FUEL CELL AND HYDROGEN VEHICLES – STATE OF THE ART AND CHALLENGES FOR IMPROVED MATERIALS

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Abstract

Fuel cell vehicles should be further improved. Key issues are cost reduction; higher power density of the primary energy converter, the fuel cell; wider operation ranges and improvement of operation parameters, e.g. higher operation temperature and starting ability in freezing conditions. Using advanced materials and construction principles is a key factor by meeting these requirements. The paper gives a short introduction to the technology of fuel cell vehicles and the most prominent fuel cell type for traction applications, the polymer-electrolyte-membrane fuel cell (PEFC). Progress in material development of a core component of the PEFC, the bipolar plate is described.

In the second part of the paper some ideas are presented, in which way material research could help to enable suitable on-board storages for hydrogen. Namely, a new approach to design compressed gas storages and new developments in materials for solid state hydrogen storage are brought to attention.

Introduction

The fuel cell is in the transformation from chemical energy to electricity a very promising primary energy converter for automotive propulsion due to their high efficiency and ultra-low emissions. The polymer-electrolyte-membrane fuel cell (PEFC) - among the different types of fuel cells - is almost exclusively discussed for applications in traction because of their rugged design and suitability for dynamic operation. Therefore this paper deals exclusively with PEFC technology. In comparative views with other vehicle power trains "tank to wheel" lowest CO₂-emissions for vehicles with fuel cell power trains were obtained with the PEFC-fuel cell technology [1]. However, extending the view to “well-to-wheel” it becomes apparent that the advantage is getting smaller or – for unfavorable fuel supply chains – CO₂-emissions could be also higher. The PEFC’s preferable fuel for is hydrogen. As fuel up-to-date almost exclusively hydrogen is used, because it has been found that the realization of gas generation systems, which convert hydrocarbons to a hydrogen rich gas on-board, is very complex [2]. Consequently, the above cited potential can only be assessed, if satisfying answers to the questions of hydrogen production, infrastructure and storage are found with regard to economics. Furthermore, technical progress is needed in fuel cell propulsion technology. Main issues are: cost of the power train; lifetime of the core components, namely the fuel cell stack; cold start ability; performance under freezing conditions; and operating range of the vehicles. Improved materials are needed to meeting the envisaged targets. This paper gives some examples for challenges in material science developing advanced PEFC-stacks and advanced hydrogen storages.
Fuel cell power train

Fig. 1 shows the scheme of fuel cell power train applied to an electrical drive train. Torque for traction is provided by an electrical engine, which is usually fed with electrical energy by an inverter. The primary energy converter, which provides the electrical energy, is a fuel cell system. The hydrogen, which is consumed by the fuel cell, is stored in a hydrogen storage.

Despite of the hydrogen supply the fuel cell system needs more sub systems: an air supply system, a heat and water management system and a control system. However, the most important component, which determines the characteristics of the fuel cell system to a wide extend is the fuel cell or fuel cell stack itself. Although the fuel cell technology has already made substantial improvements in the past; the road map of fuel cell developers foresees significant improvements e.g. cost reduction, durability, lifetime and power density until 2010. For instance in the road map of Ballard the cost target for a fuel cell stack by 2010 comes to 25 USD/kW net EOL compared to 103 USD by 2004 [3].

With regard to the hydrogen storage the target of the DOE in the United States a cost reduction to 6 $/kWh of stored energy at a recoverable hydrogen storage capacity of 4.5 wt% shall be reached by 2007 [4].

PEFC stacks

A fuel cell stack has to provide all manifold functions. Fig. 2 shows on the left side a schematic representation of a single PEFC, whereby flow of media, heat and current is indicated. This scheme is not complete and some flow directions may differ depending on specific cell designs and/or specific operating conditions. The center component of the PEFC is the proton exchange membrane, which separates the two reaction layers. The combination of the membrane and the two electrodes is often called membrane electrode assembly (MEA). On the anode fuel is oxidized, whereby electrons are dragged to an external circuit and protons are conducted through the membrane to the cathodic side. On the cathode oxygen is reduced and combined with protons from the membrane and the electrons from the external electric circuit to water. Heat is released in several reaction steps and must be removed from the location of its genesis transferred to a heat transfer fluid (htf). The heat transfer fluid flows in a cooling plate, which may serve as the so called bipolar plate (BPP) as well. The function of the layers - gas distributor and gas diffusion layer - is to distribute the reactants to the active layers (electrodes: anode and cathode) respectively to collect and remove the products or inert gases from active layers. The gas distributor is often integrated into the bipolar plate. The gas diffusion layer is also called backing. Bipolar plates interconnect electrically a number of single PEFCs forming a so-called “stack” and multiplying thereby the voltage of the stack. An example of a PEFC stack is given on the right-hand-side of fig. 2. The single cells and bipolar plates are covered on both sides with metallic end plates, which fix mechanically the stack and provide the inlets and outlets for the media. Near to each end plate one current collector (plus and minus pole of the stack) of the stack can be seen. It is obvious that within the stack manifolds are needed, which provide the media supply to each individual cell, whereby appropriate gaskets must separate the different media.
In summary the main transportation processes in the fuel cell are: (1) proton transport through the membrane from the anodic side to the catalyst surface of the cathode; (2) electrons through an external electric circuit from anodic side to the catalytic surface of the cathode (3) electrons from the cathode of one fuel cell to the anode of a second cell through the interconnecting bipolar plate, (4) the reactants and products to and from the reaction layers on the anodic and cathodic side as well; (5) heat from the membrane electrode assembly (MEA) to the htf cooling channels. There are various research activities ongoing regarding all components of fuel cells. In the following some aspects regarding material research on BPPs and polymer membranes are given.

**Bipolar Plate and Membrane**

Bipolar Plates (BPPs) contribute significantly to cost, volume and mass of fuel cell stacks. Hermann et al. report, that BBPs participate with about 80% to the stack weight and with 45% to its cost [5]. Newest research results at DLR-IFK indicate a contribution of about 33% to the stack cost [6]. A BPP fulfills multiple functions: it separates individual cells in the stack, it distributes fuel and oxidant, it may serve as a support for gaskets, it may serve as a cooling plate, it conducts electrons. Herman et al. give the following properties, which should be met by a BPP.

- Electrical conductivity: plate resistance < 0.01 Ohmcm²
- Thermal conductivity: as high as possible.
- Hydrogen/gas permeability: <10⁻⁴ cm³/(s cm²)
- Corrosion resistance: corrosion rate < 0.016 mA/cm²
- Compressive strength: >22 lb/in²
- Density: <5g/cm³

The following materials are under investigation for BPPs: non-porous graphite/electrographite; coated and non-coated metals; composite materials (polymer carbon and polymer-metal). Due to the character of the membrane, the BPP must withstand an acidic environment at temperatures around 80 °C. Because of its chemical stability and low electrical resistance, graphite has been widely used in the past as preferable BPP material for PEFC stacks. However, the mechanical properties of graphite are not favorable. It must be handled with care, manufacturing of parts with structures is very expensive and the design of the entire stack has limits given by the mechanical properties of graphite. Therefore metal and composite materials have actually drawn more attention.

Chemical stability is the main issue for metal plates, which can be shaped relatively easily. Recently the supplier Dana reported promising results for BPPs with special coatings [7]. In comparison with other BPPs the degradation of special coated plates was reduced about by a factor 6 compared to stainless steel. The observed degradation was even smaller than the degradation of a BPP made of gold.
As explained above main functions of the polymer electrolyte membrane are the conduction of protons from the anode to the cathode side of the fuel cell and the separation of the reactants. Consequently the membrane should have high proton conductivity, low gas permeability, high thermal and chemical stability, and high mechanical stability. Perfluorinated ionomer membranes like Nafion® from DuPont are widely used in PEFCs. However, the automotive industry is asking for low-cost membranes, which can be operated at higher temperatures without the need for a sophisticated water management [8]. Worldwide there are extensive research activities on advanced electrolyte membranes ongoing. An overview can be found in [9].

**Hydrogen storage**

Main requirements to on-board hydrogen storages are: (1) high mass and volume specific storage capacity, (2) highly dynamical operation to provide instantaneous hydrogen mass flow, (3) safety, (4) easy-to-maintain, (5) fast and easy refill, (6) long life time with cycling. An industrial view on hydrogen storage in vehicles can be found in [10]. Actually mainly compressed gas storages are used to store hydrogen in fuel cell vehicles. Advanced pressure hydrogen storage systems, which are manufactured with carbon fibres for a pressure range up to 700 bar, have a volumetric and mass specific storage capacity of about 4 %. Consequently 4 kg of hydrogen - equivalent to 16 l of gasoline - can be stored within a tank system volume of around 100 l at a mass of around 100 kg [11]. Liquid hydrogen storage systems with the same size and weight take about 30 % more of hydrogen. However, liquid hydrogen storage has to be stored at 20 K. This storage method uses about 30 % of the energy content of the hydrogen for liquefaction.

In comparison to the actual state of the art of technology, the storage target of the US-DOE for 2010 is to achieve a capacity of 6 wt%. Having in mind the challenging targets and the limits, which are set almost by the physical behaviour of hydrogen new approaches are needed to overcome barriers and to reach the ambitious goal.

![Fig. 3: Comparison of different pressure vessel technologies with the DLR-concept [12].](image)

Fig. 3 compares some construction principles of pressure vessels. Comparison is based on compressed natural gas vessels. With the storage of natural gas in series vehicle more experience with is already available. However, the same classification could be used for hydrogen vessels. There are 4 different vessel construction principles for cylindrical vessels. The CNG1 is full metal cylinder. It is cheap and has a high weight. Having the costs in mind, it is widely spread for usage in vehicles at pressure levels of 200 and 300 bar respectively. By substituting the metal with light-weight material and achieving the mechanical strength by applying fibre wrapping, the mass can be reduced to almost one third to the extent of higher cost. The new approach of DLR is indicated in the upper right corner [12]. It combines the advantages of cylindrical pressure vessels with a cellular structure. So, the ideal usage of material, shaped cylindrical in order to withstand the inner pressure, is kept inside the outer shell of the flat tank. Within the inner volume, where almost no pressure differences occur between
the cells, the storage volume is increased by applying quadratic shapes and the thickness of the material is reduced. Thus a flat pressure vessel is realized, which should better fit package requirements. The shape can also be customized by skipping segments, which is also indicated in Fig. 3.

In order to enable a significant cost reduction a production process, which allows mass production with short cycle times should be applied. Therefore it is intended to manufacture the pressure vessel by injection moulding using short fibre reinforced thermoplastic as material, whereby the mechanical strength should be obtained by applying endless fibre inlays (see Fig. 4).

Fig 4: Example of an arrangement with inlays made from endless fibres foreseen for injection moulding [12].

Mechanical properties of advanced short fibre reinforced thermoplastics have been determined by DLR experiments, whereby a tensile strength up to 200 MPa was obtained. FE-calculation based on these experimental data show that compressed natural gas vessel should be feasible using this new construction principle. However, it is obvious, that the mechanical properties of the material vary widely with the orientation of the fibres. Therefore, the next step is the detailed investigation of injection moulding of short fibre reinforced thermoplastics to understand how the optimal mechanical properties can be realized not only in test probes but also in the demonstrator and prototype tank size. These investigations are part of an ongoing project, which is focussing on compressed natural gas storages.

Applying the concept to compressed hydrogen storages will be a second step and an extraordinary challenge. Major issues are to further improve the mechanical properties of the material with respect to the higher pressure level of the hydrogen storage and to reduce the permeability of hydrogen through the material. The second issue could be also answered by applying a liner with low permeability.

Due to the relatively low storage capacities of low temperature metal hydrides - often less than 1 wt% - storage systems based on physisorption materials are seldom applied in vehicles. Unfortunately, promising research results with carbon based materials could not yet be confirmed. However, due to new material developments, there is an increasing interest in solid hydrogen storages. Especially the elements of group one, two and three, e.g. Li, Mg, B, Al, which form a large variety of metal-hydrogen complexes, are gaining more attraction [13]. From a practical point-of-view a major challenge of solid hydrogen storages - beside the realization of the required storage capacity – are reversibility of the reaction, compliance to the available temperature levels of the heat source and heat sink and sufficient charging and recharging times. Advanced metal-hydrogen complexes such as the so called alanate-group differ from conventional hydrides, i.e. ionic or covalent bonds are created through the hydrogen absorption process, which yields to structural change. In [13] is stated: “But up to now there has been only one compound identified which shows experimentally proven reversibility in terms of hydrogen uptake and release under moderate conditions, the sodium aluminium hydride, or sodium alanate (NaAlH4)”. This material has a maximum, theoretical, reversible hydrogen content of 5.7 wt%, meaning that from the system point of view the above cited capacity target cannot be achieved. However, considerable progress in the kinetics of those materials has been achieved by doping the base material with Ti-cluster and preparation methods as e.g. ball milling. Thereby the absorption time has been reduced by a factor of 5 to 7 min [13].
**Summary**

Material research is a key factor pushing fuel cell vehicles forward. The paper gives some spot lights regarding material research on two main components of fuel cell vehicles – on-board hydrogen storage and fuel cell stack. The manifold functions of a PEFC stack require tailor-made materials, which can be mass-manufactured in order to meet low cost targets. The bipolar plate is an excellent example, where it is tried to replace graphite by metals or compound material. However, this requires answers regarding corrosion resistance and manufacturing processes.

Looking on-board hydrogen storages, conventional storage technologies - compressed gas and liquid hydrogen - are approaching their limits, which are mainly defined by physical properties of hydrogen, when conventional solutions regarding construction principles and materials are applied. The new DLR concept for compressed gas storage could help to solve the cost and capacity issue together. However, it will be first applied to compressed natural gas vessels. Further extension of the concept to hydrogen vessels will be an extreme challenge.

Promising results on complex metal hydrides are encouraging to intensify the material research in this field. However, basic research is still needed to identify material with sufficient high, reversible storage capacities, having also a satisfying kinetics. In a next step storages in technical size could be developed.

**References**


