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REVIEW

High capacity hydrogen storage: Basic aspects, new developments and milestones

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Abstract
One of the major technical bottlenecks in hydrogen economy is hydrogen storage. None of the hydrogen absorption materials known today exclusively meets all the required properties such as storage capacity (~4.5 wt%), reaction enthalpy (15–24 kJ/mol), kinetics (0.02 g H_2/s), cycle life (>10,000 cycles), desorption temperature (~<100 °C), etc. However, there are striking recent developments; as for example, development of reactive hydride composites (RHC), nanoconfinement of hydrides by nanoscaffold materials, synthesis of new generation alkali-alkaline earth composite structures and air stable nanocomposite system, etc. All these materials are conceptually interesting candidates, but when it comes to practical reality, still significant problems need to be circumvented. The present review therefore attempts to throw some insight on almost all classes of known hydrogen storage materials. The very basic aspects of hydrogen storage are presented and the promise of state of the art candidates is indicated.

Introduction

Sustainable clean energy development is the most compelling need of the world today. In quest of developing sustainable clean energy, many alternative options such as renewable energy (wind, solar, tidal, geothermal energy), nuclear energy and hydrogen energy are extensively discussed. From the insight gained from many in-depth reviews [1–3] it appears to be that hydrogen is the best option to curb out a balanced energy mix without prompting environmental implications [4]. This is due to the fact that renewables are season/location sensitive and nuclear fuels are not safe. Hydrogen is very advantageous in the sense that (a) it is a clean burning fuel, (b) it possesses higher energy content per mass unit and (c) it is the only indigenous energy carrier existing all over the world. Nevertheless, in spite of all such merits, a flawless economic system based upon H_2 fuel (hydrogen economy) could not be readily framed due to a couple of technical challenges in areas such as hydrogen production, storage and application, etc. Among these three areas hydrogen storage presents a huge challenge. It was proposed by USDOE [5] that a hydrogen storage media with 4.5 wt% reversible hydrogen capacity under affordable conditions should be established

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for commercial applications (the USDOE's earlier target was 6 wt% gravimetric density, which was later revised to 4.5 wt%). Both high compression storage and cryogenic storage modes are considered ineffective due to high cost and safety concerns. Thus the effective means of hydrogen storage system appears to be reversible metal hydrides. Many metal hydrides have so far been investigated but none of the materials offer the required benchmark performances for onboard storage applications. High capacity light weight hydrides are therefore paid much attention; however, significant technical challenges needs to be circumvented.

After decades of extensive investigation, it is now concluded that a storage capacity of above 4.5 wt% can be achieved only through light weight materials, particularly with elements having atomic number of up to 20 [6-8]. In fact, an exhausting list of high capacity hydrogen storage materials is known with capacity even more than double the required 4.5 wt%. But, these hydrides are either too stable or too unstable and not reversible under the ideal operating conditions [9]. Therefore research efforts like catalyzing high capacity hydrides, decorating/doping the selected sites for tuning the properties, chemical modification for enhancing the thermodynamic features and tailoring of new light weight composite systems have been attempted in recent years [10-12]. The present review illustrates some of the interesting hydrogen storage candidates with special reference to hydrides formed by elements with atomic number less than 20. We initially address the basic aspects of hydrogen storage, simple thermodynamic considerations and the unique features of catalysts in metal-hydrogen interaction, etc. A brief overview of recent developments in a variety of hydrogen storage materials is sequentially indicated. We finally discussed the new interesting strategies employed by various researchers for improving the hydrogen storage capacity of state of the art materials.

Hydrogen fuel for transport applications

Hydrocarbon fuels consume oxygen and releases carbon dioxide during the combustion reaction, thereby largely disturbing the oxygen to carbon dioxide ratio in the atmosphere. The combustion reaction of hydrogen is quite neutral because the consumed oxygen again gets released during the production of hydrogen from the product (water). Moreover, the lower heating value (LHV) of the combustion of hydrogen is almost three times higher as compared to the LHV of gasoline.

$$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O \text{ (LHV} = {\sim}45\text{ kJ/g)} \quad (1)$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \text{ (LHV} = {\sim}120\text{ kJ/g)} \quad (2)$$

Hydrogen combines with oxygen to form water and generates electricity in fuel cells (cold combustion) and it can also be burnt inside the internal combustion engines or turbines (hot combustion) to power devices and motive systems. Some of the key properties of hydrogen are compared with methane and gasoline fuels in Table 1 [13]. The table clearly illustrates that hydrogen is the potential alternative to the conventional hydrocarbon fuels. Nevertheless, it is necessary to note that hydrogen is not a fuel by source, but is an energy carrier i.e. hydrogen must be initially procured to proceed with reaction (2). For understanding the number of ways practiced for producing hydrogen, the reader is referred to reviews in Ref. [14]. In-depth discussion regarding hydrogen production is beyond the scope of the present review.

Due to the low density of hydrogen, storage of hydrogen under ambient condition requires a huge volume (11.2 l for 1 g of hydrogen). High pressure storage is widely discarded since it is risky, cost-intensive and highly ineffective. In the case of cryogenic storage, the low temperature requirement (< -253 °C) for liquefaction and the requirement of super insulated containers make this mode very expensive. Handling and distribution of liquid hydrogen is also a difficult talk. Liquid hydrogen cannot easily be moved via underground pipelines and it is necessary to use special vacuum insulated hoses for moving liquid hydrogen from container to container. Thus, this option is not easily practicable [15]. The reversible reaction of hydrogen with metals, alloys or intermetallic compounds is considered as a convenient way of storing hydrogen [16]. This is due to the fact that, unit volume of a metal hydride holds more hydrogen than liquid hydrogen does.

The U.S. Department of Energy (DOE), in consultation with the U.S. Council for Automotive Research (USCAR), has established an evolving set of technical targets for the onboard hydrogen storage systems which is shown in Table 2. The previous set of these targets was established in 2003 [17]. The targets set out in the previous reports for establishing a hydrogen storage material with 9 wt% by

Table 1 Comparison of few important properties of hydrogen with hydrocarbon fuels such as gasoline and methane.

Properties	Unit	Hydrogen (H_2)	Methane (CH_4)	Gasoline (C_8H_{18})
Energy content	kWh/kg	33.33	13.9	12.4
Self ignition temperature	°C	585	540	228-501
Flame temperature (in air)	°C	2130	1960	1977
Flame temperature (in O_2)	°C	2810	2780	2200
Ignition limits in air	vol%	4-75	5.3-15	1.0-7.6
Min. ignition energy	mW s	0.02	0.29	0.24
Flame propagation in air	m/s	2.65	0.4	0.4
Detonation limits	vol%	13-65	6.3-13.5	1.1-3.3
Detonation velocity	km/s	1.48-2.15	1.39-1.64	1.4-1.7
Explosion energy	vol%	13-65	6.3-13.5	1.1-3.3