Water powered car

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Discover the energy of hydrogen

The article talks about the future, near future, energy perspectives and hydrogen technologies. A whole host of new issues will require interdisciplinary preparation of students: not only in physics and chemistry, but also economics.

The end of coal

The Ministry of Energy calls for electromobility. In a few years up to two million electric cars are to be in Poland. In Gdynia (and a few other Polish cities) trolley buses (i.e. electric buses like a tram) run - when they go down from the hill, their engines operate as generators and give electricity to the network. Among other things, thanks to trolleybuses, Gdynia has the cleanest air in Poland. But where and how is electricity generated to power trolleybuses (and future electric cars)? A thorough comparison (Fig. 1) indicates that this current is generated in Silesia, Bełchatów, and Konin. And this current is black or brown.

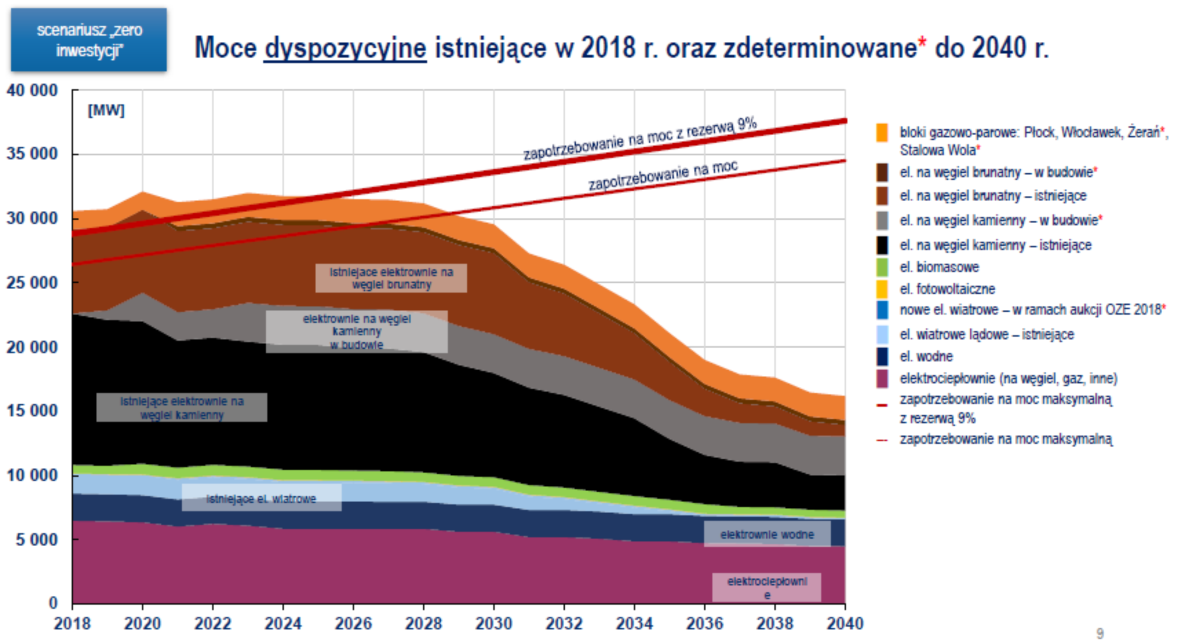

Fig. 1. Report of the Ministry of Energy (22/1/2019): forecast of electricity demand and supply in Poland by 2040. The main "sources" of energy - hard coal and lignite (black and brown stripes) are running out. https://www.gov.pl/web/energia/raport-mit-o-przyszlosci-energii-jadrowej

But from the forecast of electricity demand and supply in Poland until 2040, Fig. 1, several more pessimistic conclusions follow. The "production"[1] of electricity from hard coal and lignite will be significantly reduced: mineral deposits are simply ending. If innovative investments are not undertaken, e.g. in nuclear energy, by the eye, in 2040 there will be 50% of the necessary electric power (in Poland, the demand is about 1 GW per million inhabitants, and in the Republic of Korea it is 1.5 GW).

[1] Energy, of course, is not "produced" but only transformed from one form to another.

Coal and oil will be lacking not only in Poland. Currently, most nuclear reactors are being built in Arab countries. Of course, the governments of these countries know their own resources and plan to replace oil with other "sources" of energy on time. A nuclear reactor is not cheap - 1 GW of power costs around 4 billion euros. And Poland has just started paying fines for CO_2 emissions - a few billion euros a year. Smoking chimneys near Konin, fig. 2, must disappear, not only because of the punishment, but also by respect for the inhabitants of Pątnów and the surrounding area.

Fig. 2. According to the latest Nature report [6], Poland is one of four countries (along with Mongolia, Kazakhstan and India) that base their energy on coal. This is how the chimneys of the brown coal power plant smoke in Pątnów near Konin (photo M. Karwasz).

Getting warmer

The global rise in temperature is increasingly less denied. Anyway, physicists have no doubts. It is gases that 'send' infrared radiation back towards the Earth's surface and are responsible for the greenhouse effect. We would like to remind you that the natural (without human activities) greenhouse effect on Earth is + 33K: without it, the average temperature would not be + 15ºC, but -18ºC. And water vapor is the main greenhouse gas, as we discussed in an earlier article [1].

Physicists not only understand the mechanisms, but also can quickly estimate. An increase in the CO_2 content in the atmosphere from 270 ppm before the beginning of the industrial era to over 400 ppm is, by eye, at least 50%. So much CO_2, as the Antarctic ice research shows, has been gone for the last 400,000 years. Fortunately (?), coal, gas, oil are running out: the authoritative journal Nature has rated the world's carbon reserves for 200 years and natural gas for 55 years.[2]

[2] This was before industrial shale gas extraction began in the US. According to geologists, Poland has the largest shale gas deposits after the USA. Unfortunately, its extraction causes considerable damage to the natural environment.

Unfortunately, the temperature increase will not stop with CO_2 emissions: other gases, such as N_2O (from agricultural crops) and CH_4 (coming out of the thawing tundra and emitted by bacteria in digestive processes) are even more "greenhouse". All these gases contain polyatomic molecules: there are many different ways (modes) that atoms can vibrate in. The energy of these vibrations corresponds to the energy of infrared light quanta, so these gases do not "release" radiation heat from Earth. The CO_2 molecule has a linear, symmetrical geometry: until it vibrates, it weakly absorbs electromagnetic radiation. N_2O molecule (N = N = O), Fig. 3. although linear, has a constant dipole moment - positive and negative charge are shifted in it. As a result, its impact on the greenhouse effect is 300 times greater than CO_2 (and the time of "life" in the atmosphere reaches 144 years [2]).

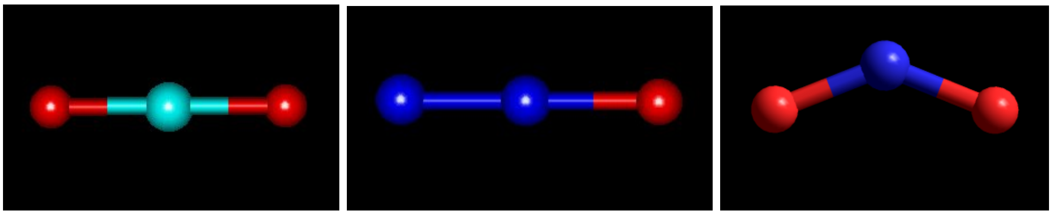

Fig. 3. The CO_2 molecule is linear and symmetrical; only when excited to bending vibrations (010) it obtains a dipole moment. The N_2O molecule is linear, but has a dipole moment. The NO_2 molecule is bent, so it has a dipole moment, though 5 times smaller than H_2O; nitric oxide is formed in urban smog and is poisonous. Scale model - HyperChem calculations.

The latest report of the Intergovernmental Panel on Climate Change (IPCC) claims that the temperature will rise by 1.5ºC by 2050 (compared to 1850). Not only "environmentalists" sound the alarm. Another prestigious journal, Science, devoted the entire August issue (No. 341) to climate change in 2013. The worst happens to polar bears: the summer ice range in the Arctic has been halved since 1980 [3] - they have no way of hunting seals.

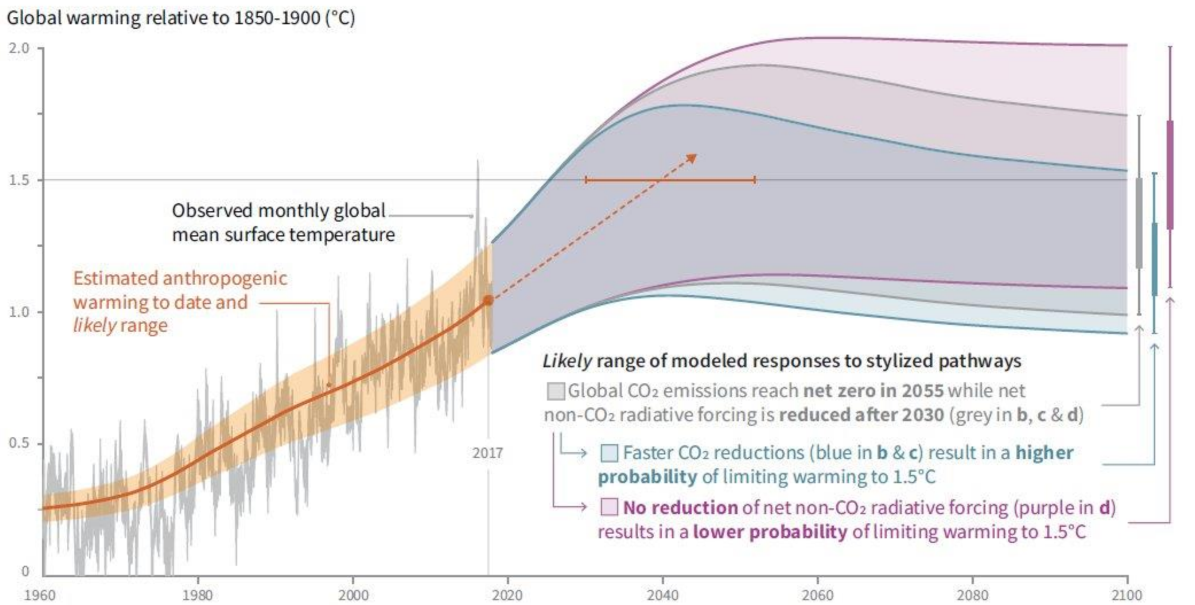

Fig. 4. The most important result of the latest IPCC report on climate change: the expected temperature increase (relative to the pre-industrial era) will be around 1-2ºC (depending on the CO_2 emission scenarios) and will reach a maximum around 2050. The model assumes reducing CO_2 emissions to zero in 2055. Source: [4]

New energies

There is no unique recipe for new energy sources. Photovoltaic panels have until recently had a payback time of 20 years; the new Nature report [4] talks about a return time of 1 year. To provide energy for the needs of one household (power used 3 kW maximum), with a panel efficiency of 10%, it is necessary to cover the part of the roof of a single-family house (we recall the value of the solar constant 1340 W, but it is the value of energy per square meter perpendicular and outside the atmosphere).

The problem of panels (and windmills) is the storage of energy in a period when the sun is not shining and the wind is not blowing. In Germany this problem is already understood as a state-wide one. A variety of options are being considered - from giant lithium batteries, to a hydrogen tank, to pump artificially produced methane into underground caverns. (In Poland, gas reserve tanks are, apparently, in salt mines in Inowrocław, but there is only enough gas for the country for 48 hours.)

The aforementioned "Nature" report lists several options for "energy sources", from nuclear power plants, to offshore wind farms, rivers, to waste incineration and methane production from biomass. The authors assume that in different parts of the world they will be somehow the law of "natural selection" developing different technologies, and in 2050 the majority of electricity will be generated from solar cells. And the main cost of the electricity bill will be its storage. One of the solutions are hydrogen technologies: production and storage of hydrogen.

Hydrogen economics

Hydrogen, despite being the main constituent of the Universe (stars) is not present in a free state on Earth: too light to remain in the atmosphere. On Earth, it is bound in the form of water (as well as carbohydrates and many different minerals). There are several methods for producing hydrogen, e.g. by pyrolysis (i.e. decomposition at high temperature) of methane $CH_4 \rightarrow C + 2H_2$ (carbon is carbon black in the waste) or through the reforming reaction $H_2O + CH_4 \rightarrow CO + 3H_2$ (also at high temperature).

The cleanest (but not the cheapest) way to produce hydrogen is water electrolysis. But an important advantage of electrolysis is that it does not require large industrial installations. As the Nobel Prize winner Jeremy Rifkin described in 2002, a new hydrogen economy appears: each household produces hydrogen for its own needs (from its own solar panels or windmills) and uses it as needed, e.g. for refueling tank in the car.

Again, the problem will not be production, but storage. Scientists are working on various solutions: injection into a cylinder (under pressure, e.g. 800 atm), liquefaction or chemical bonding in porous metals, in the form of hydrides, e.g. MgH_2. The disadvantage of the latter idea is the difficulty in fast (and regulated) hydrogen recovery, what you need, e.g. in a car. A new "engine" is also needed.

Combustion of hydrogen in a thermal engine would not make sense: the efficiency of such a process is limited by Carnot's law - the temperature difference between the engine and the radiator. In practice, the efficiency of internal combustion engines reaches about 35%. The way to achieve efficiency, theoretically up to 80%, are the so-called fuel cells, although they should be called rather "hydrogen". A hydrogen cell is nothing but reverse electrolysis. And it works like any Volta (or Galvani "battery" - the Italians themselves argue about it).

Volta cell

The prototype of the fuel cell is the Volta cell - two different metals immersed in water (with the addition of salt, acid, alkali[3]). The first link of Volta (1799) was a pile of coins - tin and silver, arranged alternately, and felt soaked in dilute acid between them (i.e. between each pair). Volta tried the link by putting pairs of coins on the tongue [6]. He noticed that if he put a tin coin on the tip of his tongue, he felt sour.[4]

Volta was right to say that the cause of electricity is the presence of two different metals. And he determined the direction of the current from silver (more expensive) to tin. Today we know that it is the opposite of the direction of electron flow. But the electron was only discovered a hundred years later.

Fig. 4a) Volta's original link from the Como Museum: a pile of zinc and copper disc pairs, postponed with felt moistened with acid. b) The same museum - two cells "piles" and a battery of glasses, electrically connected (zinc and copper plates). Photo: GK; Tempio Voltiano, Como.

It is due to chemical differences between metals, e.g. silver and tin, that one of them (tin) loses electrons more easily and the other more difficult. In the gas phase, we would talk about ionization energy. For silver it is 7.58 eV and for tin 7.34 eV. In the solid phase, the energy values necessary to knock out the electron (e.g. by photoelectric effect) are lower: 4.7 eV for Ag and 4.3 eV for Sn. (The energy values of photons necessary to knock out electrons from metal are called, after Einstein, the "work function").

The "work function" at Volta's cell - metals immersed in water - is yet another. Physicists are not yet able to calculate what voltage will arise between silver and tin or copper and zinc (this was the second version of the Volta cell - in the form of plates immersed in glasses with acid, photo 4b).

[3] This addition is due to the low electrical conductivity of clean water. To find out, just drop the battery "finger" into a glass of water: without the addition of salt we do not see bubbles of hydrogen and oxygen. And the battery itself must be new, because electrolysis requires a voltage of 1.23 V.

[4] Today this experience can be repeated with eurocents. Although they are iron, but covered by copper. We wrap them half-way with aluminum foil (like a half-moon) and touch the tip of the tongue: the sour taste (from Al^{+3} ions passing to saliva) we feel after removing the coin from the tongue.

The processes occurring in the Volta cell (actually Daniella, in a moment about this) is the donation of an electron through a zinc atom (and the passage of the resulting Zn + ion into the solution), the flow of electrons via an external copper wire, and on a copper electrode - the connection of the electron to the copper ion (metallic copper settles and the amount of Cu^+ in the solution decreases).

$Zn \rightarrow Zn^+ + e$ (chemists call it oxidation)
$Cu^+ + e \rightarrow Cu$ (chemists call it reduction)

The negative electrode in Daniella's cell is zinc (physicists call it anode) and the positive (cathode) is copper.

<u>Electrochemical series</u>

Physicists (or chemists) cannot yet calculate what voltage will arise between two different metals. It is not only metal but also the water-metal interface that determines this tension. It wasn't until a few months ago that work appeared trying to calculate the work of electron output from platinum immersed in water [7]. This result is not fully correct yet, but we are beginning to understand that the *interface* (boundary layer) between water and metal fundamentally changes the physics of the process.

If you can't count, you need to measure it with a reference point. This point is the lightest metal-non-metal, i.e. hydrogen. However, we do not have hydrogen in the form of an electrode; therefore, a platinum electrode is used (but necessarily covered with colloidal platinum, so-called platinum black). Platinum acts as a catalyst (in a moment about this), "encouraging" hydrogen to donate electrons (and before that, facilitating the breakdown of hydrogen H_2 particles into atoms, i.e. *dissociation*).

The electrochemical potentials are[5]:

Li	Al.	Zn	Fe	Sn	H_2	Cu	Ag	Au	O_2*
-3,04	-1,66	-0,76	- 0,44		-0,13	0	+0,34	+0,80	+1,23

* The reaction proceeds $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$

Lithium lies at the beginning of the Volta series, with a voltage relative to hydrogen of -3.05 V (therefore lithium batteries give the highest voltage). Zinc gives a voltage of -0.76 V and copper +0.34 V. This does not mean, however, that by inserting a copper and zinc electrode into the salt or acid solution, we get a potential difference of 0.76 + 0.34 = 1.1 V. It would be so, if there were reactions in the link like in equation (1). The cell should have two electrolyte tanks - one with zinc ions, the other with copper ions. This is the "patch" introduced to Volta's cell by John Daniell (1836): hydrogen cathode bubbles are avoided.

[5] This is a simplified version: in fact it is necessary to define what reaction is taking place. For example, the electrochemical potential is different if there are Cu^+ copper ions in the solution, i.e. the reaction is $Cu^+ + e \rightarrow Cu$ (potential +0.52 V) and different when the ions Cu^{2+} (reaction $Cu^{2+} + 2e \rightarrow Cu$, potential +0,34 V).

Without a septum (and two different electrolytes) on the positive electrode, copper will not separate because there are no Cu^{+} ions in the solution - hydrogen will be released from the water. The useful voltage will be only 0.76 V, even if we use a gold electrode as the cathode. But to close the circuit, either a porous septum is needed (to allow the flow of SO_4^{-2} ions) or even an external "ion key" filled with KNO_3 gel. Electrochemistry is a complex field of research.

Hydrogen cell

The hydrogen cell (also called "fuel cell") was proposed in 1838 by William Grove [8]. It was only during the flights that Apollo found real implementation: both oxygen and hydrogen were in the rocket tanks, the cell generated electricity and the resulting water was used for drinking.

The "fuel" cell is a reversal of water electrolysis. In electrolysis, to generate H_2 and O_2 from water, an electric voltage (minimum 1.23 V) must be applied to the electrodes. By supplying oxygen and hydrogen gas to two electrodes, we obtain a useful voltage on the electrodes. This is somewhat obvious, because the water synthesis reaction is an exothermic reaction.

This "obvious" is not so simple to implement: both hydrogen and oxygen are gases, so they must first be dissolved in water (but they are quite soluble), then you must "force" both gases, H_2 and O_2, to transition to atomic form, H and O, i.e. for *dissociation*. Appropriate catalysts are needed for this. In the case of hydrogen, platinum is used in its colloidal (nano-structural) form, called by chemists platinum black. In the case of O_2, various catalysts, both metallic (Ni) and oxide (e.g., appropriately activated tungsten oxides) are tested. However, the link has a lot of restrictions - power, construction, materials (and prices[6]).

The key to the fuel cell is the membrane separating the two areas. As in Daniella's cell, the electrical circuit is closed by SO_4^{-2} ions diffusing through the septum (or other ions in the external ion key) so in the hydrogen cell the electrical circuit is closed by the flow of H^{+} ions from the anode to the cathode: this is where the reaction of H_2O formation with H^{+} and oxygen occurs, see fig. 5.

[6] The cost analysis indicates that for powering a passenger car, the cost of the cell itself is comparable to the current cost of producing the entire "rest" of the car (body, interior, etc.).

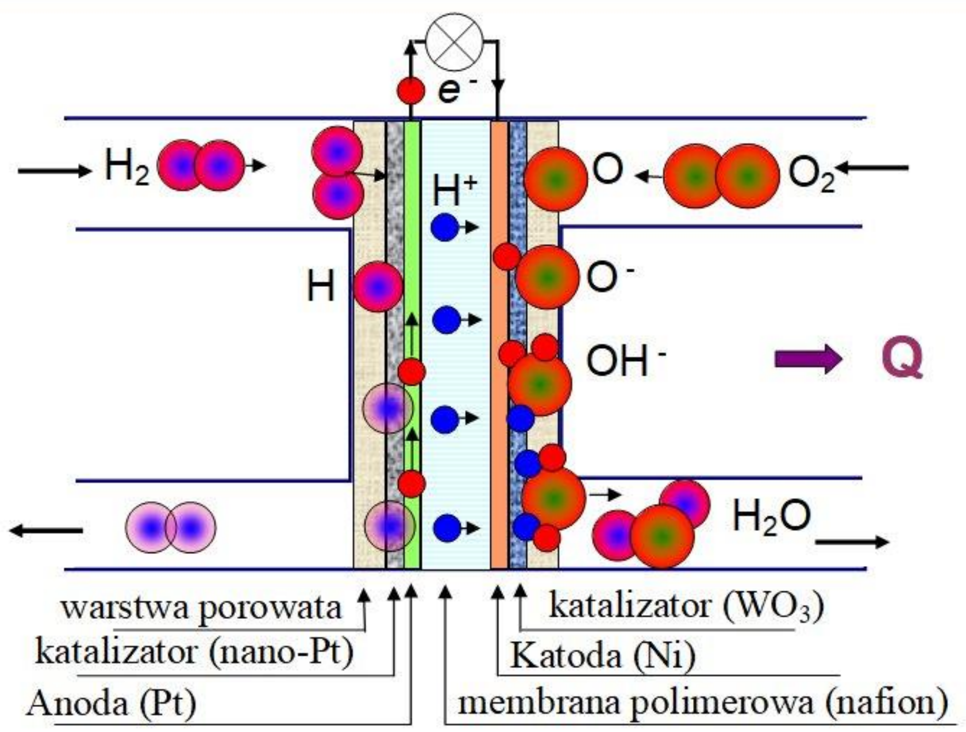

Fig.5. Fuel cell scheme (GK). Hydrogen and oxygen gas flow from two sides. The partition separating the two areas has a multilayer structure: the outer porous layers are intended to "trap" the gas so that it comes in contact with the catalyst. The membrane from nafion is 20 μm. On the hydrogen side, platinum is used (layer on the order of 1 μm), on the oxygen side various technologies are tested, such as Ni, nano-structured WO_3, Se, etc. The processes on the oxygen side are less understood than on the hydrogen side. From the hydrogen side, H_2 dissociates into H, loses an electron in contact with the catalyst (it flows to the other side of the cell through the external circuit), the H^+ proton diffuses towards the anode. On the anode side, H^+ joins with O (or OH and OH^-, it is not exactly known) to form water. In the form of faded discs we show that hydrogen was, but broke down into e^- and H^+.

H^+ ion flow (or "bare" protons, with recently measured diameter of $0{,}86 \times 10^{-15}$m) however, it is not a physical process, but rather a chemical one. In a special fluoridated polymer, with sulfonic acid groups, protons "jump" from molecule to polymer molecule. The membrane, therefore, isolate two catalysts, do not let water or gases through and transport protons. Despite many efforts, a fluorinated polymer with a sulfonic acid group remains commonly used. Nafion, 20 μm thick, see photo from the electron microscope on the Internet [8].

We don't quite understand chemistry like the physics of a hydrogen cell. It is not known whether it is the sulfone group or the fluoridation of the polymer that provides H^+ transport. Platinum is expensive. It is not known where some of the electrical voltage is lost. For the electrolysis needs 1.23 V and the highest voltage obtained from the hydrogen cell up to 1.0 V. For now, technologists call this loss "activation potential". But rather it resembles the so-called polarization voltage (0.6-0.8 V) in a silicon photovoltaic cell [9].

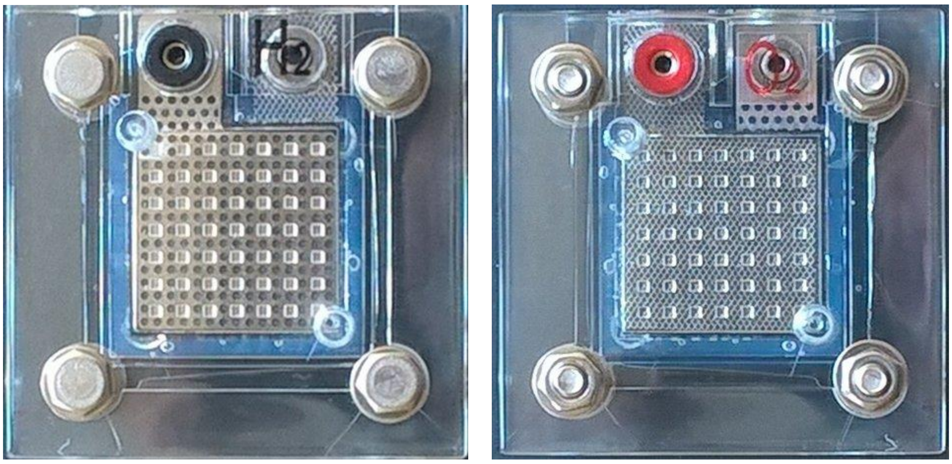

Fig.6a) H_2 side of the fuel cell from a water-based toy car model. Platinum catalyst and perforations leading to the membranę are visible. b) O_2 side - a slightly different structure is visible. Photo AK.

<u>Water powered car</u>

Fully useful "water" cars were constructed several years ago. However, there is still a lack of proper economic motivation (oil is still cheap) and technologies are not fully developed. Nafion is expensive and not very resistant to temperature (in the process of H_2O formation heat is released) not to mention the resistance of the entire cell to frost. But nafion is not the only technology possible.

Hydrogen tanks take up the entire trunk, like lead batteries in cars today, in 2019, declared at the Swiss fair as electric. Not to mention the lack of a hydrogen refueling station. The most advanced works on the construction of a fuel cell car are carried out in Korea, China and Japan.

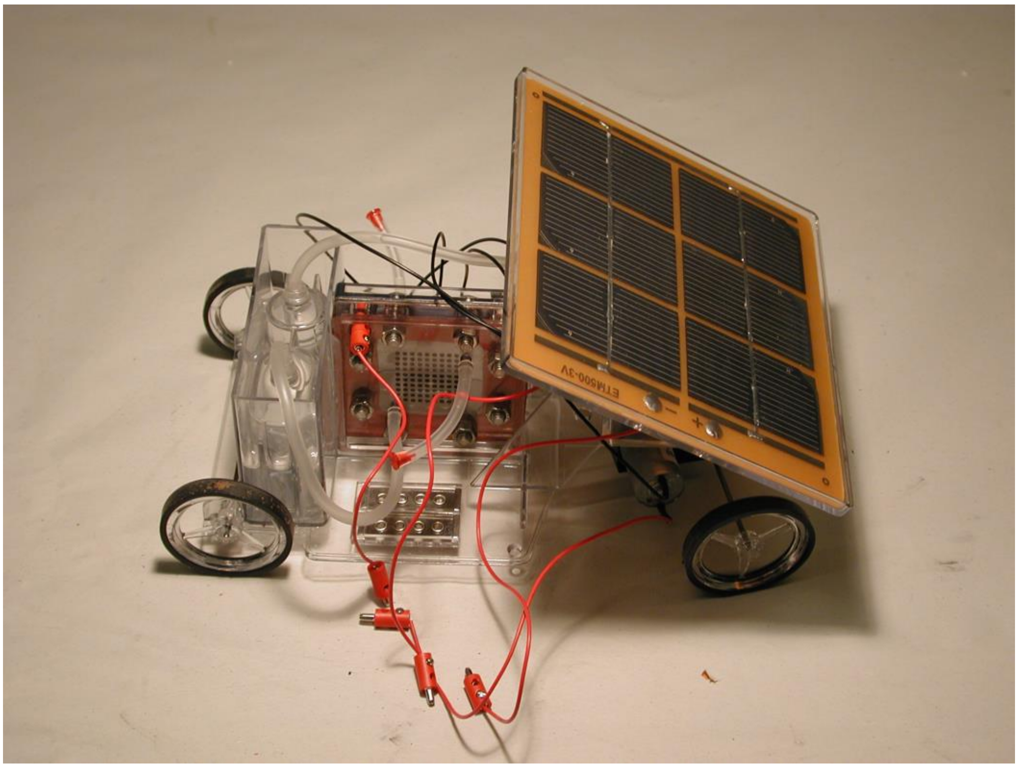

Fig. 7. Water toy car (Kosmos & Thames company). First, water (necessarily distilled) is poured into the tank on the left, connecting to the fuel cell (inside) the solar panel (on the right). The current generated in the solar panel electrolyses water (the cell works as an electrolyzer), and H_2 and O_2 go to the tanks (on the left): the H_2 tank is twice as wide). After producing (gaseous) fuel, the wires are switched so that the car's engine (under the panel) is powered by the current generated in the fuel cell. Of course, in full sun the motor can be powered directly from the solar panel (photo GK).

Experts needed

The aforementioned forecast of global "production" of energy in 2050 assumes that coal and oil are gone: 80% of global demand is covered by photovoltaic cells. This in turn raises the problem of energy storage when the sun is not shining and electricity is needed. Various ideas are being considered, such as the production (from CO_2 and H_2) of artificial methane, new tanks for pumping water, and above all hydrogen based technologies. We are also working [10] on a thermonuclear reactor synthesizing helium from heavy hydrogen.

No doubt, new ideas are needed. And new specialists. What specialists? We do not know. But knowledge of physics will be the key ability.

Fig. 8a) Aluminum and copper plate, inserted into an apple, "give" a potential difference (workshop of the Children's University of Głogów, 2011, photo Maria Karwasz). b) A pleasant surprise when you can power a fuel cell from hydrogen and oxygen and a small fan from the current (photo KW).

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