

## 9. Conversion and storage of energy

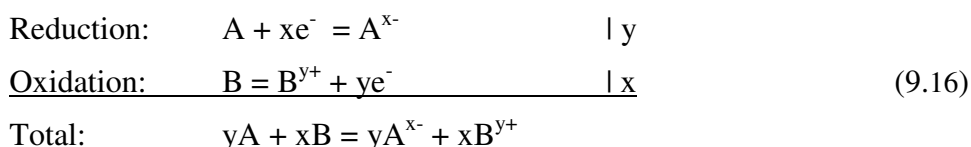
### Electrochemical energy conversion

#### What is electrochemistry?

Electrochemistry deals with the relation between chemical reactions and electrical phenomena – mainly potential and current of electrons. It is important for a large part of the metallurgical industry in which electrical energy is used to produce metals by electrolysis. Moreover, it is important for energy technology and in particular clean, sustainable energy: fuel cells, electrolyzers for hydrogen production, and batteries.

A more precise definition of electrochemistry states that *Electrochemistry is reduction and oxidation processes where reduction and oxidation takes place on different locations*. That means we must have transport of electrons and ions between these locations; in electronically and ionically conducting phases. If these phases are split into separate electronic and ionic pathways we have the possibility to convert chemical energy to electrical and *vice versa*.

In electrochemistry it is, as in red-ox-chemistry in general, useful to write the reduction and oxidation as separate half-cell reactions, like the following general example:

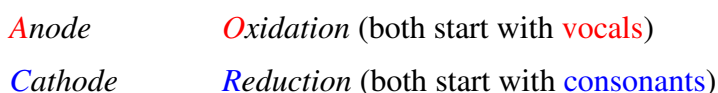


In general electrochemistry, we often represent cells by a diagram of the type



Here the phase borders are marked by single lines, while the double line mark the division between the half cells – by an electrolyte, a salt bridge, or an ion-conducting diaphragma.

The electrode where oxidation takes place is called the anode. The electrode where a reduction takes place is called the cathode:



The definition of anode and cathode is thus in general *not* defined by the sign of the voltage of the electrode, but on whether the process consumes or releases electrons.

Current may pass in the ionic and electronic pathways – driven by electrical or chemical gradients. Michael Faraday managed 200 years ago to find the relation between the magnitude of the current and the amount of chemical entities reacting. He established the constant we today call *Faraday's constant*, namely the amount of charge per mole of electrons:  $F = 96485 \text{ C/mol}$ , where C is the coulomb, the charge carried by one ampere in one second ( $1 \text{ C} = 1 \text{ A}\cdot\text{s}$ ).

A cell driven by a spontaneous electrical total reaction can deliver electrical current – it converts chemical energy to electrical. We call them *galvanic cells*. A cell in which the chemically energetic reactants are installed during manufacture and that are designed for only one discharge cycle are called primary batteries, most often simply batteries. If they can be recharged by reversing the discharge reaction, they are called secondary batteries, or accumulators. If they can accept a continuous supply of chemicals – usually fuel and oxidant such as air – they are called ternary batteries, or fuel cells.

If the cell is reversed by forcing the chemical reaction backwards – producing chemicals of higher energy level - we call it an *electrolytic cell* - we do electrolysis or charging. This is what happens when we charge an accumulator or produce metals from ore or hydrogen from water with electrical energy.

## Cell voltage

In an electrochemical cell we can do electrical work,  $w_{el}$ . It can be shown that *the electrical work we do reversibly on an electrolytic cell is equal to the increase in Gibbs energy of the cell system* (strictly speaking at constant pressure and temperature). Similarly, *the electrical work a galvanic cell does on the surroundings equals the reduction in the cell system's Gibbs energy*. Thus, generally, we have

$$\Delta G = w_{el} \quad (9.18)$$

The electrical work for each electron taking part in the reaction is given by its charge  $e$  times the potential difference between positive and negative electrode, i.e. the cell voltage  $E$ . The electrical work for the reaction is thus obtained by multiplication with the number of electrons. The work for a mole of reactions is similarly obtained by multiplying with Avogadro's number:

$$w_{el} = \Delta G = -neE \quad (\text{for a reaction with } n \text{ electrons}) \quad (9.19)$$

$$w_{el} = \Delta G = -nN_A eE = -nFE \quad (\text{for } n \text{ mole electrons}) \quad (9.20)$$

From this, the cell voltage  $E$  will, like  $-\Delta G$ , express how much the reaction tends to go forward:

$$\Delta G = -nFE \quad \text{or} \quad E = \frac{-\Delta G}{nF} \quad (9.21)$$

The standard Gibbs energy change,  $\Delta G^0$ , corresponding to the change in Gibbs energy when all reactants and products are present in standard state (unit activity) at 1 bar pressure, has a corresponding standard cell voltage  $E^0$ :

$$\Delta G^0 = -nFE^0 \quad (9.22)$$

From the relation between the Gibbs energy change and the reaction quotient  $Q$

$$\Delta G = \Delta G^0 + RT \ln Q \quad (9.23)$$

we can by combination of the above equations obtain

$$E = E^0 - \frac{RT}{nF} \ln Q \quad (9.24)$$

This widely applied and important equation is called the *Nernst-equation*.

Equilibrium means that the Gibbs energy sum of the products and that of the reactants are equal. At equilibrium we thus have  $\Delta G = 0$ , so that also  $E = 0$ :

$$E = E^0 - \frac{RT}{nF} \ln Q_{\text{equilibrium}} = 0 \quad (9.25)$$

i.e.,

$$E^0 = \frac{RT}{nF} \ln Q_{\text{equilibrium}} = \frac{RT}{nF} \ln K \quad (9.26)$$

All in all, we can give the standard data for a reaction in terms of  $\Delta G^0$ ,  $E^0$ , or  $K$ :

$$\Delta G^0 = -nFE^0 = -RT \ln K \quad (9.27)$$

Gibbs energy change for a total reaction is the sum of the change for each half cell reaction:

$$\Delta G_{\text{total}} = y\Delta G_{\text{red}} + x\Delta G_{\text{oks}} \quad (9.28)$$

or, if we use reduction data for both reactions:

$$\Delta G_{\text{total}} = y\Delta G_{\text{red1}} - x\Delta G_{\text{red2}} \quad (9.29)$$

Vi see from this that

$$E_{\text{total}} = \frac{\Delta G_{\text{total}}}{-nF} = \frac{\Delta G_{\text{total}}}{-xyF} = \frac{y(-xFE_{\text{red}}) + x(-yFE_{\text{oks}})}{-xyF} = E_{\text{red}} + E_{\text{oks}} \quad (9.30)$$

or

$$E_{\text{total}} = E_{\text{red1}} - E_{\text{red2}} \quad (9.31)$$

We can measure the total cell voltage over an electrochemical cell. But we cannot measure the voltage of a half cell alone, because we would need two electrodes to do the measurement. The absolute potential of one halfcell van thus not be known, only the difference to other half cells. To obtain a system of relative half cell voltages, we need a reference half cell. The half cell



where we use platinum as inert electrode, is much used as reference in aqueous electrochemistry. It is called the Standard Hydrogen Electrode (SHE) and is defined to have have a half cell voltage of 0 V.

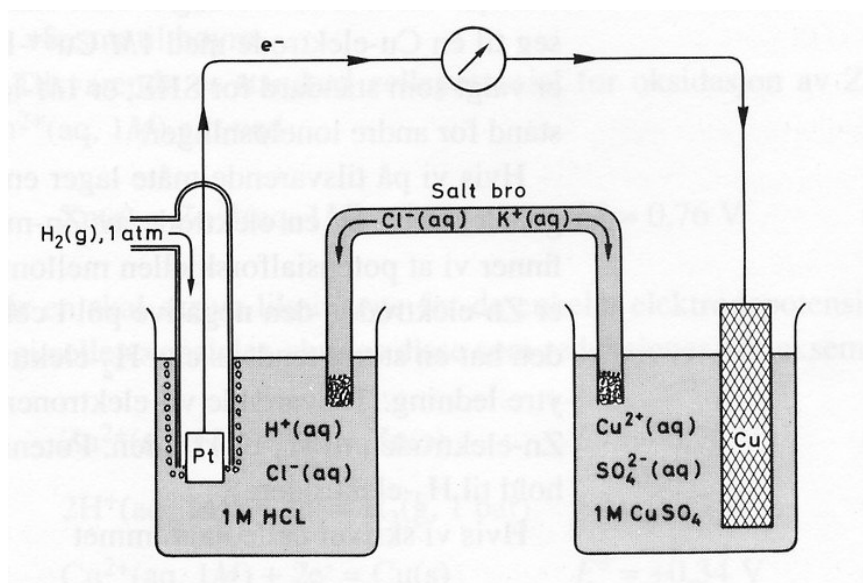


Figure 9-1. Electrochemical cell with standard hydrogen electrode (SHE), salt bridge, and a  $\text{Cu}^{2+}/\text{Cu}$ -electrode at standard conditions.

Other, more practical reference electrodes are also in use in aqueous electrochemistry, such as the standard calomel electrode (SCE).

For non-aqueous, and particularly solid electrolytes, there are no standard electrodes defined. Half-cell electrode potentials are then not used, only full cell potentials.

A total red-ox reaction does not indicate electron transfer, it does not specify the number  $n$  of electrons exchanged and can be done without an electrochemical cell. Nevertheless, we can still represent its thermodynamics by a cell voltage. The relation between Gibbs energy and the cell voltage then requires knowledge of the number of electrons  $n$  transferred in the reaction. As example, the total reaction between  $y\text{A}$  and  $x\text{B}$  above involves  $n = x \cdot y$  electrons.

The reaction between hydrogen and oxygen:



has standard Gibbs energy of  $-228.7 \text{ kJ/mol}$  at ambient temperatures. We can utilise this in a fuel cell, but what is the standard cell voltage? We may assume that the process involves  $\text{O}^{2-}$  or  $\text{H}^+$  as ionic charge carrier in the electrolyte, and thus that we get two electrons ( $n = 2$ ) per reaction unit (i.e. per hydrogen or water molecule):

$$E^0 = \frac{\Delta_r G^0}{-2F} = +1.185 \text{ V} \quad (9.34)$$

It may be useful to note that Gibbs energy is an *extensive* property. If we consider the double of the reaction above,



then Gibbs energy is twice as big;  $2 \times -228.7 = -457.4$  kJ/mol. But the number of electrons is also doubled, so the cell voltage remains constant, it is an *intensive* property:

$$E^0 = \frac{-457400}{-4F} = +1.185 \text{ V} \quad (9.36)$$

It may also be useful to emphasise that an electrochemical cell is not at equilibrium as long as the cell voltage is different from 0. Only at  $E = 0$  is the system at equilibrium and has reached a minimum in Gibbs energy, so that  $\Delta G = 0$ . Only then is the quotient  $Q$  equal to the equilibrium coefficient  $K$  for the overall reaction.

## Fuel cells

A fuel cell is a galvanic cell in which the chemicals (fuel and oxidant) are continuously supplied to the electrodes.

The fuel can be of fossil origin or come from renewable energy. With fossil origin we think primarily of gases produced from natural gas, oil, or coal. They comprise hydrogen, CO, methane or propane, methanol, gasoline or diesel, or mixtures such as syngas or coal gas (both mainly  $\text{H}_2 + \text{CO}$ ). Fuels from renewables comprise primarily hydrogen, but also a number of what we may call hydrogen carriers; methanol, ammonia, etc. Recently, focus has been put on biofuels (alcohols, biodiesel, etc.) from organic harvest of sunlight.

Fuel cells offer potential advantages in efficiency and environment-friendly operation for all types of fuels. The choice of fuel has nevertheless influence on which type of fuel cell it is most reasonable to use.

All fuel cells can use hydrogen as fuel, but hydrogen is not easy to store and transport, and there is thus a desire to use other fuels. As a general rule, the higher the operating temperature of the fuel cell, the better does the cell tolerate variation and non-hydrogen elements of the fuel. CO and many other compounds poison electrodes at low temperatures, so that organic fuels, that often contain traces of CO or form CO as intermediate combustion product, for the most part is excluded from use with low temperature fuel cells. Some poisons such as sulfur affect also high temperature cells, but the critical contents are usually higher the higher the temperature. Direct use of kinetically inert molecules such as  $\text{CH}_4$  can only be imagined in high temperature cells. Water soluble fuels such as methanol can be used below  $100^\circ\text{C}$  because they can then be supplied in an aqueous phase. Fossil fuels, forming the acidic product  $\text{CO}_2$ , can not be used in alkaline fuel cells because  $\text{CO}_2$  will react with the electrolyte. Conversely, ammonia, which is a basic gas, can not be used in phosphoric acid fuel cells or other fuel cells with an acidic electrolyte.

The discovery of the fuel cell has been attributed to Sir William Grove, who filled small containers with hydrogen and oxygen and used sulfuric acid as electrolyte and platinum for electrodes. He described that when he connected several such cells in series the voltage of the end terminals became increasingly painful to touch. He also showed that a number of such cells connected to two electrodes standing in sulfuric acid led to the production of hydrogen and oxygen over those two electrodes (electrolysis)

(see figure below). Grove published his findings in 1839 – thus usually considered the year of the discovery of the fuel cell.

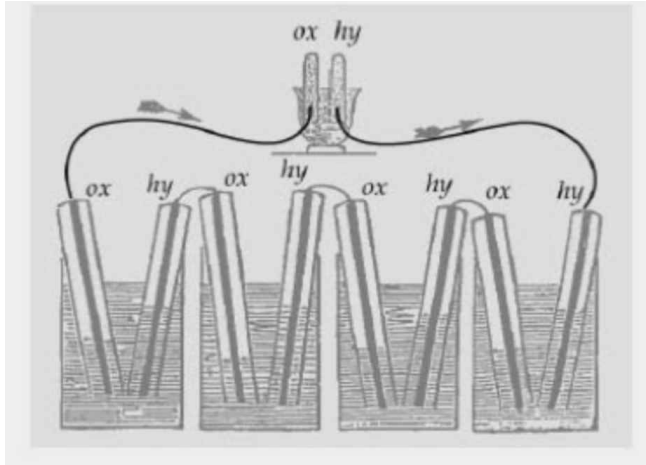


Figure 9-2. Grove's illustration of his fuel cell, consisting of four individual cells in series, and using the electrical power to electrolyse sulfuric acid.

#### *General principle of operation and requirements of materials for fuel cells*

A fuel cell consists of 4 central elements: Electrolyte, anode, cathode, and the interconnect that links stacked cells. In addition one may say that the medium of the fuel and oxidant makes up a fifth element. Each element has individual tasks and requirements.

The electrolyte must be an ionic conductor, being able to transport ions of fuel or oxidant elements to the opposite side. The ionic transport number (fraction of the total conductivity) is considered to have to be 0.99 or more, because any electronic conductivity will cause loss by partial electrical shortcircuit. The electrolyte moreover has to be very redox-stable, i.e. withstand the oxidising conditions of the oxidant as well as the reducing conditions of the fuel. The electrolyte must furthermore not react with the electrodes or have any degree of mutual solubility. If the electrolyte is solid one must furthermore appreciate the chemical potential gradient it faces. This causes the fast ions to migrate, but it also puts a similar force on the stationary ions in the material; if the metal cations of a solid electrolyte have non-negligible mobilities, the whole electrolyte membrane may move. Thus, there is a requirement on small diffusivities for stationary components.

The cathode must be an electronic conductor to transport electrons from the electrochemical reaction site to the current collector. It should also be catalytic to the electron transfer and other reaction steps. The cathode stands in the oxidant and must tolerate oxidising conditions. For this reason, metals except the most noble ones such as Pt, Au, and Ag, are excluded from use here. Instead one tends to use graphite at low temperatures and oxidic materials at higher temperatures. The cathode must not react with the electrolyte or with the interconnect (current collector). Finally, the cathode must be porous so as to allow the fuel medium to reach the reaction site and the products to diffuse away.

The anode must similarly be an electronic conductor, stable under reducing conditions. In addition to noble metals, some additional metals may be stable here, like

Ni and Cu. Like the cathode the anode must not react with the electrolyte and interconnect.

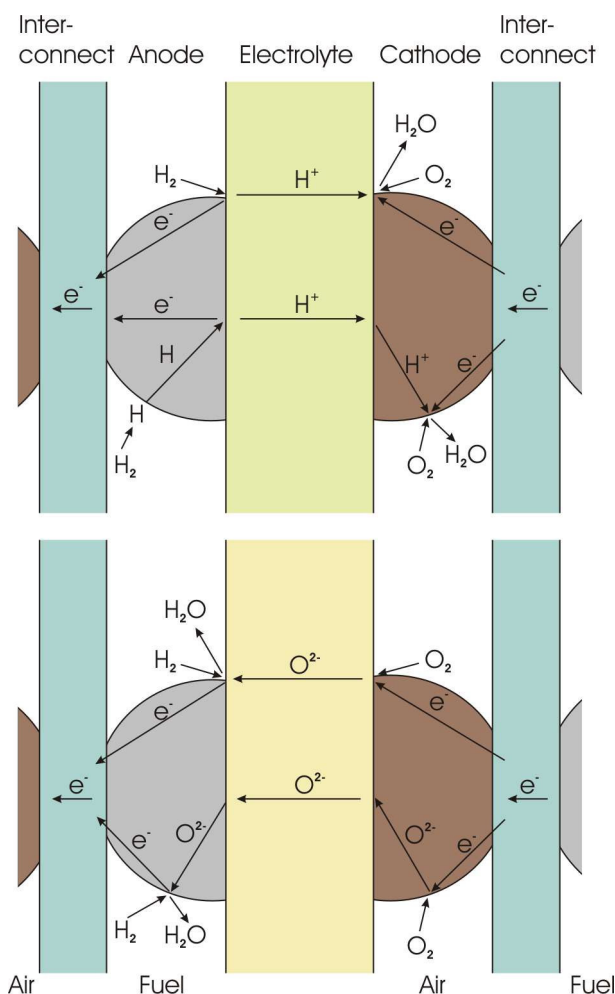


Figure 9-3. General principle of fuel cells with  $H^+$  (upper) or  $O^{2-}$  (lower) conducting solid electrolytes, running  $H_2$  and  $O_2$ (air). For each cell is shown a schematical anode and cathode electrode grain. For each of these the electrode reaction on the top of the grain is the normal three-phase-boundary reaction, while the lower part depicts extended reaction possibilities if the electrode conducts also ions or is permeable to atomic species.

One cell is usually series connected to a next cell in order to increase the overall voltage. The material that makes this connection is called an interconnect or bipolar plate and is thus placed between one cathode and the next anode. It must thus be an electronic conductor, and in this case have no mixed conduction; any transport of ions will lead to chemical short-circuit; loss of fuel by permeation. The interconnect must obviously also not react with either of the electrodes it contacts. Moreover, the interconnect separates the oxidant of one cell from the fuel in the next. This requires that it is redox stable and gas tight (and as said above also diffusion tight).

Especially in ceramic fuel cells, the thermal expansion coefficient must match between the various materials, or else delamination, bending, and cracking may result from startups, shutdowns, thermal cycling, and even load variations. This is hard, because ceramic materials usually have smaller expansion coefficients than metals. In addition to the thermal expansion, many materials also suffer from chemical expansion. One example is the swelling of polymers during water uptake. In ceramic cells, some

materials similarly expand upon stoichiometry changes. Even metals may be affected: A metal serving as interconnect may for instance dissolve hydrogen and carbon at the fuel side, and dissolve oxygen or oxidise at the air side. This may lead to expansion, stresses and bending of the interconnect and eventually cracking of the cells and stack.

*Three-phase boundaries of electrodes and ways to expand them*

Both anode and cathode are in principle rate limited by the length of the three-phase boundary, i.e. the place where electrons, ions, and reacting neutral species in gas or liquid phases can all meet. The width of the reaction zone can be increased by diffusion of adsorbed species on the surface of the electrode or electrolyte, as shown in two of the cases in the figure below.

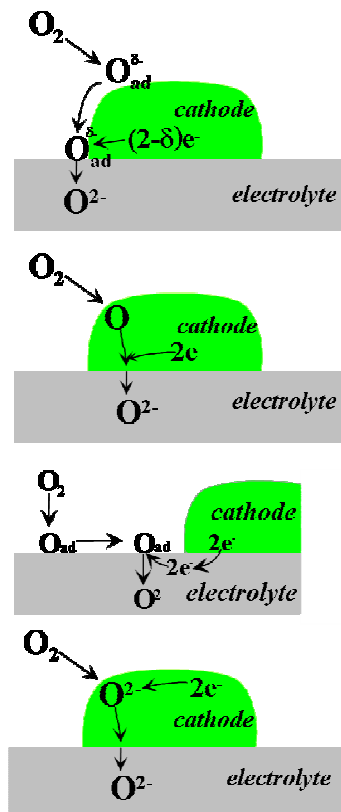


Figure 9-4. Schematic showing four ways of expanding the reaction area from a pure three-phase boundary line in solid oxide fuel cell cathodes: Cathode surface diffusion of adsorbed oxide ions or atoms; cathode volume diffusion of oxygen atoms; electrolyte surface diffusion of oxygen atoms; mixed ionic-electronic conduction in the cathode.

Diffusion of reactant atoms or molecules in the volume of the electrode increases the reaction zone inwards under the electrode. Finally, one may apply electrode materials that are mixed ionic and electronic conductors. The two latter cases are also illustrated in the figure.

From being a one-dimensional three-phase boundary line, these extra transport paths make the reaction zone transform into an area.



### Composite electrodes

In order to increase further the number of reaction sites one usually makes the electrode a porous structure of the electron conductor in which a percolating ionically conducting network is embedded and the fuel or oxidant medium can flow. With liquid electrolytes one lets the electrolyte and reactants penetrate a porous electrode. With solid electrolytes one makes a porous composite of the electron and ion conductors. This composite must have three percolating phases: The pores, the electron conductor and the ion conductor (electrolyte).

In polymer fuel cells these electrodes are called gas diffusion electrodes, made of a porous nanograined carbon-polymer composite.

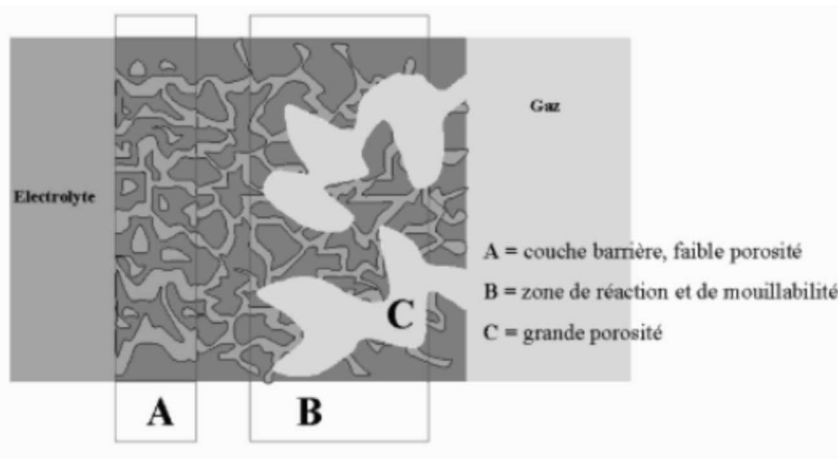


Figure 9-5. Gas diffusion electrode for polymer fuel cells: Electrolyte, finely distributed mixture of electrolyte, electrolyte and carbon+catalyst (A), The gas diffusion layer (B) is a mixture of pores.

In solid oxide fuel cell anodes one uses a cermet – a porous mixture of electrolyte ceramic and Ni metal.

Needless to say, a composite electrode gets even better if one of the two conductors exhibits more or less mixed conduction or volume diffusion of reactants. One may for instance expect that in a Ni anode cermet, hydrogen dissolves in the Ni metal and diffuses to the reaction interphases.

### Overview of fuel cell types

In the sulfuric acid fuel cell the electrolyte – sulfuric acid - works by transporting protons or more precisely  $\text{H}_3\text{O}^+$  ions. The sulfuric acid fuel cell is not pursued today. The figure below shows the main types of fuel cells considered for general energy production, classified according to the type of ionic charge carrier of the electrolyte.

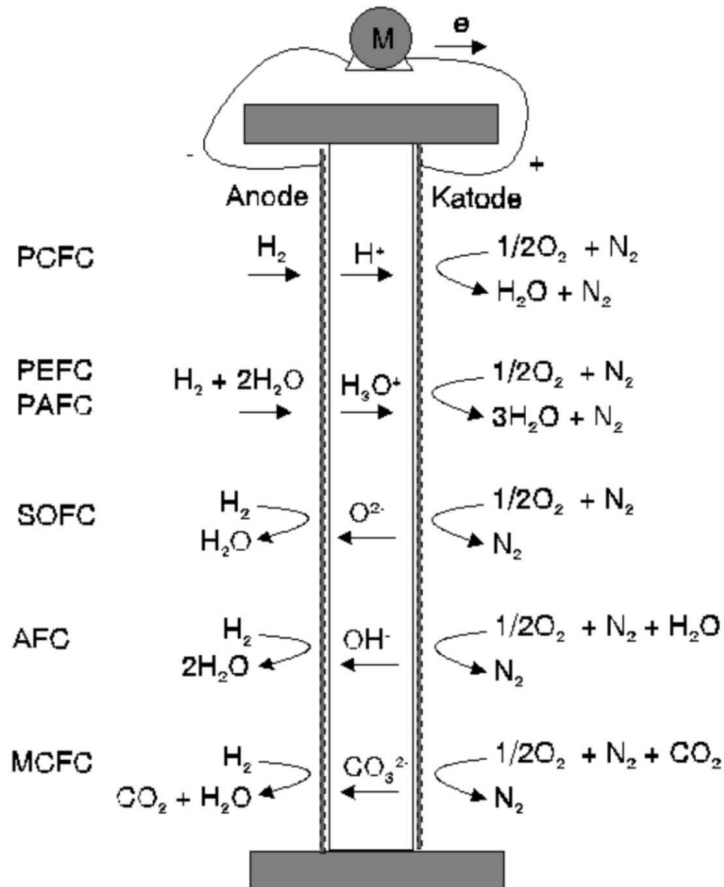


Figure 9-6. Various types of fuel cells, here in use with hydrogen as fuel and air as oxidant. PCFC = Proton Conducting Fuel Cell, PEFC = Polymer Electrolyte Fuel Cell, PAFC = Phosphoric Acid Fuel Cell, SOFC = Solid Oxide Fuel Cell, AFC = Alkaline Fuel Cell, MCFC = Molten Carbonate Fuel Cell.

In the following, we look at the various types in more detail.

#### *Proton conducting fuel cell - PCFC*

A fuel cell with a purely proton conducting electrolyte is the simplest thinkable if we want to combust pure hydrogen, and can thus be our starting point for a tour of the different fuel cell types. Pure proton conductors work at elevated temperatures (e.g.  $\text{CsH}_2\text{PO}_4$  and imidazole based water-free polymers; ca 200 °C) or high temperatures (e.g. Y-doped  $\text{BaCeO}_3$ ; 6-800 °C). The product water will thus be gaseous. The figure below shows how the PCFC is particularly simple since water is formed on the oxidant (cathode) side and no circulation of fuel is required.

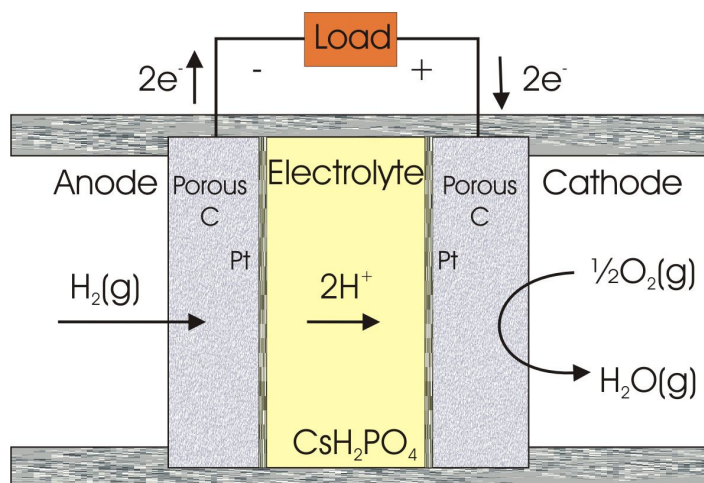


Figure 9-7. Proton conducting fuel cell (PCFC).  $\text{CsH}_2\text{PO}_4$  as example electrolyte; Pt-activated graphite as electrode materials.

PCFC with basic electrolytes like  $\text{BaCeO}_3$  can in principle use also ammonia as fuel. Fossil fuels must be pre-reformed or at least have added water vapour in order to deliver hydrogen to the anode without sooting. PCFCs are not commercialised, but there is an American initiative of developing solid acid fuel cells (SAFC) based on  $\text{CsH}_2\text{PO}_4$ -type materials (<http://www.superprotonic.com/>).

#### *Phosphoric acid fuel cell – PAFC*

The phosphoric acid fuel cell (PAFC) uses concentrated phosphoric acid  $\text{H}_3\text{PO}_4$  as electrolyte. As electrodes are used porous carbon with platinum as catalyst.

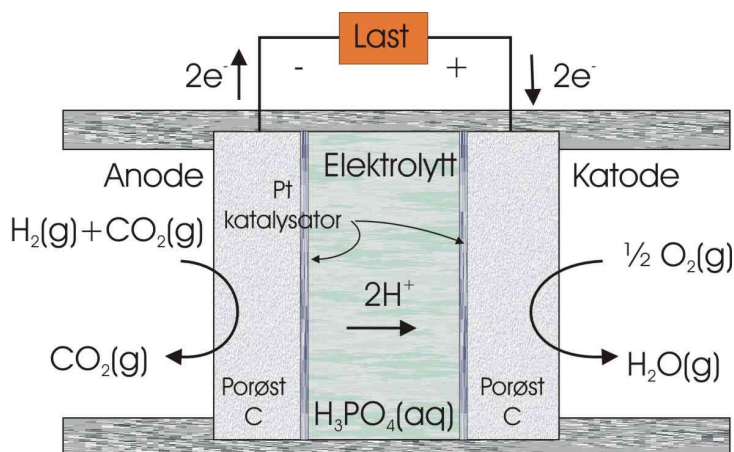


Figure 9-8. Phosphoric acid fuel cell (PAFC), drawn with  $\text{H}^+$  transport for simplicity, but in reality with  $\text{H}_3\text{O}^+$  as the mobile charge carrying ion..

PAFC operates at what we may call intermediate temperatures (160-220 °C). This enables the use of synthesis gas (reformed fossil fuels) as fuel without catalyst poisoning. Moreover, the dissipated heat is valuable for distributed heat.

As in other cells using synthesis gas,  $\text{H}_2$  is the main electroactive reactant while  $\text{CO}$  is oxidised to  $\text{CO}_2$  via the water shift reaction. In contrast to PCFC, the mobile ion in PAFC is  $\text{H}_3\text{O}^+$ .

Some of the world's largest installed fuel cell power plants are of PAFC type, but it is being delivered also for small demo units, including autonomous hydrogen-based energy systems. The technology is in other words proven, but the efficiency considered modest (40-45 %) and problems with corrosion of containers and current collectors to some extent still unresolved.

#### *Polymer electrolyte fuel cell - PEFC*

This type uses the so-called proton-exchange membranes (PEM) like Nafion® as electrolyte and are often abbreviated PEMFC. PEFC is used normally below  $100\text{ }^\circ\text{C}$  (normally  $50\text{--}85\text{ }^\circ\text{C}$ ) and in presence of liquid water. The water makes the polymer swell and form zones with liquid water inside – zones in which protons can move in. As in PAFC the mobile ions are not protons but  $\text{H}_3\text{O}^+$  ions. Each of these in turn drags another 5-6 water molecules. These will partly diffuse backwards in the polymer and partly have to be recirculated externally.

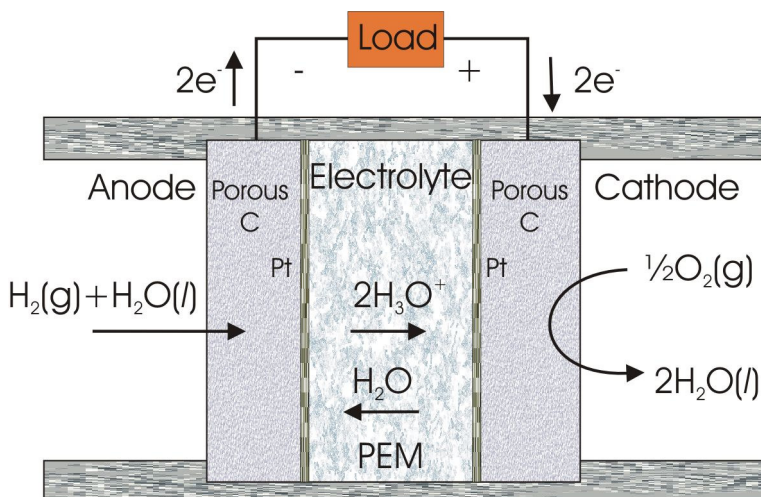


Figure 9-9. Polymer electrolyte fuel cell (PEFC, PEMFC). Each  $\text{H}_3\text{O}^+$  ion drags another 5-6 water molecules.

Also PEFC uses porous carbon as electrodes, with Pt as catalyst. The low temperature makes the catalyst sensitive to  $\text{CO}$  (adsorbs on and blocks the catalyst surface) and  $\text{H}_2\text{S}$  ( $\text{PtS}$  is very stable). The fuel must thus be clean hydrogen, with small tolerances for  $\text{CO}$  and  $\text{H}_2\text{S}$ .

The electrodes make up an interface between "solid" electrolyte and liquid water. The reactants are gases and must also reach this interface. The progress in PEFC development has for a large part reflected mastering of fine porous carbon electrodes, where the electrolyte is infiltrated in the electrode and Pt-catalyst distributed finely as nanoparticles. A number of alloying elements and additional catalysts (e.g.  $\text{RuO}_2$ ) are in use.

The value of the dissipated heat is lower for PEFC than for PAFC since it is difficult to exchange the heat from so low temperatures.

We will use the PEFC for illustrating how cells are stacked in series to obtain higher voltage. The individual cells (membrane-electrode-assemblies, MEAs) are connected together with so-called bipolar plates ("interconnects") that make electrical series contact and keep hydrogen and air separated. They contain grooves to guide the gas flow.

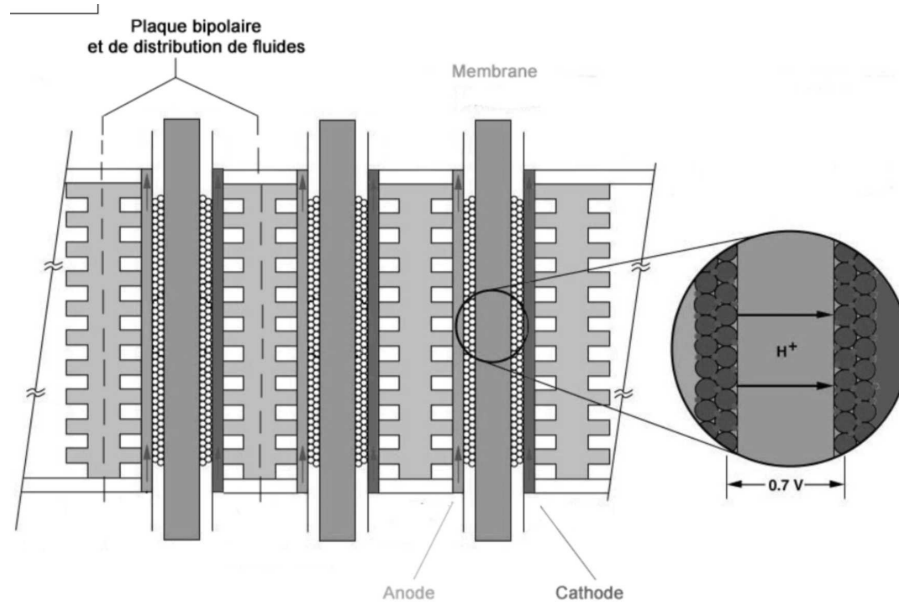


Figure 9-10. Series connection of PEFC elements into a stack. An element consists of one electrolyte membrane with electrodes and half a bipolar plate ("interconnect").

### *Direct methanol fuel cell (DMFC)*

This is a kind of PEFC, but with methanol as fuel. Normally one would think that methanol needs pre-reforming to form  $H_2$ , and that CO must be separated out before poisoning the anode. However, it is possible to send methanol directly to the anode when the anode is prepared for it, e.g. by using ruthenium as catalyst.

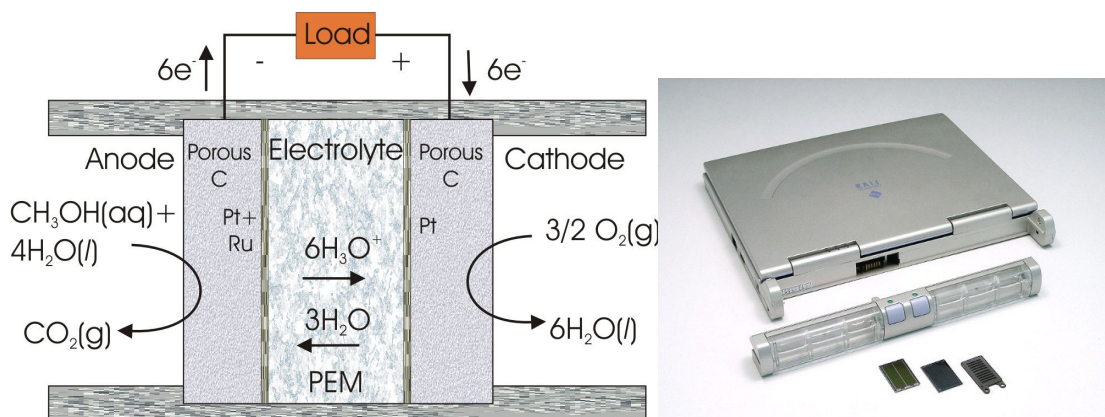


Figure 9-11. Direct-methanol fuel cell (DMFC).

The DMFC electrochemistry is aided by methanol fuel dissolving in the electrolyte. On the other hand, methanol dissolved in the electrolyte may diffuse to the cathode to be combusted there (chemical short circuit). Despite this, the cells are simple and have higher energy density than accumulators.

#### *Alkaline fuel cell (AFC)*

In an alkaline fuel cell, a strong solution of KOH is used as electrolyte, while the electrodes again can be porous carbon with fine spread platinum as catalyst. AFCs operate below the boiling point of water and have thus the same demands for fuel purity to avoid poisoning, as in PEFC systems. carbon-containing (fossil) fuels must be avoided, as  $\text{CO}_2$  in the exhaust will react with the alkaline electrolyte. On the other hand, AFC can be operated with basic fuels like ammonia and hydrazine ( $\text{N}_2\text{H}_4$ ). As for the methanol cell there are advantages and disadvantages of these fuels dissolving in the aqueous electrolyte.

Alkaline fuel cells are among the oldest technologies and have been used for a few decades onboard spacecrafts, where they are essential. They have also been tested in numerous fuel cell cars, e.g. London cabs.

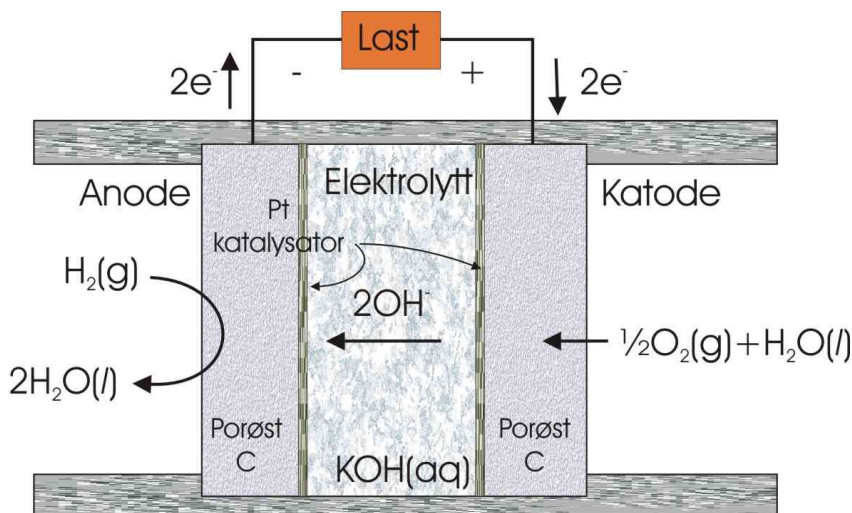


Figure 9-12. Alkaline fuel cell (AFC). The temperature of operation is 60-90 °C.

#### *Molten carbonate fuel cell (MCFC)*

MCFC and SOFC make up the so-called high temperature fuel cell technologies. They are the ones best suited for fossil fuels. MCFC utilises a melt of  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  impregnated in a porous carrier made of lithium aluminate,  $\text{LiAlO}_2$ . The anode is nickel, Ni, while the cathode is Li-doped NiO, which is a good p-type conductor. As the  $\text{CO}_3^{2-}$  ion is the charge carrier in the electrolyte,  $\text{CO}_2$  must be recirculated in the cell, from the anode back to the cathode.

MCFC is well-proven technology, installed in several large plants. However, as for the PAFC systems, the operation and lifetime is troubled by large corrosion problems at the high temperature in and around the very aggressive molten salt melt.



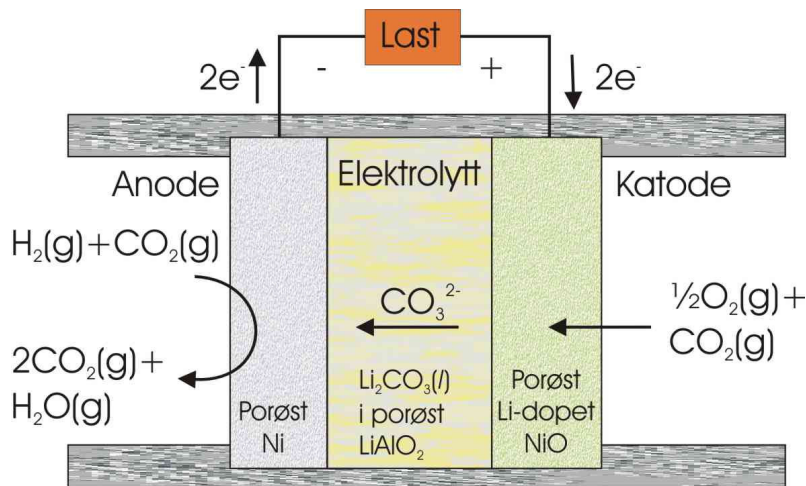


Figure 9-13. Molten carbonate fuel cell (MCFC).

### *Solid oxide fuel cell (SOFC)*

The SOFC technology has for the most part based itself on yttrium stabilised (kubic) zirconia (YSZ) as oxide ion conducting electrolyte. The cathode is typically Sr-doped LaMnO<sub>3</sub> (lanthanum manganite) or similar perovskites. As anode is most often used a cermet of nickel and YSZ. The cells operate typically at 700-1000 °C depending on the thickness of the electrolyte and quality of the electrodes.

The SOFC can, like other fuel cells run pure H<sub>2</sub> as fuel. Compared with the purely proton conducting fuel cell, the SOFC is characterised by forming water at the anode (fuel) side.

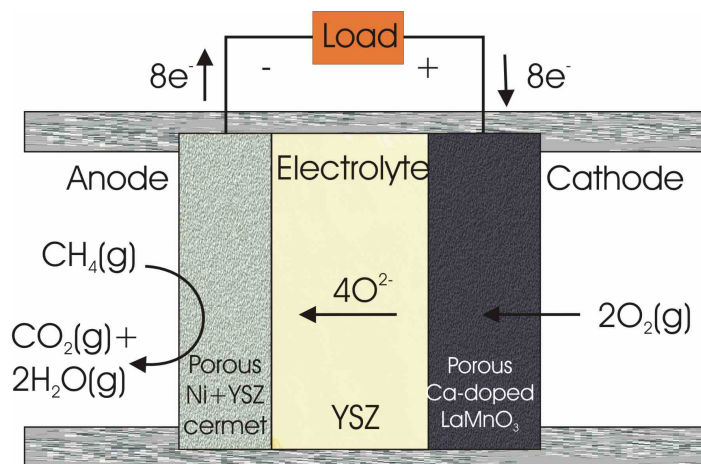


Figure 9-14. SOFC with methane as fuel and internal reforming over the anode.

The figure shows an SOFC that uses CH<sub>4</sub> as fuel: CH<sub>4</sub> reacts (is reformed) with H<sub>2</sub>O over the anode whereby the H<sub>2</sub> is oxidised electrochemically to H<sub>2</sub>O. This is used in its turn to reform more CH<sub>4</sub> and to shift CO to CO<sub>2</sub> + H<sub>2</sub>. In practice we must add H<sub>2</sub>O (steam) to the CH<sub>4</sub> before the cell, because we otherwise get too reducing conditions with too high carbon activities, giving sooting in the fuel inlet.

SOFCs can in principle be used with all kinds of fossil fuels, because the fuel is reformed on its way to and over the anode. In reality we have as mentioned some problems with sooting in the fuel inlets. Moreover, the reforming reaction is endothermic. This may cool the cells anode too much at the inlet and we may get cracks because of the thermal stresses. One may design the cell such that the cooling from the reforming just balances the heating from the ohmic losses, but one usually chooses to do the reforming in a separate reactor *before* the cell.

It has been speculated and tested whether one can oxidise the  $\text{CH}_4$  molecule *directly* on the anode (without reforming). However, such a process from  $\text{CH}_4$  to  $\text{CO}_2 + 2\text{H}_2\text{O}$  is an 8-electron process – a very unlikely pathway. Thus, intermediate reforming and shift by the formed water and subsequent oxidation of  $\text{H}_2$  and possibly  $\text{CO}$  is probably inevitably the reaction path in operation on an SOFC anode.

The materials and ways of assembling them in SOFC concepts are many and challenging. As electrolyte is used Y- or Sc-doped  $\text{ZrO}_2$ , or other oxide ion conductors (based e.g. on  $\text{CeO}_2$  or  $\text{LaGaO}_3$ ). These must be sintered gastight, typically at  $1400^\circ\text{C}$ , and in thin layers as possible.

As anode is used Ni-YSZ-cermet. These are fabricated as a fine grained mixture of NiO and YSZ powders that is sintered onto the YSZ electrolyte at high temperature (typically  $1400^\circ\text{C}$ ). NiO is then reduced to Ni metal under the reducing conditions at the anode, at around  $800^\circ\text{C}$ . Ni is a very good catalyst for reforming of methane and for electrochemical oxidation of hydrogen. Because the Ni metal has higher thermal expansion coefficient than YSZ it is a challenge to fabricate constructions of YSZ+Ni/YSZ that can be cycled in temperature without cracking.

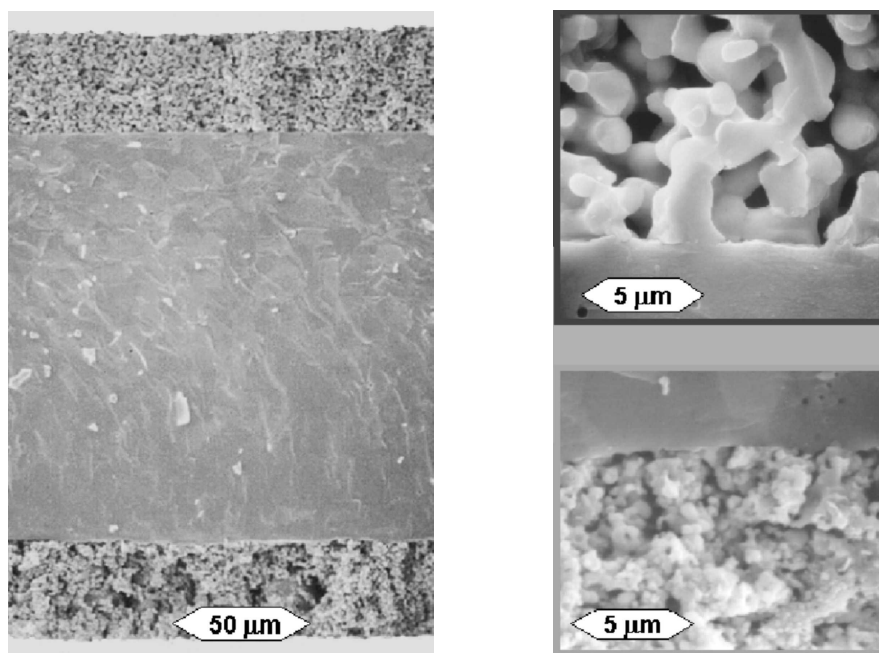


Figure 9-15. Cross section of SOFC single cell with self-supported gastight YSZ electrolyte in the middle, porous  $\text{LaMnO}_3$  based cathode (top) and porous Ni/YSZ cermet anode (bottom). The magnifications to the right show the interfaces between electrolyte and electrodes, the critical place for mechanical strength and adhesion and electrochemical kinetics (E. Ivers-Tiffée *et al.*, Universität Karlsruhe).



As cathode is used  $\text{LaMnO}_3$  and similar perovskites, doped with acceptors to give high electronic p-type conductivity.  $\text{LaMnO}_3$  has a thermal expansion similar to that of YSZ.

SOFC, like other fuel cells, need interconnects to connect single cells in stacks and to separate the gases.  $\text{LaCrO}_3$  doped with an acceptor is a perovskite material with a high electronic (p-type) conductivity from reducing to oxidising conditions and it has TEC similar to that of YSZ. The problems with it is the cost; it is expensive to sinter dense and to machine. It has limited stability and low heat conduction. One thus seeks to develop metallic interconnects for SOFCs: With that one can achieve better electrical and thermal conduction and the materials have in principle easier and cheaper machining. But the metals (except noble metals) that can withstand 800-1000 °C without oxidising – and where the protective oxide layer is conducting – are Cr-rich Fe-Cr-superalloys, that form  $\text{Cr}_2\text{O}_3$  as protective layer. These are expensive and very hard. Moreover, chromium compounds evaporate and deposit on and poison the  $\text{LaMnO}_3$ -cathode. To solve the problem with the hardness one have to form the parts using powder metallurgy. To reduce evaporation one covers them with a a layer of  $\text{LaCrO}_3$ . Today the temperature for SOFC is sought brought down to 600°C. If that succeeds we can imagine using ordinary stainless steel qualities as interconnects. These then have sufficiently low corrosion rates, and are machinable and more affordable in every sense than the superalloys. The desire for lower temperatures (often referred to as intermediate temperature SOFCs) does however put severe demands on the conductivity of electrolytes and the kinetics of electrodes.

SOFC-modules can be built along various design classes. The first with any success was the tubular design, introduced by Westinghouse (now Siemens-Westinghouse). Here, carrier tubes are made of a porous cathode material, closed in one end. Electrolyte is deposited as a thin layer by chemical vapour deposition (CVD), whereafter the anode is sprayed on as a slurry and sintered. A stripe is left without electrolyte and anode and instead covered with an interconnect. The tubes are stacked so that the cathode has contact to the next anode through the interconnect stripe. This makes the series connection that builds voltage. At the same time the tubes are placed in parallel to increase the current, se figure.

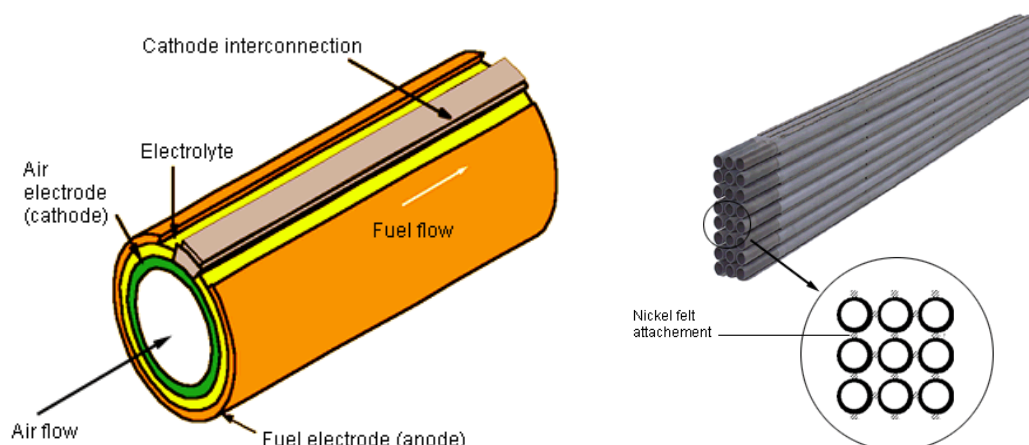


Figure 9-16. The construction of SOFC tube (left) and stacking (right) in series (upwards) and parallel (sideways). From Siemens-Westinghouse.

The figure below shows how a stack like this is operated. Notice how some used fuel is recirculated for use in reforming of new fuel, and how rest air and rest fuel are mixed and burned after the fuel cell to provide heat to preheating of ingoing air and fuel. In the tubular design sealing and manifolding is relatively unproblematic, but the packing density of cells is poor.

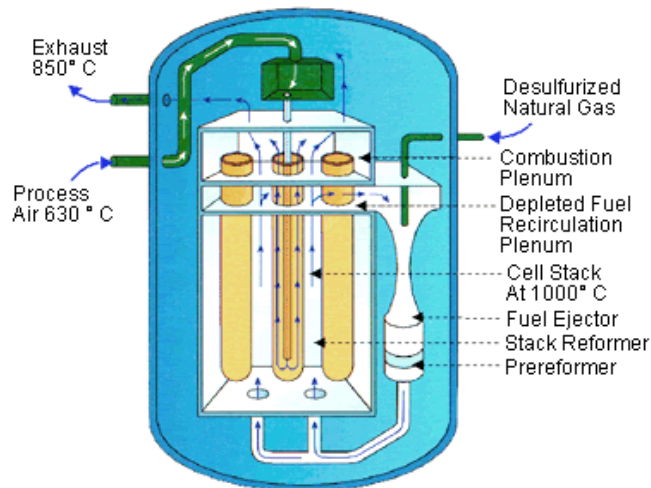


Figure 9-17. Schematic illustration of how a stack of tubular SOFC can be operated. From Siemens-Westinghouse.

In the so-called *planar concept* thin plates of cathode-electrolyte-anode are stacked, connected and separated by bipolar interconnect plates. The packing density becomes very good, while the challenge is the sealing between the layers. The sealing can be for instance glass, glass-ceramic, or a noble metal such as gold or silver.

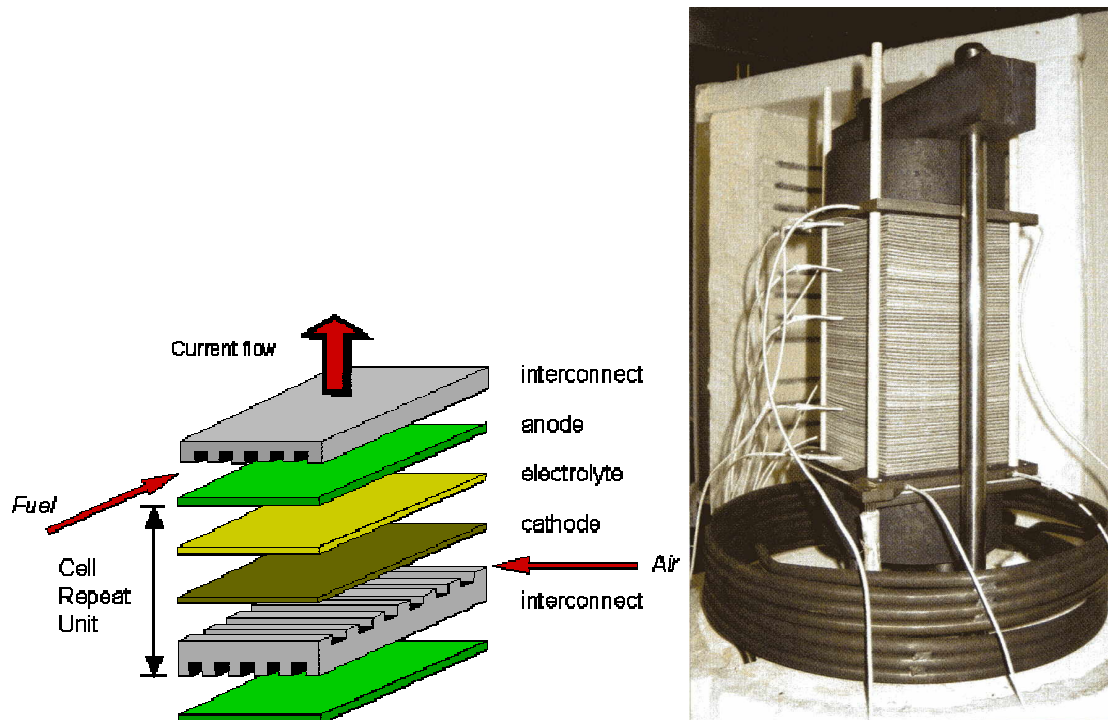


Figure 9-18. Left: Schematic principle of planar SOFC stack. Right: SOFC stack under mounting at Haldor Topsøe AS, Denmark. From S. Harris, *Fuel Cell Review*, 1[1] (2004) 31-32.

Most SOFC development projects today work within planar concepts. Some apply variations over planar and tubular concepts. Siemens-Westinghouse has flattened their tubes so that they can be packed better. Rolls Royce additionally uses short and flat tube segments with bipolar connecting between each segment.



Figure 9-19. Fabrication of Rolls Royce SOFC stacks. From Rolls Royce.

One of the problems with today's SOFC-technology is the use of nickel. If we run the cell too hard and oxidise the fuel too much, Ni oxidises to NiO. Moreover, Ni is a (too) good catalyst for reforming reactions, leading to spot cooling. It is also a good catalyst for carbon deposition (sooting). Therefore we are looking for new anode

materials. Candidates are oxides with high conductivity under reducing conditions, so far with limited success, however.

### *Losses*

There are many sources of loss of energy in the fuel cell process:

The first is the so-called IR-loss, from the current running in the cell, and that is proportional to the resistivity and thickness of the electrolyte. It is inversely proportional to the membrane area.  $U_{IR} = IR$  and  $R = \rho d / A$ .

There may also be ohmic resistances to electronic flow in the electrodes or current collectors, not easily distinguishable from the electrolyte resistance.

Next come the overpotential losses. These arise from the limiting kinetics at the electrodes. They can be represented as electrochemical resistances. They are non-linear except at low currents.

Another source of loss is the change in Nernst voltage that arises from production of products, and thus changing the reaction quotient. This is usually seen as a change in cell voltage (and seemingly a high resistance) at small currents.

Finally, we have the mass transport limitations, that restricts the supply of fuel and oxidant and the transport away of the products. This eventually limits the current of the cell; the limiting current.

### *Potential and current; loss and effect*

There are many ways of displaying the performance of a fuel cell. The most fundamental and scientific is the potential vs current plot. We shall use the plot in the figure below to illustrate this. It shows cell voltage falling with increasing current, from open circuit voltage of close to 1.1 V (the Nernst voltage), to 0 V at the short circuit current close to 450 mA/cm<sup>2</sup>. The slope is given by the total resistance in the cell. The figure shows also the potential drop over the cathode – its overpotential – which increases with increasing current, due to the limiting kinetics for reduction of oxygen gas. Likewise, there is an anode overpotential for hydrogen oxidation. A third loss is the so-called IR-loss given by the resistance to ionic transport in the electrolyte. In the experiment plotted in the figure, the anode overpotential and IR drop were measured together. The two overpotentials and the IR loss come out as heating.

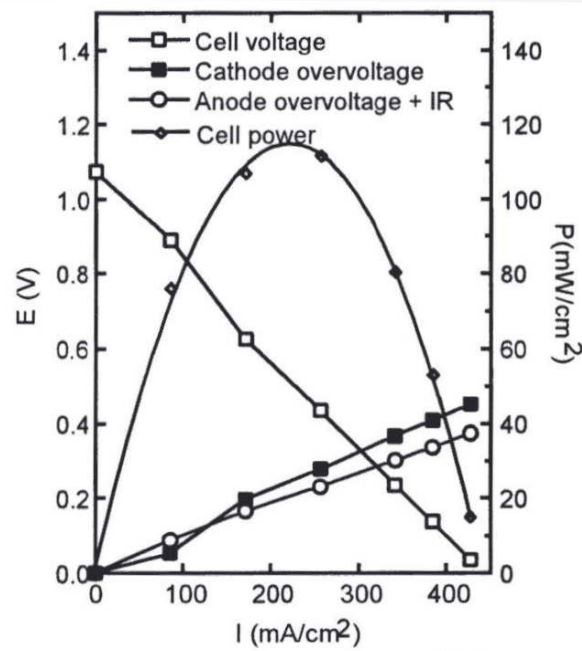


Figure 9-20. Potential (left axis) and power density (right axis) vs current density for a cell with 1 mm thick YSZ electrolyte and Ca-doped  $\text{LaCrO}_3$  as anode and cathode. Fuel:  $\text{H}_2$ , oxidant: air.  $T=1000^\circ\text{C}$ . T. Norby et al., *Proc. 1st European SOFC Forum*, Oct. 1994 (U. Bossel, ed.) (1994) 217-26.

How much effect can we extract from the cell? The effect is given by the cell voltage  $U$  that we can apply to the external load, multiplied with the current:  $P = I \cdot U$ . The plot shows an effect curve (area specific). It starts at zero at zero current. It then rises to a maximum, typically at halved cell voltage. Then it decreases again as the cell voltage approaches zero, at the short circuit current.

When we extract relatively little current, the cell is very efficient; most of the energy is extracted as electrical effect. When we reach the maximum in effect, we lose half the energy as heat. At short circuit, we lose everything as heat. From this it is clear that it is not optimal to run the cell at maximum power; half the energy would be lost. The operation point is a compromise between efficiency and investment in more or bigger cells: Usually one operates around 2/3 of the open circuit voltage, or ca. 0.7 V for a  $\text{H}_2\text{-O}_2$  fuel cell.

#### *Fuel utilisation*

The fuel cell plotted in the figure above can look OK, but the plot itself says less about the overall efficiency than we might have pretended; It does not say what the fuel utilisation is. Often such tests are carried out with a large surplus of fuel, meaning that most of it is wasted. In order to properly characterise a fuel cell, the fuel utilisation  $u_f$  (a unitless ratio) must be specified. The fuel utilisation can in most cases not be drawn towards 1 (= 100 %), because if products dilute the fuel, the cell voltage at the outlet is close to zero, and this dramatically lowers the electrical output. Instead a practical compromise has to be chosen, and the remaining fuel must be burnt in an afterburner. This restriction is not applicable to purely proton conducting fuel cells running on pure hydrogen; here the fuel utilisation can in principle be 100 %.

### Efficiency

The electrical effect  $P_e$  we can get is given by

$$P_e = \eta_G u_f P_{in} \quad (9.37)$$

where  $\eta_G$  is the Nernst efficiency,  $u_f$  is fuel utilisation, and  $P_{in}$  is the effect in the fuel and oxidant that we supply (energy per time unit).

The Nernst efficiency is electrical energy delivered by the cell divided by consumed chemical energy. The chemical energy is close to equal to the enthalpy (heat value) that the reactants would have delivered if they reacted with each other in a simple combustion process. The electrical energy is on the other hand equal to the electrical work that the cell does on the surroundings, in turn equal to the Gibbs energy change for the process. Dependent on the entropy change, the Gibbs change can be larger or smaller than the enthalpy change and the Nernst efficiency thus smaller or bigger than 100 %.

The overall efficiency for the cell is  $P_e/P_{in} = \eta_G u_f$ . This is the number that should be referenced and that typically ends up around 50 % - because of electrical loss as heat and because of finite fuel utilisation. When fuel cells offer superior efficiency it is usually after taking the heat value also into account, and using afterburners or a gas turbine + generator running on the rest fuel. The heat can be utilised in remote heat systems, in steam turbines, etc.

The figure below estimates and compares the overall electrical efficiency of various power technologies.

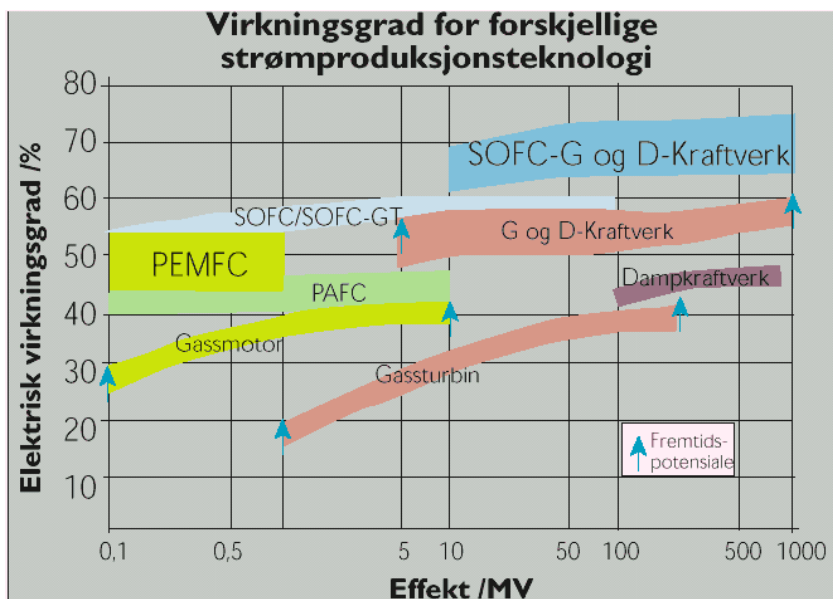


Figure 9-21. Estimate of overall electrical efficiency ( $P_e/P_{in}$ ) for various power technologies as a function of produced effect. From Bellona.

For use of pure hydrogen as fuel, the fuel cells are clearly competitive (gas turbines and engines do not tolerate well pure hydrogen) so that fuel cell cars will probably eventually become dominating. But for the fossil and biological fuels the fuel cells so far has difficulty to compete with engines for large scale as well as mobile power. Also rechargeable batteries is a hard competitor for mobile applications. Fuel

cells have their potential in the near future perhaps mostly for auxiliary power units (APUs) and small distributed power applications.

### *From DC to AC*

Fuel cells produce direct current (DC). In many applications – such as load by AC motors in electrical vehicles or application to a distributed AC electricity grid, it needs to be converted to alternating current (AC). This is done by so-called inverters. This is power electronics that alternatingly reverses the current and smooths it into a sine curve. If applied to a grid it needs to be synchronised with the grid before application to it.