Plastics in Fuel Cells

Electromobility Arguments in Favor of a Future with Hydrogen

Electromobility, whether based on batteries or hydrogen fuel cells, permits zero-emission driving and the integration of the transport sector into an overall concept with a high share of renewable energy. Fuel cell technology will play a key role here, not only because of its long-range capability. However, the deciding factor will be the use of high-quality, but also cost-effective, materials and production processes to offer reliable, affordable products. This will place demands on plastics technology, in particular.

Injection-molded bipolar plate of plastic-carbon compound (© JRF e.V.)

The transport sector's current dependence on oil as energy source is regarded as problematic for both ecological and economic reasons. The pollutant emissions from transport are harmful to health and reduce life expectancy while making a significant contribution to CO_2 emissions. Politics and industry must therefore focus on developing alternative drive concepts, for both personal mobility and the transport system.

Mobility Structures for Battery Vehicles and Fuel Cell Vehicles

Along with other criteria (**Table 1, p. 21**), battery-electric vehicles are now regarded as mainly suitable for short distances; for long-range journeys and applications in the transport and logistics sector, on the other hand, it is unlikely that solutions based purely on battery technology will offer user-friendly solutions. A climate-friendly, clean and economically attractive alternative to oil is offered by hydrogen. It can be manufactured renewably in situ and, in particular, can be filled rapidly. Converting hydrogen into electricity with low-temperature fuel cells is one of the most efficient and quiet concepts for ecologically sound long-range mobility.

The fuel cell technology is well on the way to sustainably changing mobility structures. All the major automotive companies are working on the technology. The first fuel cell vehicles are already commercially available. Trains and buses with hydrogen fuel cells are already successfully used in scheduled operation, in the medium term, trucks and even aircraft and ships are to be equipped with low-emission fuel cell drives.

Applications and Development Status of Hydrogen Technology

Internationally, the fuel cell is already technically mature and established on the market in stationary applications, but also for material handling and backup power supply. In Japan, over 290,000 CHP (combined heat and power) fuel cell systems were installed by the end of 2018, providing a highly efficient supply of power and heat to households. In the field of material handling, forklift trucks and electric lifting trucks operate emission-free 24/7 without charging or complicated battery changing processes. Over 20,000 such systems are in use in the USA. In backup power supply, over 8500 fuel cell systems are currently installed globally due to their very high availabilities and long bridging times [1].

The fuel cell is currently being introduced into mobile applications. Despite the low production rates of only a few thousand fuel cell cars to date, the transport sector already dominates the global stack power due to the high installed system performance per vehicle (**Fig. 1**). »

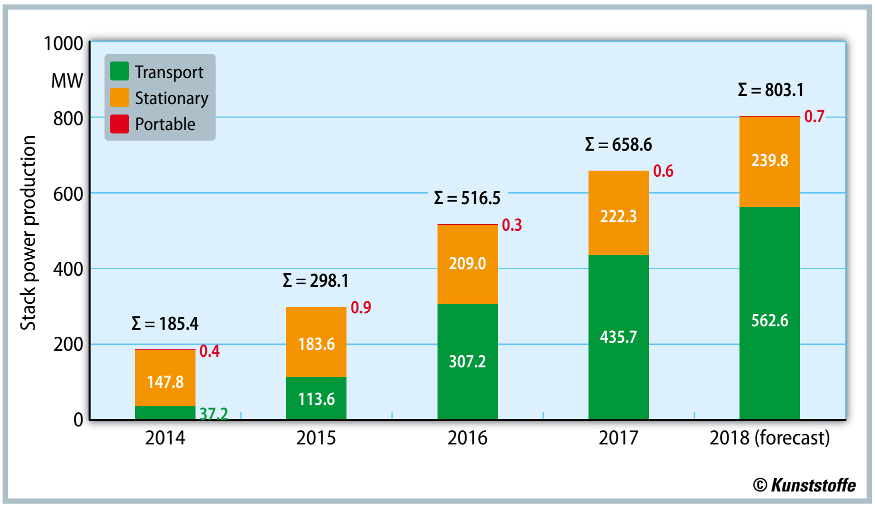

Fig. 1. Global stack power production from fuel cells, according to application [1] (source: E4tech)

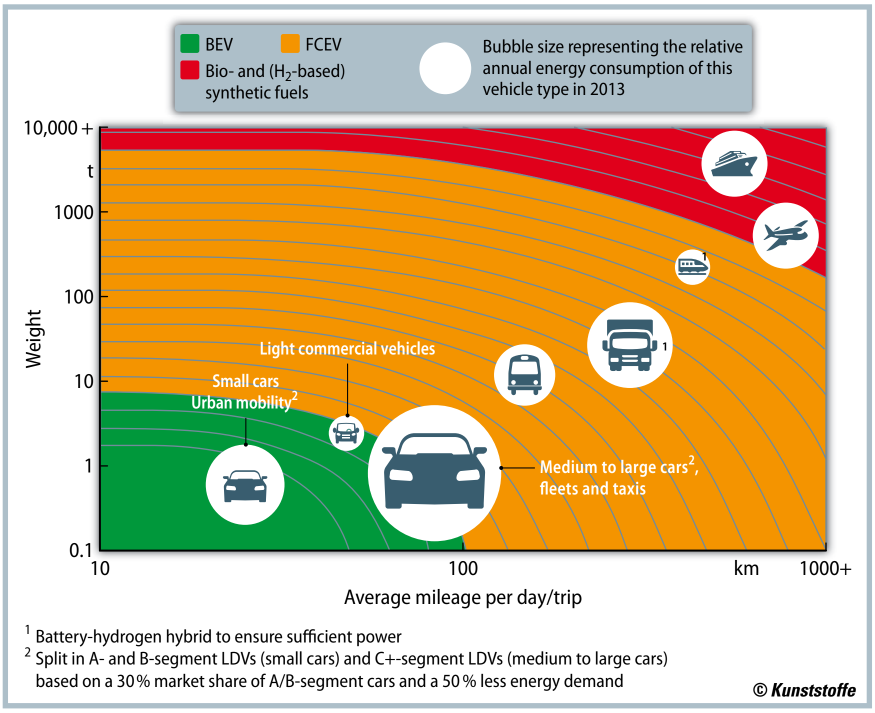

Fig. 2. Current and future application fields of fuel cells in the transport sector [4] BEV: battery electric vehicles; FCEV: fuel cell electric vehicles (source: Hydrogen Council)

Automotive manufacturers are planning the market introduction of larger quantities as of 2020. For example, as of 2020, Toyota, for example, intends to increase the production of fuel cell vehicles to 30,000 units per year [2] – thereby, solely through Toyota's activities, increasing the globally produced stack power of fuel cells more than fivefold, from its current 650 MW to approx. 3500 MW. Hyundai is investing approx. EUR 6 billion in production capacities to 40,000 fuel cell systems per year by 2022, and 700,000 by 2030 [3].

The PEM (polymer-electrolyte-membrane) fuel cell already dominates the market. This trend will be reinforced with the continued growth of the transport sector, in which the PEM fuel cell will be almost exclusively used, particularly due to its high dynamics and excellent cold start behavior. In mobile applications, fuel cell technology is particularly suitable, especially for applications requiring long ranges and short refill times. Besides the larger long-distance-capable cars, this also includes lightweight commercial vehicles, buses, trucks, trains through to aviation and shipping (**Fig. 2**). Other fuel cell technologies, such as the phosphoric acid fuel cell (PAFC), the molten carbonate fuel cell (MCFC) or the solid oxide fuel cell (SOFC) are used, particularly in stationary applications, predominantly in relatively large performance classes.

The energy density of current automotive fuel cell systems, incl. hydrogen tank is already significantly higher than the energy density of battery systems in battery-electric vehicles. In addition, similar performance densities are achieved (**Fig. 3**). The advantage of fuel cell systems is that, independently of one another, the system performance can be designed in advance via the dimensioning of the fuel cell stack, and the amount of energy or range respectively can be designed via the dimensioning of the hydrogen storage. This permits compact, emission-free electrical powertrain systems with low weight to be provided, even in the commercial vehicle range, where there is a high energy requirement.

The Membrane Fuel Cell

With the development of the polymer membrane, which is suitable for use as a proton-conductor electrolyte, the membrane fuel cell has started its triumphal rise. The cell type can now be found in home energy systems, in fuel cell vehicles and in off-grid power supply systems. According to the application, the lifetime, the power density or other system aspects are optimized. The common feature of all applications is the demand to reduce costs, which mainly come from the automotive industry.

The construction of a membrane fuel cell is characterized by a layer system; the membrane electrode unit with five to seven functional layers forms the heart of the cell [6, 7]. The proton-conductor, solid membrane electrolyte has a catalyst layer on both sides. The membrane and catalyst form the reaction layers in which the electrochemical reactions of hydrogen oxidation and oxygen reduction take place. A large active surface of the so-called 3-phase zone between the combustion gases, the catalyst as electron conductor and the electrolytes as ion conductor is important to obtain high power densities.

Adjacent to the catalyst, there is a microporous layer and a gas diffusion layer, whose function consists in conducting the electrons from the catalyst to the cell frame and being permeable for the reaction gases and for the reaction product water. The properties of these layers make a considerable contribution to the water management of the cells. On one hand, sufficient moisture must be provided in the membrane in order to achieve the required high ion conductivity and on the other hand to avoid water accumulating in the gas channel structures.

The electrochemical reaction in the membrane fuel cell (**Fig. 4**) takes place in two sub-processes: hydrogen is oxidized at the anode, and oxygen from the supplied air is reduced at the cathode. The reaction product is water:

$$H_2 \longleftrightarrow 2\,H^+ + 2\,e^-$$
$$\tfrac{1}{2}\,O_2 + 2\,e^- + 2\,H^+ \longleftrightarrow H_2O$$
$$H_2 + \tfrac{1}{2}\,O_2 \longleftrightarrow H_2O$$

The reaction releases electrical energy and heat energy. The performance of a cell is characterized by the current density-voltage curves (**Fig. 5**).

The open-circuit voltage of a cell is about 1 V. Under load, the voltage is further reduced until the maximum electrical power is reached at approx. 0.5 V. In parallel with the dropping cell voltage, the electrical efficiency of the cell also falls, which, in simplified form is derived as the voltage efficiency – expressed as a quotient of the measured cell voltage for theoretical voltage of 1.25 V, which can be calculated from the lower heating value of the hydrogen of $\Delta_R H_u$ = -241.8 kJ/mol.

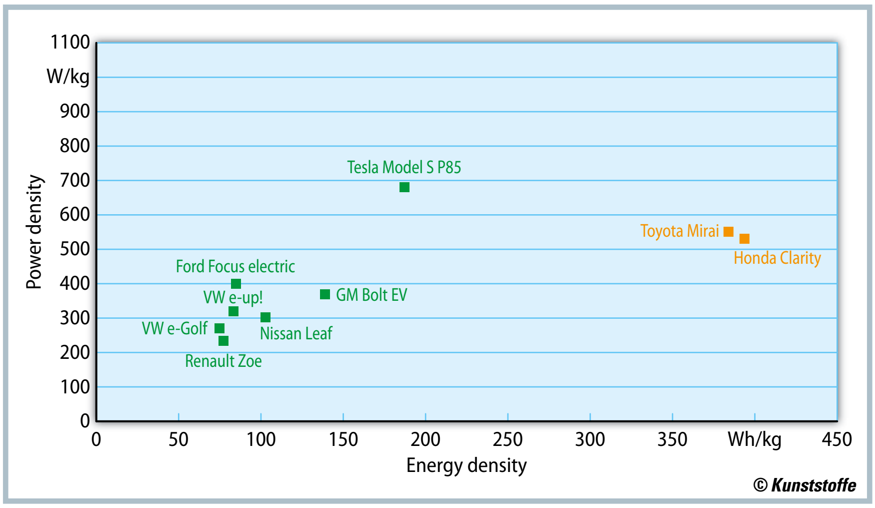

Fig. 3. Comparison of commercial automotive battery (green) and fuel cell systems (orange), incl. hydrogen stores with 5.7 wt.% H_2 acc. to [5] (source: ETI Group)

The Membrane as a Plastic Element of the Fuel Cell Stack

A fuel cell essentially consists of two functional elements: the membrane-electrode unit as an electrochemically critical component and the bipolar plates, which form the key mechanical element, on one hand, and, on the other hand both supply the cell with the process media and efficiently take off the energy.

The development of polymeric proton conductors has led to commercially available membranes, in which polymers with a perfluorinated backbone with side chains bearing sulfonic acid groups are still the standard [8]. Besides high proton conductivity, the chemical and mechanical stability, as well as the gas permeability, are important properties of these components. The proton conductivity is dependent on the water content, as well as the equivalent weight and thickness of the membrane. For the automotive industry, ever thinner membranes have been successfully developed, which can increase current density as well as achieve the performance targets of 1.2 W/cm^2.

Despite the low thickness of the membrane (approx. 20 µm), reliable operation, in particular gas-tightness, must »

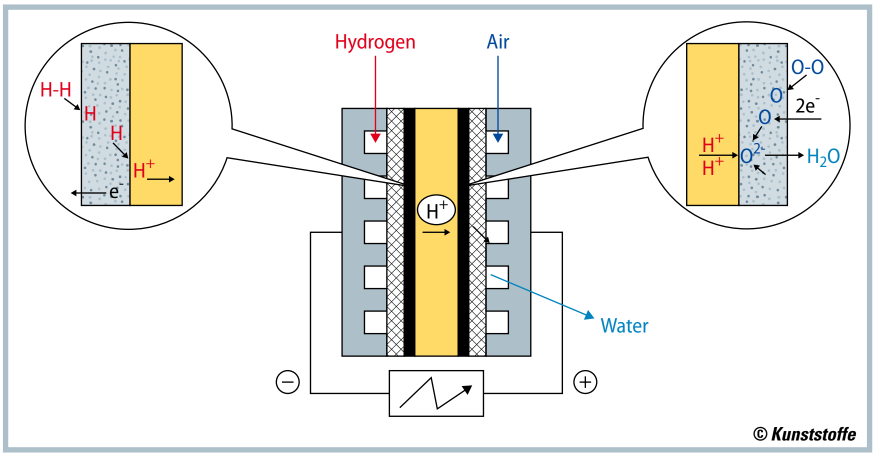

Fig. 4. Schematic view of the construction and the electrochemical reactions of a membrane fuel cell (source: A. Heinzel)

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- Read the German version of the article in our magazine ***Kunststoffe*** or at ***www.kunststoffe.de*** be ensured over the lifetime of a fuel cell vehicle. Degradation and accelerated aging tests are therefore highly important [9]. Mechanical stress due to moisture cycles or frost-thaw cycles and chemical degradation, particularly as a result of free-radical intermediate products, such as the OH radical, as well as thermal aging, can thin the membrane material locally and eventually initiate defects. Such chemical attack can also be caused by media supplied externally.

As an indicator of the membrane aging, the presence of released fluoride-containing compounds in the reaction water, a rise in the hydrogen permeation and a reduction of the electron resistance of the membrane electrode unit can be measured. The introduction of expanded PTFE films [3], inorganic nanomaterials [10] or nanofibers through to a combined manufacturing process comprising electrospinning and ink-jet printing of a composite membrane [11] are approaches that are being pursued by the various work groups, with promising results.

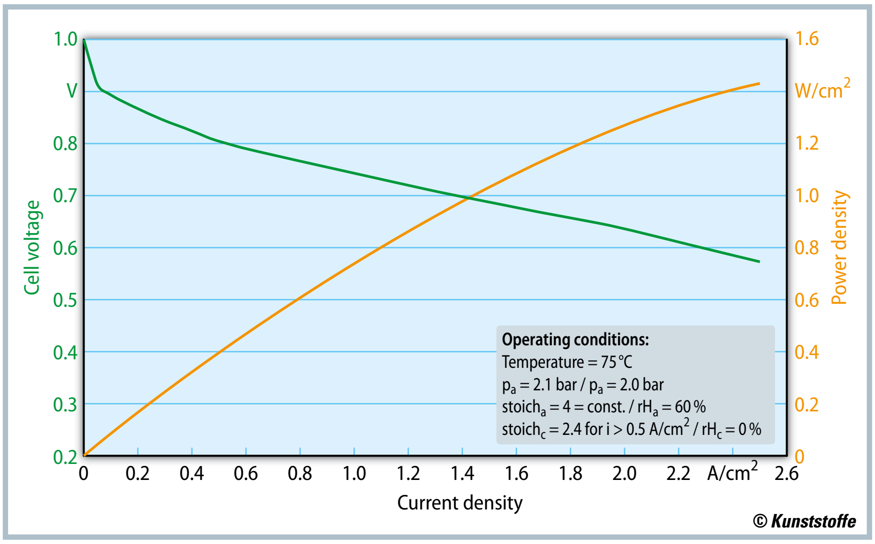

Fig. 5. Current density-voltage curve of a PEM fuel cell (source: ZBT, Dr. Jörg Karstedt)

Bipolar Plates as another Plastic Element

Apart from the fact that they conduct electrical current, the bipolar plates also have other important functions. They distribute the reaction gases over the electrode surface, at both the anode and cathode side, and cool the fuel cell stacks. For this purpose, components are produced consisting of two plates and containing different structures for gas distribution and the channels for the cooling structure. For the different applications in stationary areas and electromobility, two different types are currently used:

- Bipolar plates produced from metal foils and
- those produced from a plastic-carbon compound (**Title figure**).

Because of their significantly lower construction volume, the former are used, in particular, for car applications with planned lifetimes of 8000 operating hours at most. Compound bipolar plates, by contrast, have the advantage of greater chemical stability and are therefore preferred for applications with longer planned lifetimes in stationary applications, but also in the transport sector (trains, trucks).

Despite high carbon or graphite content – filler loadings of up to 85 % – thermoplastic materials can still be processed by plastics technologies [12]; however injection molding requires, e.g., a plate thickness of 2 to 3 mm. Injection molding introduces the desired gas distribution structures and seal grooves into the surfaces of the plates. Subsequent surface treatment ensures low contact resistances with respect to the adjacent gas diffusion layer.

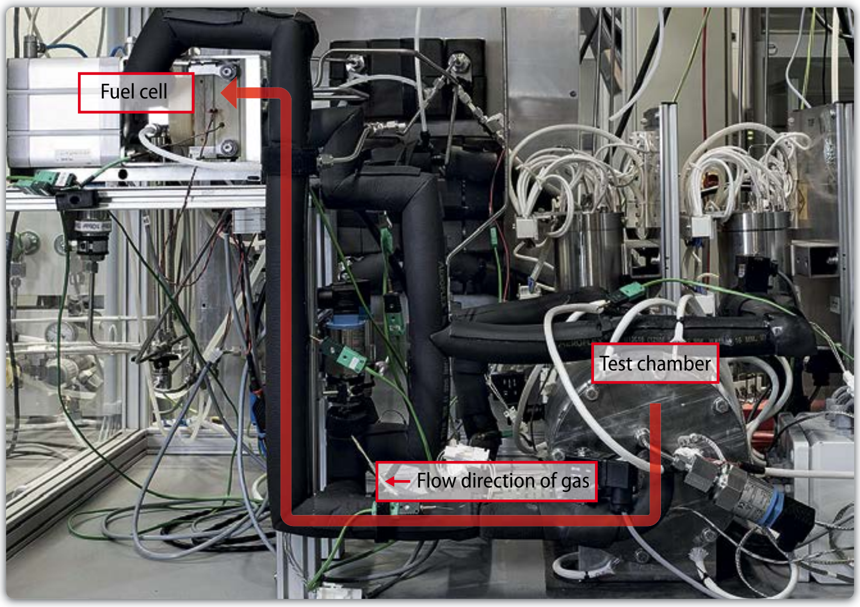

Fig. 6. Set-up for investigating material samples for fuel cell suitability (source: ZBT, A. Kayser)

Cost Reduction in the Fuel Cell System with Alternative Materials

The operation of fuel cell stacks requires numerous additional ancillary components, which are intended to supply the stack with the reactants hydrogen and (atmospheric) oxygen, as well as with the coolant. This includes actuators (e.g., pumps, compressors, valves), connecting elements and sensors. As the technical maturity of fuel cell systems improves, the component costs must be significantly reduced – the future task is therefore to increasingly install inexpensive materials in fuel cell stacks and the surrounding ancillary equipment.

However, the influence of external contaminants introduced into the cell from the materials used or from the environment is currently a significant accelerator for the degradation of fuel cells. The

	With fuel cell	With battery
Advantages	■ High energy densities permit use in cars, but also in trucks, buses, trains, ships and aircraft ■ Long ranges ■ Short filling times (**Fig. 8**) ■ High share of value creation in European industry ■ Hydrogen is a large-scale storage option for fluctuating renewable energy	■ Greatest efficiency when renewable power is used ■ Existing production infrastructure, which is successively expanded ■ Higher number of cars already available on the market ■ For smaller market shares simple expansion of the charging infrastructure
Challenges	■ Production capacities for stack components are currently still being built up ■ High costs due to the current low quantities ■ Hydrogen infrastructure must be expanded	■ Space and weight ■ Charging times ■ Costs of the charging infrastructure, in particular for fast charging ■ Resource availability of important raw materials

Table 1. The main pros and cons of battery-operated vehicles compared to fuel cell vehicles (source: ZBT)

Fig. 7. Test rack within the test chamber with the possibility of positioning a total of 27 material samples (© ZBT, A. Kayser)

qualification or suitability testing of such materials and the components they are used to make is therefore an important task, both during development and as part of quality assurance during subsequent production processes.

At the hydrogen and fuel cell center ZBT in Duisburg, Germany, in the "Validate" project, carried out jointly with the partners Volkswagen AG and SGS Fresenius, the focus is on researching validation methods to analyze the influence of materials in the media supply circuits of the fuel cell system, and the stack, for potential damage to the fuel cell. The aim of the joint project is to develop test processes and draw up test specifications for qualifying materials and stack and system components.

The key element of the scientific analyses at the ZBT is characterization of different material samples (thermoplastics, elastomers, thermosets, but also metals). They are introduced into the media supply circuit under conditions typical of the fuel cell, and then the media are supplied directly to the fuel cell (**Fig. 6**). This allows the effect on the performance of the fuel cell of any pollutants that may potentially be released to be determined.

The core element of the test set-up is a test chamber, which can be separately heated. Within the test chamber, there is a rack, with the aid of which a total of 27 test samples can be positioned on nine layers (**Fig. 7**). This permits flow over a large material surface area, thus accelerating the test procedures. This test set-up correspondingly permits a rapid suitability test for the particular material to be performed. The first studies demonstrate the suitability of the method. Whereas sulfur-vulcanized EPDM positioned in the test chamber led to severe loss of performance within a few hours, studies with polyphthalamide (PPA) did not result in any negative effects on the test fuel cell.

This in-situ test method permits OEMs and suppliers to subsequently qualify new materials under defined conditions for their suitability for use in the fuel cell system, and, during the subsequent production process, to perform spot checks on batches of already qualified materials and components.

This enables the supplier industry to purposefully develop cost-efficient system and stack components, using the test specifications, with no impairment of the lifetime of the fuel cell system. The background to the performance deficits that may potentially be introduced may be contaminants leached out of the components by the media (ultrapure water, cooling media or gases).

Fig. 8. Filling a Hyundai IX35 at the hydrogen filling station in Mülheim an der Ruhr, Germany (© Jorgo Chatzimarkakis, Hydrogen Europe)

Summary

Plastics technology already plays an important role in the fuel cell. The key components of the stack are only made possible thanks to plastics, likewise connecting elements, actuators and sensors in the media supply are often at least partly made of polymeric materials. The upcoming mass production requires lower material and production costs – and new, cost-effective materials must be used for this. However, this runs the risk of contamination, and thereby a shorter lifetime for the fuel cell. For quality assurance, a method will therefore be established for testing new components and materials at an early stage. ■