Fuel cells and hydrogen energy

Introduction

A fuel cell is a device that converts chemical energy of a fuel directly into electrical energy by an electrochemical process. In conventional processes for generation of electricity form a fuel, the fuel is combusted, and the heat liberated is converted to mechanical energy in a heat engine (a turbine or a piston engine). The mechanical energy is converted further into electricity by means of a generator. A fuel cell is capable of extracting the chemical energy or part of it directly while converting the fuel to its reaction products. These reaction products are in most cases, although not all, the same as if the combustion products. The two pathways are visualized in Figure 1.
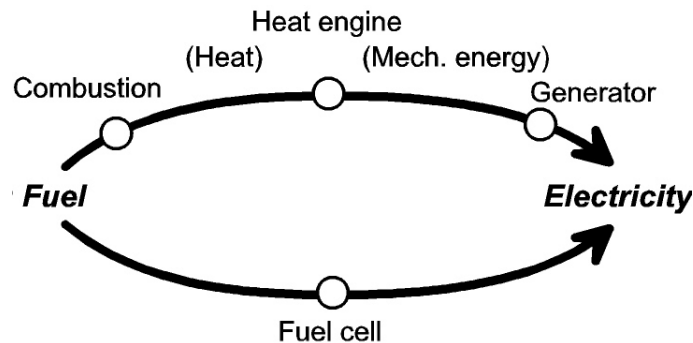

Figure 1. The traditional pathway from chemical energy to electrical energy and the direct conversion pathway in a fuel cell.

The process that liberates energy from a fuel is shown in a generalized form in (1) for a fuel constituting carbon, hydrogen and oxygen (e.g., coal, hydrocarbons or alcohols). When reacted with oxygen, energy is liberated because the chemical bonds in CO_2 and water are stronger than the chemical bonds in the fuel (more correctly, the sum of the bonding energy in all the product molecules is larger than that of all the reacting molecules)

$$\text{Fuel} + xO_2 \rightarrow yCO_2 + zH_2O + \text{energy} \tag{1}$$

This reaction is the same regardless if the fuel is combusted or converted in a fuel cell.

Since conversion in a fuel cell does not happen through a state of thermal energy (heat), the Carnot limitation does not apply to a fuel cell and the ultimate thermodynamic conversion efficiency - fuel to electricity - is only limited by the Gibbs free energy change of the equivalent combustion process. This limitation naturally also applies if the fuel is combusted, but the Carnot limitation is always more demanding. The independence of the Carnot limitation gives the fuel cell a potential for higher electrical

efficiency than a system working via a heat engine. However, due to imperfections in both systems, the race is not necessarily decided based on thermodynamics alone.

Fuel cells have fascinated scientists, engineers and other people with an interest in technology for decades since their early applications as power sources in the space programmes. The main advantages are

- The possibility for higher electrical efficiency that thermal engines
- Full scalability from below 1 W to kW or even MW with practically the same performance characteristics. In contrast, combustion engines gain efficiency with size, mostly due to lower relative heat loss (The huge shipping engines are actually very efficient)
- Silent operation and no vibrations with "no moving parts" (not quite true when the system around with blowers is considered)
- The perfect match with hydrogen as fuel with emission of only pure water - the clean hydrogen energy concept.

Fuel cells can in principle be constructed to convert any fuel, or any energy releasing chemical process in which electrons are exchanged between species, but most commonly they are powered by hydrogen.

The concept of hydrogen energy is simple and appealing. Hydrogen is a gaseous fuel. When combusted, it produces only water as the combustion product. We cannot mine or extract hydrogen from wells like we do with coal, oil and gas, but we can extract it from water by electrical energy in an electrolyzer. The electrolyzer is actually a fuel cell in reverse mode. The reaction (2) is simply reaction (1) with hydrogen as the fuel. It proceeds left in the electrolyzer and right in the fuel cell.

$$H_2 + \tfrac{1}{2}O_2 \rightleftarrows H_2O + \text{energy} \tag{2}$$

In a future energy system based on renewables, the major sources of energy (solar and wind) produce electricity and production of hydrogen makes it possible to store the energy and to use it in applications where cables are not practical, in particular transport. If nuclear energy is considered, the situation is the same. Moreover, the chemical starting material is the cheapest and most abundant that we can imagine, water. Silly rumours appear regularly that cars running on just water have been developed, and the hydrogen energy idea is probably the closest we get making that come true. The only thing to add is that we need to "power up" or "charge" the water with energy and this is done by separating hydrogen from oxygen and allow the two elements to combine when we need to reclaim the energy. The full hydrogen cycle is shown schematically in Figure 2. In the figure, hydrogen is produced in the electrolyzer and stored in a tank. The by-product, oxygen, can be stored too, but normally it is let out because it is available most places in a sufficient concentration in the surrounding air of which about one fifth of the molecules are oxygen.
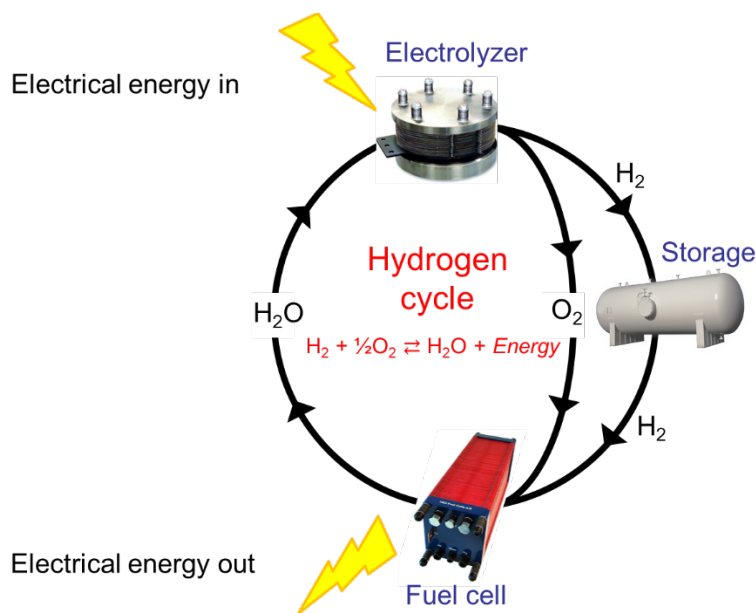
Figure 2. The hydrogen energy cycle. Production from water and electrical energy in an electrolyzer, storage in a tank and conversion back to water and electricity in a fuel cell.

The function of a fuel cell

Grabbing the electrons

Electrical energy can be extracted from a chemical process as long as it involves transfer of electrons. The trick in the fuel cell is to utilize the transfer of electrons, i.e., the oxidation and reduction of species. Oxygen is the oxidant that oxidizes the fuel. This means that oxygen increases the oxidation state of the atoms it reacts with (or some of them) by taking two elections. There is a strong chemical driving force for oxygen to receive two electrons[1]. In the hydrogen combustion process, the two electrons are taken from hydrogen forming two positive hydrogen ions, H^+, which are actually only protons since the hydrogen atom has only one electron in the first place. In a normal combustion process, as in (2), this happens too, but is not clearly seen from the reaction because hydrogen and oxygen combine to water as part of the process. In the water molecule, the electron are only partly shifted from hydrogen to oxygen and still part in the chemical bond. One could say that they belong more to oxygen than to hydrogen.

In the fuel cell, the oxidation and reduction processes are separated, and the electrons are transferred through an external circuit. The driving force for electron transfer is then the driving force for pushing electrons through the external circuit and it is quantified by the cell voltage, E. Electrons are generated or liberated at the anode (the electrode where the oxidation process takes place), which is the hydrogen electrode.
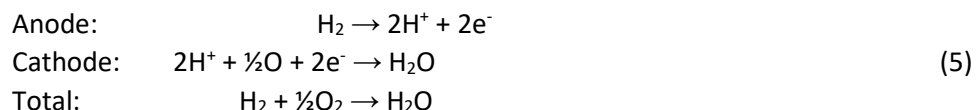
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[1] Like many other atoms, oxygen "likes" to have 8 electrons in its outer electron shell. The nucleus charge of oxygen is +8, but the inner electron shell takes the first two, so only 6 electrons are available for the outer shell and thus two more negative charges are highly desired. Adding these makes it an ion O^{2-}. In molecular oxygen, the two oxygen atoms share 4 electrons by the chemical double bond, and thus both atoms see 8 electrons.

$$H_2 \rightarrow 2H^+ + 2e^- \tag{3}$$

On the other electrode, the cathode (where reduction takes place), oxygen ions might be expected, but the process is slightly different. The protons take part in the reduction process forming water.

$$2H^+ + \tfrac{1}{2}O_2 + 2e^- \rightarrow H_2O \tag{4}$$

The total reaction scheme becomes

$$
\begin{aligned}
\text{Anode:} \quad & H_2 \rightarrow 2H^+ + 2e^- \\
\text{Cathode:} \quad & 2H^+ + \tfrac{1}{2}O + 2e^- \rightarrow H_2O \\
\text{Total:} \quad & H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O
\end{aligned}
\tag{5}
$$

These processes are energetically favoured over forming hydrogen ions and oxygen ions separately and then forming water.[2]

The single cell

The core of the fuel cell is the electrode and the electrolyte that separated them. See Figure 3. Hydrogen is oxidized at the anode and oxygen is reduced at the cathode. The generation of electrons at the anode charges the electrodes negatively with respect to the cathode at which electrons are consumed. Protons formed at the anode are needed for the process at the cathode, but the electrode cannot be in direct contact because that would cause a short circuit for the electrons. The electrolyte serves as a selective barrier that prevents transfer of electrons but allows transfer of ions. It is an ion conductor and an electronic insulator.

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[2] If we for a moment imagine that oxygen ions, O^{2-}, were formed along with protons, $2H^+$, they would subsequently need to combine to form water, which we know is the end product. This reaction, $2H^+ + O^{2-} \rightarrow H_2O$, liberates very much energy as thermal energy which would not be utilized. This energy can only originate from the chemical energy of the overall process and in that there is simply not enough energy available to generate this ion pair separately. In a chemical environment where hydrogen ions are stable, oxygen ions are highly unstable and will not be formed (or will be consumed before they are fully generated. Likewise in a different environment where oxygen ions are stable, hydrogen ions are very unstable and will not be formed. In solid oxide fuel cells, oxygen ions are formed instead of hydrogen ions. This will be explained later.
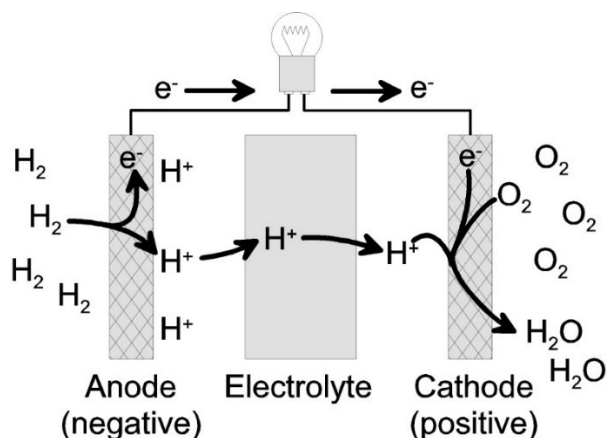
Figure 3. Schematic of a fuel cell with a proton conducting electrolyte.

Electrolytes

Electrolytes can be liquids contained in a porous matrix or they can be solids. They are capable of conducting specific ions. Liquid electrolytes can be aqueous solutions of acid or base. Acidic electrolytes conduct protons and alkaline (i.e., basic) electrolytes typically hydroxide ions, OH^-. The most common solid electrolytes are the proton exchange membrane, a specialty polymer which conducts protons, and the solid oxide electrolyte which is a ceramic oxide ion conductor. The reactions in (5) are for a cell with a proton conducting electrolyte, i.e., an acidic liquid electrolyte or a proton conducting membrane electrolyte. In Table 1, the reaction schemes for cells with different ion conducting electrolytes are listed. Note that the total reaction is the same in all cases. That is the combustion process of hydrogen. Note also that the product water is formed at the cathode in some cases and at the anode in others.

Table 1. Reaction schemes for fuel cells with different ion conducting electrolytes.

Proton conducting electrolyte (acidic)	
Anode:	$2H_2 \rightarrow 4H^+ + 4e^-$
Cathode:	$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$
Total:	$2H_2 + O_2 \rightarrow 2H_2O$
Oxide ion conducting electrolyte	
Anode:	$2H_2 + 2O^{2-} \rightarrow H_2O + 4e^-$
Cathode:	$O_2 + 4e^- \rightarrow 2O^{2-}$
Total:	$2H_2 + O_2 \rightarrow 2H_2O$
Hydroxide ion conducting electrolyte (alkaline)	
Anode:	$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$
Cathode:	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Total:	$2H_2 + O_2 \rightarrow 2H_2O$
Carbonate conducting electrolyte	
Anode:	$2H_2 + 2CO_3^{2-} \rightarrow 2H_2O + 2CO_2 + 4e-$
Cathode:	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$
Total:	$2H_2 + O_2 \rightarrow 2H_2O$

Electrodes

Fuel cell electrodes are complex structures. Figure 4 shows the different layers in a fuel cell. The electrochemical reactions take place in the catalyst layers in close contact with the electrolyte. Behind the catalyst layers gas diffusion layers ease distribution of the reacting gasses (hydrogen and oxygen respectively), and outermost, massive channel plates supply gasses to the diffusion layers by the channels while the ribs or land separating the channel collect the electronic current passing through the cell.

The catalytic reaction sites must be accessible to the reacting gas (hydrogen or oxygen respectively) and be in ionic contact with the electrolyte to be able to exchange generated or consumed ions. At the same time, the sites must be in good electronic contact with the channel plate that is the current collector. Heat is generated at the reaction sites and in the electrolyte and this heat is conducted to the channel plates which are cooled. See Figure 5. Altogether, simultaneous transport of gasses, ions, electrons and heat requires percolating transport pathways of gaseous, solid and ion conducting phases, which all meet at the reaction sites. The catalytic sites where the gas phase, the ion conducting phase and the electron conducting phase meet is called the *triple phase boundary*.[3]
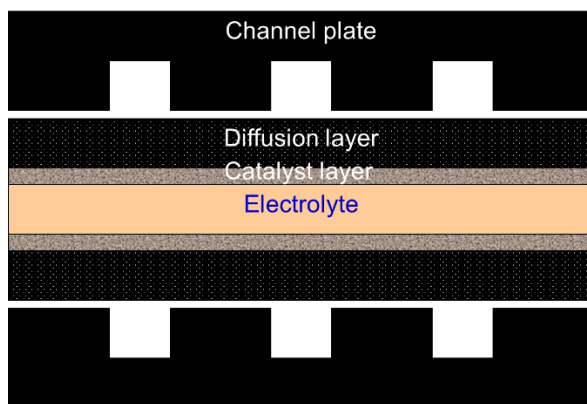

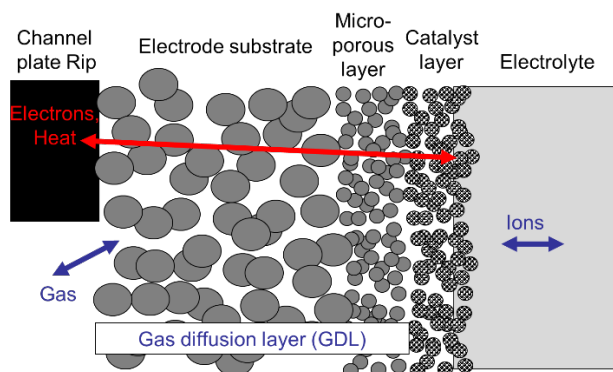Figure 4. The functional layers of a fuel cell.

Figure 5. Principal sketch of a fuel cell electrode with the various transport processes indicated.

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[3] In some cases, materials with mixed ionic and electronic conductance can be applied or a thin film of electrolyte may cover the catalyst and the gasses dissolve in this film and reach the reaction site as dissolved gas. In such cases, only two phases meet.

Stacking fuel cells

Fuel cells are nearly always applied in a stack of cells connected in series. This way, a higher and more useful voltage is obtained. Electrochemical cells only generate voltages in the order of up to a few volts at maximum and despite the theoretical cell voltage of a hydrogen powered fuel cell is 1.23 V, the practical voltage is significantly below 1 V, typical in the range from 0.5 to 0.8 V. The current-voltage characteristics of a fuel cell will be treated later. In principle, it is possible with power electronics to step up a voltage (at the cost of the current), but when starting from less than 1 volt it is not practical and at least very inefficient. Moreover, with a power density in the order of 1 W cm^2 then 100 kW, a typical power rating for a fuel cell vehicle, requires 10 m^2 of fuel cells. The manufacture of such a large cell would be difficult and one single cell would have to be rolled or folded anyway to fit in into an application. Additional advantages of stacking fuel cells are that they are efficiently connected and that the stack is very compact.

Many different stacking concepts have been developed, but the prevailing one is with planar cells separated by bipolar plates as shown in Figure 6. The channel plates that secure gas supply and current collection are paired with the plate from the adjacent cell forming a *bipolar plate*. It is labelled "bipolar" because it connects a positive electrode in one direction and a negative electrode in the other. The bipolar plates can be manufactured as one piece or as two pieces with channels for a coolant in between. The bipolar plates must be completely gastight and conduct electrons and heat well.

The stack ends with a rigid end plate in each end to ensure even compression by long spring-loaded bolts or similar means.
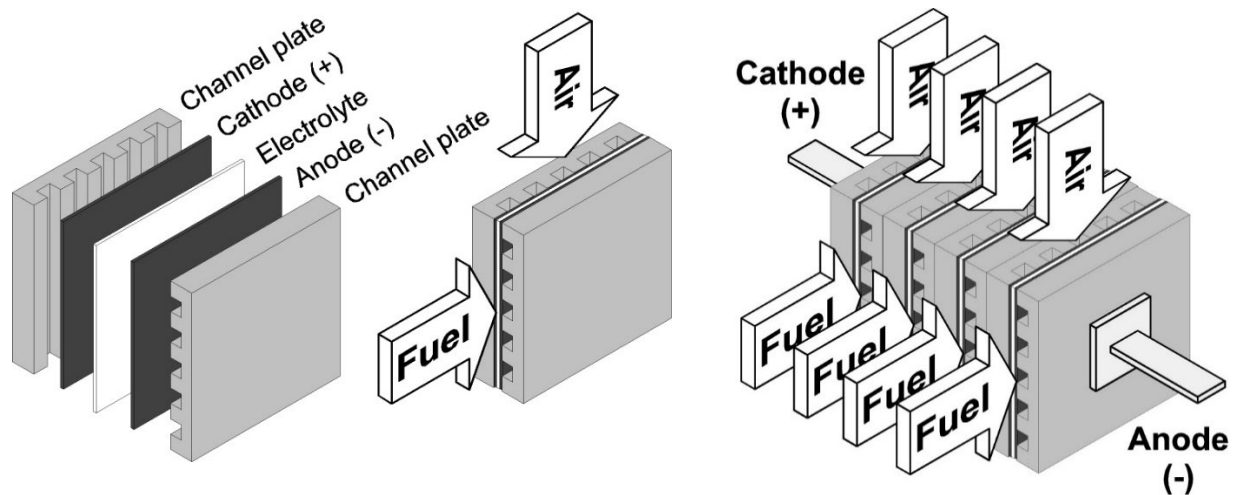

Figure 6. Stacking fuel cells. The stack is closed in each end by a rigid end plate (not shown) and fixed with long bolts.

In Figure 6, the channels for inlet and outlet of gasses are open and proper gas manifold must be applied. The usual way is to integrate gas manifolds in the bipolar plates as internal manifolds connected via channel along the stack formed when stacking the bipolar plates. See Figure 7. The long supply channels are then connected to the individual cells. The channels across the bipolar plate may take many different shapes optimized with respect to pressure drop and gas distribution. The extremes are

either one long serpentine channel or straight parallel channels (like in Figure 6). In Figure 7 the pattern on the plate in font is a combination, parallel/serpentine, meant for a gas and the plate behind has straight parallel channels for a coolant (water).

Between all the cells and plates proper sealing must be applied. These can be made from elastomers ("rubbers") for low temperature stacks and from soft glasses for high temperature stacks.

Figure 7. Left: commercial bipolar plates of a carbon composite for a PEM fuel cell stack. Right: PEM fuel cell stack from IRD Fuel Cells. The PEM fuel cell works with a proton conducting membrane (first set of reactions in Table 1).

Thermodynamics and cell voltage of fuel cells

The total energy release by combustion of hydrogen or conversion in a fuel cell equals the standard enthalpy of reaction (ΔH_r^0). The maximum work obtainable from the fuel cell equals the Gibbs free energy of reaction (ΔG_r^0). The values are listed in Table 2 with respect to product water generated as liquid or vapour, i.e., with respect to higher and lower heating values.

Efficiency is "what you get" divided by "what you pay" and in a fuel cell, you get the work and pay the fuel. Consequently, with the ultimate work obtainable given by the free energy of reaction and the total energy of the fuel by the enthalpy of reaction, the ultimate thermodynamic efficiency, $\eta_{\max}$, must be

$$\eta_{\max} = \frac{\Delta G_r^0}{\Delta H_r^0} \tag{6}$$

This value is included in Table 2 for with both heating values as reference.

Table 2. Standard enthalpy (ΔH_r^0) and Gibbs free energy (ΔG_r^0) of reaction and thermodynamic conversion efficiency (η_{max}) for a hydrogen powered fuel cell. Based on higher and lower heating values, respectively.

(25 °C, all at 1 bar)	HHV based	LHV based
Reaction	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$
ΔH_r^0	-285.8 kJ mol^{-1}	-241.8 kJ mol^{-1}
ΔG_r^0	-237.1 kJ mol^{-1}	-228.6 kJ mol^{-1}
η_{max} ($\Delta G_r^0/\Delta H_r^0$)	83 %	98 %

The Enthalpy of reaction is only a very mild function of temperature. This is because it is dictated by the chemical bond strengths. In contrast, The Gibbs free energy is declining (numerically) with temperature. This is because of the temperature dependence of the entropy of reaction, which the free energy depends on. These temperature dependencies are shown in Figure 8. It is clearly seen that the maximum obtainable work of a hydrogen powered fuel cell becomes smaller as the temperature increases. Equation (7) translates the free energy directly into a reversible cell voltage, which can be read from the ΔG_r curve on the secondary vertical axis.

$$E_{cell} = \frac{-\Delta G_r}{nF} \tag{7}$$

This lowering of the reversible cell voltage implies that the ideal (maximum) conversion efficiency, fuel to electricity, also decreases with temperature.

Figure 8. The energy functions of the combustion reaction of hydrogen. Note that the units are negative. On the secondary axis, the reversible cell voltage can be read from the free energy curve.
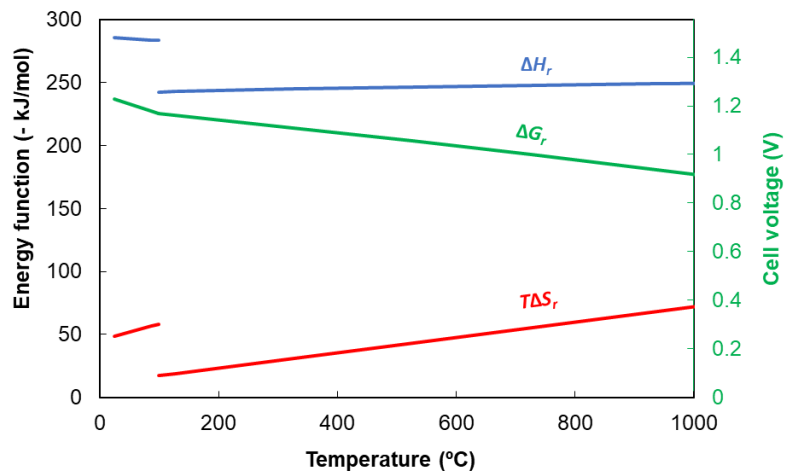
When including the temperature dependence of the free energy, equation (6) becomes

$$\eta_{\max}(T) = \frac{\Delta G_r\ (T)}{\Delta H_r^0} \qquad (8)$$

Note that the (mild) temperature dependence of the reaction enthalpy is not included. This follows logically from the fact that the universal energy value of a fuel should be measured at a fixed state and not depend on the temperature at which the fuel is used.

We can now plot the fuel cell efficiencies together with Carnot efficiencies (with different lower temperatures) as a function of temperature. This is done in Figure 9. The declining trend is a direct consequence of the declining free energy. The two curves represent higher and lower heating value equivalents of the enthalpy.
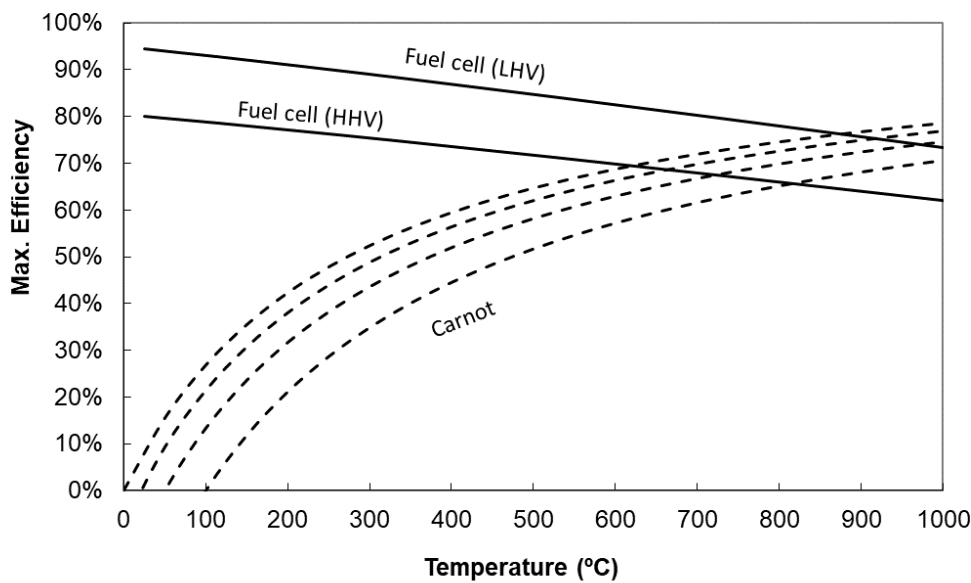

Figure 9. The maximum conversion efficiency of a hydrogen powered fuel cell based on either higher or lower heating value as function of temperature (solid lines). Carnot efficiencies with the higher temperature directly on the primary axis and the lower temperature read where the curves cross the primary axis at zero efficiency (hatched lines)

The thermoneutral voltage

It is clear from Figure 9 that a hydrogen powered fuel cell is always less that 100 percent efficient. We know from thermodynamics that this is because operating the fuel cell results in a net reduction in the number of gas molecules and that the following loss of entropy has to be balanced by dissipation of

some of the energy as low temperature heat. At higher temperatures, the entropy generated by dissipation of heat is less, because the generated entropy is the heat dissipated divided by the temperature at which it happens (cf. Clausius' inequality).

Now let us for a moment imagine that all the enthalpy of reaction could be converted to work or electricity. Then there would be no heat to dissipate, and the cell would neither cool nor heat up. This is not possible as it violates the second law by leading to destruction of entropy, but we can still use this abstraction as a reference point for a state of 100 pct. conversion to work and thus 100 pct. voltage efficiency. We can even calculate the reversible voltage the cell would attain if all the enthalpy was put behind the electrons.

$$E_{TN} = \frac{-\Delta H_r}{nF} \tag{9}$$

This voltage, E_{TN}, is called the *thermoneutral voltage* because at this voltage the cell would be completely balanced thermally with constant temperature and no need for heating or cooling since all fuel energy leaves the cell as electricity. The thermoneutral voltage depends on whether water is produced as vapour or liquid because of the enthalpy difference between these two forms. See Table 3.

For hydrogen powered fuel cells, the thermoneutral voltage is never obtained but only used as a benchmark for 100 pct. efficiency. The cell voltage in real cells is always below an even below the reversible cell voltage due to a variety of imperfections as we shall see it the next part. The actual conversion efficiency, η_{actual}, or voltage effceiency can be found at any real cell voltage, E_{cell}, by (10).

$$\eta_{actual} = \frac{E_{cell}}{E_{TN}} \tag{10}$$

While the thermoneutral voltage is an abstraction for a hydrogen powered fuel cell, it is real and obtainable in the equivalent electrolyzer.

Table 3. The thermoneutral voltages, E_{TN}, if water is produces as liquid or vapour.

(25 °C, all at 1 bar)	HHV based	LHV based
Reaction	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$
E_{TN}	1.48 V	1.25 V

Polarisation curves

Fuel cells are characterized by their polarization curves or current voltage characteristics. The cell voltage is measured as a function of current (or current density, i.e., current per electrode area, to make

11

the measurements more comparable) or vice versa. A fictive example of such a polarisation curve can be seen in Figure 10. The characteristic features are that (1) it is below the reversible cell voltage at any current density. Imperfections in the form of internal resistances cause this by consuming part of the energy fighting internal resistance. (2) The curve follows an S-shaped profile, which is described well by rather simple yet physically founded mathematical models that are left out in this context.

The main sources of *voltage loss* or *overvoltages* are explained in the chapter on thermodynamics and electrochemistry and repeated here for the reader's convenience:

The physical origin of overvoltages is:

- Voltage loss due to the ohmic resistance in the electrolyte and in cables and connection. This loss is purely ohmic, i.e., it follows Ohms law, which dictates that the voltage loss is proportional with the current.
- Electrochemical losses at the electrodes. The charge transfer process can be slow and by polarizing the electrode (changing its potential) electron transfer in one direction is favoured and the process is accelerated. This contribution is not at all ohmic but follows a logarithmic like characteristic with current density. This overvoltage is referred to as *charge transfer overvoltage*, *kinetic overvoltage* or simply *anodic or cathodic overvoltage*.
- At high currents, transport of species to and from the reaction sites on the electrodes can be a limiting factor. This may in some cases result in *transport overvoltages*, which are also called *concentration overvoltages*.
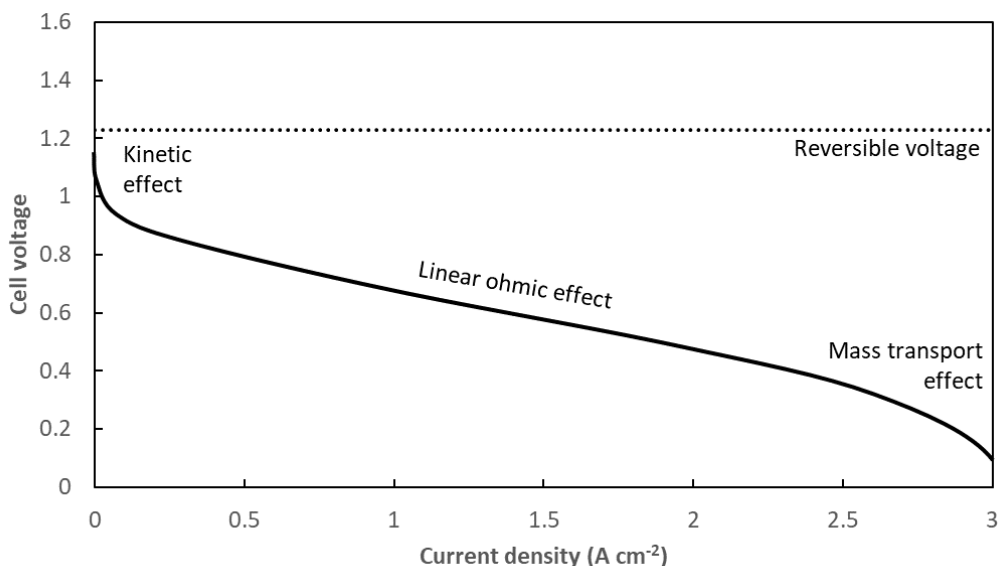

Figure 10. Polarization curve of a typical fuel cell. The dominant origins of the overvoltages (voltage drops) are indicated along the curve.

On Figure 10, the polarization curve begins at zero current density by facing an immediate significant drop. This is due to the electrode processes, mostly that for oxygen reduction and can be labelled a kinetic overvoltage. In the successive linear part, the kinetic drop does not develop further, and the curve is dominated by a purely ohmic development mostly caused by the electrical resistance in the electrolyte. When the curve begins to drop faster than that at high current density, it indicates problems of mass transport, i.e., transport of hydrogen or oxygen to the reaction sites. If this transport cannot keep up with the consumption, the cell voltage cannot be maintained and will drop even more. In the most extreme case (not shown) the cell reaches the so-called limiting current completely controlled by mass transport. The limiting current cannot be exceeded by additional polarization because all reactants are already consumed on arrival and the polarization curve becomes vertical.
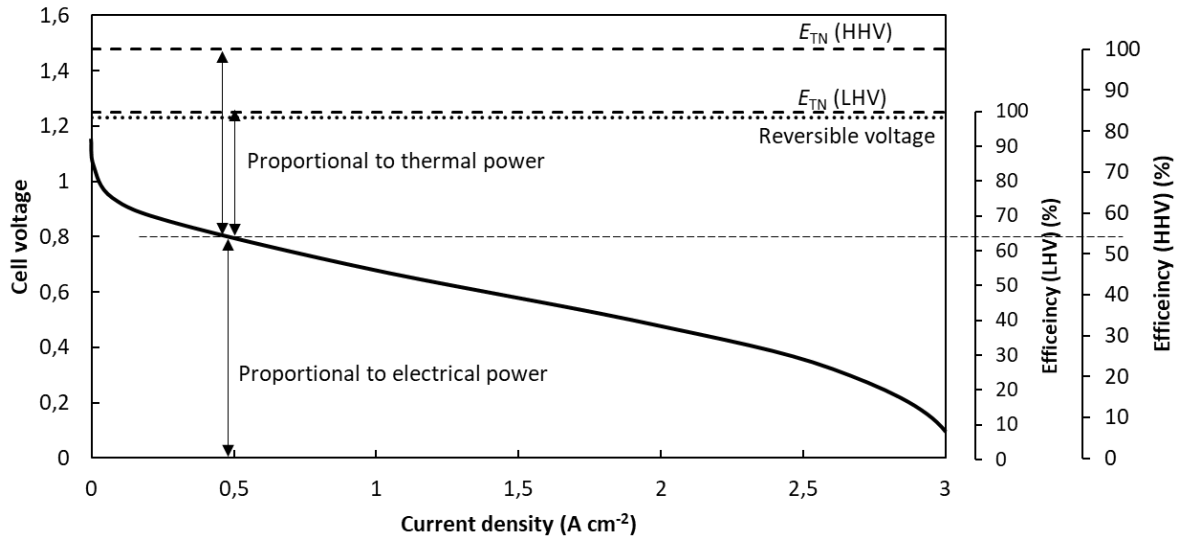

Figure 11. Reading voltage efficiency from a polarization curve.

The polarization curve can be used for a direct visual reading of the voltage efficiency my means of the principle of equation (10). Actually, any energy (ΔH_r, ΔG_r, the electrical energy at a give working point, etc.) corresponds to a voltage in a cell when divided by the charge transferred in the cell, similar to (9).

$$E_{\text{any}} = \frac{|\text{Any energy}|}{nF} \tag{11}$$

In Figure 11, the two thermoneutral voltages are added to the figure at 100 pct. efficiency based on HHV and LHV. The division of the reaction enthalpy between electrical work and heat is clearly seen and the efficiency at any chose working point can be read directly on the efficiency axes to the right. In the chosen example, a cell voltage of 0.8 V corresponds to an efficiency of 54 % (HHV) and 64 % (LHV). Both are correct, just with different reference points. Note also that the efficiency corresponding to the reversible voltage of 1.23 V are 83 % (HHV) and 98 % (LHV), respectively, in agreement with Table 2.

Yet another characteristic of the polarization curve is that the fuel cell is most efficient at low load (low current density). This is opposite to an internal combustion engine, which is most efficient at moderate to high load and extremely inefficient when idling. An implication of this is that the efficiency superiority of a fuel cell vehicle as compared to an internal combustion engine vehicle is more pronounced during city driving than on the highway.

Types of fuel cells

Fuel cells can be constructed in many ways, each with advantages and disadvantages. When treating the electrode reactions above, it already became evident that they depend on which ions are exchanged between the electrodes and thus the electrolyte applied. Moreover, the electrolyte decides the working temperature or temperature. Some volatile components (like water) may limit the upper temperature, while others require high temperature to attain sufficient ionic conductivity (mobility). Therefore, fuel cells are named and classified based on their electrolyte. In Table 4 the most common fuel cell types are listed. Systems working at temperatures up to about 200 ^{o}C are called low temperature fuel cells and above 600 ^{o}C we have the high temperature cells.

Table 4. The main types of fuel cells, their typical working temperature and their electrolyte.

Type	Abbreviation	Temperature	Electrolyte	Charge carrier
Low temperature systems				
Polymer fuel cell	PEMFC (PEFC)	60-80 ^{o}C	Polymer	H^+
Phosphoric acid fuel cell	PAFC	200 ^{o}C	Phosphoric acid	H^+
Alkaline fuel cell	AFC	60-100 ^{o}C	Aqueous Potassium hydroxide	OH^-
High temperature systems				
Solid Oxide fuel cell	SOFC	700-900 ^{o}C	Ceramic oxide	O^{2-}
Molten carbonate fuel cell	MCFC	650 ^{o}C	A molten carbonate mix	CO_3^{2-}

Note: The abbreviation PEMFC stands for "proton exchange membrane fuel cell" or "polymer electrolyte membrane fuel cell". Some sources use PEFC for "polymer electrolyte fuel cell".

The most common fuel cell is the PEMFC and the SOFC is in its early commercialization. PAFC and MCFC were initial stationary demonstrators in the multi-kW range, but their importance is declining. In the following the main fuel cell types are treated individually.

Polymer fuel cell (PEMFC)

The PEMFC is by far the most common fuel cell today. It has high power density exceeding 3 kW L^{-1} for optimized automotive stacks, which makes it the first choice for vehicles. The thin polymeric electrolyte has low ohmic resistance (proportional to thickness) and makes the cell flexible and easy to stack.

The membrane
The proton conducting membrane is an ion-exchange membrane. This means that it can bind and release ions.[4] The ion-exchange capability is bought about by immobilized sulfonic acid ions bonded to the polymer backbone. The backbone is a fully fluorinated (perfluorinated) hydrocarbon string. This is the same chemical structure as for PTFE (polytetrafluoroethylene) also known as Teflon. This backbone is chemically resistant but not conductive at all. The ion conductivity comes with the side chains terminated by a sulfonic acid (-SO$_3$H). See Figure 12. The backbone is hydrophobic (water repelling), and the acid is hydrophilic (water loving). When the membrane is cast, the side chains tend to stick together in some domains that can take up water. Protons cannot jump between the acid groups, since protons don't jump and since all positions are already filled. Conductivity depends strongly on humidification of the membrane. When the membrane takes up water (and swells) it happened in the hydrophilic domains with the side chains. Then the protons of the sulfonic acid, which is a very strong acid, is donated to water molecules[5] and the water molecules transport the proton through the membrane via the wetted domains, either by the *transport mechanism* when the proton "rides on the back" of a water molecule as a hydronium ion, H$_3$O$^+$, or via the *Grotthuss mechanism* where protons are exchanged between water molecules. It is obvious that if the membrane dries out, the conductivity is lost and proper control of the humidity in the cell is crucial (called *water management*). Many different proton conducting membranes are available from different suppliers each with different length and frequency of the side chains. The most common make is Nafion.

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[4] Ion exchange materials are normally used for desalination of water by exchanging metal ions, like Na$^+$ and Mg^{2+} with protons (H$^+$) in one material and negative ions, like Cl$^-$ and CO$_3^{2-}$ with hydroxide (OH$^-$) in another. The exchanged ions form water.
[5] An acid (in the Brøndsted sense) is a molecule (or a similar functionality) that easily donates a proton. A base is then a similar acceptor of a proton. A strong acid binds its proton weekly and is ready to donate it to almost any other molecule.
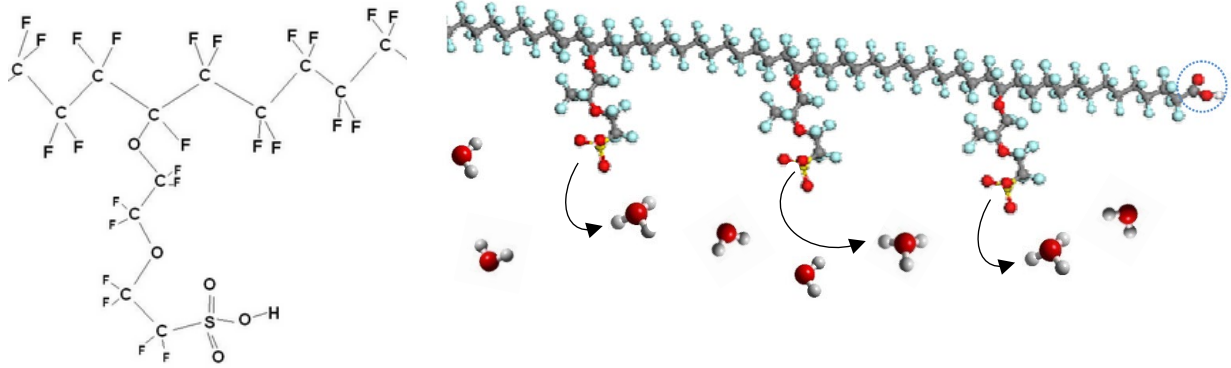
Figure 12. The perfluorosulfonic acid (PFSA) polymer used in PEMFC. Left: the chemical composition. Right: another graphical representation including water molecules. Note that the side chains are not exactly the same in the two figures. The one to the right bears the well-known tradename Nafion.

Electrodes

In PEMFC electrodes, the electrode backing and gas diffusion layers are made from carbon fibres. The catalyst is platinum or platinum alloys for both electrodes. With the high cost of platinum in mind it is important to use as little as possible and since catalysis is a surface process it is only the surface of the platinum that is utilised while the bulk platinum is "dead weight" economically. The optimum solution is to use nanoparticles of a few nm supported on larger carbon particles. See Figure 13.
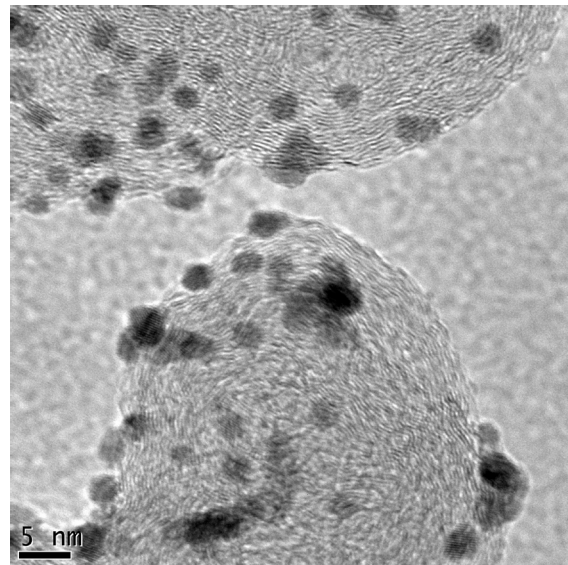

Figure 13. Transmission electron microscope images of platinum nanoparticles on carbon. The dark spots are the platinum particles.

Stacks

PEMFC cells are stacked with either carbon based or metallic bipolar plates. Plates of a carbon composite are shown in Figure 7. The sealing is done with elastomers. Two examples of modern stacks are shown in Figure 14.

The development has been largely driven by automotive use and the sub-zero starting capability was a challenge for a long time but has now been addressed so that fuel cell vehicles can start in cold climates at -20 °C.

Key characteristics of the PEMFC

|	
Cathode:	A carbon fibre based structure
	Platinum nanoparticles on carbon powder
Cathode reaction:	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Anode:	A carbon fibre based structure
	Platinum nanoparticles on carbon powder
Anode reaction	$H_2 \rightarrow 2H^+ + 2e^-$
Electrolyte:	A H^+ conducting polymer. Perfluorosulfonic acid. Commercial membranes: Nafion, Aquivion
Temperature:	60-80 °C
Typical power rating:	From 1W to 200 kW
Applications:	Transport (cars, busses, trucks and forklifts)
	Small stationary (domestic heat and power, auxiliary and backup power)
	Portable (electronics and drones)
Commercialization status:	The most common of the fuel cells.
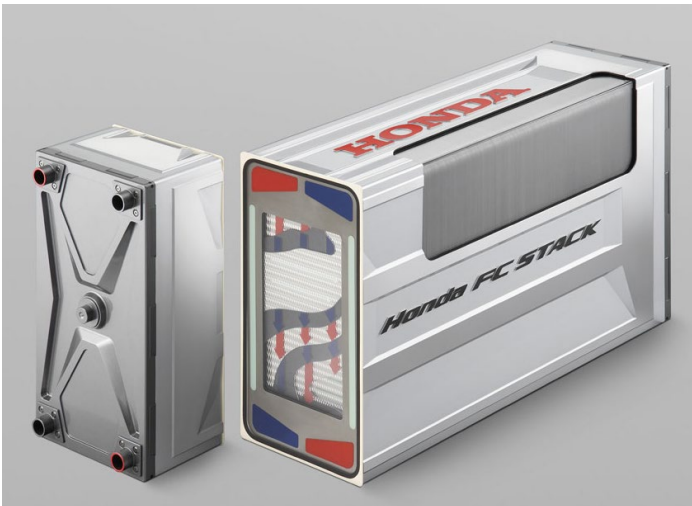
Figure 14. Left: automotive PEMFC stack from Honda. Left small portable stack from Horizon Energy Systems.

Direct methanol fuel cells

A subclass of PEMFC is the direct methanol fuel cell (DMFC). The anodic process is

$$H_3COH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{12}$$

where water needs to be supplied with the methanol to balance oxygen if carbon shall be oxidized all the way to CO_2. The reversible cell voltage is 1.21 V, almost the same as for hydrogen.

The cell is a PEMFC in which the anode catalyst is optimized for conversion of methanol. It is platinum alloyed with ruthenium. Ruthenium is better at binding the oxygen that is needed for forming CO_2 (the Langmuir–Hinshelwood Mechanism)

Another difference is that the DMFC is fed with a liquid solution of methanol in water. With no need for access of gasses, the anode can be completely flooded, and the electrode is made hydrophilic instead of hydrophobic.

The anode process is naturally more complicated than the conversion of pure hydrogen and the overvoltage is significantly larger. Moreover, methanol crossover (passage through the membrane) affects the oxygen process as well and altogether, the DMFC has much lower cell voltage than a hydrogen powered fuel cell. This make it unsuitable for applications where energy efficiency is important (like in vehicles). The advantage is that it does not depend on the availability of hydrogen and that methanol has a higher energy density than hydrogen and is easy to store and fuel. DMFC have been developed for a long time aiming at powering portable electronic devices, but still the market penetration is pending.

High temperature PEMFC

Another sub-class of the PEMFC is the high-temperature PEMFC (HT-PEMFC). This cell is operated at temperatures around 160 °C. The membrane of a normal PEMFC would dry out and malfunction at this temperature, but in the HT-PEMFC water in the membrane is replaced by phosphoric acid, which is much less volatile and a good proton conductor well-known from the phosphoric acid fuel cells. The membrane material is also different to withstand the higher temperature. The polymer polybenzimidazole (PBI, Figure 13) is used doped with a significant amount of phosphoric acid. The electrodes and catalysts are similar to those of the normal low-temperature PEMFC, i.e., made from platinum and carbon.

Figure 15. PBI (Poly (2,2´-*m*-(phenylene)-5,5´-bibenzimidazole), the polymer mostly used in HT-PEMFC after doping with phosphoric acid.
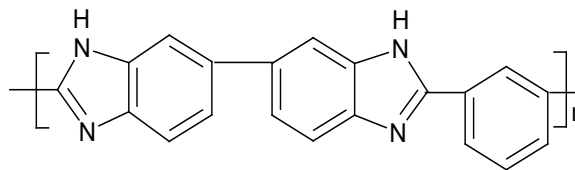
One might expect that a HT-PEMFC outperforms a normal PEMFC due to improved kinetics at the elevated temperature, but instead the cell voltage is somewhat lower. The reason is that phosphoric acid to some extend blocks the platinum catalyst.

The advantage of the HT-EMFC is primarily the higher temperature, which makes integration with a reformer very easy. A reformer converts a carbon containing fuel to hydrogen and CO_2, but due to the chemical equilibria, some CO (carbon monoxide) is always formed too. CO is a strong poison, not only to

humans, but also to a platinum catalyst. And the traces in the reformer gas (perhaps 0.5 %) kills the platinum catalyst. This is mitigated by purification of the reformer gas to levels below 20 ppm. In a chemical plant producing hydrogen this is not a problem, but in small reformer systems like one for use in a vehicle, this is complicated and costly. At 160 $^\circ$C, the poisoning effect is much less and a HT-PEMFC can be operated on reformer gas with 0.5-1 % CO without purification. This makes it possible to run a PEMFC on methanol via reforming with a much higher efficiency than with a DMFC.

Solid Oxide fuel cell (SOFC)

The SOFC is the only system with an oxide ion conductor. It is also the only one with a real solid state ion conductor in the sense of a crystalline solid[6]. The entire cell was initially made from different ceramic materials and formidable challenges in the form of matching thermal expansion coefficients, handling thin layers of brittle materials under compression, and limiting interdiffusion of ions between adjacent materials have all been overcome.

Oxide ion conduction
Oxide ions move through the crystalline metal oxide structure jumping between the positions between the positive metal ions in the lattice. For this to be possible, vacant positions (vacancies) must be available. Vacancies are a kind of lattice defects and are generated by a deliberately induced mismatch between charge balance and a preferred crystal structure. A very stable crystal structure, like the perovskite structure, ABO_3, is used. A and B are metal ions with the charges +2 and +4 respectively (Figure 13). With oxygen as O^{2-}, charge balance is fulfilled (The original mineral perovskite awarding its name to this large group of crystals is $CaTiO_3$ with exactly the charges, +2, +4 and -2, respectively.) Now, if some of the A or B metal ions are replaced with ions of a different charge, and if we assume that the perovskite structure is still formed because of its stability, then charge balance can only be maintained if the number of either metal ions or oxygen ions are correspondingly off with respect to the ideal perovskite structure and vacancies are formed. If the material is short of oxide ions, the formula may be written $A1_{1-x}A2_xB1_{1-y}B2_yO_{3-\varepsilon}$. ε indicate that some oxide ions are missing. A neighbouring oxygen ion can fil the vacancy forming an adjacent vacancy which then again can be filled by a next neighbour. With an electrical field across the material, oxygen will tend to move according to that, and oxygen ions are conducted. The energy needed for the oxygen ion to leave its position in a crystal lattice is high and despite the fact that it is liberated again when the ion settles at its new equivalent position, this *activation energy* must be there to begin with as thermal energy in the lattice (vibrations). This is why SOFC only works at high temperatures. Another benefit of the high temperature is that the kinetics of the electrode reactions become very fast. The kinetic overpotentials are low in an SOFC and thus the conversion efficiency can be high. In brief, the kinetics gain from temperature more than outweighs the poor starting point dictated by thermodynamics (the low free energy at high temperature).

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[6] The polymer electrolyte of the PEMFC is practically regarded a solid but is actually a gel when swollen with water.
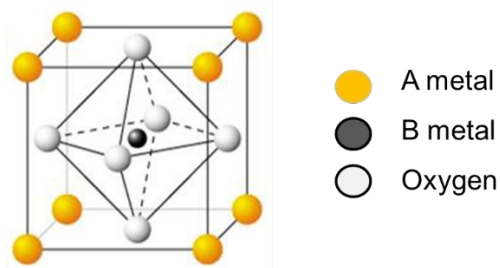
Figure 16. The perovskite structure, ABO_3.

The most common electrolyte in SOFC is yttria stabilised zirconia (YSZ) (yttria is yttrium oxide and zirconia is zirconium oxide). Zirconia, ZrO_2, is not a perovskite, but the principles with oxygen vacancies are the same when part of the Zr^{4+} is replaced by Y^{3+}. The material is called yttria stabilised zirconia because yttrium also stabilizes the desired cubic fluorite structure that is otherwise only stable at higher temperature.

Electrodes
The electrodes gain their ionic conductivity by the same principles as the electrolyte. The cathode is made from a substituted perovskite (e.g., $La_{1-x}Sr_xMnO_3$), which like many perovskites also have high electronic conductivity. It is thus a mixed conductor and cannot be used as electrolyte for that reason. Many perovskites moreover have good catalytic properties, so it possesses all three properties (ionic and electronic conductivity and catalytic activity for oxygen reduction)

The anode is typically made from YSZ which has no electronic conductivity. Electronic conductivity and catalytic activity are provided by a thin layer of nickel. This materials i called a *cermet*, a contraction of the words ceramic and metal.

Electrodes and single cells are made by a sequence of ceramic processing steps in which electrodes and electrolyte are applied layer by layer with intermediate sintering.

Stacks
Stacking is made with ceramic bipolar plates, but if the temperature is low enough, they can be replaced by metallic plates. This adds mechanical stability to the otherwise brittle cell components and makes the stack more compact. Today the cells are stacked as flat plates like the PEMFC, but in the early days a tubular design was developed that made sealing easier. The high temperature excludes polymeric sealing materials. Instead, glass which softens without melting at the working temperature is used.

Today, the SOFC is characterized by high conversion efficiency. The high working temperature sets a lower limit the size of stacks. At the same time, it is still an open question how to scale the cells to sizes suitable for high power applications in a practical way.

An elegant feature of SOFC that should be mentioned is that the cells often work very well in reverse mode, i.e., as electrolyzers. The low kinetic overvoltages make the changes of electrode potentials moderate and this protects the metal oxide from being oxidized or reduced when changing mode. Additionally, and in contrast to low-temperature cells, the electrodes face only gasses. In typical cells with liquid water, the electrodes need to be flooded in electrolysis mode and prevented from flooding in fuel cell mode. This is controlled in fuel cells and electrolyzer by making the electrodes hydrophobic and

hydrophilic, respectively, you cannot do both at the same time. With only a gas phase, this is not an issue.

Key characteristics of the SOFC

Cathode:	A porous ceramic. Made from mixed oxides like $La_{1-x}Sr_xMnO_3$
Cathode reaction:	$O_2 + 2e^- \rightarrow O^{2-}$
Anode:	Yttria stabilized zirconia (YSZ) and nickel
Anode reaction	$O^{2-} + H_2 \rightarrow H_2O + 2e^-$
Electrolyte:	Ceramic electrolyte. Yttria stabilized zirconia (YSZ). An oxide ion conductor.
Temperature:	700-900 ^{o}C
Typical power rating:	1 kW – 1 MW
Applications:	So far stationary application (domestic heat and power, larger power supplies). Larger vehicles and ships are considered
Commercialization status:	Early commercialization. Growing roll-out

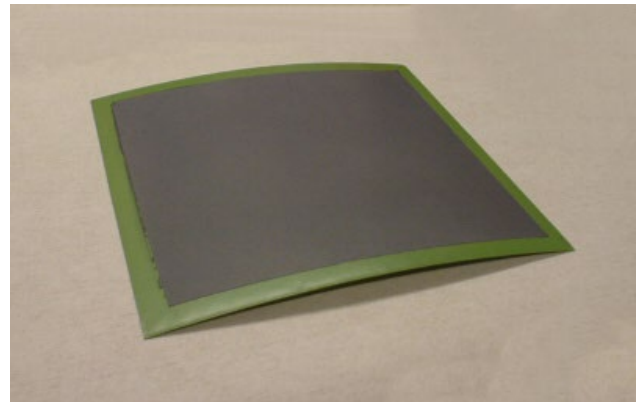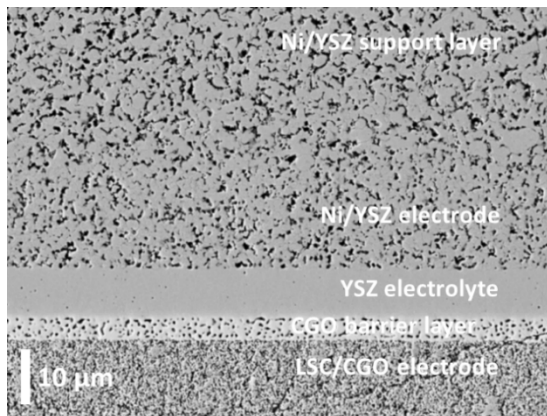*Note. Yttria is yttrium oxide and zirconia is zirconium oxide.*

Figure 17. Left: cross section of an SOFC with the different layers identified. Right: an SOFC single cell. (DTU Energy)

Figure 18. 20 kW SOFC power supply.
(Wärtsila/Haldor Topsoe)

Alkaline fuel cell (AFC)

The alkaline fuel cell was e first useful system. It was developed by Thomas Francis Bacon in the late 50's with a performance of up to 0.5 W cm^{-2}, which is quite decent, even today. The technology was developed further by Pratt & Whitney for the space mission in the 60's. It is actually a system with many advantages. It can work without the use of noble metals and the kinetics of the oxygen reduction process is good in the alkaline environment.

Carbonization
The main reason that it is not more common today is that it cannot tolerate CO_2 from the air. CO_2 is acidic and reacts readily with the hydroxide of the alkaline electrolyte forming bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), which reduces the conductivity of the concentrated KOH (i.e., K^+ and OH^- ions in water). Moreover, the solubility of potassium carbonate ($K_2CO_3^{2-}$) is lower than that of KOH and therefore K_2CO_3 precipitates and fil the pores in the catalyst layer. The reaction are the following

$$CO_2 + OH^- \rightarrow HCO_3^- \qquad\qquad (13)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \qquad\qquad (14)$$

$$2K^+ + CO_3^{2-} \rightarrow K_2CO_3 \text{ (s)} \qquad\qquad (15)$$

As long as the stacks are operated on pure oxygen, as in a spacecraft when there is no point in carrying air with all the useless nitrogen, they work fine. For terrestrial use with air, the air must be scrubbed for CO_2 and this complicates the used and it becomes more obvious to choose the PEMFC.

AFC based on anion-exchange membranes
Recently, as the manufacturing cost of PEMFC has been reduced significantly, platinum is gradually becoming a cost driver. This has spawned a renewed interest in the alkaline system, which works quite well without noble metals. The main showstopper besides the carbonization problem is that a highly conductive and durable membrane similar to the PFSA membrane used in PEMFC has not yet been

developed for the alkaline system. The aim is to have a thin polymeric membrane with immobilized cations (positive ions) like the negative immobilized anions and a PFSA membrane. The immobilized cations will be balanced by OH^- ions and with a fully humidified environment in the membrane, OH^- can be conducted in the wetted domains like H^+ in the wetted domains of a PFSA membrane. Such a membrane is called an anion exchange membrane because it exchanges anions (negative ions like OH^-) and then the proton exchange membrane (PFSA) is a cation exchange membrane. The immobilized ions are typically quaternary ammonium ions, which are quaternarily coordinated nitrogen like the ammonium ion NH_4^+ only with three or more of the H replaced by carbon based moieties. With the immobilized ammonium ion as counter ion to OH^-, there is no need for the K^+ ions that make carbonate precipitate. Some claim that the carbonization problem is less because if this, but formation of carbonates from OH^- and CO^2 can still take place, cf. (13) and (14).

Key characteristics of the AFC

|	
Cathode:	Pt, Ag or metal oxides on Ni or carbon
Cathode reaction:	$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow + 2OH^-$
Anode:	Pt or Ni on Ni or carbon
Anode reaction	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
Electrolyte:	Aqueous KOH (ca. 30 w%) in a porous matrix
Temperature:	60-100 ^oC
Typical power rating:	1 kW to 100 kW
Applications:	Early applications in space. Later used in the space shuttle. Most application on pure oxygen
Commercialization status:	Not very common.
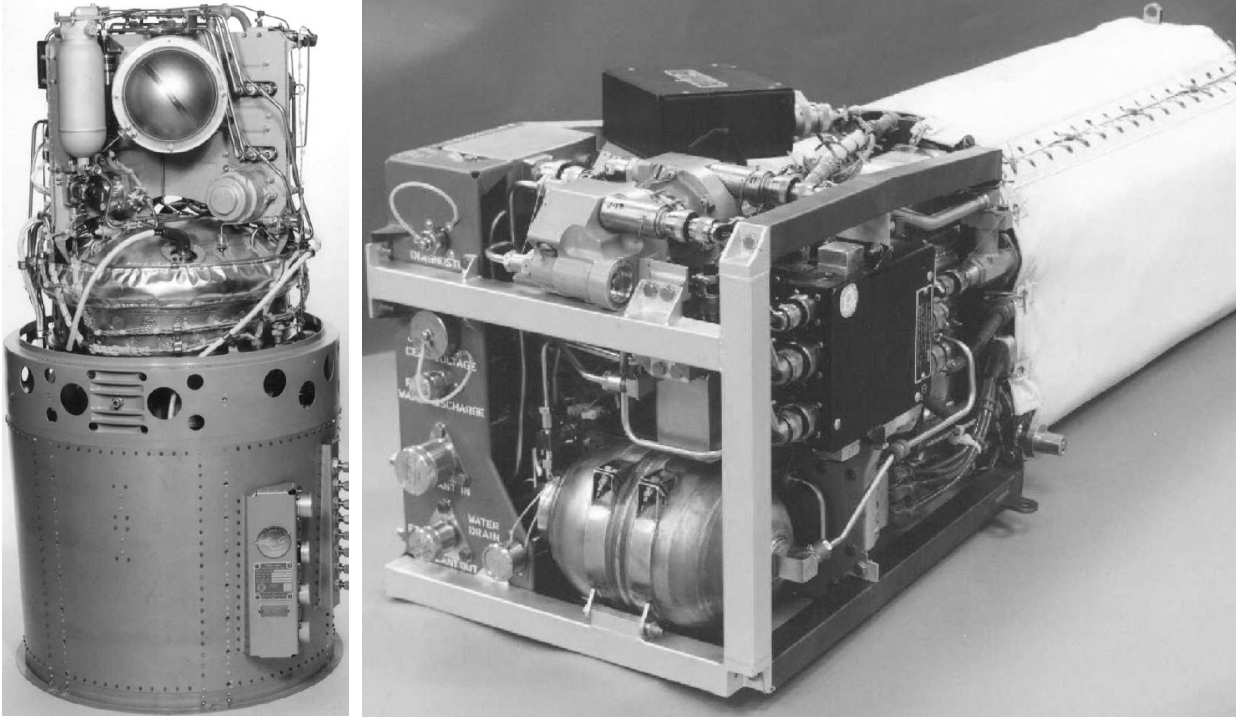
Figure 19. Left: AFC from the Apollo programme. 563 to 1420 W (2300 W peak) (Pratt & Whitney). Right: 12 kW AFC from the space shuttle.

Phosphoric acid fuel cell (PAFC)

The PAFC was the first fuel cell system that was installed around the world. It was developed I the 60's and containerized 200 kW units were installed during the 70's. Later the rated power was increase to 400 kW. The units contained a natural gas reformer to produce the hydrogen for powering the fuel cells. This way, the lack of a hydrogen infrastructure was circumvented. Over 245 units have been delivered worldwide, but today the system is considered less important, partly due to limited conversion efficiency. The catalysts are the same as for PEMFC and the electrodes quite similar.

Key characteristics of the PAFC

Cathode: Carbon fibre based structure
                               Platinum nanoparticles on carbon powder

Cathode reaction: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Anode: Carbon fibre based structure
                               Platinum nanoparticles on carbon powder

Anode reaction $H_2 \rightarrow 2H^+ + 2e^-$

Electrolyte: Pure phosphoric acid (H^+ conducting) contained in a porous matrix of
                               silicon carbide.

24

Temperature: 200 ^{o}C

Typical power rating: 100 to 400 kW

Applications: Stationary heat and power. Fuelled by natural gas via reforming

Commercialization status: First fuel cell to be commercialized during first wave of fuel cell roll-out in the 70's. Still produced. Limited share.

Figure 20. The ONSI PC25 system. 200 kW PAFC with natural gas reformer. For heat and power. (UTC+Toshiba)

Molten carbonate fuel cell (MCFC)

The molten carbonate fuel cell differs from the other cells by the ion conduction concept, which involves CO_2. The ionic transfer is via carbonate ions, CO_3^{2-}. CO_2 is added with the oxygen and carbonate is formed in the cathodic process. The electrolyte is a molten mixture of different carbonates (Li_2CO_3, Na_2CO_3 and K_2CO_3) contained in a porous ceramic matrix.

The MCFC can besides hydrogen convert natural gas, CO and alcohols. It is still produced, but is expected to be replaced by SOFC in the future.

Key characteristics of the MCFC

Cathode: Lithiated NiO

Cathode reaction: $\frac{1}{2}O_2 + 2e^- + CO_2 \rightarrow CO_3^{2-}$

Anode: Ni-Cr or Ni-Al alloy

Anode reaction $\qquad$ $CO_3^{2-} + H_2 \rightarrow H_2O + CO_2 + 2e^-$

Electrolyte: $\qquad$ Molten salt of Li, Na, K carbonate. A CO_3^{2-} conductor.

Temperature: $\qquad$ 650 °C.

Typical power rating: $\qquad$ 1-10 MW

Applications: $\qquad$ Power stations. Only large scale.

Commercialization status: $\qquad$ Several units installed over the years. Decaying importance.
The largest fuel cell plant is a 58.5 MW MCFC plant powering 140,000 households in South Korea (POSCO Energy).

Figure 21. MCFC module. MTU Friedrichshafen