Discover the energy of hydrogen

Grzegorz Karwasz

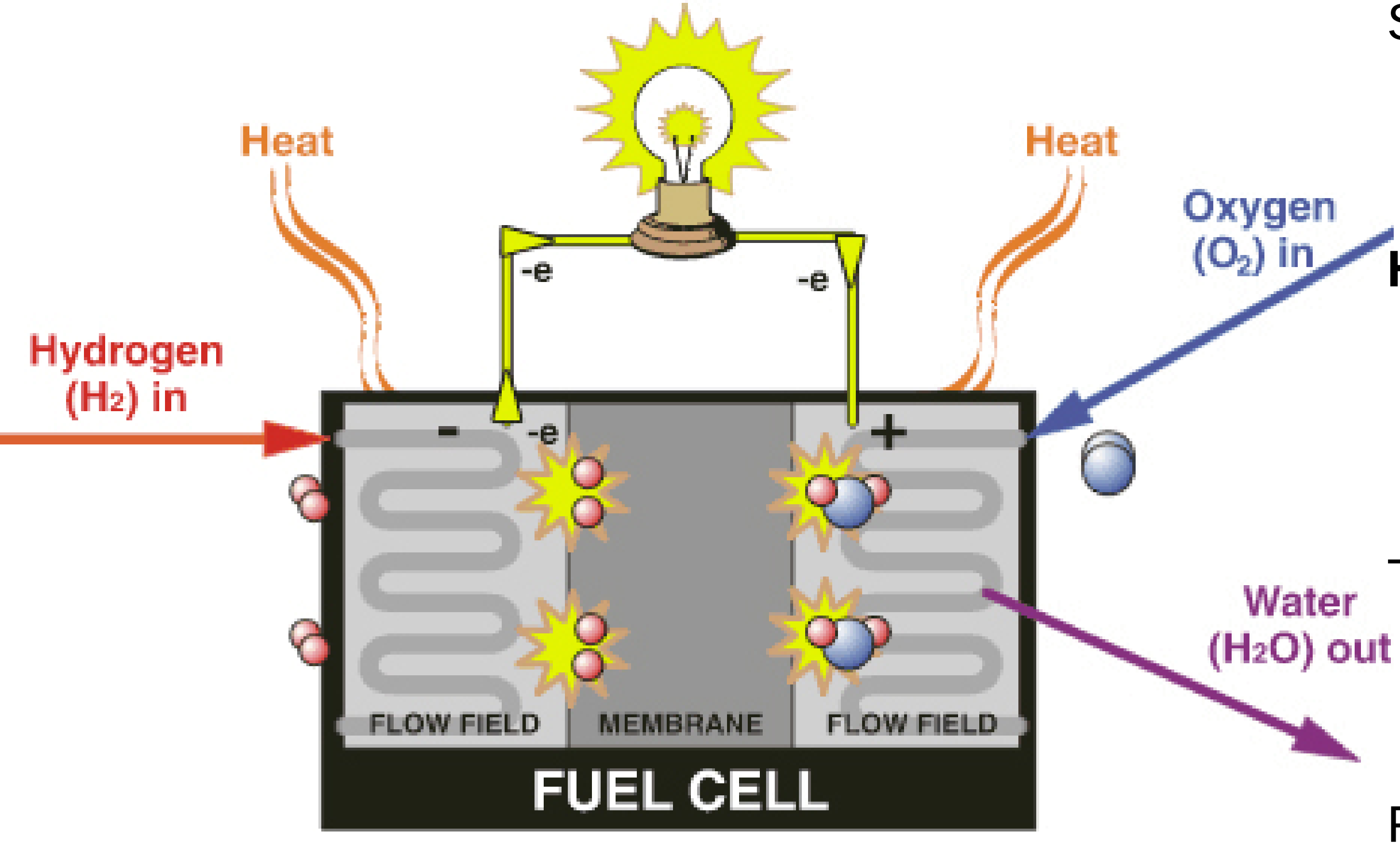
Kamil Fedus

University Nicolaus Copernicus

Didactical material: Secondary School

Part IV: Hydrogen fuel cells

Hydrogen fuel cell



Shortly, a fuel cell is Volta's pile, in which instead of two metals (like Zn and Cu), gaseous elements are used (hydrogen and oxygen, for example).

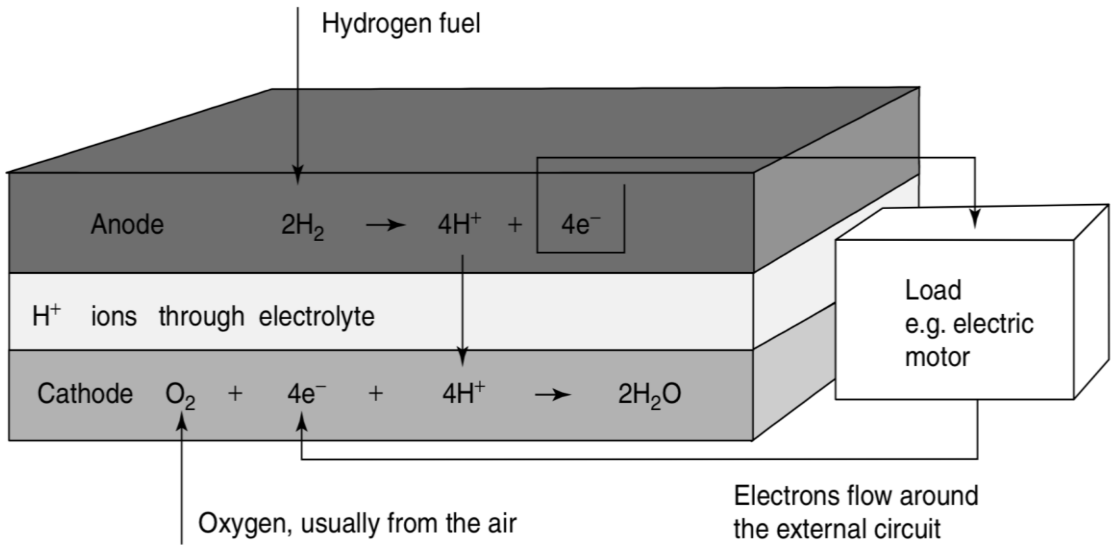
Hydrogen fuel cell can be considered as *inverting* the electrolysis: in electrolysis we supply the current and produce two gases, in fuel cell oxygen and hydrogen combine, **giving the electrical current**.

The main advantage of fuel cells is their high efficiency: as far as direct burning hydrogen (in oxygen) would give the efficiency of some 30%, **fuel cells can arrive to 80%.**

Finally, the process is **clean and quite**: water is the only by-product.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen fuel cells – definition and basic principles



J. Larminie, A . Dicks, *Fuel Cell Systems Explained*, John Wiley & Sons (2000)

A fuel cell by definition is an electrical cell, which unlike storage cells can be continuously fed with a fuel so that the electrical power output is sustained indefinitely.

Fuel cell converts hydrogen, or hydrogen-containing fuels, directly into electrical energy plus heat through the electrochemical reaction of hydrogen and oxygen into water. The process is that of electrolysis in reverse:

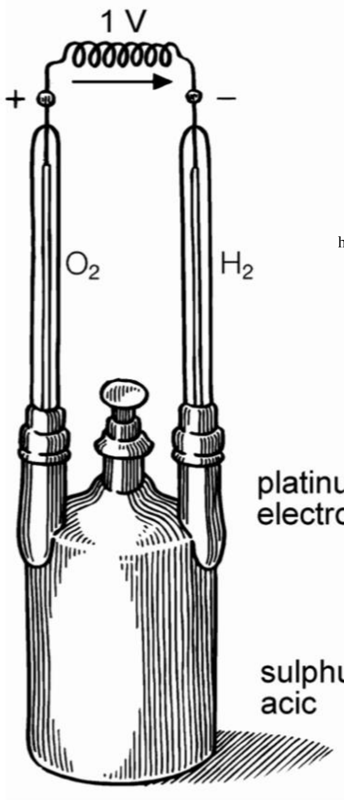
$$2\ H_{2(gas)} + O_{2(gas)} \square\ 2\ H_2O + energy$$

Because hydrogen and oxygen gases are electro-chemically converted into water, fuel cells have many advantages over heat engines. These include: high efficiency, virtually silent operation and, if hydrogen is the fuel, there are no pollutant emissions. If the hydrogen is produced from renewable energy sources, then the electrical power produced can be truly sustainable.

B. Cook, *An Introduction to Fuel Cells and Hydrogen Technology*, Engineering Science and Education Journal 11 (6): 205 - 216 · (2003)

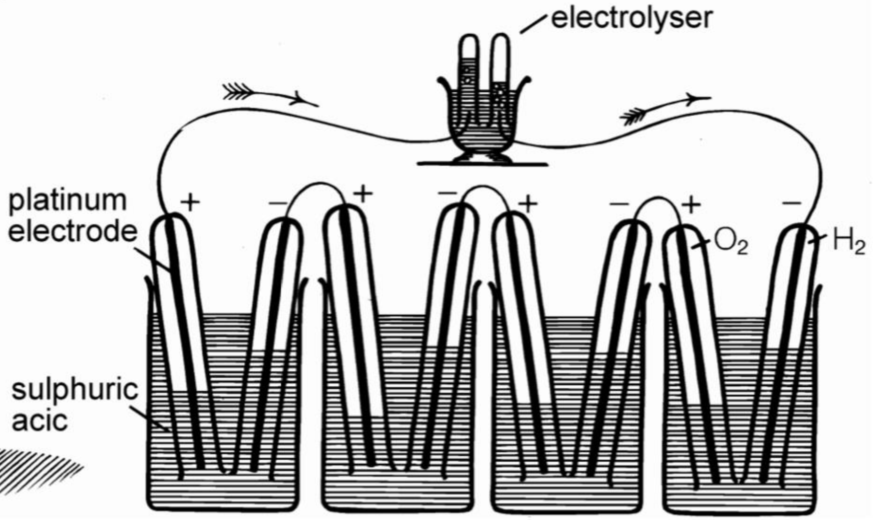
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

„Gas battery“ – the first fuel cell



Sir William Grove

https://pl.wikipedia.org/wiki/William_Grove#/media/Plik:William_Robert_Grove.jpg



Grove’s ‘gas battery’ (1839) produced a voltage of about 1 volt, shown left. Grove’s ‘gas chain’ powering an electrolyzer (1842), shown right.

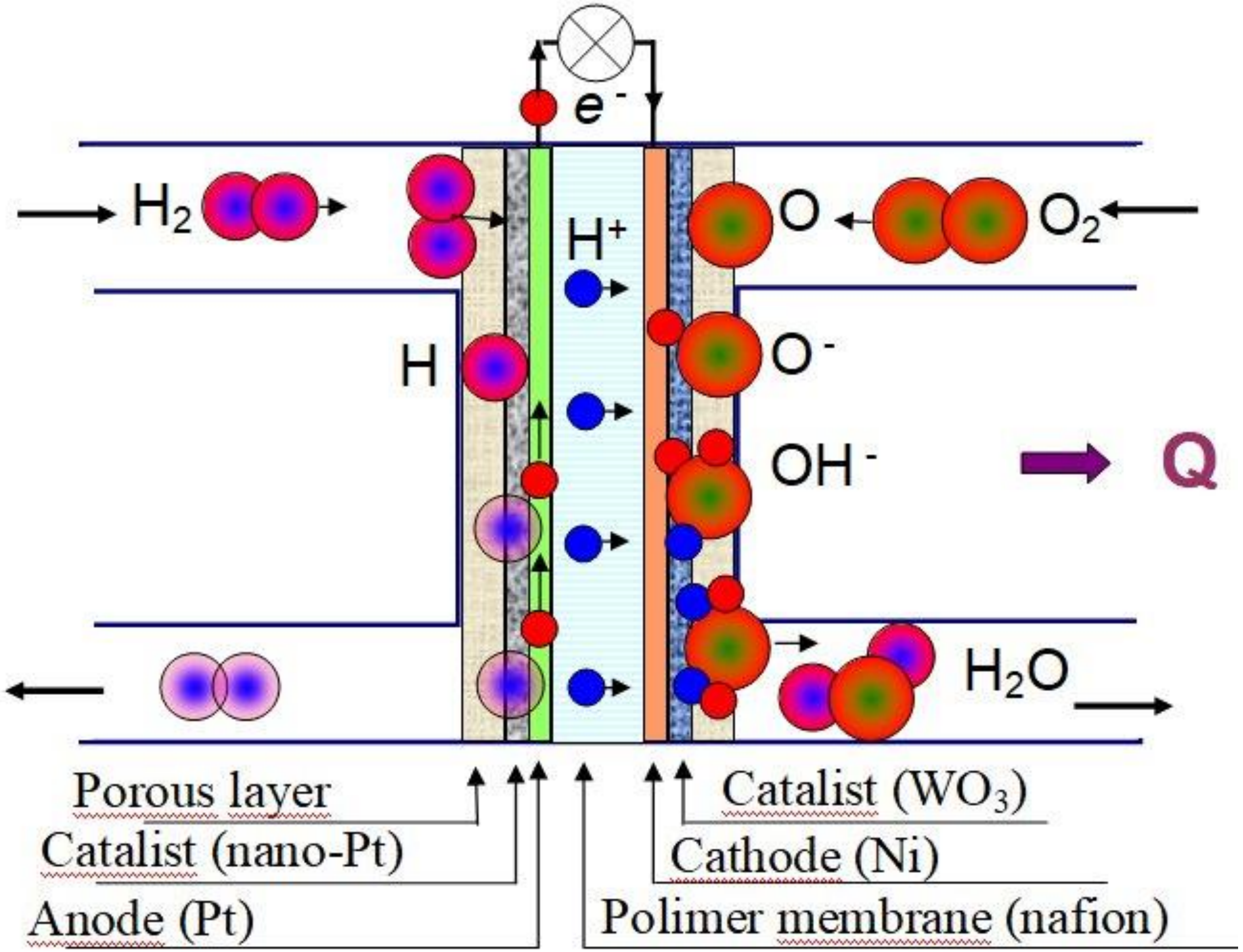
Sir William Grove (1811-96), a British lawyer (and amateur scientist) developed a first fuel cell in 1839. The principle was discovered by accident during an electrolysis experiment. When Grove disconnected the battery from the electrolyzer and connected the two electrodes together, he observed a current flowing in the opposite direction, consuming the gases of hydrogen and oxygen. His gas battery consisted of platinum electrodes placed in test tubes of hydrogen and oxygen, immersed in a bath of dilute sulphuric acid. It generated voltages of about one volt.

In 1842 Grove connected a number of gas batteries in series to form a ‘gas chain’. He used the electricity produced from the gas chain to power an electrolyzer, splitting water into H and O. However, due to problems of corrosion of the electrodes and instability of the materials, Grove’s cell was not practical. As a result, there was little research and further development of fuel cells for many years to follow until the mid-twentieth century.

B. Cook, *An Introduction to Fuel Cells and Hydrogen Technology*, Engineering Science and Education Journal 11 (6): 205 - 216 · (2003)

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union’s Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen fuel cell - scheme



By bleached symbols we show „ghosts” of H_2 molecules: H_2 disappeared, disintegrating into protons and electrons

Similarly to the practical implementations of PV cells, also the construction of the hydrogen fuel cell is multi-layer, and quite complex.

Several processes must be accomplished:

1. Hydrogen and oxygen must diffuse towards electrodes (must be captured by some porous layer)
2. Hydrogen and oxygen must dissociate into atoms, a process that requires in gas phase quite a bit of energy; in fuel cell this process must catalyzed
3. Protons (H^+) from hydrogen must be captured by the membrane (nafion) and be transported towards cathode; such a ionization $H \rightarrow H^+ + e^-$ in gas phase again would require energy
4. Electrons, left after ionization of H, must be transported (in a metal layer) to the external electrical circuit.
5. On oxygen side, similar processes must occur.

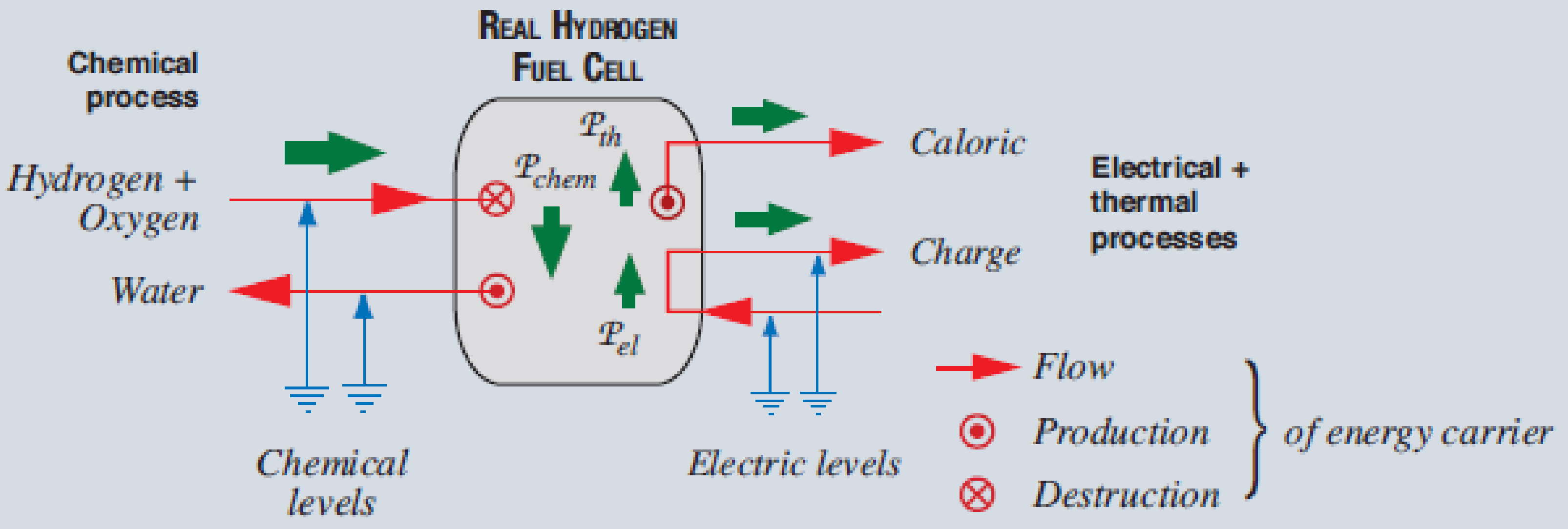
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen fuel cell: energetics

FCHgo! Discover the energy of hydrogen

T Real hydrogen fuel cells

A real (hydrogen) fuel cell is fed with hydrogen and oxygen. Their reaction drives an electric and a thermal process in parallel.



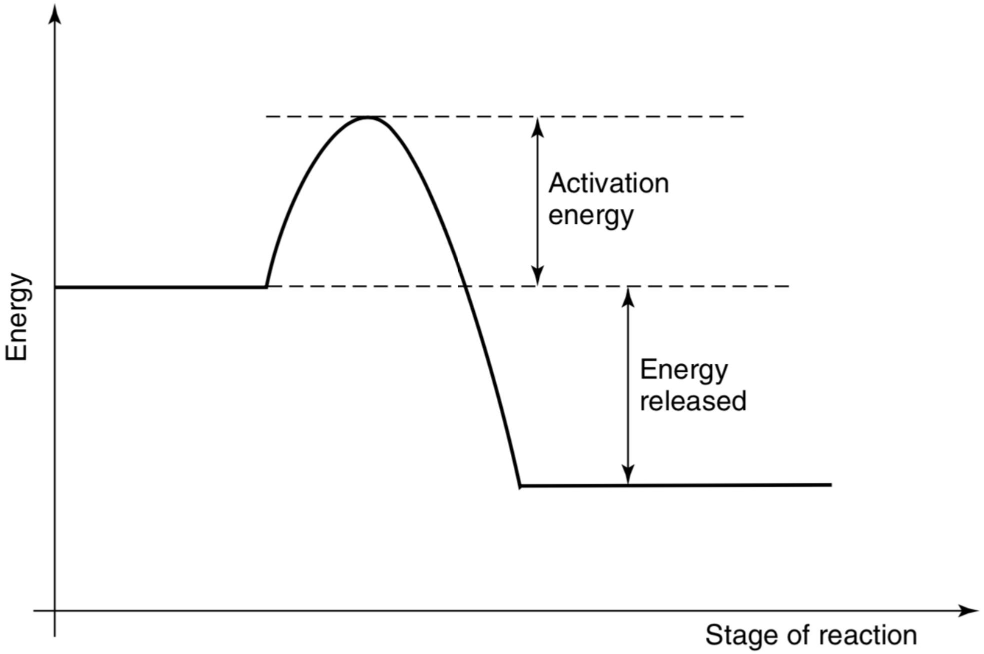
Formation of H_2O from H_2 and O_2 in gas phase is endothermic, i.e. produces the heat. It is similar in the fuel cell, even if the overall efficiency is higher (80%), i.e. the amount of heat produced is smaller.

The diagram here show the clue of the FC process: the chemical energy transforms into the electric current (flow of the electrical charge) and the outflow of heat

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen fuel cells in details

What limits the current?



The difference between the peak of activation energy and the reaction end-point explains also the heat produced in fuel cells: the electrical potential comes from the difference between the entrance and exit levels and the surplus gives the heat.

At the anode, hydrogen reacts, releasing energy. However, just because energy is released, it does not mean that the reaction proceeds at an unlimited rate. To initiate reactions, the 'activation energy' must be supplied to get over the 'energy hill'. If the probability of a molecule having enough energy is low, then the reaction will only proceed slowly. Except at very high temperatures, this is indeed the case for fuel cell reactions.

The three main ways of dealing with the slow reaction rates are

- the use of catalysts,
- raising the temperature,
- increasing the electrode area.

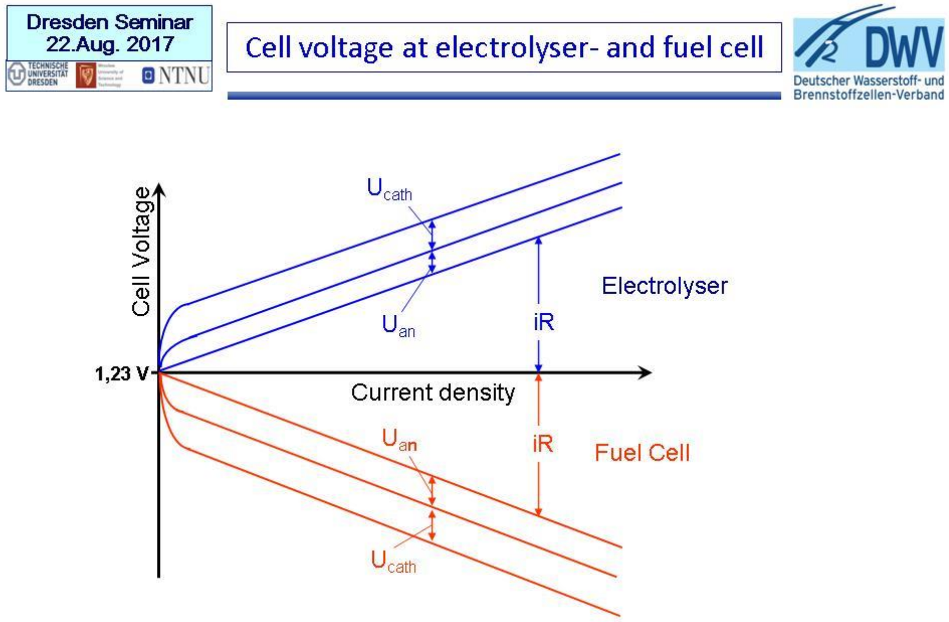
The first two can be applied to any chemical reaction. However, the third is special to fuel cells and is very important.

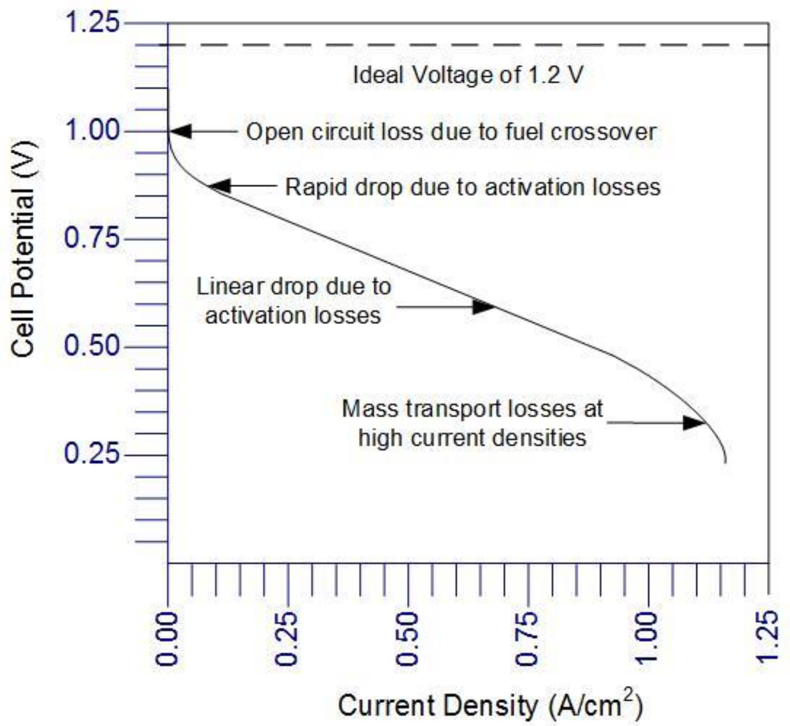
J. Larminie, A . Dicks, *Fuel Cell Systems Explained*, John Wiley & Sons (2000)

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen fuel cells in details

What limits the voltage?





The electrical power from the FC is limited not only by its construction but also by the very the basis of physical and chemical processes. As in electrolysis the theoretical potential needed is 1.23 V but in practice a fraction of volt more is required [see experiment], the same in fuel cells: the voltage obtained is never higher than 1.0 V [see experiment]. This is some analogy to the bias voltage in PV cells.

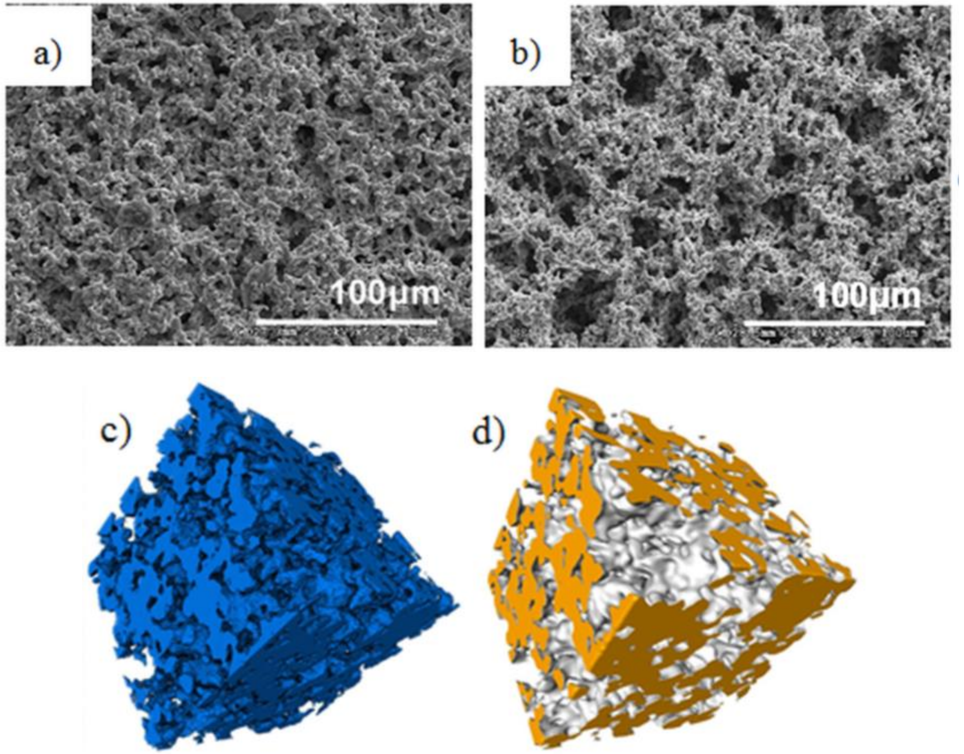
Then, as in any electrical circuit, an external load (i.e. the current sunk) lowers the delivered potential. In „normal" batteries we would call it the *internal resistance*, see the right panel.

Courtesy: Dr Johannes Töpler, Deutscher Wasserstoff-und Brennstoffzellenverband/ https://www.fuelcellstore.com/blog-section/polarization-curves

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen fuel cells in details

Porous electrodes



(a): SEM image of the anode.
(b): SEM image of the cathode.
(c): 3D micro-computer tomography (CT) image of the cathode.
(d): 3D vector-like model of the cathode microstructure based on micro-CT image

T. Wejrzanowski et al., Journal of Power Technologies 96 (3) (2016) 178–182

The low 'contact area' between the gas, the electrode, and the electrolyte is the main reason for the small current. To overcome this problem the structure of the electrode is porous so that both the electrolyte from one side and the gas from the other can penetrate it. This is to give the maximum possible contact.

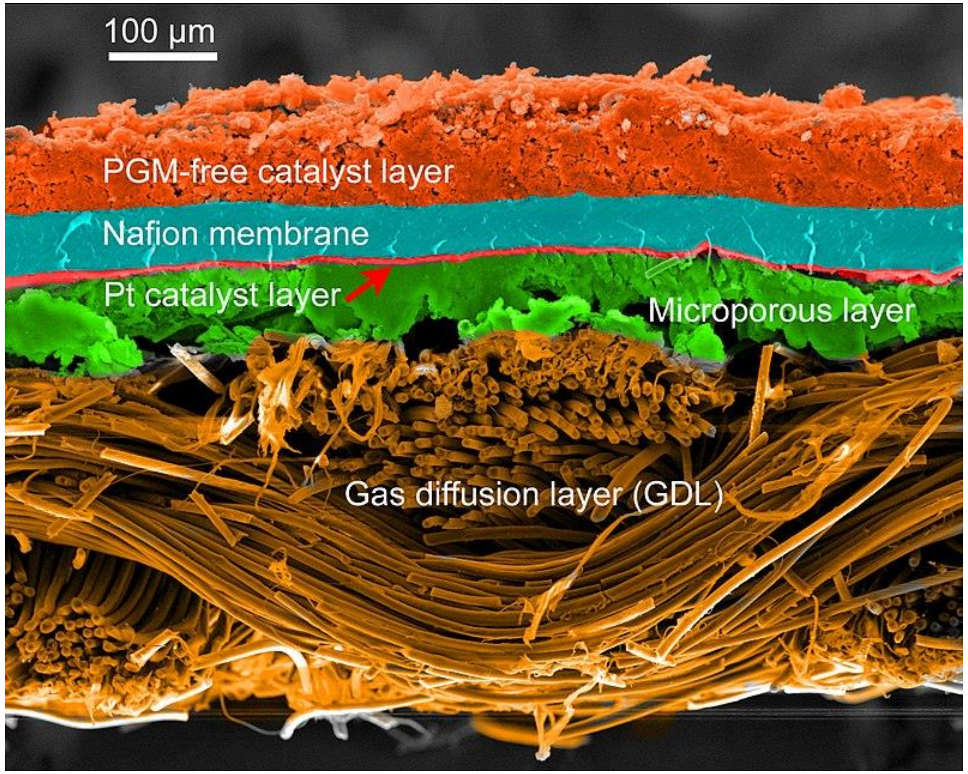
Modern fuel cell electrodes have a microstructure that gives them surface areas that can be hundreds or even thousands of times their straightforward 'length × width' area. The microstructural design and manufacture of a fuel cell electrode is thus a very important issue for practical fuel cells. In addition to these surface area considerations, the electrodes may have to incorporate a catalyst and endure high temperatures in a corrosive environment.

J. Larminie, A . Dicks, *Fuel Cell Systems Explained*, John Wiley & Sons (2000)

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen fuel cells in details

Catalysts



Transversal section of the FC central assembly (i.e. membrane) in false colours. Source: Wikipedia

Several atomic processes must occur on electrodes:

On anode (i.e. the negative pole of the battery):

1. Dissociation of H_2 molecules to atoms $H_2 \rightarrow H + H$
2. Ionization of hydrogen atoms $H \rightarrow H^+$ (i.e. proton) + e^+

On cathode:

1. Capture of proton and electron by oxygen atoms
   $O + H^+ + e^- \rightarrow OH$
2. Attaching of the second pair H^+ and e^- to make H_2O

As far reactions on cathode are exothermic (releas the energy), reaction on anode require energy. In gas phase the required energy would be quite big – few eV.

In the liquid phase, or better ionic reactions, the energies are lower, like it is in Volta's pile. Now a catalyst can work.

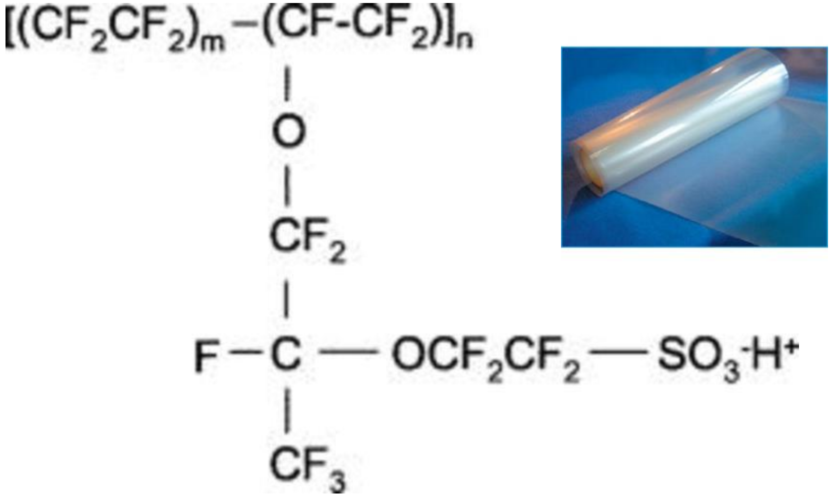
Nanostructured platinum (black) is the most versatile catalyst.

Unfortunetely, also quite expensive

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen fuel cells in details

Proton-exchange membrane

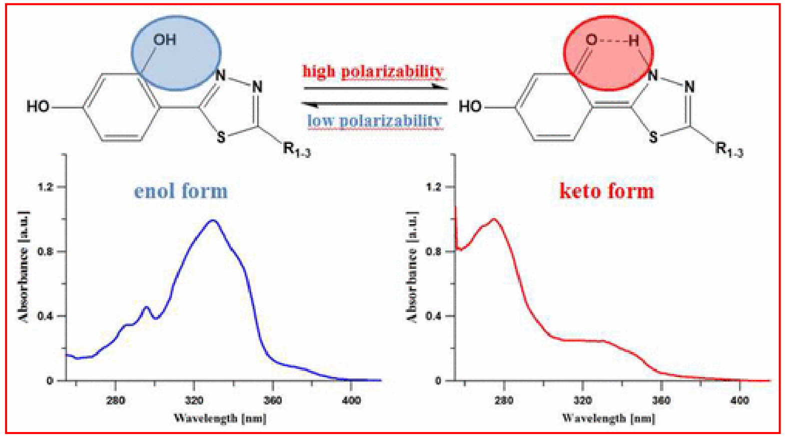


As far as colloidal platinum catalyst is expensive, the key element of hydrogen low-temperature cell is a special membrane, which prevents mixing of gases, is non-conductive for electrons but transports protons.

The chemical structure is shown here: this is a type of fluorinated polymer, like „teflon” (TM DuPont) but contains additionally the sulphonic-acid group. Is thet group that allow „hopping” of H^+ from one polymer chain to another?

Jumping of protons is quite common in chemistry. In the molecule below the external environment (the solvent) can induce the proton transfer between two neighbouring functional groups and in this way change the chemical nature (and the colour) of the molecule.

Finally, sharks use their front „radar” to detect weak electrical signals from a frightened fish hidden in sand. The radar is extremely efficient as protons in a special gel are charge carriers. Shall we use this gel in fuel cells?



Source: Wikipedia / A. Matwijczuk, …, G. Karwasz, M. Gagoś, J. Fluorescence (2017)

http://physicsworld.com/cws/article/news/2016/may/23/protons-swim-with-ease-through-shark-jelly

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union’s Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen production & storage

One of major problems in practical implementation of hydrogen-based mobility is the gas storage.

The simplest way would be a pressurized tank, but as seen from the figure it takes comparatively the biggest volume.

H_2 can be also liquefied: this creates additional problems with cryogenic isolation etc.

H_2 can be captured in a kind of chemical sponges: nanostructured metals (Mg, LaNi); the problem is the release of the gas when needed (when the car accelerates, for example).

Scientific and technical works are under way.

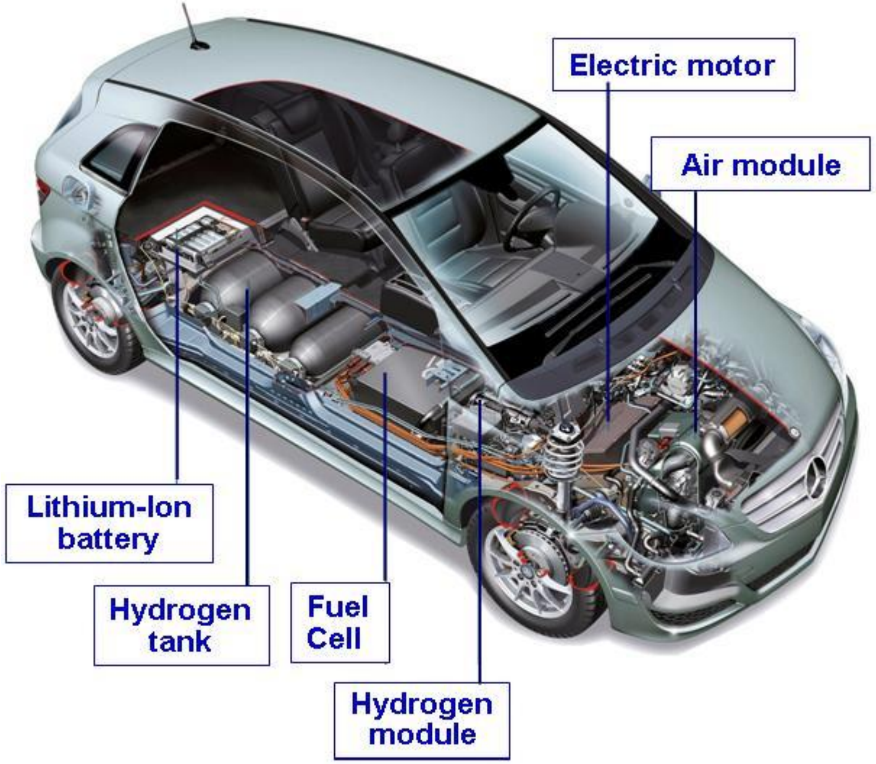
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

From a prototype…

FCHgo! Discover the energy of hydrogen

Fuel Cell vehicle
Mercedes-Benz B-Class

DWV Deutscher Wasserstoff- und Brennstoffzellen-Verband



Essential Facts

1) Vehicle is constructed, fabricated and approved under serial condititions.
2) It was tested by a turn of 125 days around the world with 30.000km

Start of serial production of Fuel-Cell cars at Daimler in 2017

Biggest car producers started practical implementations of hydrogen fuel cells.

Technical problems are numerous: from hydrogen storage, flexible delivery of hydrogen to the fuel cell, the durability of the cell itself, the whole system of control and security, electrical engines and „buffor" Volta's like batteries.

Mercedes-Benz developed a prototype in 2017, but it is still not available on the market.

Courtesy: Dr Johannes Töpler, Deutscher Wasserstoff-und Brennstoffzellenverband

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Hydrogen-fuelled car

Toyota Mirai

Solid polymer hydrogen fuel cell, electric engine 150 hp

Hydrogen tank 37 l, @ 70 atm. pressure, filling time 5 minutes.

Cruising range 300 miles

Acceleration 0-60 mph – 9 seconds

Your, with 389 $/month for 36 months [lease] or 58,500 $ (only)

https://ssl.toyota.com/mirai/fcv.html

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

The network of „good will"

„Phileas-Bus" in Cologne
in daily use in public trafic

Deutscher Wasserstoff- und Brennstoffzellen-Verband

Source: HyCologne -Wasserstoff Region Rheinland

Diesel engines in buses produce not only CO_2 but also quite frequently huge amounts of carbon-like nanoparticles, that are cancerogenous. They are commonly classified as PM10 but are much more dangerous than a common (silica-like) dust.

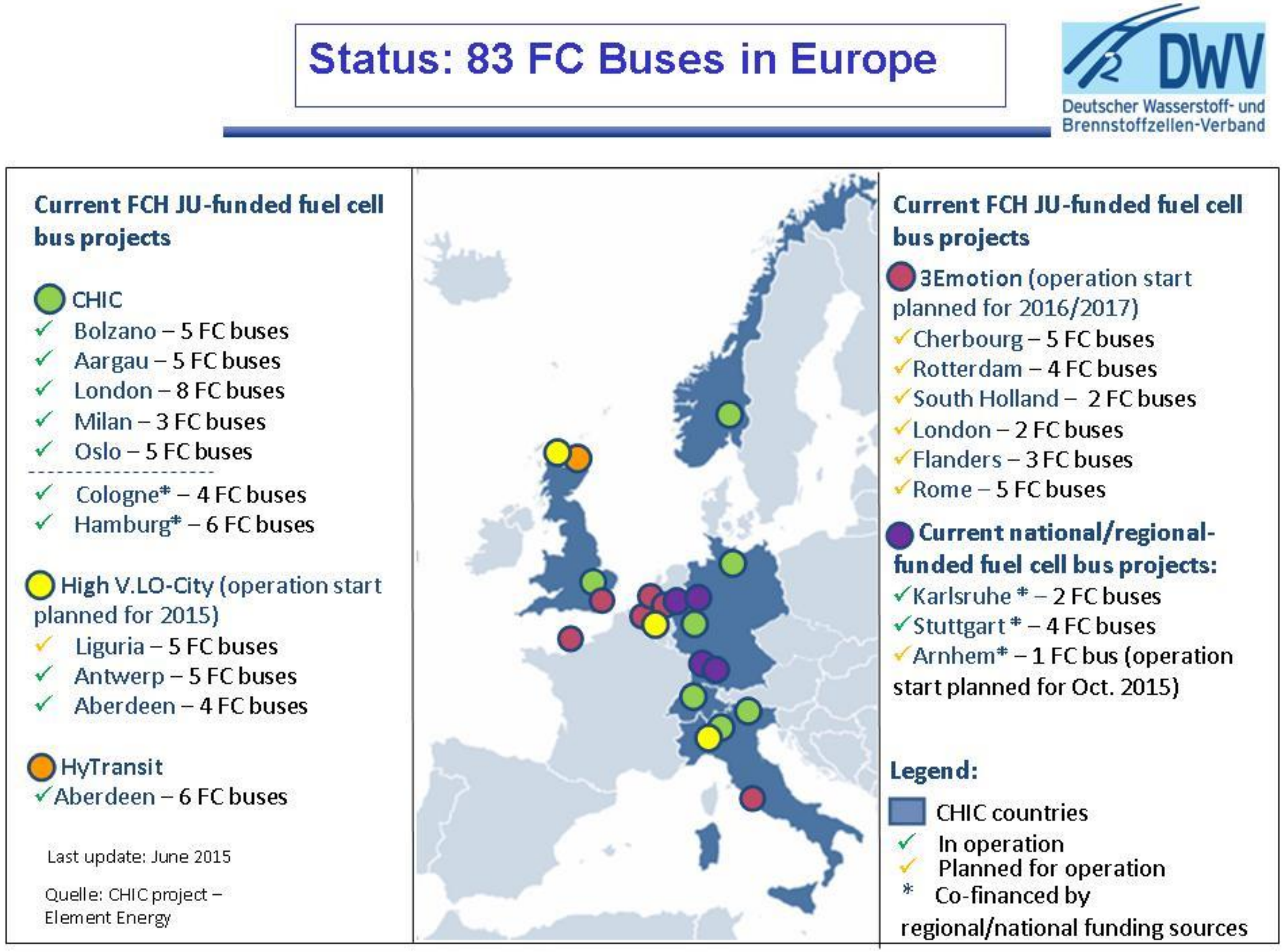
The hydrogen bus in Köln now is 2-3 times more expensive than traditional buses, but this happened always with new technologies.

Photo GK, this time not in Poland

Courtesy: Dr Johannes Töpler, Deutscher Wasserstoff-und Brennstoffzellenverband
G. Karwasz worked as expert for Provincia Autonoma of Trento, in subject of air pollution.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

The network of „good will”



The problem of urban pollution is urgent all over in Europe (see next slide for Poland).

Dense urbanisation, landscape specificity, the technical conditions of cars etc. cause ine many European aglomerations the quality of air be below permitted limits.

At this stage, any attempts to remove burning petrol are welcome and costs are not the priority.

A whole line of countries decided to test hydrogen-fuelled buses, from Norway to Italy. Now also Poland.

Courtesy: Dr Johannes Töpler, Deutscher Wasserstoff-und Brennstoffzellenverband

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union’s Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Exporting urban smog

The title says „Poland in top of air polluting countries in Europe”

The map shows concentrations of benzopirene (cancerogenous) coming from burning coal.

Poland not only produces huge amount of benzopirene (mean concentrations ten time over the permitted health limit) but also „exports” it, freely, to neighbours.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union’s Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

In ships…

The first fuel cell passenger ship in Hamburg

Deutscher Wasserstoff- und Brennstoffzellen-Verband

72,500 kg of CO_2
1000 kg of NOx
220 kg of SOx
40 kg of particles
will **not** be emitted per year!

Source: Alster Touristik GmbH

Ships use very powerful Diesel engines that are particularly polluting. One does not feel this pollution being on water. But satellite images show traces of clouds where ships passed over an open ocean.

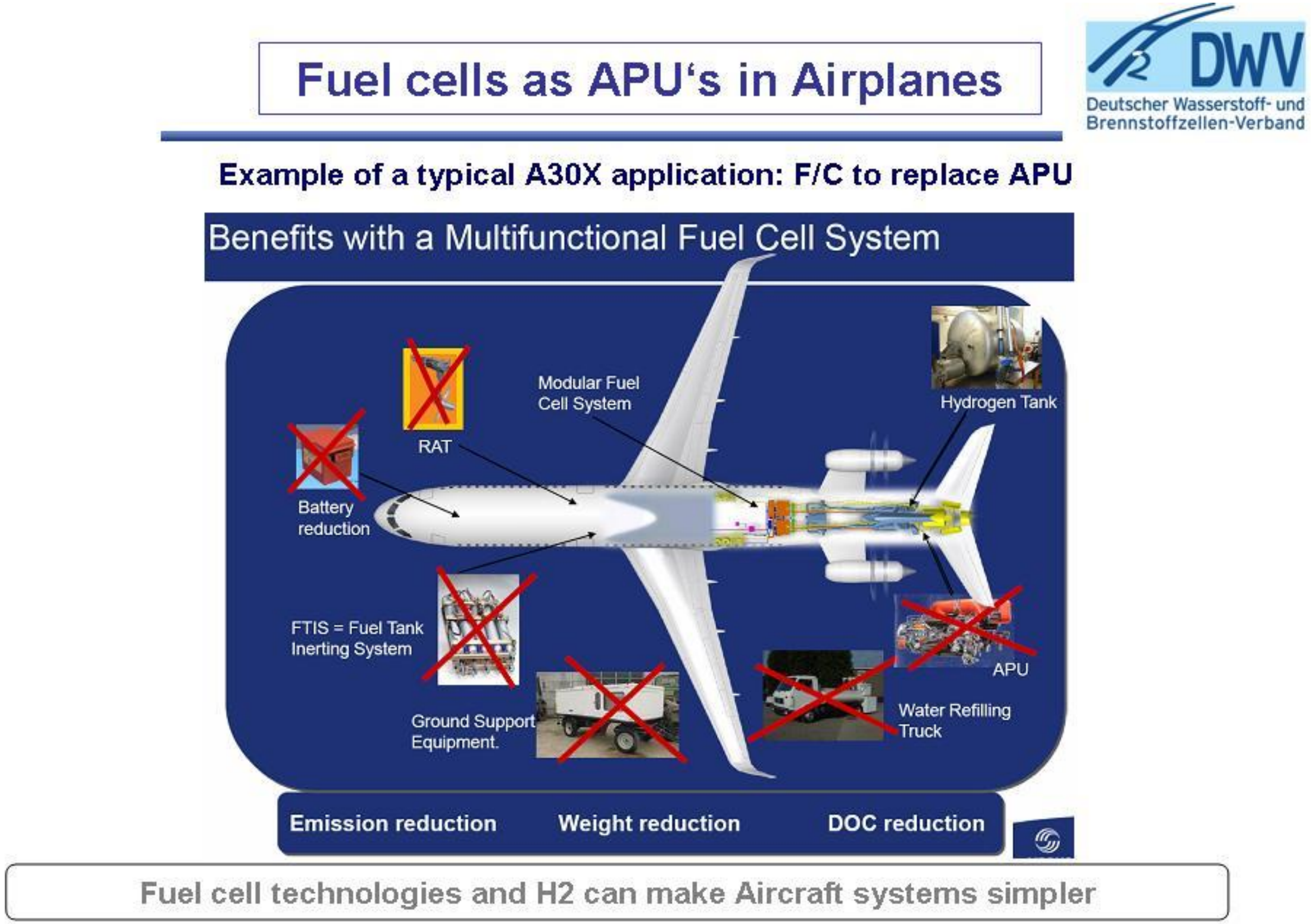
Diesel engines produce also huge amounts of gases, that being polyatomic, bring long-term (270 yrs in case of N_2O) global warming. NO_2, in turn, contributes to the tropospheric ozone which is cancerogenous.

SO_2 is highly corrosive: its emission on Northern Hemisphere „mitigated” the GH effect in mid of XXth century.

Courtesy: Dr Johannes Töpler, Deutscher Wasserstoff-und Brennstoffzellenverband

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union’s Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Even in ariplanes…



A number of applications are under study: an airplane can be a very far future vision, but compared to the cost of detailed projecting, a *vision* is low-cost research.

Airplanes, in particular military, will be probably last to abandon petrol, but the huge amount of the passenger traffic make producers of aircraft think seriously about hydrogen as propellent.

And probably quite close is the use of fuel cells as electrical current generators in aircrafts (here Airbus A30X).

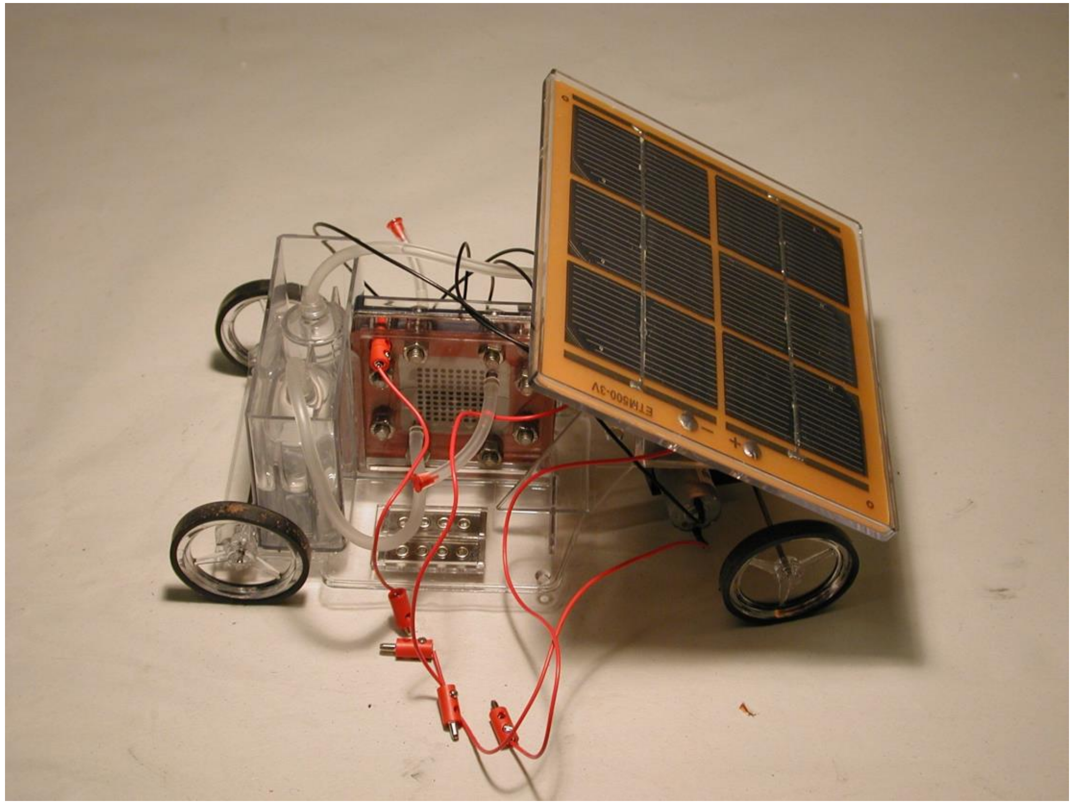
On the other hand, FC technologies took-off when they were used in Apollo flights.

Courtesy: Dr Johannes Töpler, Deutscher Wasserstoff-und Brennstoffzellenverband

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Water-fuelled car: didactics

FCHgo! Discover the energy of hydrogen



All us (maybe with the exception of politicians, but also them only when they wear a tie) we are aware of global warming, local air pollution and economical issues (including political dependences) related to the use of petrol.

Didactically, this model that comes from „Kosmos and Thames” is impressive: while making a lecture, say „now we fuel it with pure water”. During from that water bottle before (remember that it must be distilled water).

Do not forget also a lamp on the lecture desk, apparently for reading. And keep the car under this lamp. As soon as you notice that enough hydrogen and oxygen is produced, make necessary connection and leave the car ride over the lecture hall.

The effect on the public is astonishing.

Experience of author from a public lecture in Trento, Italy, 2003

FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union’s Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Resuming…

Arguments in favor of FCH-Technology

1. Hydrogen is a renewable fuel.
2. Burning hydrogen, or using it in fuel cells, only produces water.
3. Hydrogen working in fuel cells is potentially highly efficient.

FCHgo! Discover the energy of hydrogen

There are at least three arguments in favor of Fuel Cell and Hydrogen Technology (FCH-T):

The fuels currently used are mostly non-renewable. Coal, oil, and natural gas have been laid down in the Earth’s crust a very long time ago, and once used up, they won’t come back.

Burning the usual fuels creates substances that harm the environment in several ways. For example, they pollute the air we breathe and the water we drink. Most importantly, carbon dioxide produced by burning coal, oil, and natural gas is making our planet warmer at a rate that will not be acceptable to future generations—and should not be acceptable to us.

From a physical and technical viewpoint, burning fuels is wasteful—producing heat is not what we should be doing. There are better ways, at least theoretically, from a basic scientific and engineering perspective, to use fuels.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union’s Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.

Debate for students

Find as many as possible practical applications (or prototypes of applications) of hydrogen fuel cells.

Bring for the next lesson different pieces of polymer foils: check their thickness and surface roughness. Compare with nafion foil (from teacher).

See a separate presentation for experiments with fuel cells.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 826246.
The JU receives support from the European Union's Horizon 2020 research and innovation programme and Italy, Denmark, Poland, Germany, Switzerland.