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Recent developments in hydrogen storage applications based on metal hydrides

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Abstract

Metal hydrides have been commercialized for battery applications for more than 8 years. In case of storage applications, metal hydrides were extensively evaluated in combination with combustion engines. The relatively low gravimetric energy density of hydride tanks based on low temperature metal hydrides prevented the commercial use of that technology. Recently, lasting progress in the PEM fuel cell technology offers chances for metal hydride storage systems mainly for low power applications, but also for niche markets. The paper describes promising projects on metal hydride storage technology and gives an outlook about improvements of both the metal hydride alloy performance and the performance of metal hydride storage tanks.

Keywords: Metal hydride; Hydrogen storage; Fuel cell; Energy supply

1. Introduction

The first studies for industrial use of metal hydrides for hydrogen storage were made by Daimler Benz in the eighties by combining metal hydride tanks with combustion engines in mini vans [1]. This project was technically successful, but has been stopped because of the relatively low energy efficiency of the storage tank and high costs of the storage system. Serious efforts to increase the storage capacity of low temperature metal hydrides have been made. However, the development of low temperature metal hydride materials for hydrogen storage applications has been almost stagnant for more than 10 years. The maximum hydrogen storage capacity of low temperature metal hydrides still remains below 2 wt.%. The resulting energy density is too low for the economic support of hydrogen fuel for mobile applications.

As an alternative, high temperature metal hydrides mainly based on magnesium and Mg alloys have been investigated for hydrogen storage applications because of their high storage capacity up to 7.6 wt.% in case of pure MgH_2. Various binary and ternary Mg alloys have been characterized in regard to their hydrogen storage properties. The main objective was to reduce the high Mg–H binding energy by alloying techniques in order to decrease the working temperature. Up to now there is no record of success [2,3]. If the working temperature is decreased below 200°C, the hydrogen storage capacity drops down dramatically.

A novel group of reversible hydrogen storage materials, the so called alanates (alkali metal aluminum hydrides), have been investigated during the last few years [4]. Several compositions ($NaAlH_4$, Na_2LiAlH_6 and others) are known and offer reversible hydrogen storage capacities up to 6 wt.%. The main problem of alanates is that the melted alkali metal alloys can not be hydrided from the gas phase but have to be prepared by chemical procedures. If an alkali metal aluminum hydride is formed, the material can be cycled like a normal metal hydride. Whilst Mg based alloys show low plateau pressures at working temperature (ca. 1–5 bar at 300°C), the alanates have relatively high plateau pressures (ca. 10–200 bar at 200°C). Some alloy compositions form multiple plateaus.

However, a major drawback for magnesium based hydrides and alkali metal aluminum hydrides is the high sorption temperature of >200°C, whereas 80°C is required for applications. Moreover, these hydrides have not been considered competitive because of their rather sluggish sorption kinetics, which is mainly controlled by diffusion [5,6].

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2. Fast kinetics light weight metal hydride alloys with high storage capacity

In order to overcome the poor kinetic properties of high temperature metal hydride alloys new materials concepts have been developed. Because the sorption kinetics of Mg based alloys is diffusion limited, nanocrystalline materials are very promising candidates. Diffusion can be very fast in the grain boundaries, which exceed up to 30% of the total volume of nanocrystalline powders. Several nanocrystalline MgNi powders have been synthesized by mechanical alloying [7].

By keeping the high hydrogen storage capacity, the sorption kinetics could be increased by orders of magnitude (see Fig. 1). At a temperature of 300°C and under 1.2 MPa hydrogen pressure the absorption is very fast. After only 1 minute a hydrogen content very close to the theoretical value is reached, whereas the as cast polycrystalline material is much slower. That means nanocrystalline Mg based alloys manufactured by mechanical alloying or high energy ball milling offer very fast kinetics which would be sufficient for practical applications.

The addition of catalysing substances to metal hydrides seems also to be a promising way to increase the sorption kinetics of metal hydride alloys. It is well known that Pt, Pd or Ni at the surfaces of metal hydrides can improve the kinetics [8]. However, Mg_2Ni shows catalytic effects in both Mg based alloys and AB_2 type alloys (Laves phase alloys) [6,9].

The developments on hydrogen storage materials can be summarised as follows:

- Metal hydrides based on the Fe–Ti system, on AB_2 Laves phases, and also on the $LaNi_5$ system have not been remarkably improved during the last 5 years.
- The maximum hydrogen storage capacity of room temperature alloys is still lower than 2 wt.%
- A novel material group (alkali aluminum hydrides) has been developed for reversible hydrogen storage applications at about 200°C which probably has the potential for a further decrease in the working temperature. The hydrogen capacities are in the range of 4–6 wt.%.
- Nanocrystalline Mg based alloys have been developed. These materials show very fast kinetics but still need sorption temperatures in the range of 250°C.

3. Metal hydrides and fuel cells

During the last years, large progress has been made in the development of the PEM fuel cell technology, which is now at the stage of commercialization. The most important car manufacturers worldwide intend to present a fuel cell powered car by the year 2005. Therefore there will be a strongly increasing demand for hydrogen supplying systems. As mentioned above, metal hydride tanks based on state-of-the-art low temperature metal hydride alloys (AB, AB_2 and AB_5) can not meet the requirements regard to the energy density. The car industry is focused on methanol reformers and cryotanks as competing systems to metal hydrides. New materials (fiber reinforced plastics) increased the energy density of gas pressure tanks. Fig. 2 shows the state-of-the-art energy densities of the different hydrogen storage systems. In order to power a fuel cell, a metal hydride storage tank has remarkable advantages in regard to cryo- or pressure tanks:

- no additional power supply is required
- no loss of hydrogen
- hydrogen can be supplied at an optimum and constant pressure
- safety

On the other hand, the low gravimetric energy density of metal hydride tanks, especially from automotive applications is a major drawback. The first German prototype hydrogen powered bus is running in the city of Erlangen (Germany) using liquid hydrogen and a combustion engine [10]. This project is part of the Euro-Quebec Hydro-Hydrogen Pilot Project. New buses with both combustion engines and fuel cells using liquid hydrogen and pressurized hydrogen as well are planned to run in 1999 [11].

If the main technical advantage of the metal hydride storage tanks (high volumetric energy density) can be used, there are real chances for niche market applications,

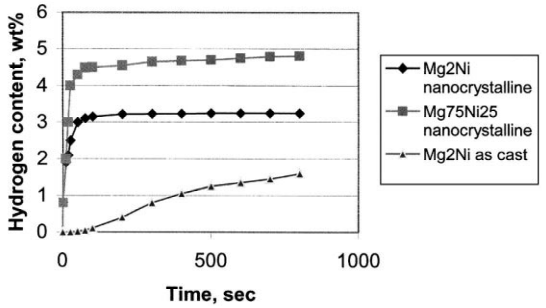

Fig. 1. Absorption kinetics of MgNi alloys at 300°C and 1.2 MPa [7].

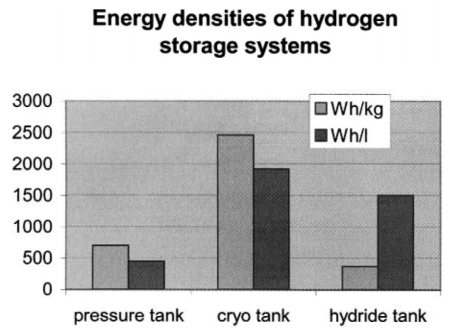

Fig. 2. Competing hydrogen storing systems.

as soon as the high power PEM fuel cell technology is ready for commercialization:

- fuel cell powered submarines. After the successful tests of a submarine powered by a Siemens PEM fuel cell using a GfE metal hydride tank system, a small series of submarines will be manufactured during the next years by Howaldtwerke Deutsche Werft AG.
- fuel cell powered fork lift. A Siemens 10 kW PEM fuel cell powered fork lift has been successfully tested in the Bavarian Solar Hydrogen Centre in Neuenburg v. Wald. The weight of the GfE metal hydride tank storing about 45 m^3 hydrogen is of advantage for this application.

The combination of small metal hydride tanks and PEM fuel cells in the low power region (up to some W) can replace reversible batteries for different applications:

- notebook computers
- cellular phones
- cordless tools

At the Hannover Fair 1998 a Siemens Nixdorf laptop computer was demonstrated (see Fig. 3), which was powered by a laboratory PEM fuel cell (FhG ISE Freiburg, Germany) and a commercial metal hydride tank SL002 (GfE Metalle und Materialien GmbH, Germany), which has been developed for demonstration models (see below). The total energy density of the system was 222 Wh/l and 73 Wh/kg, respectively. The energy densities of the relating Li-ion battery are 181 Wh/l and 93 Wh/kg. It is expected that the final energy densities of the fuel cell/metal hydride system will be increased to about 500 Wh/l and 160 Wh/kg in the near future. Such high energy densities can not be reached by a reversible electrochemical battery.

A teaching model for demonstrating the opportunities of the hydrogen based energy system has been developed by GfE Metalle und Materialien GmbH and H_2 Interpower GmbH (Germany) and is distributed by a market chain (Conrad Electronic, Hirschau, Germany) and other suppliers as well. The hydrogen kit consists of an SL002 metal hydride tank (20 l), a 100 mW PEM fuel cell and a small consumer (mini fan). A 10 days continuous run of the fan is possible without recharging the metal hydride tank.

Hydrogen storage tanks may play an important role for establishing decentralized energy supply in less industrialized areas. The hydrogen produced by using photovoltaic, electrolysis and drying systems can easily be stored in metal hydride tanks without the need of additional energy sources.

4. Summary

Metal hydride storage systems based on room temperature alloys have been successfully used to supply hydrogen for high power PEM fuel cells for special niche applications (submarines, fork lifts). Depending on the cost decrease, mainly in regard to the high power PEM fuel

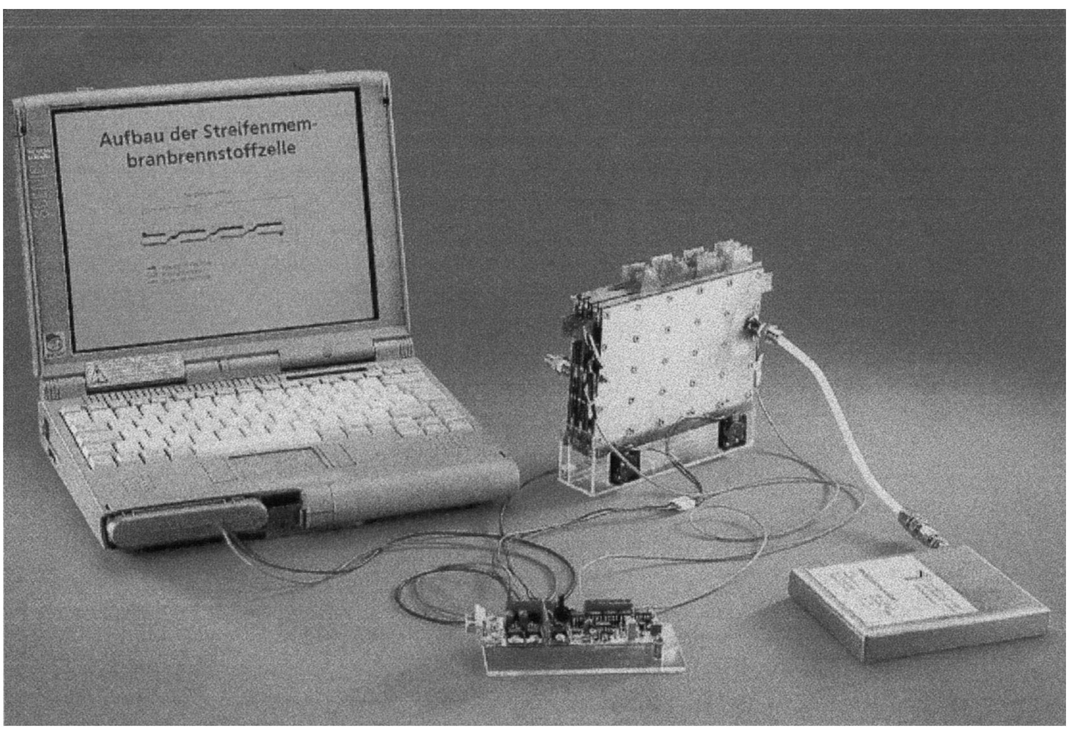

Fig. 3. Siemens Nixdorf Notebook powered by a PEM fuel cell/metal hydride tank.

cell, there seems to be a small market potential for these special applications in the near future.

Because of the low gravimetric energy density it is expected that the metal hydride tank will not be a practical solution for supplying fuel cell powered cars.

Metal hydride tanks based on a new generation of fast kinetics nanocrystalline light weight hydride alloys have a good chance to compete with cryotanks as well as pressure tanks for powering combustion engines, because waste heat can be used for desorption.

Because of the very high energy densities, the combination of a metal hydride tank with a low power PEM fuel cell is a very attractive alternative to rechargeable batteries and has therefore the highest potential for commercialization. However, such a system is not yet reversible.

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