



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

Maximilian Fichtner\*

Karlsruhe Institute of Technology, Institute of Nanotechnology, Postfach 3640, 76021 Karlsruhe, Germany

## ARTICLE INFO

### Article history:

Received 28 September 2010

Received in revised form

17 December 2010

Accepted 24 December 2010

Available online 31 December 2010

### Keywords:

Conversion materials

Energy storage

Hydrogen storage

Batteries

Ball milling

Metal hydrides

Fluorides

## 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.

© 2011 Elsevier B.V. All rights reserved.

## 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:

\* Tel.: +49 0 724782 5340; fax: +49 0 724782 6368.

E-mail address: [m.fichtner@kit.edu](mailto:m.fichtner@kit.edu)

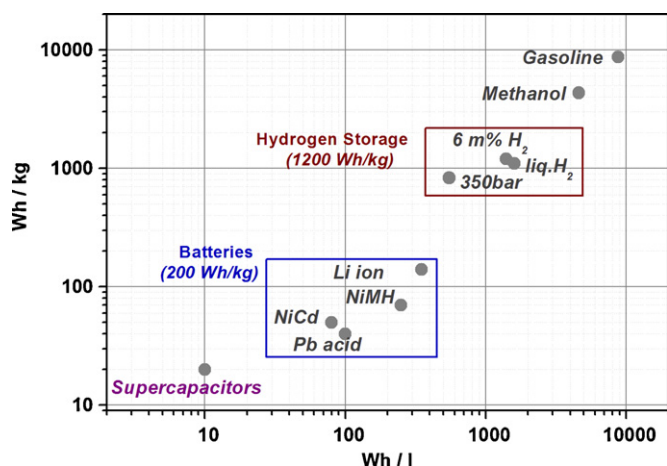


Fig. 1. Gravimetric and volumetric system densities for various energy storage methods.

- 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<sub>2</sub> 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 torned 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<sub>2</sub> 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<sub>2</sub> 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

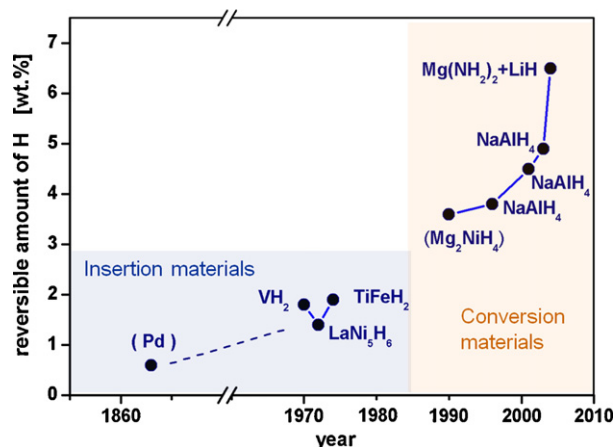
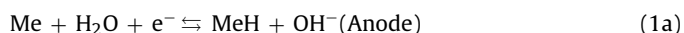
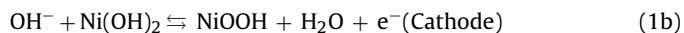


Fig. 3. Historical development of low and medium temperature hydrides.

the Ni–MH battery which contains a misch metal alloy, the storage mechanism is based on the following electrochemical reactions at the electrodes (Eq. (1)):



and



Beyond Ni–MH batteries, the systems with the highest gravimetric and volumetric energy density on the market are Li-ion batteries which are also based on insertion materials. Here, lithium is intercalated in the host structure of the cathode (e.g. lithium cobalt oxide or lithium iron phosphate) or the anode material (graphite). However, due to the limited number of lattice sites for lithium ions or lithium atoms, the storage capacity of such systems is in the order of the already achieved values which are considered as too low for mid-sized full electric vehicles with interurban or long distance driving ranges [7].

Similar to the development of H storage materials, there are strategies for improving the storage density in batteries, which include the search for new intercalation compounds which allow for higher packing densities of lithium. An alternative approach having the potential to considerably increase energy densities is making use of several oxidation or reduction steps so that more

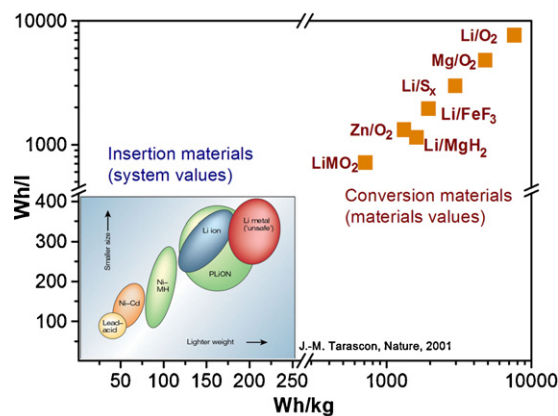
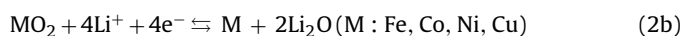
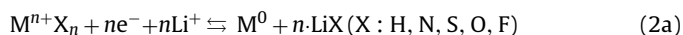


Fig. 5. System values for energy density versus specific energy of existing batteries on a linear scale (inset, taken with permission from [14]) and physical limits for materials based on conversion reactions, on a logarithmic scale.

than one electron (or Li) can be transferred by a metal atom in the electrode. This may be possible by solid-state conversion reactions in reactive nanocomposites based on metal hydrides, nitrides, metal chalcogenides, or metal fluorides, for example. It should be noted that storing several electrons per atom in an electrode material is comparable to binding several H atoms to a central atom in a complex hydride. The general equation of the process at the electrodes can be described by Eq. (2a), an example for metal oxide conversion electrode is shown in Eq. (2b) [8], a sketch describing the solid state process of a fluoride-based system is shown in Fig. 4:



The physical limit of conversion-based battery materials can exceed the energy density of a hydrogen storage material and may be very high when compared to the state-of-the-art batteries, see Fig. 5. It should be noted that the inset of the figure depicts system values. However, system values cannot be given for the conversion-based batteries in the diagram due to the lack of systems at the moment and the values on the double logarithmic scale are theoretical materials values. The system density of a later battery can only be estimated in these cases and is presumably in the order of 20–25% of the materials value.

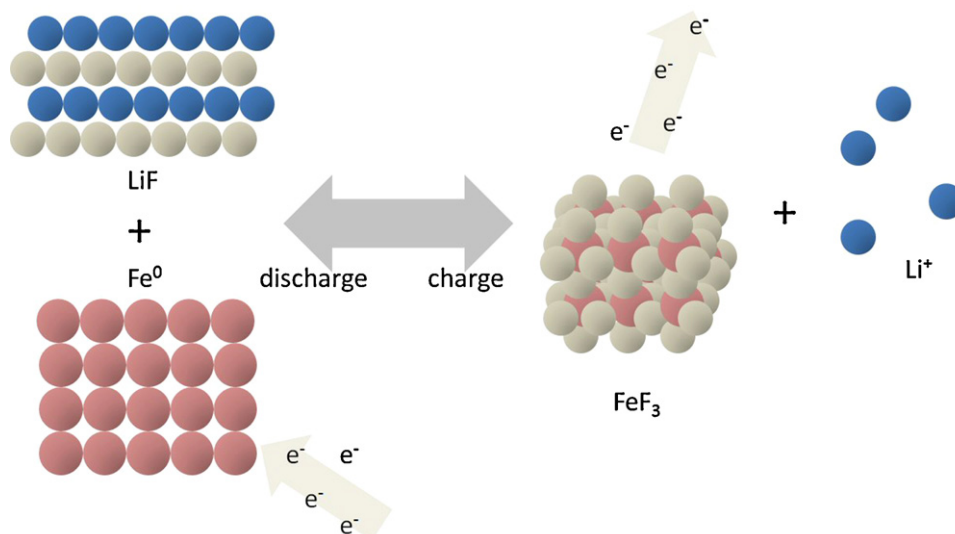


Fig. 4. Simplified representation of materials transformation in the conversion reaction of the Fe/LiF system.

### 3. Conceptual aspects

Similar fundamental relationships describing the thermodynamics, the kinetics, and the energy density of conversion materials apply for H storage and electrochemical applications.

#### 3.1. Thermodynamics

Fundamental equations describing the equilibrium conditions of an H storage system are the well-known relations for the enthalpy (3a) and the entropy of reaction (3b), the Gibbs Equation (4), and the Van't Hoff Equation (5).

$$\Delta H_{\text{reaction}} = \sum_i H_{f,\text{reaction}}^i(\text{product}) - \sum_i H_{f,\text{reaction}}^i(\text{educt}) \quad (3a)$$

$$\Delta S_{\text{reaction}} = \sum_i S_{f,\text{reaction}}^i(\text{product}) - \sum_i S_{f,\text{reaction}}^i(\text{educt}) \quad (3b)$$

$$\Delta G_r = \Delta H_r - T\Delta S_r \quad (4)$$

$$d \ln p = -\frac{\Delta H_r}{RT} + \frac{\Delta S_r}{R} \quad (5)$$

Eq. (4) describes the interplay of temperature-dependent forces which tend to increase the entropy by dissociation of the hydride and the release of H<sub>2</sub> molecules, and the counteracting binding forces which sum up in the binding enthalpies of the partners. Eq. (5) describes the equilibrium H<sub>2</sub> pressure which is obtained by these competitive forces, at a reaction temperature *T*.

In batteries, the available energy is also determined by the reaction equation, the thermodynamics, and the kinetics of the conversion reaction. A certain difference is that in this case, the theoretical energy content cannot be obtained directly from the reaction equation as in the case of H storage systems. Only the number of charge carriers or electrons stored in the reaction can be derived, see Eq. (6). The relation can be transformed to obtain the frequently used theoretical specific capacity (Eq. (7)).

$$It = \frac{m}{M} nF \quad \text{in [Ah] or [mAh]} \quad (6)$$

(with *I* = electric current, *t* = time, *m* = mass, *M* = molar mass, *n* = number of electrons transferred, *F* = Faraday constant)

$$\frac{It}{m} = \frac{nF}{M} \quad (\text{in [Ah/kg] or [mAh/g]}) \quad (7)$$

In order to calculate the energy content of the system the number of charge carriers has to be multiplied with their energy level i.e. the electromotive force or voltage of the cell. This, in turn, can be derived from the (standard) Gibbs free energy of the reaction (Eq. (8)). The obtained theoretical voltage is characteristic for each electrochemical couple.

$$\Delta G_r^0 = -nFU^0 \quad (8)$$

As is obvious from above, the thermodynamics are key for the available energy from both H storage materials and batteries at *p* and *T*. In both cases the reaction enthalpy and reaction entropy are determined by the enthalpy of formation of the reaction partners and can thus be modified as has recently been demonstrated for complex hydride based reaction systems [11,12]. These reaction systems were designed with the aim to lowering the reaction enthalpy which is high for certain complex hydrides such as LiBH<sub>4</sub> and Ca(BH<sub>4</sub>)<sub>2</sub> leading to high working temperatures and/or low equilibrium pressures for hydrogen. In the case of batteries, reaction systems would be desirable where the reaction enthalpy is increased rather than decreased because a higher voltage (see Eq. (8)), and, thus, higher energy output can be obtained.

#### 3.2. Kinetics

The energetic barriers which interfere with an easy storage of hydrogen or electrons are similar in nature for battery materials and H storage materials and are governed by interface processes and materials transport. There is an additional complexity for batteries because not only Li (or another ion) has to be transferred to every volume element of an electrode material, the same volume element must also be accessible by electrons in order to enable the oxidation or reduction of the material when the charge transfer ion is stored or released. In general, the following steps may be rate determining in the case of H storage materials:

- H<sub>2</sub> diffusion
- H<sub>2</sub> adsorption
- H<sub>2</sub> splitting and chemisorption of H
- Mass transfer of H from interface to bulk
- Bulk transport in the solid
- Nucleation of new phases
- Mass transfer for phase segregation and growth

For Li ion batteries based on conversion materials this is very similar:

- Li transport in the electrolyte.
- Li transfer from the electrolyte to the particle interface.
- Li transfer from the interface to the bulk.
- Li transport in the bulk
- Nucleation of new phases
- Mass transport due to phase segregation and growth.

In addition, the following electronic barriers have to be taken into account:

- Electron transfer from the collector to conductive parts of the electrode material.
- Electron conduction in the conductive part of the material.
- Electron transfer to the non-conductive, active material.
- Electronic transport in the active material.

In case of the batteries the above mentioned kinetic barriers lead to so-called 'polarization' or 'overpotentials' which means that the voltage necessary for charging the battery is higher than the voltage which is obtained when current is drawn from the battery. The kinetic limitations are different in nature. Depending on the partial step, a transport or reaction effect may be the origin of the respective barrier and there has been a classification in basically three types of polarization: The activation polarization is related to the charge transfer reactions at the electrode/electrolyte interface; the ohmic polarization is due to the ohmic resistance of different cell components and/or due to contact problems; the concentration polarization is related to mass transport limitations when the cell is charged or discharged. For conversion systems, an additional kinetic limitation may have to be taken into account in case the phase transformation including nucleation and growth is a rate determining process.

A voltage hysteresis is generally observed between discharge and charge of conversion materials, which lowers the efficiency of the electrode and, thus, hampers the transfer to commercial applications. The origins of this hysteresis are not well understood and are a matter of research at the moment. First studies indicate that not only kinetic factors play a role such as electrode conductivity. In addition, the hysteresis may be due to different paths of reaction, interfacial thermodynamics or mobility of the species during phase transformation.



To summarize, the theoretical energy content of H storage materials can be derived from the reaction equation which contains the number of released  $H_2$  molecules per mass of the reaction partners. The thermodynamics determine the maximum availability or partial pressure of the hydrogen at a given temperature whereas the kinetics decides upon the real availability of the hydrogen in an experiment at a given temperature  $T$ .

In the case of battery materials the energy content is determined by the reaction equation (i.e. mass of the reaction partners and number of electrons transferred) and the change of the free energy of the reaction. The stoichiometry of the electrochemical reaction and the reaction thermodynamics together determine the maximal available electric energy of the system. The kinetics control the real voltage and, hence, the available energy of a real system.

#### 4. Materials aspects

Materials for hydrogen storage which are based on the principle of intercalation exhibit the highest volumetric densities which can be obtained for hydrogen. The next neighbor distance of H is close to the theoretical limit of 2.1 Å in some of the alloys and cannot be further reduced. As mentioned above, the major drawback is the heavy weight of the transition metal host structure leading to a reversible storage capacity below 2.3 mass% H. Conversion-based complex hydrides or reaction systems consisting of lighter elements are an option to solve the problem, however, at the cost of still higher working temperatures and pressures. In addition, the volumetric density of hydrogen may be less in complex hydrides.

A prominent example for such a material is  $NaAlH_4$  which decomposes in a first step into a nanoscale heterogeneous mixture of  $Na_3AlH_6$  and Al when heated while half of the bound hydrogen (3.8 mass% H) is released [9]. In a second step, the hexahydride compound further decomposes into NaH and Al and another quarter of the bound hydrogen (1.9 mass% H) is released. With an appropriate, catalytically active dopant such as Ti or Ce the reaction is well reversible and the tetrahydride compound forms back under a hydrogen pressure. Many other compounds based on B (tetrahydroborates) and N (amides) have been synthesized and tested in the meantime [10].

It is obvious that the discovery of conversion materials for H storage with their different reaction mechanism has led to a paradigm change in research and development of H storage materials and meanwhile a big part of the H storage community is working in this area. A further generalization of the conversion concept is the use of hydrides which react with other hydrides in a chemical reaction between the solid phases and hydrogen which can be absorbed or desorbed depending on the conditions. Such reaction systems based on complex hydrides have first been presented by Chen for amides [11] and Vajo for tetrahydroborates [12].

A principle limitation of the established Li ion concept is that typically only one electron per transition metal atom is exchanged or stored. Furthermore, lattice sites for lithium in the host matrix are limited, not densely packed, and cannot always be filled completely.

Conversion reactions may circumvent these limitations and calculated theoretical capacities are above those of lithium cobalt oxide, lithium iron phosphate, or graphite by a factor of 5–10. This is due to a complete electrochemical reduction with the transfer of several electrons per 3d transition metal ion typically leading to metal nanoparticles which are embedded in a host matrix of the lithium compound.

This concept is valid for both cathode and anode materials such as transition metal oxides, nitrides, and sulphides. Especially the oxides of iron and manganese may be interesting due to their potential, their low cost, low toxicity and their theoretical spe-

**Table 1**

Characteristics of metal/ $O_2$  couples. OCV: open circuit voltage.

Metal/ $O_2$ couple	Idealised cell reaction	Calculated OCV (V)	Theoretical specific energy (Wh/kg) <sup>a</sup>
Li/ $O_2$	$4Li + O_2 \rightarrow 2Li_2O$	2.91	13,000
Al/ $O_2$	$4Al + 3O_2 \rightarrow 2Al_2O_3$	2.73	8100
Ca/ $O_2$	$2Ca + O_2 \rightarrow 2CaO$	2.99	4600
Zn/ $O_2$	$2Zn + O_2 \rightarrow 2ZnO$	1.65	1300
Mg/ $O_2$	$2Mg + O_2 + H_2O \rightarrow 2Mg(OH)_2$	3.1	6800
Fe/ $O_2$	$4Fe + 3O_2 \rightarrow 2Fe_2O_3$	1.3	1200

<sup>a</sup> Without  $O_2$ .

cific capacities which are 1007 mAh/g ( $Fe_2O_3$ ) and 1233 mAh/g for  $MnO_2$ .

A special case of conversion systems with very high theoretical capacities are metal/ $O_2$  batteries, sometimes also called metal/air batteries. The reaction partner  $O_2$  is not taken into account in the weight calculation of the materials which is one of the reasons for their very high theoretical energy densities, see Table 1.

While the theoretical capacities of conversion systems are highly attractive, it is evident from the first work in this field that there are also drawbacks associated with the currently investigated conversion systems. The following problems have already been identified and are subject of research:

- *Limited reversibility*, which is often caused by the large volume changes that may be associated with conversion reactions or by irreversible chemical reactions of the electrode with the electrolyte.
- *Voltage difference* between charge and discharge curves leading to lower energy efficiencies.
- *Power rate*, which may be low in the case of most conversion materials. The origin has not been elucidated in detail but it is likely that the complexity of the various transfer and transformation processes is a main reason.

The limited reversibility is an issue which is quite familiar in the research on complex hydrides and there are similar reasons such as kinetic barriers, reaction pathways, thermodynamically stable intermediates, grain or particle growth etc. In the case of batteries, there is an additional complexity coming from microstructural transformations which may affect the electronic transport to and from the particles of the active and normally non-conducting material: the volumes of the reacting particles may change considerably in the conversion reaction, so that the electric connection, which is normally provided by the addition of conducting carbon, may be disrupted and the cyclic capacity fades. Moreover, it is essential for hard nonconductor materials that the particles are sufficiently small in order to provide a charge transfer to and from the particle. Reversibility, cycle life and power rate are issues which may be strongly influenced by the microstructure of the functional material.

While promising results have already been obtained in increasing the cycle life by tailored nanostructured electrodes, the polarization seems to depend on the particular ionic nature of the M–X bond (X=halide, oxide, nitride sulphide, phosphide) which makes new battery chemistries necessary in order to circumvent that problem.

A recent work in our own laboratory showed that also conversion based systems can work very stable and at high capacities. Here, the Fe/LiF system (see Eq. (9)) was encapsulated in multiwalled carbon nanostructures leading to a very stable cycling behavior with a capacity loss of 3% between the 10th and the 300th cycle, at a level of 280 mAh/g, in a voltage window between 1.3 and

4.5 V [13].



The theoretical capacity is 712 mAh/g of this system which is by a factor of 5 above that of  $\text{LiFePO}_4$ . However, the performance is also influenced by kinetic factors and a certain hysteresis of the voltage and a significant influence of the charging current on the storage capacity can be observed.

## 5. Conclusions

From the current state-of-the-art in the development of H storage materials and battery materials it may be concluded that both fuel cell driven and full electric vehicles will be developed and introduced, which is mainly due to the limited energy storage capacities of current batteries. In the case of hydrogen storage systems, the hybrid concept seems to have advantages due to the better safety and much higher volumetric capacity when compared to pressurized tanks.

Materials are needed which allow for better storage capacities for both H storage and electrochemical storage. A material with higher reversible gravimetric capacity for hydrogen could cancel out the disadvantage of the higher weight of a hybrid system. An electrode material with higher specific energy density could increase the driving range of FEVs and/or decrease the costs, thus enabling new application areas for the battery car.

It seems that conversion-based material systems are the only way at the moment to increase both storage capacities 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. However, the development has just begun and no systems have been presented yet

with an acceptable maturity for industrial applications. Finally, it is apparent that the seemingly competing 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.

## Acknowledgment

This work was supported by the European Commission under the 'NanoHy' project (grant agreement no.: 210092).

## References

- [1] <http://inventors.about.com/library/weekly/aacarselectrica.htm>.
- [2] [http://en.wikipedia.org/wiki/Bertha\\_Benz](http://en.wikipedia.org/wiki/Bertha_Benz).
- [3] International Energy Agency (IEA), World Energy Outlook 2009, Paris, France.
- [4] (a) <http://www.greencarcongress.com/2009/09/h2-mobility-20090910.html>;  
(b) <http://www1.eere.energy.gov/hydrogenandfuelcells/accomplishments.html>.
- [5] U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem. Int. Ed.* 48 (2009) 2–25.
- [6] D. Mori, *Metallic Hydride R&D for Vehicular Hydrogen Storage*, Gordon Research Conference on Hydrogen-Metal Systems, Barga, Italy, 2009.
- [7] A. Nistroj, *The Electrification of the Automobile – Technical and economical challenges*, World Hydrogen and Energy Conference, Essen, Germany, 2010.
- [8] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, *Nature* 407 (2000) 496–499.
- [9] B. Bogdanovic, M. Schwickardi, *J. Alloys Compd.* 253–254 (1997) 1–9.
- [10] (a) S. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel, C.M. Jensen, *Chem. Rev.* 107 (2007) 4111–4132;  
(b) M. Fichtner, *Adv. Eng. Mater.* 6 (2005) 443–455.
- [11] (a) P. Chen, Zh. Xiong, J. Luo, J. Lin, K.L. Tan, *Nature* 420 (2002) 302–304;  
(b) P. Chen, *Metal Nitrides and Imides as Viable Hydrogen Storage Materials*, MRS Fall meeting Boston, U.S.A. 2003.
- [12] (a) J.J. Vajo, F. Mertens, C.C. Ahn, R.C. Bowman Jr., B. Fultz, *J. Phys. Chem. B* 108 (2004) 13977–13983;  
(b) J.J. Vajo, S.L. Skeith, F. Mertens, *J. Phys. Chem. B* 109 (2005) 3719–3722.
- [13] R. Prakash, A.K. Mishra, A. Roth, Ch. Kübel, T. Scherer, M. Ghafari, H. Hahn, M. Fichtner, *J. Mater. Chem.* 20 (2010) 1871–1876.
- [14] J.-M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.