CLEAN ENERGY GENERATION, INTEGRATION AND STORAGE (EEE-801)

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➢ **Fuel cells are hardly a new idea. They were invented in about <mark>1840, but they are yet to really make their mark as a power source for electric vehicles</mark>.**

➢ **However, this might be set to change over the next 20 or 30 years. Certainly most of the major motor companies are spending <mark>very large sums of money developing fuel cell powered vehicles</mark>.**

➢ **The <mark>basic principle of the fuel cell is that it uses hydrogen fuel to produce electricity in a battery like device. The basic chemical reaction is:</mark>**

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

Introduction: Fuel Cell (Cont)

➢ **The product is thus water, and energy. Because the types of fuel cell likely to be used in vehicles work at <mark>quite modest temperatures (~85∘C)</mark> there is <mark>no nitrous oxide produced by reactions between the components of the air used in the cell</mark>.**

➢ **A fuel cell vehicle could thus be described as zero-emission. Furthermore, because they run off a fairly normal chemical fuel (hydrogen), very reasonable energies can be stored, and the range of fuel cell vehicles is potentially quite satisfactory.**

➢ **They thus offer the only real prospect of a silent zero-emission vehicle with a range and performance broadly comparable with IC engine vehicles.**

➢ **It is not surprising then that there have, for many years, been those <mark>who have seen fuel cells as a technology that shows great promise, and could even make serious inroads into the domination of the internal combustion engine</mark>.**
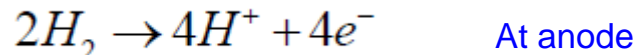
Introduction: Fuel Cell (Cont)

➤ There are many problems and challenges for fuel cells to overcome before they become a commercial reality as a vehicle power source. The main problems centre on the following issues.

➤ **Cost:** Fuel cells are currently far more expensive than IC engines, and even hybrid IC/electric systems.

➤ **Water management:** It is not at all self-evident why water management should be such an important and difficult issue with automotive fuel cells.

➤ **Cooling:** The thermal management of fuel cells is actually rather more difficult than for IC engines.

➤ **Hydrogen supply:** Hydrogen is the preferred fuel for fuel cells, but hydrogen is very difficult to store and transport. There is also the vital question of 'where does the hydrogen come from' these issues are so difficult and important, with so many rival solutions.

➤ However, there is great hope that these problems can be overcome, and fuel cells can be the basis of less environmentally damaging transport.
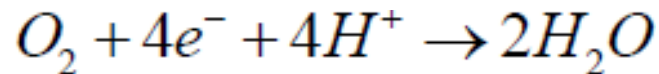
Electrode reactions

➢ **We have seen that the basic principle of the fuel cell is the release of energy following a chemical reaction between hydrogen and oxygen. The key difference between this and simply burning the gas is that the energy is released as an electric current, rather that heat.**

➢ **How is this electric current produced?**

➢ **To understand this we need to consider the separate reactions taking place at each electrode. These important details vary for different types of fuel cell, but if we start with a cell based on an acid electrolyte, we shall consider the simplest and the most common type.**

➢ **At the anode of an acid electrolyte fuel cell the hydrogen gas ionizes, releasing electrons and creating H+ ions (or protons).**

$$2H_2 \rightarrow 4H^+ + 4e^-$$ At anode

➢ **This reaction releases energy. At the cathode, oxygen reacts with electrons <mark>taken from the electrode, and H+ ions from the electrolyte, to form water.</mark>**

At cathode

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

➢ **Clearly, for both these reactions to proceed continuously, electrons produced at the anode must pass through an electrical circuit to the cathode. <mark>Also, H+ ions must pass through the electrolyte. An acid is a fluid with free H+ ions, and so serves this purpose very well. Certain polymers can also be made to contain mobile H+ ions.</mark>**
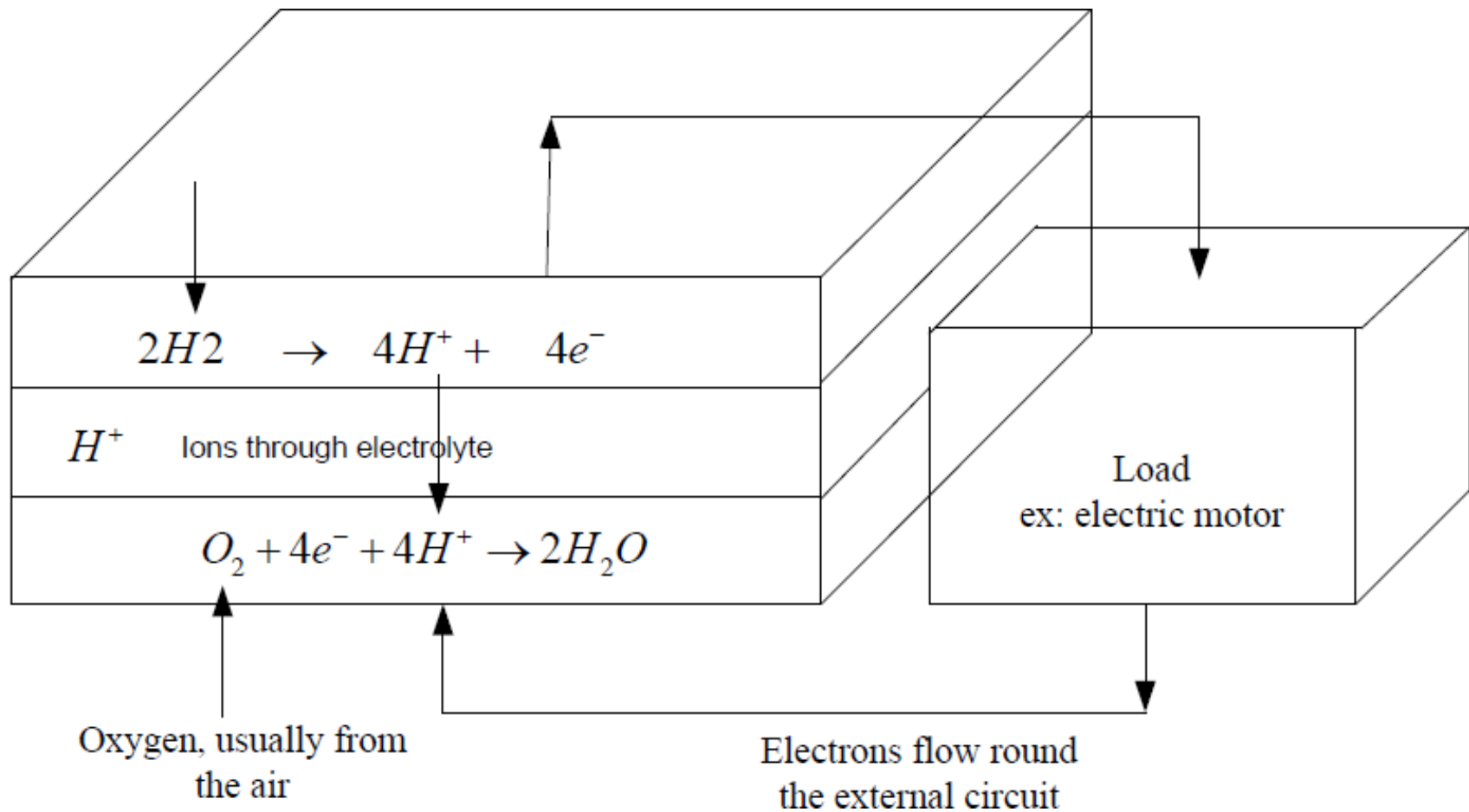
Different electrolytes:

➢ **The reactions given above may seem simple enough, but they do not proceed rapidly in normal circumstances. Also, the fact that hydrogen has to be used as a fuel is a disadvantage.** Why?

➢ **To solve these and other problems many different fuel cell types have been tried. The different types are usually distinguished by the electrolyte that is used, though there are always other important differences as well.**

Introduction: Fuel Cell (Cont)

- The situation now is that six classes of fuel cell have emerged as viable systems for the present and near future. Basic information about these systems is given in Table on next two slides.

- As well as facing up to different problems, the various fuel types also try to play to the strengths of fuel cells in different ways. The PEM fuel cell capitalizes on the essential simplicity of the fuel cell. The electrolyte is a solid polymer, in which protons are mobile. The chemistry is the same as the acid electrolyte fuel cell of Figure on next slide. With a solid and immobile electrolyte, this type of cell is inherently simple; it is the type that shows by far the most promise for vehicles, and is the type used on all the most impressive demonstration fuel cell vehicles.

- PEM fuel cells run at quite low temperatures, so the problem of slow reaction rates has to be addressed by using sophisticated catalysts and electrodes. Platinum is the catalyst, but developments in recent years mean that only minute amounts are used, and the cost of the platinum is a small part of the total price of a PEM fuel cell.

$$2H2 \quad \rightarrow \quad 4H^+ + \quad 4e^-$$

H^+ Ions through electrolyte

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

Load
ex: electric motor

Oxygen, usually from
the air

Electrons flow round
the external circuit

Fuel cell type	Mobile ion	Operating temp.	Applications and notes
Alkaline (AFC)	OH^-	50–200°C	Used in space vehicles, e.g. Apollo, Shuttle.
Proton exchange membrane (PEMFC)	H^+	30-100°C	Vehicles and mobile applications, and for lower power CHP systems
Direct methanol(DMFC)	H^+	20-90°C	Suitable for portable electronic systems of low power, running for long times
Phosphoric acid (PAFC)	H^+	220°C	Large numbers of 200kW CHP systems in use
Molten carbonate (MCFC)	CO_3^{2-}	650°C	Suitable for medium to large scale CHP systems, up to MW capacity
Solid oxide (SOFC)	O^{2-}	500-1000°C	Suitable for all sizes of CHP systems, 2 kW to multi MW

➢ **One theoretically very attractive solution to the hydrogen supply problem is to <mark>use methanol1 as a fuel instead</mark>. This can be done in the PEM fuel cell, and such cells are called direct <mark>methanol fuel cells.</mark>**

➢ **'Direct' because they use the methanol as the fuel as it is, in liquid form, as opposed to extracting the hydrogen from the methanol using one of the methods. <mark>Unfortunately these cells have very low power, and for the foreseeable future at least their use will be restricted to applications requiring slow and steady generation of electricity over long periods.</mark>**

➢ **A demonstration <mark>DMFC powered go-kart</mark> has been built, but really the only likely application of this type of cell in the <mark>near future is in the rapidly growing area of portable electronics equipment</mark>.**

➢ **Although PEM fuel cells were used on the first manned spacecraft, the alkaline fuel cell was used on the Apollo and is used on the Shuttle Orbiter. The problem of slow reaction rate is overcome by using highly porous electrodes, with a platinum catalyst, and sometimes by operating at quite high pressures.**

➢ **Although some historically important alkaline fuel cells have operated at about 200∘C, they more usually operate below 100∘C. The alkaline fuel cell has been used by a few demonstration electric vehicles, always in hybrid systems with a battery. They can be made more cheaply than PEMFCs, but they are lower in power, and the electrolyte reacts with carbon dioxide in the air, which make terrestrial applications difficult.**

Fuel cell electrodes:

➢ **Figure on next slide is another representation of a fuel cell. Hydrogen is fed to one electrode, and oxygen, usually as air, to the other.**

➢ **A load is connected between the two electrodes, and current flows. However, in practice a fuel cell is far more complex than this. Normally the rate of reaction of both hydrogen and oxygen is very slow, which results in a low current, and so a low power.**

➢ **The three main ways of dealing with the slow reaction rates are: the use of suitable catalysts on the electrode, raising the temperature, and increasing the electrode area.**
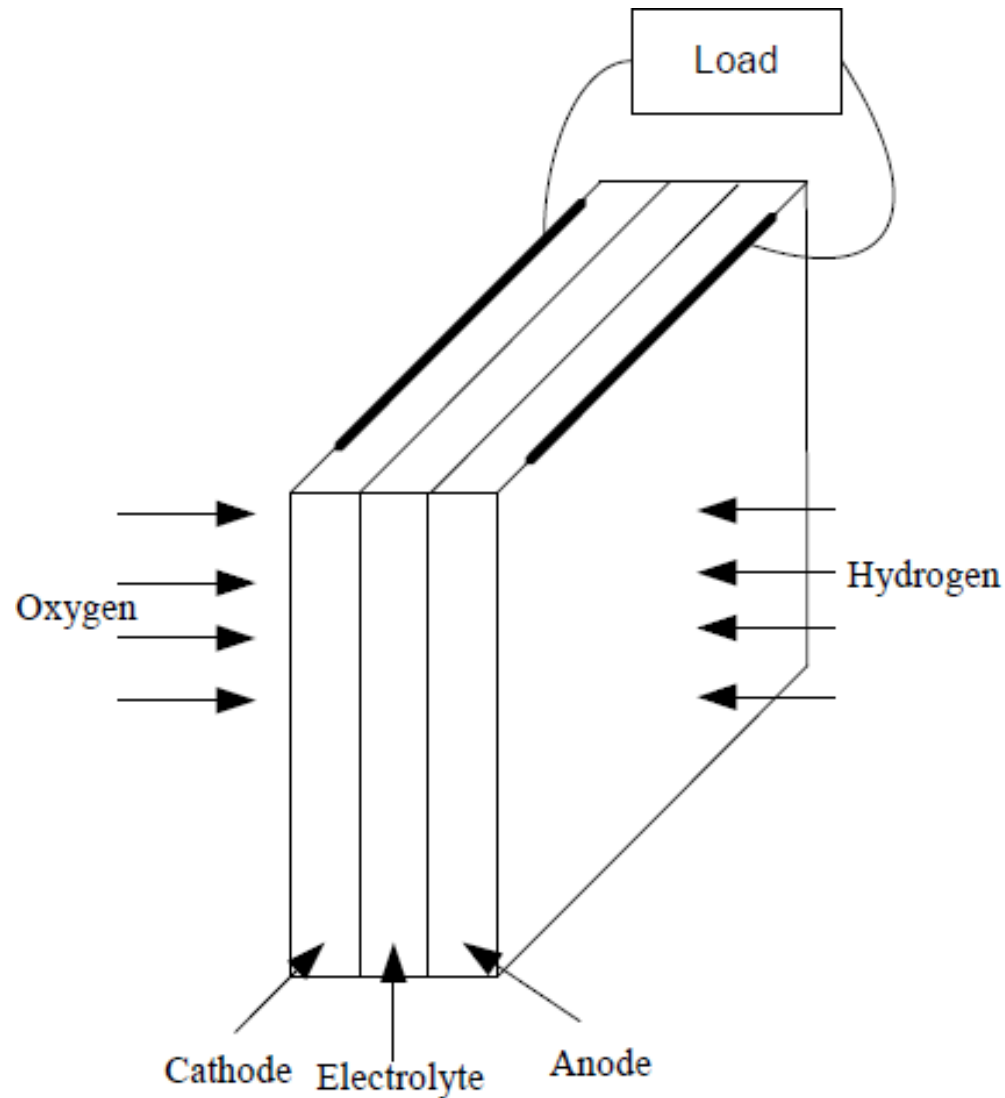
➢ **The first two can be applied to any chemical reaction. However, ==the third is special to fuel cells and is very important==.**

➢ **If look at chemical reactions, we see that ==oxygen gas, and H+ ions from the electrolyte, and electrons from the circuit are needed, all three toge==ther.**

➢ **This 'coming together' must take place on the surface of the electrode. ==Clearly, the larger the electrode area, the more scope there is for this to happen and the greater the current. This is very important.==**

➢ **Indeed, electrode area is such a vital issue that the performance of a fuel cell design ==is often quoted in terms of the current per cm^2.==**

➢ **The structure of the electrode is also important. It is made highly porous so that the real surface area is much greater than the normal length × width.**

➢ **As well as being of a large surface area, and highly porous, a fuel cell electrode must also be coated with a catalyst layer.**

Proton-exchange membrane fuel cells (PEMFC)

➢ **In the case of the PEMFC this is platinum, which is highly expensive. The catalyst thus needs to be spread out as finely as possible. This is normally done by supporting very fine particles of the catalyst on carbon particles.**

➢ **The reactants need to be brought into contact with the catalyst, and a good electrical contact needs to be made with the electrode surface.**

➢ **Also, in the case of the cathode, the product water needs to be removed.**

➢ **These tasks are performed by the 'gas diffusion layer', a porous and highly conductive material such as carbon felt or carbon paper, which is layered on the electrode surface.**

Fuel cell efficiency and efficiency limits:

➢ **One of the attractions of fuel cells is that they are not heat engines. Their thermodynamics are different, and in particular their efficiency is potentially greater as they are not limited by the well-known Carnot limit that impinges on IC and other types of fuel burning engines.**

➢ **However, as we shall see, they do have their own limitations, and while fuel cells are often more efficient than IC engines, the difference is sometimes exaggerated.**

➢ **At first we must acknowledge that the efficiency of a fuel cell is not straightforward to define. In some electrical power generating devices it is very clear what form of energy is being converted into electricity.**

➢ **With a fuel cell such energy considerations are much more difficult to visualize. The basic operation has already been explained, and the input and outputs are shown in Figure on next slide.**

➢ **The electrical power and energy output are easily calculated from the well known formulas:**

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

Hydrogen enrgy=?

Oxygen energy=?

Fuel cell

Electricity energy=VIt

Heat

Water
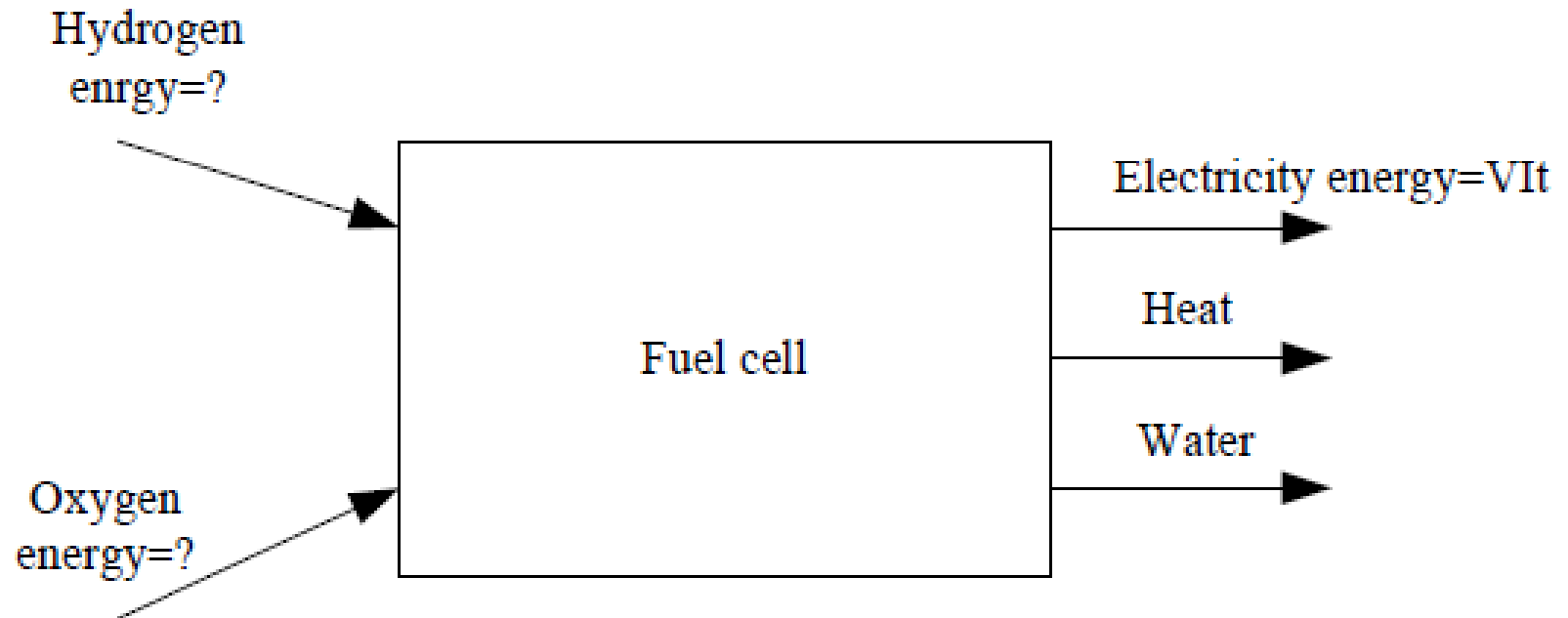
➢ **However, the energy of the chemical inputs and output is not so easily defined. At a simple level we could say that it is the chemical energy of the H2, O2 and H2O that is in question.**

➢ **The problem is that chemical energy is not simply defined, and terms such as enthalpy, Helmholtz function and Gibbs free energy are used.**

➢ **In recent years the useful term 'energy' has become quite widely used, and the concept is particularly useful in high temperature fuel cells, though we are not concerned with these here. There are also older (but still useful) terms such as calorific value.**

➤ **In the case of fuel cells it is the Gibbs free energy that is important. This can be defined as the energy available to do external work, neglecting any work done by changes in pressure and/or volume.**

➤ **In a fuel cell the external work involves moving electrons round an external circuit; any work done by a change in volume between the input and output is not harnessed by the fuel cell.**

➤ **Energy is all the external work that can be extracted, including that due to volume and pressure changes. Enthalpy, simply put, is the Gibbs free energy plus the energy connected with the entropy.**

➤ **The enthalpy H, Gibbs free energy G and entropy S are connected by the well-known equation:**

$$G = H - TS$$

➤ **The energy that is released by <mark>a fuel cell is the change in Gibbs energy before and after a reaction</mark>, so the energy released can be represented by the equation:**

$$\Delta G = G_{outputs} - G_{inputs}$$

➤ **However, <mark>the Gibbs free energy change is not constant, but changes with temperature and state</mark> (liquid or gas). Table on next slide shows ΔG for the basic hydrogen fuel cell reaction for a number of different conditions. <mark>Note that the values are negative, which means that energy is released</mark>.**

$$\Delta G = \Delta H - T \cdot \Delta S$$

ΔG = Gibbs free energy
ΔH = Change in enthalpy
ΔS = Change in entropy
T = Temperature in K

Form of water product	Temperature ($^{\circ}$C)	ΔG (kJ/mole)
Liquid	25	- 237.2
Liquid	80	-228.2
Gas	80	-226.1
Gas	100	-225.2
Gas	200	-220.4
Gas	400	-210.3
Gas	600	-199.6
Gas	800	-188.6
Gas	1000	-177.4

➢ **The energy that is released by a fuel cell is the change in Gibbs energy before and after a reaction, The reaction can be represented by the equation:**

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$
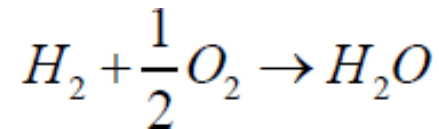
➢ **If there are no losses in the fuel cell, or as we should more properly say, if the process is reversible, then all this Gibbs free energy is converted into electrical energy. We could thus define the efficiency of a fuel cell as:**

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

➢ **Since a fuel cell uses materials that are usually burnt to release their energy, it would make sense to compare the electrical energy produced with the heat that would be produced by burning the fuel.**

➢ **This is sometimes called the calorific value, though a more precise description is the change in enthalpy of formation. Its symbol is ΔH.**

➢ **As with the Gibbs free energy, the convention is that ΔH is negative when energy is released. So to get a good comparison with other fuel using technologies, the efficiency of the fuel cell is usually defined as:**

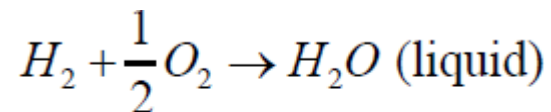$$\frac{\text{electrial energy produced per mole of fuel}}{-\Delta H}$$

➢ **However, even this is not without its <mark>ambiguities</mark>, as there are two different values that we can use for ΔH. For the burning of hydrogen:**

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \text{ (steam)}$$
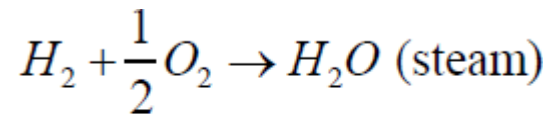
$$\Delta H = -241.83 \ kJ / mole$$

➢ **whereas <mark>if the product water is condensed back to liquid, the reaction is:</mark>**

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

$$\Delta H = -285.84 \ kJ / mole$$

➢ **The difference between these two values for ΔH (44.01 kJ/mole) is the molar enthalpy of vaporization of water.**

➢ **We can now see that there is a limit to the efficiency. The maximum electrical energy available is equal to the change in Gibbs free energy, so:**

$$Maximum \; efficiency \; possible = \frac{\Delta G}{\Delta H} \times 100\%$$

➢ **This maximum efficiency limit is sometimes known as the thermodynamic efficiency. Table on next two slide gives the values of the efficiency limit, relative to the higher heating value, for a hydrogen fuel cell.**

➢ **The maximum voltage obtainable from a single cell is also given. The graphs in Figure on next slide show how these values vary with temperature, and how they compare with the Carnot limit, which is given by the equation:**

$$Carnot \lim it = \frac{T_1 - T_2}{T_1}$$

➢ **where T1 is the higher temperature, and T2 the lower, of the heat engine. The graph makes clear that the efficiency limit of the fuel cell is certainly not 100%, as some supporters of fuel cells occasionally claim. Indeed, above the 750 degree Celsius the efficiency limit of the hydrogen fuel cell is actually less than for a heat engine. Nevertheless, the PEM fuel cells used in vehicles operate at about 80 degree Celsius and so their theoretical maximum efficiency is actually much better than for an IC engine.**
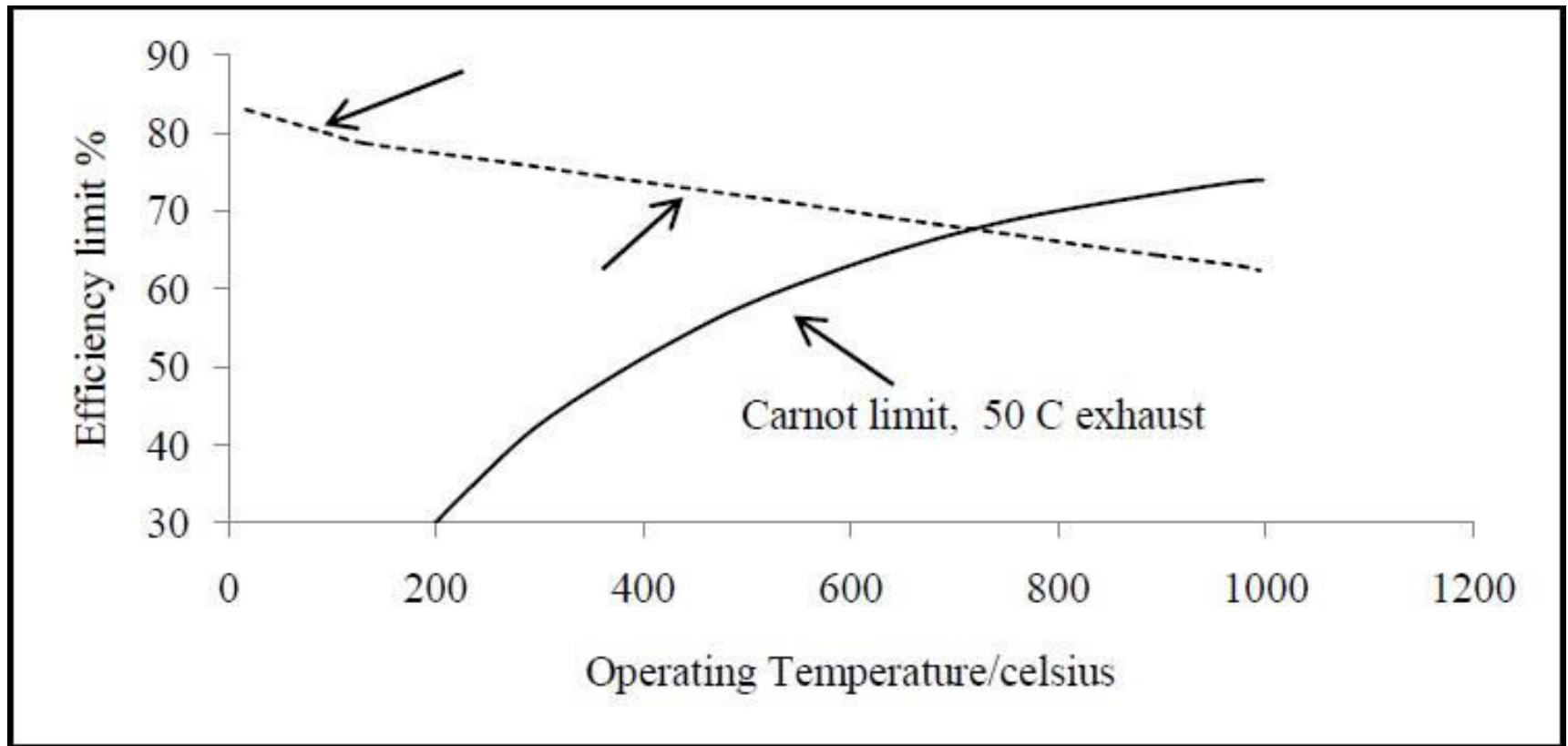
Form of water product	Temp °C	ΔG kJ/mole−1	Max. EMF	Efficiency limit
Liquid	25	-237.2	1.23V	83%
Liquid	80	-228.2	1.18 V	80%
Gas	100	-225.3	1.17 V	79%
Gas	200	-220.4	1.14 V	77%
Gas	400	-210.3	1.09 V	74%
Gas	600	199.6	1.04 V	70%
Gas	800	-188.6	0.98 V	66%
Gas	1000	-177.4	0.92 V	62%

Efficiency and the fuel cell voltage:

➢ **A very useful feature of fuel cells is that their efficiency can be very easily found from their operating voltage.**

➢ **The reasoning behind this is as follows. If one mole of fuel is reacted in the cell, then two moles of electrons are pushed round the external circuit;**

$$Energy = Ch\arg e \times Voltage$$

➢ **The Faraday constant F gives the charge on one mole of electrons. So, when one mole of hydrogen fuel is used in a fuel cell, if it were 100% efficient, then we would be able to say that:**

$$Energy = 2F \times V_{100\%} = \Delta H$$

$$V_{100\%} = \frac{\Delta H}{2F}$$

➢ **The two values for ΔH given above, we can easily calculate that the '100% efficient' voltage for a single cell is 1.48V if using the HHV or 1.25V if using the LHV.**

➢ **Now of course a fuel cell never is, and we have shown in the last section never can be, 100% efficient. The actual fuel cell voltage will be a lower value, which we can call Vc.**

➢ **Since voltage and electrical energy are directly proportional, it is clear that**

$$Fuel\,cell\,efficiency = \frac{Vc}{V_{100\%}} = \frac{Vc}{1.48}$$

➢ **Clearly it is very easy to measure the voltage of a fuel cell. In the case of a stack of many cells, remember that the voltage of concern is the average voltage one cell, so the system voltage should be divided by the number of cells.**

➢ **The efficiency can thus be found remarkably easily. It is worth noting in passing that the maximum voltage of a fuel cell occurs when 100% of the Gibbs free energy is converted into electrical energy.**

➢ **Thus we have an equation, giving the maximum possible fuel cell voltage:**

$$V_{\max} = \frac{\Delta G}{2F}$$

Practical fuel cell voltages:

➤ **In practice the actual cell voltage is less than this. Now of course this applies to ordinary batteries too, as when current is drawn out of any electric cell the voltage falls, due to internal resistances.**

➤ **However, with a fuel cell this effect is more marked than with almost all types of conventional cell. Figure on next slide shows a typical voltage/current density curve for a good PEM fuel cell.**

➤ **It can be seen that the voltage is always less, and is often much less, than the 1.18V that would be obtained if all of the Gibbs energy were converted into electrical energy.**
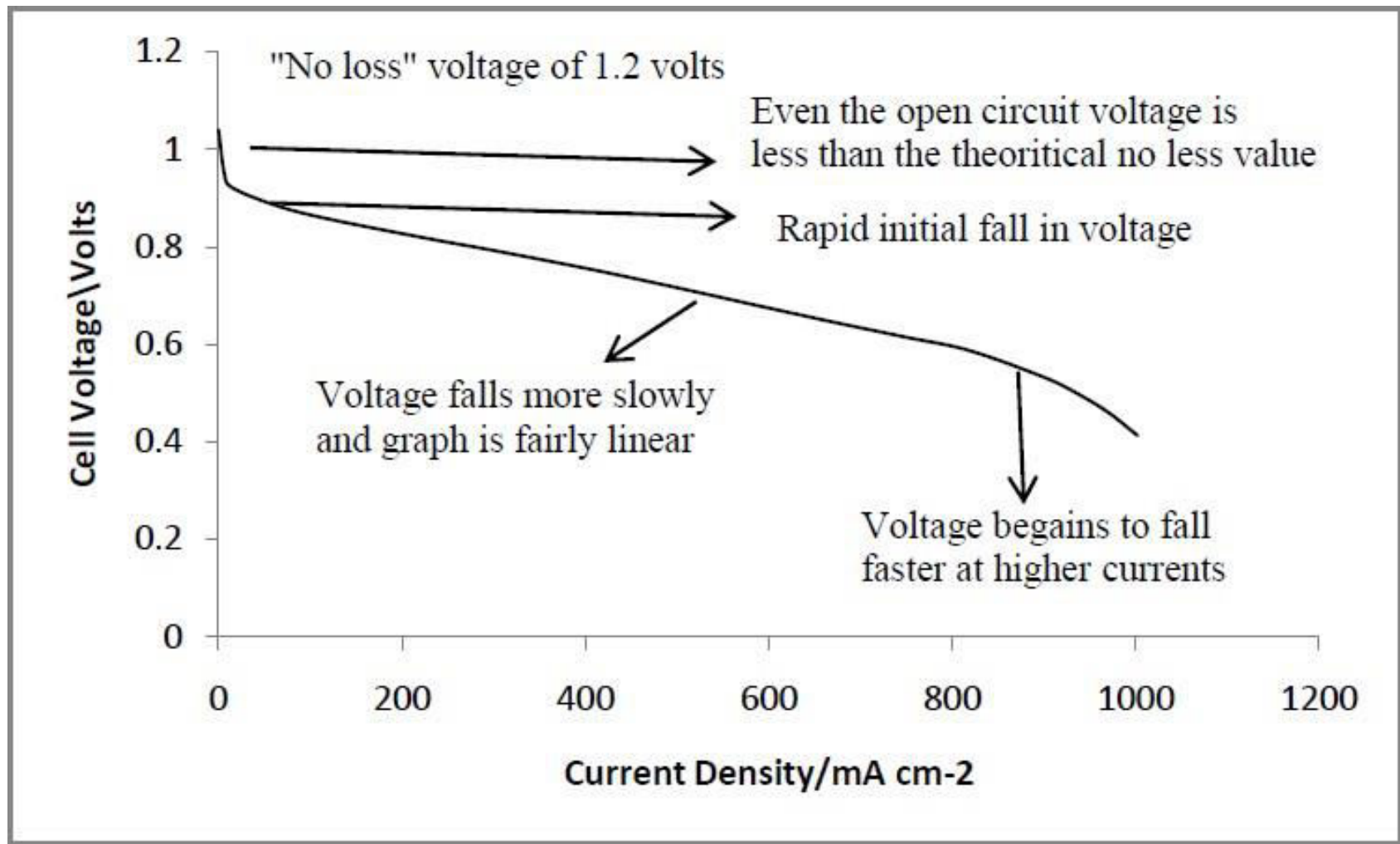
There are three main reasons for this loss of voltage, as detailed below.

➢ The energy required to drive the reactions at the electrodes, usually called the activation energy, causes a voltage drop. This is especially a problem at the air cathode, and shows itself as a fairly constant voltage drop. This explains the initial fall in voltage even at quite low currents.

➢ The resistance of the electrolyte and the electrodes causes a voltage drop that more or less follows Ohm's law, and causes the steady fall in voltage over the range of currents. This is usually called the Ohmic voltage loss.

➢ At very high currents, the air gets depleted of oxygen, and the remnant nitrogen gets in the way of supplying fresh oxygen. This result is a fall in voltage, as the electrodes are short of reactant. This problem causes the more rapid fall in voltage at higher currents, and is called mass transfer or concentration voltage loss.

The effect of pressure and gas concentration:

➢ **The values for the changes in the Gibbs free energy given in Tables are all concern pure hydrogen and oxygen, at standard pressure, 100 kPa.**

➢ **However, as well as changing with temperature, as shown in these tables, the Gibbs energy changes with pressure and concentration.**

➢ **A full treatment of these issues is beyond a book such as this, and it can easily be found elsewhere.**

➢ **Suffice to say that the relationship is given by a very important fuel cell equation derived from the work of Nernst. It can be expressed in many different forms, depending on what issue is to be analyzed. For example, if the change of system pressure is the issue, then the Nernst equation takes the form:**

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

➢ **Where ΔV is the voltage increase if the pressure changes from P1 to P2. Other causes of voltage change are a reduction in voltage caused by using air instead of pure oxygen.**

➢ **The use of hydrogen fuel that is mixed with carbon dioxide, as is obtained from the 'reforming' of fuels such as petrol, methanol or methane, also causes a small reduction in voltage.**

➢ **For high temperature fuel cells the Nernst equation predicts very well the voltage changes. However, with lower temperature cells, such as are used in electric vehicles, the changes are nearly always considerably greater than the Nernst equation predicts.**

➢ **This is because the 'activation voltage drop' mentioned in the last section is also quite strongly affected by issues such as gas concentration and pressure. This is especially the case at the air cathode.**

➤ **The voltage increase resulting from a doubling of the system pressure would be:**

$$\Delta V = \frac{8.314 \times (273 + 80)}{4 \times 96485} \ln(2) = 0.0053V \ per \ cell$$

➤ **However, in practice the voltage increase would typically be about 0.04 V, nearly ten times as much. Even so, we should note that the increase is still not large, and that there is considerable energy cost in running the system at higher pressure.**

➤ **Indeed, it is shown elsewhere that the energy gained from a higher voltage is very unlikely to be greater than the energy loss in pumping the air to higher pressure.**