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Conversion materials for hydrogen storage and electrochemical applications—Concepts and similarities

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ABSTRACT

Conversion-based material systems seem to be the only way at the moment to increase energy densities of H storage materials and battery materials considerably. In the case of H storage materials, the complex hydrides and related reaction systems are still a matter of research. For battery materials there are promising options to increase the energy density of a battery material by a factor 5–10 but the development has just begun and no systems have been presented yet which would have an acceptable maturity for commercial applications. It will be shown that the developments of H storage materials and electrode materials have many historical and conceptual similarities and there are similar goals and challenges in the development in both areas.

1. Introduction

There has been a debate about the future of the hydrogen technology in general and of solid hydrogen storage in particular when compared to battery technology. The discussion has been fueled by still existing technical or economical hurdles for the introduction of a hydrogen economy and by the fact that car manufacturers have started strong activities to develop battery-driven electric cars and get them on the market.

In that context, this contribution will discuss the potential of the two options for energy storage in vehicles and the possible role of hydrogen storage materials in comparison to batteries. With respect to the technological development in both areas it will be shown that there are common features of solid H storage systems based on complex hydrides/reaction systems and of novel conversion materials for electrochemical energy storage. Both methods, hydrogen storage and the storage of electrons are based on similar thermodynamic and kinetic principles and suffer from similar limitations. In the case of batteries, an additional complexity has to be taken into account due to the necessity of an electronic conductivity in every volume element of the material. Nevertheless, the progress which has been made and the knowledge that has been gained with H storage materials may be beneficial also for the development of future electrode materials which are based on the conversion principle.

1.1. *Situation in the automotive sector*

The current way of using liquid organic fuels for the propulsion of cars, trucks, ships, and airplanes is both familiar and extraordinary. It is familiar for long because there has been a technical development over centuries which started from early fossil and renewable sources such as coal and wood for steam engines. Only for a short period of approximately 20 years in the late 1800s there were also electric cars on the road where the energy was stored mostly in lead batteries [1]. However, long charging periods, low power and the short driving ranges let them soon fall behind new gas engines and gasoline powered cars which became increasingly reliable and powerful and which had only a small and lightweight tank which was easy to refuel, in pharmacies at the beginning [2]. The relatively high safety of the cars, the availability of large oil resources and an easy-to-install infrastructure were cofactors which contributed to the success of this technology. Hence, already over more than four generations, we have been familiar with using liquid organic fuels for combustion engines in vehicles.

Nowadays, there is an increasing pressure to replace these fuels by sustainable energy carriers, mainly for the following reasons:

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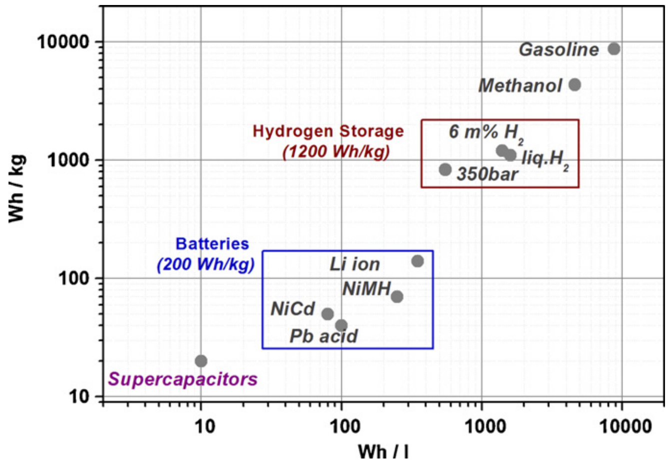

Fig. 1. Gravimetric and volumetric system densities for various energy storage methods.

- Limitation of oil reserves and expected “peak-oil” before 2020, with an expected oil prize of 200 US$ per barrel in 2030 [3]. Man-made climate change caused by CO_2 emission.
- Already occurring or expected environmental disasters such as off-shore oil spills and mining of tar sands.
- Saving fossil fuels as a carbon source for the production of chemicals, plastics, medicals, for future generations.

Fig. 1 depicts an overview of different systems for storing energy in vehicles, sorted according to their gravimetric and volumetric energy density. The diagram clearly shows that the current technology which is so familiar to us, is extraordinary at the same time because existing alternative methods reach only system densities which are by a factor of 8 (H storage) or 50 (batteries), or 500 (supercapacitors) lower than those of a diesel or a gasoline tank at the moment. Clearly, chemical storage methods offer by far the highest energy densities among the different alternatives.

1.2. Applicability of H storage and batteries

These facts have an impact on the projected applicability of the different drivetrain concepts and, apparently, the international car companies have similar ratings of the expected application of battery driven cars (FEV, full electric vehicles) and electric cars with fuel cell powered (FCV, fuel cell vehicle). According to a recent evaluation by Daimler AG mainly micro compact cars, compact cars, and light duty trucks are foreseen as FEV, see Fig. 2. Batteries are currently limited in their energy content and it is unclear at the moment whether and when energy densities can be offered which are by a factor of 3–5 higher than those at the moment. Nevertheless, this would be necessary in order to be competitive with hydrogen based drivetrains in the respective applications. In certain areas of the world this has already led to a renaissance of hydrogen applications, supported by an increasing technical maturity and decreasing manufacturing costs for fuel cells and tanks [4]. Hence, hydrogen is still considered as a viable option for storing energy on board of a car.

The current storage technology of FCV is mostly based on 350 bar and 700 bar hydrogen tanks which have been regarded as sufficiently safe. However, to the knowledge of the author, this does not include heavy accidents where a controlled release of hydrogen is not possible anymore. A typical, relatively frequent scenario of such an accident is a passenger car which is overrun by a fast train. It is likely that a pressurized hydrogen tank is teared very quickly and completely and that the train with its passengers may be affected, too. The mechanical power of the compressed gas, the low ignition energy of hydrogen, its large flammability limit and the high detonation sensitivity of hydrogen are critical factors which may then cause a severe incident. If train passengers are severely affected and if this happens repeatedly, such incidents may be a show stopper for the technology. Hence, it may be necessary to develop alternative tank systems which offer a much lower release rate for hydrogen in case of a sudden rupture of the tank.

Tanks based on metal hydrides may be such an alternative. Interestingly, a tank-to-wheel comparison published by Eberle et al. [5] shows that a current 700 bar tank system which contains 6 kg H_2 has a mass of 125 kg and a volume of 260 L. A so-called hybrid tank from TOYOTA which consists of 28 Al tubes filled with metal hydride under an overpressure of several 10 bars carries 5 kg H_2 in a volume of only 95 L but has a mass of 220 kg [6]. The volume of this system is only two times the one of a comparative gasoline tank and is therefore highly competitive especially for small and mid-sized cars. The weight is still an issue which may be addressed by developing hydrides with a higher gravimetric capacity.

As a first conclusion, both hydrides and batteries remain interesting for automotive (and stationary) applications in the future. Interestingly, materials for hydrogen storage and electrode materials for batteries have similarities and there are several viewpoints under which the two areas may be compared. Hence, the main part of the paper will deal with historical, conceptual, and materials aspects.

2. History and recent developments

Fig. 3 shows a diagram which depicts a selection of low temperature and medium temperature hydrides, their reversible hydrogen content, and the time of publication. The development started in 1869 where the first metal hydride, palladium hydride was discovered. In the later decades other metals and alloys were developed as H storage materials which were all based on the same principle of intercalation of the hydrogen in the metallic host lattice. In the early and mid 90s of the last century, a sudden increase could be noticed when a new type of material was introduced, the so-called complex hydrides. In these materials, the hydrogen is covalently bound to a central atom such as Al, B, N, forming a negatively charged complex anion. The charge of the anion is compensated by a cation so that the material has salt-like properties. Such a material undergoes drastic changes when converted, see below.

In the battery field a similar development seems to loom at the horizon. The batteries which have been commercialized are currently all based on intercalation materials. A prominent example is

	Micro-Compact	Compact	Middle	Luxury- & Family	City-Bus	Interurban Bus	Light duty truck	Medium duty	Heavy duty
Fuel Cell vehicle	(✓)	✓	(✓)	(✓)	✓	SOFC	✓	✓	SOFC
Battery vehicle	✓	(✓)	-	-	-	-	(✓)	-	-

Fig. 2. Expected applicability of future battery cars and fuel cell cars (according to [7]). √: possible; (√): possible, with limitations; -: in general not possible or not possible as of today’s assessment; SOFC: solid oxide fuel cell