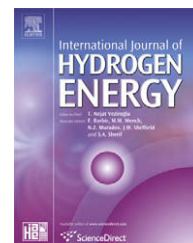


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Recent challenges of hydrogen storage technologies for fuel cell vehicles

D. Mori*, K. Hirose

Toyota Motor Corporation, Fuel Cell System Development Division, 1200, Mishuku, Susono, Shizuoka, 410-1193 Japan

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ABSTRACT

Fuel cell vehicles have a high potential to reduce both energy consumption and carbon dioxide emissions. However, due to the low density, hydrogen gas limits the amount of hydrogen stored on board. This restriction also prevents wide penetration of fuel cells. Hydrogen storage is the key technology towards the hydrogen society. Currently high-pressure tanks and liquid hydrogen tanks are used for road tests, but both technologies do not meet all the requirements of future fuel cell vehicles. This paper briefly explains the current status of conventional technologies (simple containment) such as high-pressure tank systems and cryogenic storage. Another method, hydrogen-absorbing alloy has been long investigated but it has several difficulties for the vehicle applications such as low temperature discharge characteristics and quick charge capability due to its reaction heat. We tested a new idea of combining metal hydride and high pressure. It will solve some difficulties and improve performance such as gravimetric density. This paper describes the latest material and system development.

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1. Introduction

Mobility is one of human beings' fundamental desires. Along with the progress of the world economy it is likely to expand further in the future, and people demand mobility everywhere in the world. However, it should be clean and safe as well as inexpensive. The increase of personal mobility mainly derived from automobiles raises environmental concerns such as exhaust emission and global warming. Transport consumes about one quarter of the world total energy. In the case of internal combustion engines, a large part of the fuel energy is emitted as heat due to friction loss and exhaust gas. So higher efficient technologies such as fuel cell vehicles are hoped for [1]. With this scope, hydrogen is expected to be a clean and recyclable energy carrier after the fossil fuel. However, the development of fuel cell vehicle is facing a big barrier of on-

board hydrogen storage due to its gaseous property of low density. The cruising range of vehicle is limited by the amount of hydrogen on board. It has only 1/10 of energy compared with gasoline from the same volume. Fuel cell vehicle's high efficiency can only compensate for part of this disadvantage. Therefore, it is necessary to increase both storable hydrogen and efficiency to achieve comparable range as gasoline vehicles. In other words, hydrogen storage is the key technology for the introduction of the hydrogen society. We need a new material and concept to meet vehicle requirements. We engineers are trying to design a new tank system to store more hydrogen on board. In order to draw a new tank design, we need several fundamental data such as material density, heat conductivity, volumetric change, heat of absorption or dehydrogenation energy, as well as gravimetric density and hydrogen uptake [2–7]. From those data we can propose new

* Corresponding author. Tel.: +81 55 997 9740; fax: +81 55 997 7120.

E-mail address: mori@daigoro.tec.toyota.co.jp (D. Mori).

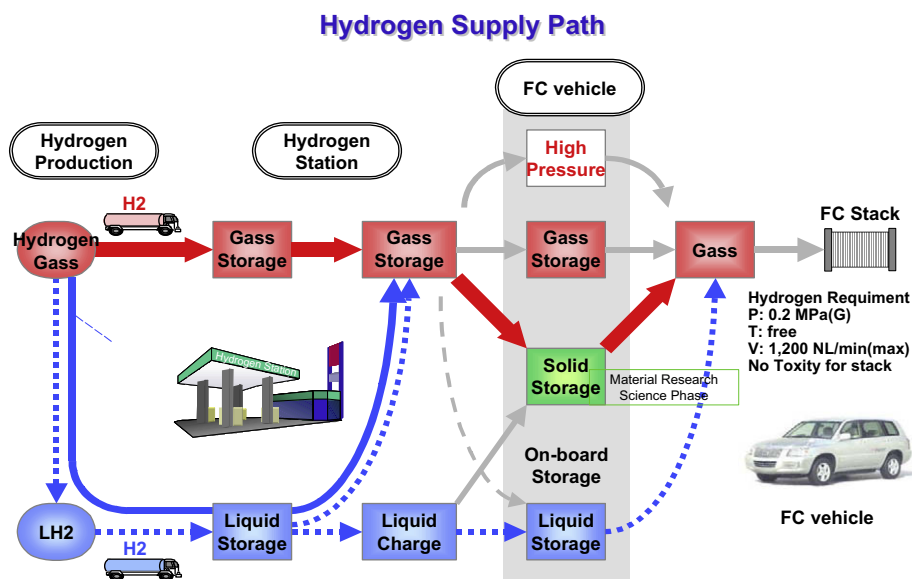


Fig. 1 – Total hydrogen path from production to FC vehicle.

direction of development. We also need collaboration with material scientists and engineers from the early stage in order to develop new practical ideas. We hope this will happen soon and realize the hydrogen society in the near future.

2. Hydrogen and infrastructure

Fig. 1 shows the total hydrogen path from production to on-board vehicle consumption. It is very important to consider this whole picture when we discuss about hydrogen storage. It is preferable to keep the low-pressure gaseous form in terms of efficiency. However, vehicles cannot store enough hydrogen, so we need either to compress hydrogen gas or to make it absorbed into a solid material. Otherwise it is not preferable from the viewpoint of energy but to liquefy the hydrogen then transport and store as a liquid phase. In the later case, on-board storage is available in either liquid or evaporated gaseous form. The solid form is preferable for the on-board storage but it is still in the scientific phase. On-board storage technologies must meet several requirements simultaneously, including the infrastructure, cost and charging capabilities. Hydrogen storage technologies shall be considered from the energy production to the end usage.

From the vehicle side, the following requirements are presented:

- 1) Safety
- 2) Performance (Charge/discharge, weight volume)
- 3) Cost
- 4) Technical adaptation for the infrastructure
- 5) Scalability (applicable to small and large vehicles)

Currently no candidate exists to meet all the requirements. However, since many efforts are being made in both the fields

of material science and engineering, we anticipate the further research.

3. Current status of hydrogen tank systems

Fig. 2 shows the current technologies in the engineering phase and the gap from the targets indicated. High-pressure tanks of 35 MPa and 70 MPa, liquid hydrogen tank and hydrogen-absorbing alloy tank as well as chemical storage are shown in the chart.

3.1. High-pressure tank system

Most vehicles currently in the on-road testing phase are equipped with a composite high-pressure tank. This is because of its simple structure and charge-discharge easiness.

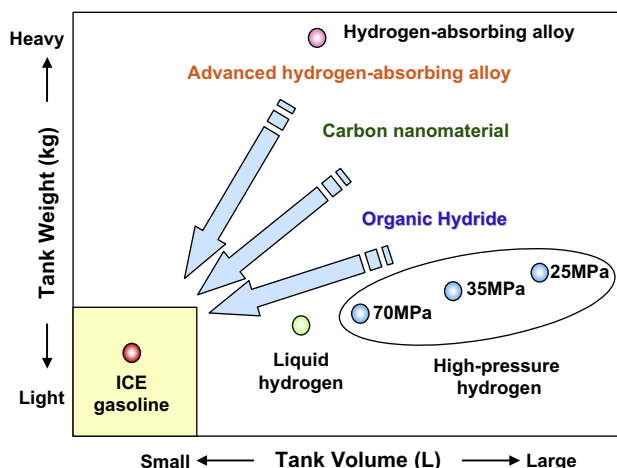


Fig. 2 – Hydrogen storage technologies and targets.

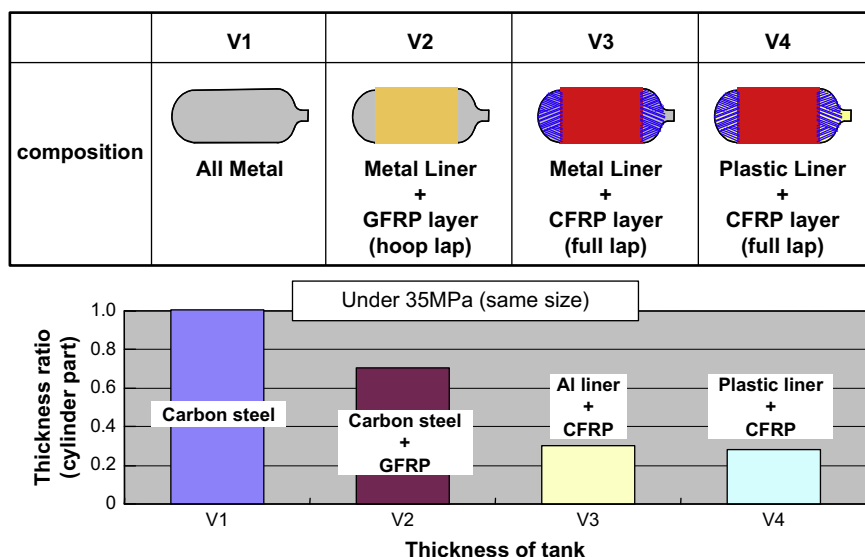


Fig. 3 – Wall thickness of different types of tanks.

High-pressure tanks can be categorized into four types from the regulation (Fig. 3). The mainstream of the hydrogen tank is carbon composite V3 and V4. This is different from the compressed natural gas vehicle, which mainly employs type V1 and V2. It is because the hydrogen vehicle uses higher pressure than the natural gas vehicle, which is normally compressed to 20–25 MPa. Recently there is a trend to move to 70 MPa tank to carry more hydrogen in order to extend vehicle range. However, pressure of this range makes the relationship between the hydrogen amount and pressure un-linear. Double pressure cannot lead to the storing of twice much hydrogen, and only results in 40–50% increase. Fig. 4 shows the latest tank we have developed in-house. Optimization of material and winding strategy has resulted in 65% more

hydrogen storable for the same vehicle [8]. The weight of the tank may have more possibility to be lightened if the material durability is assured. However, high-pressure tanks cannot be shrunk further because of its physical property. Volumetric property of the high-pressure tank must be compromised with the vehicle architecture in order to extend the range of the vehicle.

3.2. Liquid hydrogen tank

Hydrogen exists in a liquid form when it is cooled down to 20 K at atmospheric pressure, and its density is much higher than the gaseous form. Liquid hydrogen is attractive for the extension of vehicle driving range because of its high

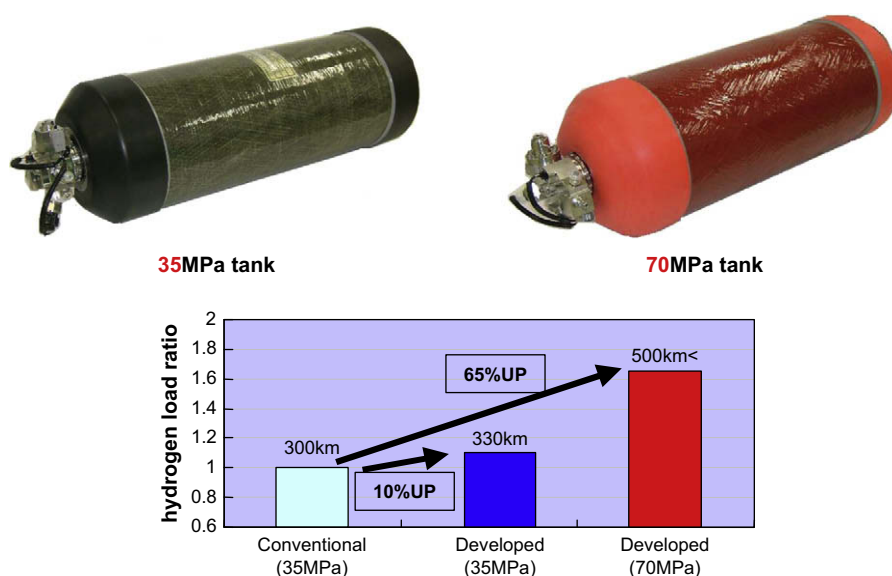


Fig. 4 – Improvement of storage capacity by new tank.

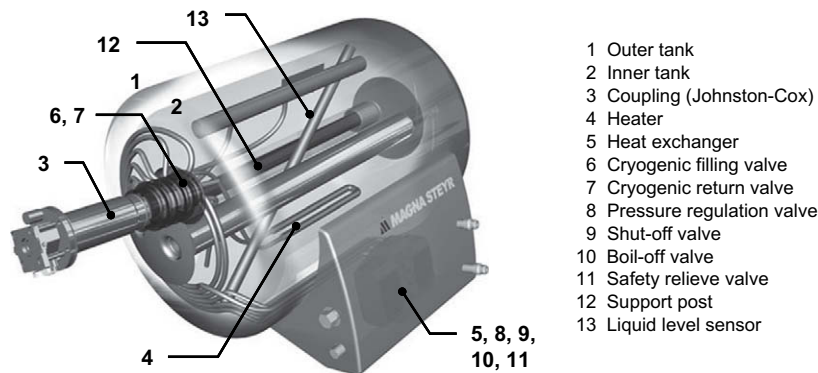


Fig. 5 – Liquid hydrogen tank system (Source: Magna Steyr and BMW).

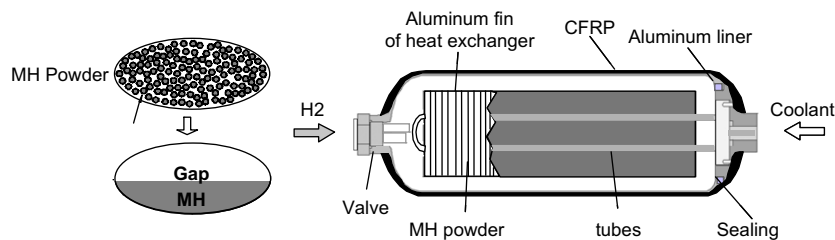


Fig. 6 – Schematic view of high-pressure MH tank.

density, and thus it has potential of storing a large amount of hydrogen on board. In addition, from the infrastructure point, the potential of a large amount of hydrogen that can be easily stored and transported is also very attractive. Some studies show the extra energy consumption of the liquefaction can be compensated by the easiness of delivery and storage.

Liquid hydrogen tanks have a double wall construction to keep the ultra low temperature with the thermal insulation. Thermal insulation minimizes the heat conductivity with the vacuum multi-layer insulation (MLI). MLI consists of a thin metal layer on the spacer material to prevent both radiation and thermal irradiation between the layers. It also prevents heat intrusion from irradiation and gaseous convection. The latest tank has a capability of limiting the heat flow to a few watts per second, resulting in the liquid hydrogen evaporation of a few percent per day. Liquid hydrogen tank has a relatively long history but products and suppliers are limited for lack of data and experiments. Further development is anticipated with the latest thermal insulation technologies, as well as an advanced liquefaction and charge–discharge strategy. Fig. 5 illustrates the latest liquid hydrogen tank (curtesy of Magna Steyr and BMW) [9].

3.3. Hydrogen-absorbing alloy tank

Hydrogen-absorbing alloy tanks have an advantage of storing hydrogen more dense than the liquid hydrogen, thus the tank can be built small and has a characteristic of reversible

hydrogen charge and discharge capability. However, it has a low gravimetric density (hydrogen weight per tank weight).

Several attempts have been made to increase the density [10]. Materials such as Ti–V–Mn, Ti–V–Cr, Ti–V–Cr–Mn and Ti–Cr (MoRu) are being developed and are known to have a capability up to 2.8 mass% [11–13]. However, vehicle tests showed some difficulties such as handling of a large amount of heat while absorbing hydrogen (which requires refrigerator for the quick charge), and low hydrogen release in the cold environment.

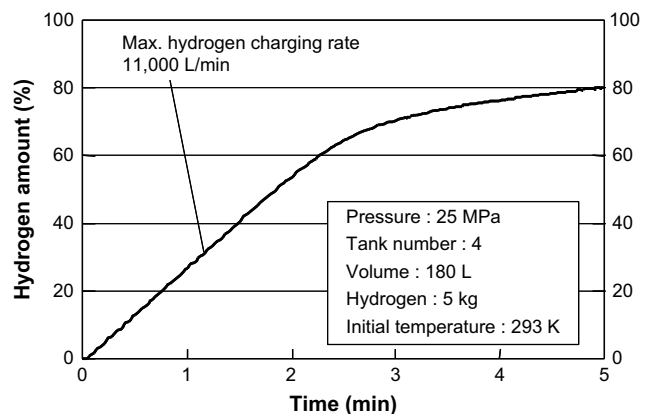


Fig. 7 – Hydrogen charging speed of high-pressure MH tank.

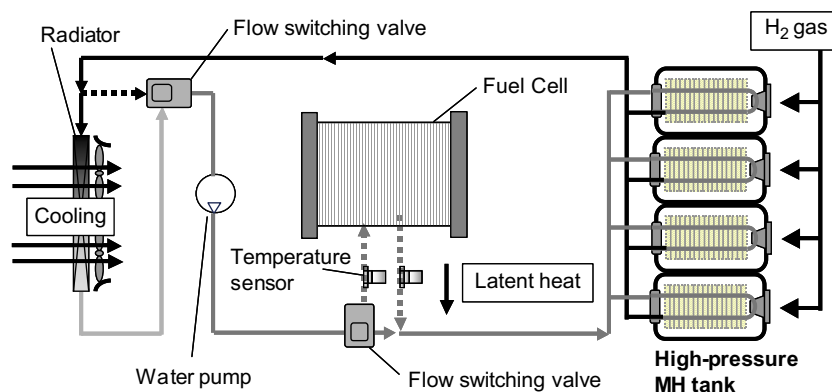


Fig. 8 – Concept of charge and discharge system.

4. Hybrid tank system, high-pressure hydrogen-absorbing alloy tank

A new system has been tested in order to improve charge-discharge characteristics. It combines a high-pressure tank and high-pressure equilibrium type absorbing alloys. This idea is presented to have an improved characteristic of higher volumetric density [14–16].

4.1. Experiment

A full size high-pressure tank was prototyped with the heat exchanger and metal hydride ($\text{Ti}_{1.1}\text{CrMn}$) inside (See Fig. 6) [17,18]. This alloy can absorb 1.9% hydrogen. A vehicle-sized heat management system, such as a radiator and fan, is used for the experiment.

4.2. Results and discussion

Fig. 7 shows the result of hydrogen storage capacity from the 180 L tank. About 7.3 kg of hydrogen can be stored with the pressure of 35 MPa. This is 2.5 times more hydrogen stored in comparison with a 35 MPa high-pressure tank. Even a larger amount of hydrogen can be stored. The tank can be charged with hydrogen to 80% capacity in just 5 min. At the temperature -30°C , the tank is still capable of supplying the required hydrogen. The heat exchanger and radiator are the actual vehicle size and performance level.

Fig. 8 shows the result of an on-board charging test. A vehicle-sized radiator is able to remove heat from metal hydride and give 80% charge within 5 min. High-pressure hydrogen environment helps MH absorb hydrogen quickly and it acts as a reservoir for the case of discharge.

Thus this approach solves the difficulty of classical metal hydride and creates practical hydrogen storage for the hydrogen-powered fuel cell vehicles.

Table 1 shows the comparison of high-pressure tank, hydrogen-absorbing alloy tank and high-pressure hydrogen-absorbing alloy tank system. This new approach (Hybrid Containment) will give a new scope on the use of existing simple containment (high pressure and liquid hydrogen tank) and future chemical containment such chemical hydride and complex hydride. This is the example of close collaboration of material research and engineering. It will give further extension of the potential of materials.

5. Future

Fig. 9 summaries the hydrogen uptake and ΔH , energy to take out hydrogen from hydride. There is a relation between them. It may tell that higher the hydrogen uptake more energy necessary to take out. At this moment there are no concrete theory to support. Even we are trying to find a material in the unstable area in the chart. We engineers have to prepare certain amount of heat management for the future hydrogen

Table 1 – Specification of each tank system

	Low-pressure MH tank	High-pressure tank	High-pressure MH tank
Hydrogen storage capacity	3.5 kg/tank; 120 L	3 kg/tank; 180 L	7.3 kg/tank; 180 L
Tank weight	300 kg	<100 kg	420 kg
Hydrogen filling time	0.5–1 h; With external cooling facility	5–10 min	5 min/80%; Equal to high-pressure tank without external cooling facility
Hydrogen release at low temperature	Impossible at low temperature	Possible	Possible even at 243 K
Control ability	Difficulty in acceleration	Good	Good; Equal to high-pressure tank
Safety	Low pressure (<1 Mpa)	High pressure (35 Mpa)	High pressure (35 Mpa)

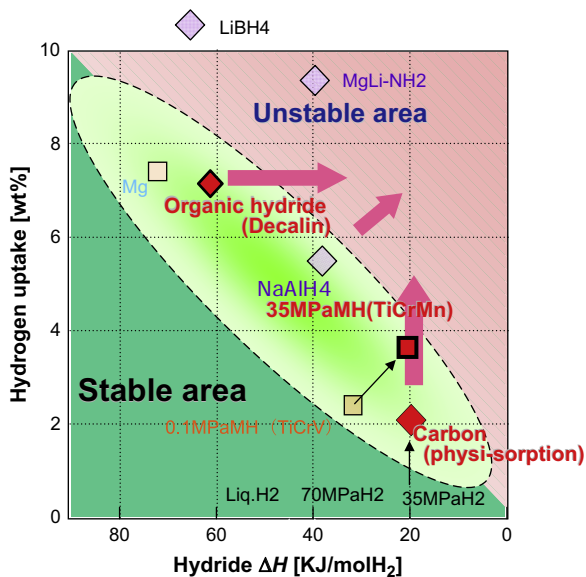


Fig. 9 – Hydrogen uptake and energy.

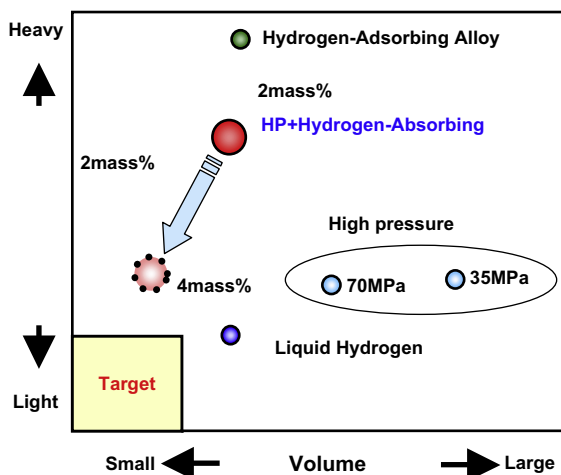


Fig. 10 – New status of storage technologies.

storage. If the new material reaches 4 mass% level, the tank system reaches a very attractive area (Fig. 10).

In between the simple containment and chemical containment, there can be a new area of hybrid containment where new idea/concept can be raised by the close collaboration of scientists and engineers.

Acknowledgement

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