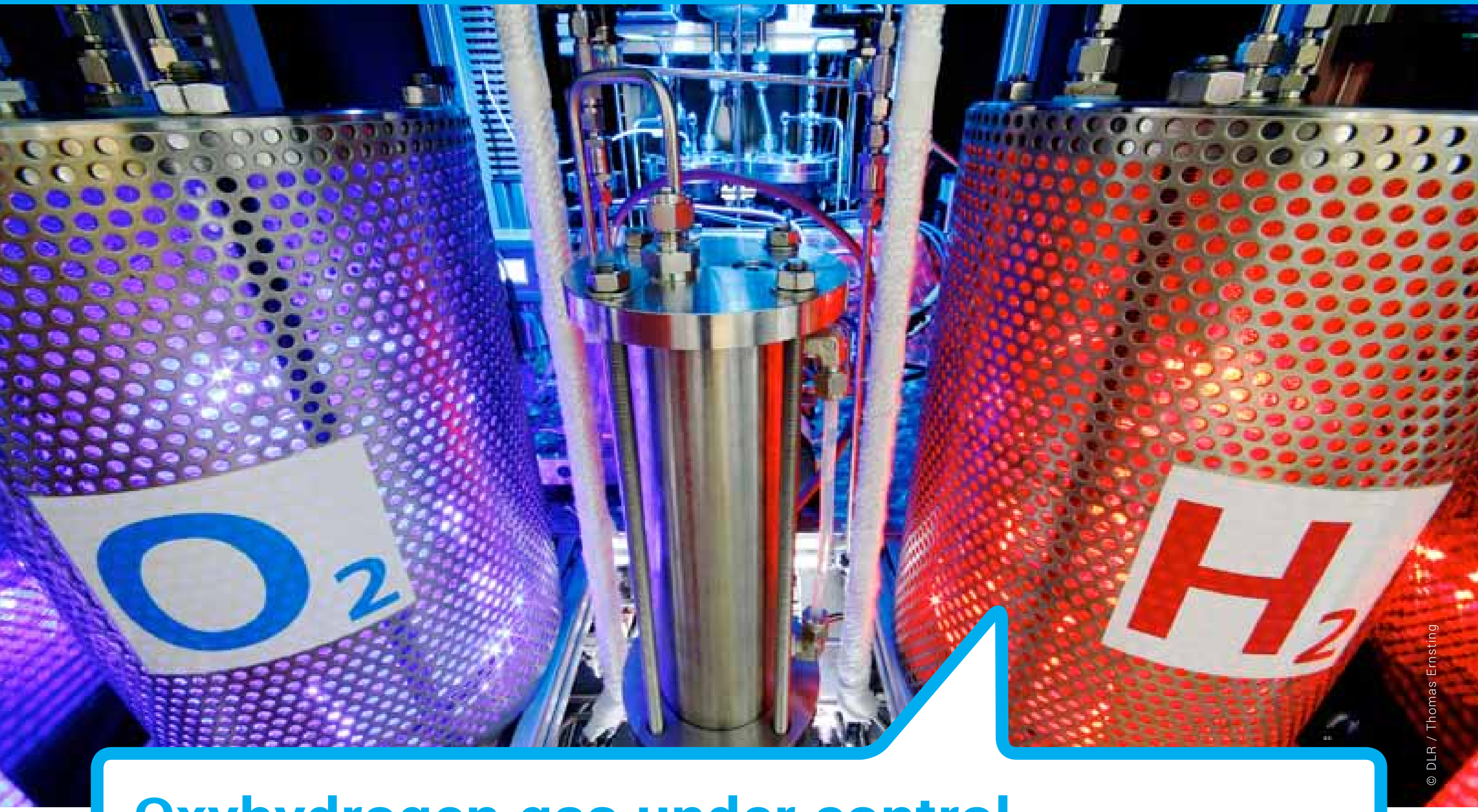
CURIOUS ABOUT SCIENCE

techmax

Issue 16 // Summer 2020



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Oxyhydrogen gas under control –

making fuel cells fit for widespread use

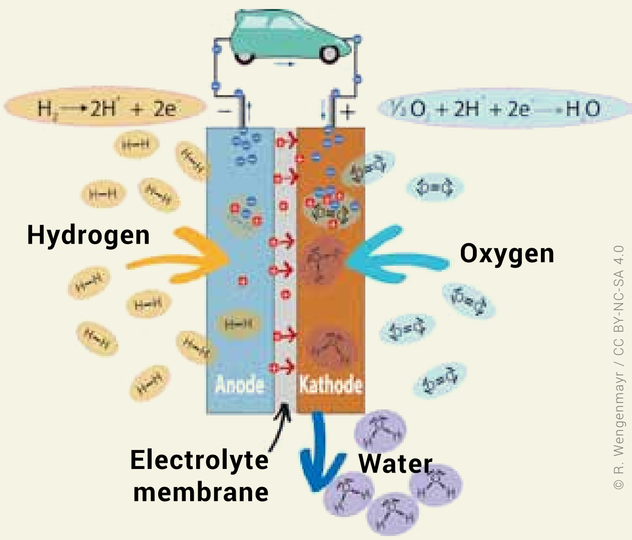
„Houston, we have a problem." With this simple message from Apollo 13, fuel cells were suddenly making headlines. On 11th April 1970, an oxygen tank exploded on board the spacecraft on its way to the moon. Strangely, this meant that there was no on-board electric power generation. So what does oxygen have to do with electric power? Television viewers watching anxiously learned that a „fuel cell" used oxygen and hydrogen to generate electricity. Plus the system had a practical advantage – the by-product of this chemical reaction was drinking water for the astronauts.

The first fuel cell was constructed by Christian Friedrich Schönbein in 1838. Electric power can be used to split water molecules into hydrogen and oxygen, and Schönbein reversed this **electrolysis** (see cover image). He placed two platinum wires in hydrochloric acid and directed a stream of hydrogen along one wire and oxygen along the other. He was able to measure an electric voltage between the wires. Sir William Grove in England had the same idea at almost the same time. Today, they are both considered the fathers of the fuel cell. The energy potential contained in a hydrogen fuel cell can be demonstrated in a school experiment: If a gaseous hydrogen and oxygen are mixed and this oxyhydrogen gas is then ignited, an explosion results. In this reaction, two hydrogen atoms combine chemically with one oxygen atom to form a water molecule. This releases a large quantity of energy in the form of heat. A fuel cell controls this violent chemical reaction, forcing it to release most of its energy in a usable form: electricity.

Like batteries, fuel cells are **electrochemical cells**. They convert chemical energy into electrical energy. Some batteries can also be recharged by reversing this process (see Techmax 13). In contrast to batteries, fuel cells must receive a continuous external supply of two electrochemically active substances – oxygen and fuel – in order to function. Only then can they produce electrical energy.

Like batteries, fuel cells have two electrodes that are electrically connected via an **electrolyte**. They also need a connection for the fuel, usually pure hydrogen. They must be able to absorb

FIG. A: HYDROGEN FUEL CELL



Caption: Basic principle of the low-temperature hydrogen fuel cell. In the anode on the left, the hydrogen gas H_2 (H-H) is split into two protons (H^+, red) and two electrons (e^-, blue). The electrons flow through an electrical load circuit, where they perform work. The protons in the electrolyte migrate through the membrane to the cathode (right). There they meet the electrons leaving the load. They then combine with oxygen (O_2) from the intake air to form water (H_2O).

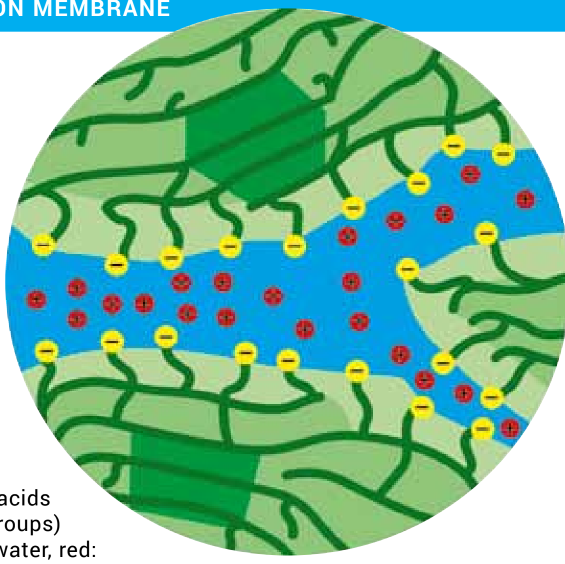
oxygen from the air through a different opening. The exhaust gas produced in the hydrogen fuel cell is pure water vapour.
The cell electrodes are designed to be porous, enabling air, the fuel and the exhaust gas to flow through them as easily as possible. For example, they may be made from microscopic grains of carbon that are compressed. These grains are also coated with catalyst particles that are roughly ten times smaller than the grains themselves. The catalyst plays a key role in accelerating the electrochemical reaction (see Techmax 10). Hydrogen fuel cells need precious metals such as platinum for this, which is expensive.
The team headed by chemist Klaus-Dieter Kreuer at the Max Planck Institute for Solid State Research is working to improve **low temperature fuel cells**. The operating temperature of such cells is normally below 100 °C, which is the boiling point of water at normal atmospheric pressure. Their compact design permits tremendous power densities. In contrast to high-temperature fuel cells, which operate at up to 1000 °C, they respond quickly to load changes, such as when vehicles accelerate or brake. This makes them especially suitable for electric cars and electric trains on routes that don't have overhead lines.
Kreuer's team is focusing on a central component of low-temperature fuel cells: a gossamer-thin plastic membrane. This membrane must efficiently separate the fuel cell's two electrode chambers. Such fuel cells are therefore also known as polymer membrane fuel cells. „Currently, these membranes are as thin as ten microns," explains Kreuer. A human hair is roughly ten times as thick. Because there is still room for improvement in the membranes used to date, the chemists in Stuttgart have been researching new membrane materials for many years.

To understand what a membrane like this has to do, let's first look at the basic principle of how a hydrogen fuel cell works. Two simple chemical half-reactions take place within the fuel cell, physically separated at the two electrodes **(Fig. A)**. At the **anode**, the hydrogen gas H_2 is electrochemically split into two atomic hydrogen nuclei, i.e. protons (H^+), and two electrons (e^-). This type of reaction is called **oxidation**. From the anode contact, the electrons (e^-) flow through the external circuit and perform work. For example, they drive the electric motor in a car. They then flow back to the cell via the **cathode** contact. At the cathode, the electrons again join with the protons. The cell also draws in air and thus oxygen (O_2) via this electrode. The second half-reaction takes place in the cathode. Here, the oxygen molecule is dissociated on the surface of the catalyst into two oxygen atoms that each combine with two protons and two electrons to form water molecules (H_2O). This half-reaction represents a chemical **reduction**. The cell gives off pure water vapour together with excess air as exhaust gas. Theoretically, a cell of this type generates a voltage of 1.23 volts at room temperature. However, in practice, losses due to electrical resistance draw this down to less than 1 volt.
How do the protons get to the cathode? This is where the **membrane** comes into play. As an electrolyte, it must provide the protons with the fastest possible path from the anode to the cathode. This is because the flow of protons through the electrolyte is just as high as the flow of electrons through the load. The membrane must simultaneously prevent electrons from flowing straight through the cell. It is therefore an insulator for electrons. An electronic short-circuit through the membrane would be dangerous. The electrons must also perform work in the electric circuit outside of the cell. This outer circuit must therefore conduct the electrons well. This is ensured by metals like copper in the cables and motor windings, for example. In turn, these metals do not conduct protons, so they act in reverse as proton insulators.

THE HOTTER THE CELL, THE MORE EFFICIENT IT IS

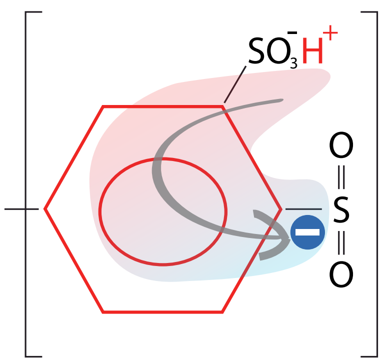
Electric vehicles that use fuel cells have some key advantages over conventional combustion engines. If the hydrogen fuel is produced using renewable energy sources, pure hydrogen fuel cells do not emit any climate-damaging carbon dioxide (CO2). This can be achieved by using surplus electricity from wind energy or photovoltaic systems, for example. An electrolysis plant uses this electricity to split water molecules into hydrogen and oxygen. Fuel cells can also be operated with methanol as the fuel, but then they do not operate CO2-free. Moreover, the methanol must be dissociated into hydrogen and CO2, which increases the technical complexity of the process. Another advantage of the fuel cell is its high efficiency, which can be increased still further. Kreuer explains that a modern, low-temperature fuel cell can convert roughly half the chemical energy stored in its fuel into usable electrical energy. Additional losses such as compression of the hydrogen in the pressurized tank reduce the final result to only about 40 percent. This is still far better than diesel-powered vehicles, which have an efficiency of roughly 25 percent.

FIG. B: NAFION MEMBRANE



Microstructure of a Nafion membrane. The hydrophobic molecule chains are green and the hydrophilic superacids (sulphonic acid groups) are yellow. Blue: water, red: positively charged protons.

FIG. C: THE STUTTGART MEMBRANE



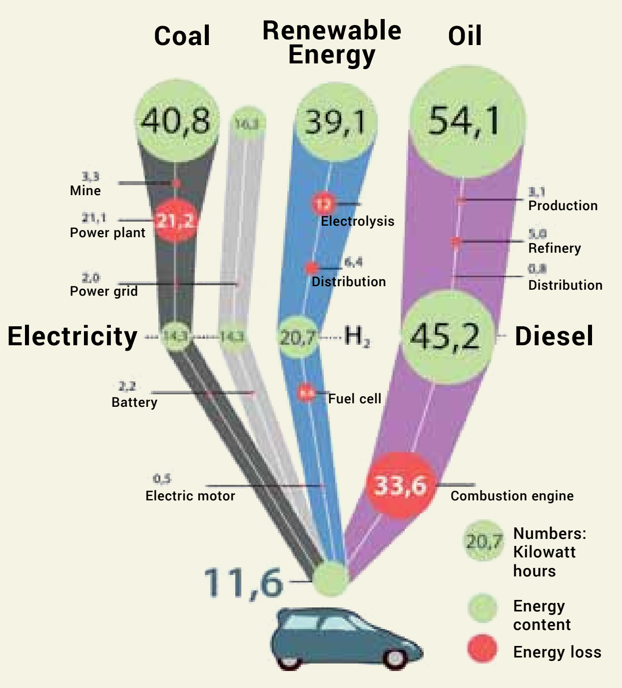
A monomer building block from the polymer chain in the new plastic for the Stuttgart membrane. Top right: Sulphonic acid group. This becomes a proton-donating superacid because the SO2 group (right) partially attracts an electronic charge (blue dot with minus) through the phenyl ring (centre). This in turn loosens the proton (H+) in the sulphonic acid group, which can easily be released.

However, this efficiency advantage and climate-friendliness are still insufficient to compensate for the disadvantages. Manufacturing costs are still high, and there is still no infrastructure for transporting hydrogen from production to the filling station. If low-temperature fuel cells were even more efficient and cost-effective, then cars powered by fuel cells would have greater success in establishing themselves on the market. One way to achieve this is to raise the cell's operating temperature. The hotter a cell is, the faster the electrochemical processes take place within it. This increases its efficiency. On the other hand, too high a temperature is dangerous for the cells. Depending on the manufacturer, the plastic membrane softens at the latest at 100 °C, and loses some of its proton conductivity as it dries out. The cell also produces waste heat that cannot be adequately discharged to the outside by the water vapour as exhaust gas. That is why low-temperature fuel cells need an elaborate cooling system. A higher operating temperature would simplify this. It would also reduce the quantity of expensive platinum needed as a catalyst, because the reaction would proceed more effectively. This in turn would significantly reduce the costs of a fuel cell system.

THE NEW MEMBRANE FROM STUTTGART

Kreuer's team is therefore conducting research to find alternative plastic materials. A few years ago, they succeeded in developing a plastic membrane that can withstand temperatures of up to 180 °C. It is also much more efficient in preventing the passage of gaseous hydrogen and oxygen. When these gases encounter each other on the catalysts, they react there to form aggressive radicals. „These attack the membrane," explains Kreuer. About 15 years ago, this limited the service life of fuel cells to less than 2000 hours. Now, radical scavengers are used, increasing service life to a more practicable 10,000 hours.
The original membrane material is called Nafion. All membranes currently in use are chemically related to it. The material was developed by American chemists in the 1960s. They forced two opposing partners together to form a single molecule: Teflon and sulphonic acid. Teflon is extremely water-repellent, **hydrophobic**, while the sulphonic acid group absorbs water very readily, making it **hydrophilic**. It turns into a **superacid** in the new molecule. A superacid is more acidic than concentrated sulphuric acid.
Because the two unequal partners strongly repel each other, the hydrophobic parts of the molecules organize in a fine network (Fig. B). In this process, the acid groups force them to the surface of this network. In the presence of water, the acid groups trap water molecules, forming a water structure that infuses the entire network. Like all Brønsted acids, these superacids readily release protons into water. This renders the finely dispersed water within the membrane conductive for protons. The membrane has to have an optimal water content to operate efficiently in the fuel cell.
However, the Teflon fraction in Nafion has two disadvantages. First, as a chlorofluorocarbon, it is not environmentally friendly. Second, this chemical structure causes Nafion to become critically soft even at the relatively low temperature of 80 °C. Although more modern variants are more thermally stable, it's still game over by 100 °C at the latest. The much more thermally stable membrane developed in Stuttgart is based on a more environmentally friendly hydrocarbon. Polyphenylene is a polymer made up of long chains of individual phenyl molecules. Each building block (monomer) also contains a sulphonic acid group (Fig. C). However, the polymer is much stiffer than Nafion. This means that the polymer network and the aqueous part with the ions cannot separate from each other as easily. The acid groups are therefore less well combined. Kreuer's team came up with a trick to compensate for this: they incorporated many more sulphonic acid groups into the material than Nafion contains. They were thereby able to achieve an even higher proton conductivity than that in Nafion.
A significant risk in operating polymer membrane fuel cells is of either the membrane drying out or becoming too heavily flooded. If the cell then has to operate at full power, the membrane material ages prematurely. A diagnostic system developed by a team headed by Tanja Vidakovic-Koch at the Max Planck Institute for Dynamics of Complex Technical Systems in Magdeburg should prevent this deterioration. Conventional diagnostic methods send electrical signals through the elect-

FIG. D: ENERGY CONVERSION CHAINS



From top to bottom: Energy conversion chains from primary resources to the amount of energy (11.6 kWh) needed to drive a car 100 km. The hydrogen (blue chain) and electricity (light grey chain) come from renewable energy sources. The greater the starting amount of energy in the top circle, the greater the losses.

rodes in the fuel cell and measure their electrical „response". This indicates whether the cell is working well or if it has a water problem.

„But it's not possible to distinguish whether the membrane is dried out or flooded," explains the engineer. The new diagnostic method now makes this possible. The Magdeburg researchers equip the cell with a sensor that records the flow of oxygen into it. The diagnostic system also uses the measured data to determine the flow of water through the cell. Yet another trick is needed to determine the health of the cell: The flow of oxygen and water into the cell must increase and decrease in waves.

These waves are sinusoidal, for example. The fuel cell reacts to this like a musical instrument. Depending on the frequency, the electrical response of the fuel cell attenuates or reinforces the input signal like a resonating body. This response now varies, depending on whether the membrane is „too dry" or „too wet." In this way, a future diagnostic system in a car could automatically determine how well its fuel cell is functioning. If it detects a critical condition early enough, even incipient damage to the membrane can be „healed", explains the scientist.

OPTIMAL FOR HEAVY ELECTRIC VEHICLES

Fuel cells face fierce competition from batteries in the transport industry. Both systems have advantages and disadvantages. In vehicles with fuel cells, the hydrogen gas is stored at 700 bar in a solid pressure tank that is protected against accidents. In this state, hydrogen has an energy density almost 200 times higher than that of lithium ion batteries. But even adding the weight of the pressure tank, an electric car carries a far greater battery weight relative to the amount of energy it stores than a battery-operated vehicle. On the other hand, it has the advantage of being able to store electric power without greater losses.

Conversely, the electricity for the fuel cell must first be used to produce hydrogen by electrolysis **(Fig. D)**. This hydrogen must in turn be used to generate electrical energy in the fuel cell. „Because of this detour, the efficiency level from the wind turbine to the wheel on the vehicle is two to three times lower than for a battery-powered vehicle," says Kreuer. However, these advantages and disadvantages depend on the size and weight of both types of electric vehicles. For a truck, a battery enabling useful transport ranges weighs many tons. A truck powered by fuel cells does not have to carry this „dead" weight around, nor does it need the same dense network of hydrogen filling stations that passenger cars do. So buses, trains and trucks could therefore help promote market penetration by fuel cells.

Keywords

anode, cathode, diagnostic system, electrochemical cell, electrolyte, high temperature/low temperature fuel cell, hydrogen fuel cell, low temperature fuel cell, membrane plastics, oxidation, reduction

Further reading

- *Books and articles on hydrogen and fuel cells*
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Links

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Videos

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