RECENT DEVELOPMENTS ON HYDROGEN STORAGE SYSTEMS

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Introduction

Protection of earth is one of the main issues to be solved for human race. However, the fast growing world population, an increasing globalization and the emerging nations on the threshold to a highly mobile society will yield more and more atmospheric pollution. Thus, hydrogen energy systems have been proposed as a means to reduce greenhouse gas and other harmful emissions from stationary and mobile sources, also aiming at a higher energy independence from the short-running fossil fuels and their uncertain sources. Moreover, the car manufactures would like to increase their rate of "zero-emission vehicles" in their car fleet.

For realizing hydrogen energy systems in near future, we have to establish suitable energy storage and transportation technologies. One of the key technologies on that way is the development of high performance hydrogen storage (H-storage) systems.

For stationary applications, weight is not a key problem. But especially for mobile applications, e.g. in fuel-cell electric vehicles (FCEV), or cars with hydrogen-fueled internal combustion engine, fuel tanks have to be a compact, lightweight, safe and affordable containment as an on-board H-storage system. As technical realizations, high-pressure hydrogen, liquid hydrogen, absorbed hydrogen in metal hydrides, chemical hydrides and nano-structured carbons will be discussed, omitting on-board reforming of hydrogen from methanol or other liquid fuels.

High-pressure hydrogen

Classical high-pressure gas cylinder tanks made of inexpensive steel are regularly filled up to 15 or 25 MPa in most countries. To run a compact car for 400 km, approximately 4 kg of hydrogen for a FCEV or 8 kg for an internal combustion engine are required[1]. If 4 kg of hydrogen is stored in its gaseous form and compacted at a pressure of 20 MPa, an internal volume of 220 liters would be necessary, a space clearly not available in standard compact cars.

Therefore, novel high-pressure tanks involving fiber-reinforced composite materials are being developed; normally these new tanks consist of an inner liner, onto which the fibers are wound. They are tested up to a maximum pressure of 60 MPa and for regular use filled up to 35 MPa (5,000 psi)[2]. However, even for that pressure, the fuel tank would have a too large volume for a compact FCEV. To overcome this disadvantage, very-high-pressure tanks up to 70 MPa (10,000 psi) for mobile and 82.5 MPa (12,500 psi) for stationary application[3] have been considered and exist as prototypes. These tanks are envisaged to have a weight of 110 kg, equivalent to a technical efficiency of 0.70 m^3/kg[4]. But even at these high pressures, at the current technical status, the gas cylinders will be a factor of three more inefficient than liquid hydrogen tanks[4]. However, besides the fact that there remains always a considerable risk in using very-high-pressure vessels, the most dangerous and complicated part is the compression itself. In addition, compressing the hydrogen up to 70 MPa (10,000 psi) would require almost the same energy as its liquefaction and some problems concerning the high-pressure container itself remain to be solved[5].

Liquid hydrogen

Liquid hydrogen has an over 800 times higher density than in its gaseous state. Therefore, liquefaction of hydrogen is particularly attractive from the point of view of improving the mass per volume ratio. However, the condensation temperature of hydrogen at 0.1 MPa is -253 °C and the unavoidable heat transfer even through a super-insulated container leads directly to loss of hydrogen due to boil-off. Larger containers have a better surface to volume ratio than smaller ones, reducing the loss of hydrogen due to evaporation. Therefore, huge hydrogen containers are used for commercial transportation of liquid hydrogen inside ships and delivery by trailers or for stationary storage systems. For small tanks inside sedans, the manufactures are currently working on reducing the boil-off rate[6]. For example, Linde AG, Germany, is using a newly patented re-cooling system, so the loss due to evaporation can be minimized. The stand-by time of a parked car can so be extended from before 3 days to more than 12 days, before evaporation losses occur[6]. Additionally, major advances in motor development like direct fuel injection and new valve generations for hydrogen have been made, improving the maximum available torque and power of the car engine, by simultaneously reducing the fuel-consumption[7].

Metal-hydrides

It is well known that metal-hydride (MH) systems can store more hydrogen than in liquid hydrogen in a safe and efficient way. However, those materials with good storage capabilities and reversibility only desorb hydrogen at relatively high temperatures, too high for fuel cell application. On the other hand, materials fitting these requirements are too heavy or too expensive for a commercial application.

Therefore, all over the world hydrogen research teams have been initiated: In 1996, the IEA (International Energy Agency) program[8] has established an international hydrogen storage task force to search for innovative materials with high H-storage capacity. Since 1995, the DOE (Department of Energy) is progressing the research program on hydrogen storage materials[9]. In Japan, since 1994 the R&D-program of developing hydrogen storage and transportation systems using metal hydrides has been set up in the WE-NET (World Energy-Network) project[10]. In addition, the research program on new advanced H-storage materials has been launched in the Priority Areas Project "New Protium Functions in Materials" by the Ministry of Education, Science, Sports and Culture of Japan. The above projects are aiming at the development of high performance H-storage materials applicable to FCEV. To overcome the disadvantages in conventional heavyweight metal hydrides, new materials using lighter elements have been investigated in the recent years.

One attractive light-element metal hydride is MgH_2, since it is directly formed from the reaction of bulk Mg with gaseous hydrogen, reaching hydrogen concentrations up to 7.6 wt.% of hydrogen. However, like in many other metal hydrides, the reaction is too slow and needs 300 °C for progressing the hydrogen desorption reaction.

A reduction of the metal grain sizes to nanocrystalline dimensions can significantly improve the thermodynamic and diffusional properties in MgH_2 and enhances the H-storage features[11]. Therefore, different processes to obtain micro- or nano-structured Mg have been investigated to overcome the above-mentioned drawbacks.

Recently, Pd-coated nano-structured Mg films prepared by a RF sputtering method have been reported to absorb ~5 wt.% at 100 °C under hydrogen atmosphere of 0.1 MPa and to completely desorb below 100 °C in vacuum[12]. These catalyzed nano-structured Mg composites are now developed as one of the H-storage materials aiming at large-scale production. Moreover, in another work, the kinetics of MgMH with a maximum H-storage capacity of 7.5 wt.%

could be drastically improved by ball-milling Mg together with nanometer size catalysts of Ni and Fe under an H_2-atmosphere of 1 MPa. The grinding time could be shortened from 10 hr to 15 min by simultaneously optimizing the Ni nanoparticle amount to 0.5 at%[13].

Recently, it has been found that Cr-Ti-V bcc alloys absorb and desorb effective hydrogen up to 2.6 wt% at 313 K under ambient pressure, which is the highest hydrogen capacity in the metal hydrides applicable for fuel cell cars at present[14].

Carbon-related storage materials

In the first work on H-storage in single-walled nanotubes (SWNT) in 1997, a H-storage capacity between 5 to 10 wt.% was reported[15]. This, and the stunning result of up to 67 wt.% at room temperature in carbon nanofibers by another group[16], have triggered many laboratories around the world to focus their research on that class of materials. (For a review on the vast area about H-storage in carbon nanostructures, see [17, 18] and [19]). Unfortunately, these first experimental results could not be repeated or confirmed independently in other laboratories up to now. Some of the reported storage capacities could be even solely caused by Ti-alloy impurities introduced by the special sonication process, which is applied to open the caps of the nanotubes[20]. Currently, the opinions about the ability of H-storage in carbon nanotubes and –fibers are still controversially discussed[21] and are as widespread as the experimental results.

Instead, nano-structured graphite, mechanically milled under a hydrogen atmosphere of 1 MPa, has been reported and confirmed to absorb hydrogen up to 7.4 wt.%[22, 23]. However, still some progress should be done in improving the yet too high desorption temperature for H storage.

Chemical hydrides

Complex metal hydrides, also called chemical hydrides, have a high theoretical H-storage capacity (e.g. the "alanate" $NaAlH_4$: 5.6 wt.%) and their feedstock is relatively cheap. But for complex aluminum hydrides, for example, the comprised hydrogen was presumed to be stored irreversibly. The material was only used, after being added to water, as a "one-shot" hydrogen releasing material[24]. Additionally, hydrogen was released only at temperatures above their melting point. Therefore, the chemical hydrides were assumed an unsuitable material for reversible H-storage. In 1995, Bogdanović et al. have shown in their pioneering work, that Ti-doping of $NaAlH_4$ renders the reaction reversible and kinetically enhances the hydrogen release already at near-ambient temperatures[25]. At present, research groups are now investigating improved catalysts for optimizing the dehydriding characteristics not only of the alanates. However, a H-storage system applicable to FCEV has not been established yet because the reaction rate and temperatures are still too inadequate for application in an on-board storage system. Moreover, it is currently still unknown what the effective catalyst mechanism is and how it contributes to the process[26]. In addition, the hydrogen release is not yet optimized, because either the full storage capacity is lost after the first cycle or the initial H capacities are low[26]. However, if the reaction is improved and becomes significantly fast, the chemical hydrides will play a dominant role as H-storage media in mobile applications.

Conclusion

Currently, in the hydrogen research laboratories all over the world new non-traditional and nano-technological techniques are applied to design high performance H-storage materials. We believe that, due to this research effort, one day better hydrogen-storage materials, which absorb and desorb at least 5 wt.% hydrogen at temperatures below 100 °C, will be discovered and developed.

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