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Chapter 1

Hydrogen Economy: Modern Concepts, Challenges and Perspectives

Vladimir A. Blagojević, Dejan G. Minić,
Jasmina Grbović Novaković and Dragica M. Minić

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1. Introduction

Identifying and building a sustainable energy system are two of the most critical issues for any modern society. Ideally, current energy system, based mostly on fossil fuels, which have limited supply and considerable negative environmental impact, would be replaced with a system based on a renewable fuel. Hydrogen, as an energy carrier primarily derived from water, can address the issues of sustainability, environmental emissions and energy security. If one assumes a full hydrogen economy the size of United States, the amount of hydrogen for just purposes of transportation would be about 150 million tons per year, which would amount to consuming, with current production efficiency, between 2 and 5 billion tons of water. As a comparison, current water consumption in United States for purpose of thermoelectric power generation in power plants is around 300 billion tons, with another 1.2 billion tons consumed for gasoline production. Therefore, rather than consume, a hydrogen economy would most likely significantly reduce water consumption for purposes of energy generation (Turner, 2004).

Hydrogen is the most abundant element in the universe, burns clean, producing only water and has the highest energy density per unit mass. This is why hydrogen is considered most suitable to replace fossil fuels as the primary energy material for the mobile industry (Šušić, 1997c). However, hydrogen is not an energy source, only an energy carrier, and it is not freely available in nature and needs to be produced, either from water or other compounds. If it is produced from water, it costs more energy to produce it than one would recover burning it. This is why, ideally, a hydrogen cycle would include hydrogen produced by splitting water using electrolysis with solar energy and stored reversibly in a solid. However, there are considerable difficulties associated with efficient hydrogen production, storage and use in fuel cells. Among them, hydrogen storage for mobile applications is currently the most difficult obstacle.

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Gasoline has very high energy density of 31.6 MJ/L, compared to 4.4 MJ/L of compressed hydrogen and 8.8 MJ/L of liquid hydrogen. In addition, gasoline tank has extremely short filling time, is capable of providing energy at low temperatures and provides excellent control of energy discharge, allowing rapid acceleration, high sustained speed and considerable range. These are the challenges that a successful hydrogen tank has to meet, too. US Department of Energy (DOE) target requirements for a hydrogen tank require hydrogen gravimetric density of 7.5 mass% and volumetric density of 70g/L, operating temperature between 233 and 358K, minimum delivery pressure of 12bar (1.2MPa) and fueling time of 3min. In addition, the storage system should be safe, durable (1500 operational cycle life) and cost effective. None of the existing systems meet these requirements.

In order to achieve the hydrogen economy, there are some obstacles that need to be overcome to make hydrogen a viable energy carrier. They are characterized by four main aspects of hydrogen use and some of these will be addressed here:

1. Production – since hydrogen needs to be produced, ideally from water, it is necessary to develop production methods that would consume the least amount of energy and provide ability to produce hydrogen renewably on a large scale.
2. Storage – fuel needs to be easily stored for use and transport, where one of the main requirements is that it is readily available, which requires not just short charge/discharge times, but also excellent control of charge/discharge process coupled with sufficient energy and gravimetric/volumetric density.
3. Power generation – once hydrogen is ready to be consumed, it is necessary to do so in the most effective way: the power generation system that uses hydrogen needs to be both efficient and, for mobile application, lightweight.
4. Safety – hydrogen use and storage comes with some risks (flammability) which necessitate certain precautions and safety measures; another aspect related to this is environmental impact of the hydrogen cycle, which depends on the methods used to produce, store and use it.

Since hydrogen is thought to be a renewable fuel for the future, it is only appropriate that, when we consider all the challenges associated with its production, storage and use, we keep in mind that when we consider proposed systems, efficiency is only one of the factors that will determine the success of these systems. Other important aspects are production cost (both financial and in resource), durability, stability of operation and safety, and these can, more than efficiency, determine the success or failure of any of the proposed solutions for a part of the hydrogen cycle.

2. Hydrogen production

There are several potential sources of hydrogen on our planet, although these are exclusively hydrogen compounds, necessitating extraction of hydrogen at energy cost. The most abundant is water, while hydrogen can also be obtained from hydrocarbons, either fossil fuels or biomass. While production from water is clean and renewable, with no CO_2

emission, production from fossil fuels generates similar or even higher levels of CO_2 emissions as burning of coal and gasoline. Hydrogen production from biomass is carbon-neutral, since plants and organisms used during the process sequester approximately the same amount of CO_2 during their growth as it is emitted during the process of extraction of hydrogen from them. However, their negative environmental impact is considerable due to the fact that they require large land surfaces for growth.

From water. Although many technologies have been explored for production of hydrogen by splitting water into hydrogen and oxygen, these processes have yet to achieve the necessary efficiency and scalability for industrial application. The main advantage of hydrogen production from water is that it is clean, renewable and has little or no negative environmental impact, although the energy cost of its production is currently too high. There are several processes of interest, like electrolysis, catalytic thermolysis, photocatalytic water splitting and sulfur-iodine cycle.

Electrolysis of water is used today to produce around 5% of all industrial hydrogen. There are several types of cells in use: solid oxide electrolysis cell, alkaline electrolysis cell and polymer electrolyte membrane cell. These cells operate at elevated temperatures (350-570K) and contain high electrolyte concentrations and catalysts (typically yttrium-stabilized zirconium oxide mixed with nickel). Efficiency of typical electrolysis processes is usually between 50-80%, when inefficiencies of production of power used for electrolysis are not taken into account. With these taken into account, the energy efficiency would decrease to 30-45% for a typical nuclear or thermal power plant used as the power source, or even lower for a typical solar cell or array (Hauch et al., 2008).

Water thermolysis is thermal dissociation of water, which occurs spontaneously around 2800K. Although this temperature is too high for practical applications, significant effort has been invested into research of catalysts to reduce water thermolysis temperature and make it an industrially viable process. The goal is to use water thermolysis either in solar concentrators or in nuclear power plants to produce hydrogen directly using thermal energy. Solar concentrators can produce very high temperatures (over 1800K) by concentrating sunlight using a system of mirrors. Next generation nuclear power plants will be operating at lower temperatures (1000-1300K), but it is hoped that new catalysts will make it possible to use them for direct hydrogen generation using water thermolysis.

Photocatalytic water splitting is a process of directly producing hydrogen using solar energy. It relies on use of photocatalyst to capture the solar energy and use for water dissociation (Ni et al., 2007). There are two principal types of catalysts: photoelectrochemical and photobiological (discussed in biohydrogen production section). Photoelectrochemical (PEC) systems can be divided further into four groups:

- Type 1 – a single electrolyte-filled reactor containing a colloidal suspension of PEC nanoparticles producing a mixture of H_2 and O_2 gas;
- Type 2 – dual electrolyte-filled reactor beds containing a colloidal suspension of PEC nanoparticles, each carrying out half of the reaction process (one producing oxygen, the other hydrogen from H^+ produced in the first reactor bed);

- Type 3 – fixed PEC planar array using multi-junction photovoltaic/PEC cells immersed in electrolyte reservoir;
- Type 4 – PEC solar concentrator system, using reflectors to focus the solar flux at 10:1 intensity onto multi-junction photovoltaic/PEC cell receivers immersed in electrolyte reservoir and pressurized to 2MPa.

Estimated hydrogen production costs for these systems are: 1.63-10.36\$/kgH_2 depending on the type of system. DOE target for 2015 price of hydrogen was originally set at 1.50\$/kgH_2, but it was increased in 2005 to 2-3\$ per kgH_2, which means that some of these systems already meet that modified requirement. The main issues in these systems remain separation of O_2 and H_2 from the product for Type 1, ionic conduction (through ionic bridge) between two reactor beds for Type 2, improvement of PEC cell structure to reduce cost for Type 3 and new composite concentrator structure and high pressure PEC operation for Type 4. Potential benefits are clean and renewable direct hydrogen production with relatively low cost, although efficiency, depending on the system, is in range of 5-25% for the entire system.

Sulfur-iodine cycle is a thermochemical process which produces hydrogen from hydrogen iodide at much higher efficiency than water splitting, and at lower temperature (700K). One of its advantages is that sulfur and iodine are recovered and reused during the process and not consumed. It is usually coupled with concentrating solar power systems to produce hydrogen using solar energy, providing clean and renewable source of energy.

From fossil fuels. Fossil fuels are the dominant source of industrial hydrogen today. Hydrogen can be produced from natural gas with efficiency of around 80% and from other hydrocarbon sources with a varying degree of efficiency.

Most widely used method of hydrogen production today is steam reforming of methane or natural gas. At high temperatures (1000-1300K), water vapor reacts with methane to yield syngas (mixture of hydrogen and carbon monoxide), which can be used to produce more hydrogen through reaction of water and carbon monoxide (also known as water gas shift reaction, performed around 400K). The drawback of this process is that it produces CO_2 waste (Lee & Lee, 2001).

Other methods of hydrogen production from fossil fuels are partial oxidation of hydrocarbons, which includes partial combustion of fuel-air mixture at high temperatures or in a presence of a catalyst, plasma reforming (Kvaerner process), which produces hydrogen and carbon black from hydrocarbons (no CO_2 waste), and coal gasification, where coal is converted to syngas and methane.

Biohydrogen production. Biological H_2 production represents an effort to harness biological processes to generate hydrogen on the industrial scale. Although they have found no industrial application, there are a number of processes for conversion of biomass and waste streams into biohydrogen. Some of them are the same as the ones described above for fossil fuels, except they use biomass in place of fossil fuel (biomass gasification, steam reforming), while others use biological conversion of solar energy (Tao et al., 2007). Biological

conversion is process where biological organisms (usually plants) convert sunlight into hydrogen through their metabolic processes (Melis, 2002).

There are variety of pathways for biological conversion that include unicellular green algae, cyanobacteria, photosynthetic bacteria and dark fermentative bacteria. Photobiological production of hydrogen offers a perspective of operating with solar energy conversion efficiency to H_2 as high as 10%, if some of the barriers could be overcome, like slow H_2 production rate, or discontinuity of H_2 production due to co-generation of O_2 (Maness, 2002). Another challenge represents system engineering for cost-effective photobiological H_2 production. Because of an excellent variety of different bacteria, which absorb light in different spectral regions, it is hoped that, ultimately, a mixture of bacteria tailored to maximize sunlight absorption would be used to improve efficiency. This level of adaptability is one of the advantages of photobiological hydrogen production. There are no photobiological hydrogen production systems that are even close to being competitive with other methods of hydrogen generation, while relatively low overall efficiency would require large surface areas for harvesting and conversion of sunlight. On the other hand, biological production would probably have positive impact on environmental pollution and potentially serve as a source of high value bio-products, which could be useful in the food and synthetic chemistry industries. However, the main limitation of biological production is that it ultimately depends on availability of land for biomass production. This means that it cannot provide the amounts of hydrogen needed by an entire civilization, especially taking into account the fact that we live in a food-limited world with increasing population.

3. Hydrogen storage

Hydrogen storage is a problem that has been a focus of scientific research for decades (Minić & Šušić, 2002). During this time a variety of methods have been investigated, although, none of these have accomplished the required performance level so far. Current methods for hydrogen storage can be broadly separated into:

- mechanical storage: storage in a tank of compressed gas or liquid hydrogen;
- physisorbtion: storage in a solid material through physisorbtion; includes:
- graphene and other carbon structures
- metals and metallic nanocrystals and composites
- metal-organic frameworks, zeolites;
- hydrogen: storage in solid or liquid material of chemically bound hydrogen that is released on decomposition; includes:
- light metal hydrides (e.g. alkaline hydrides, alanates, alane)
- borohydrides
- amines and imides
- amino borane.

Each of these methods has its advantages and disadvantages, but all on-board storage technologies have to meet the following requirements:

- safety

- performance
- cost
- technical adaptation for the infrastructure
- scalability (application in both small and large vehicles).

3.1. Mechanical storage

Low-pressure gaseous form of hydrogen is preferable in terms of efficiency. However, since vehicles cannot store enough hydrogen in this form, compression or liquefaction of hydrogen represents a relatively straightforward way of increasing vehicle on-board capacity. Mechanical storage methods store hydrogen by confining its gas or liquid form in a mechanical tank, similar to how gasoline is stored. The advantages are relatively good charge/discharge time and durability, but the capacity of the tanks is limited by relatively low energy density of hydrogen gas and liquid. In addition, the weight of tank is considerably larger than the gasoline tank due to demands of safe hydrogen storage.

There are currently three broad methods of mechanical hydrogen storage:

- high-pressure tank systems
- hydrogen-absorbing alloy tank system
- liquid hydrogen tanks.

Most current vehicles using hydrogen are equipped with a composite high-pressure tank, due to its simple structure and ease of charge-discharge cycle. Standard high-pressure tanks store hydrogen at 35MPa (350bar) pressure, which provides vehicle autonomy of 300-350km. Tanks have been developed recently to store hydrogen at 70MPa (700bar) pressure.

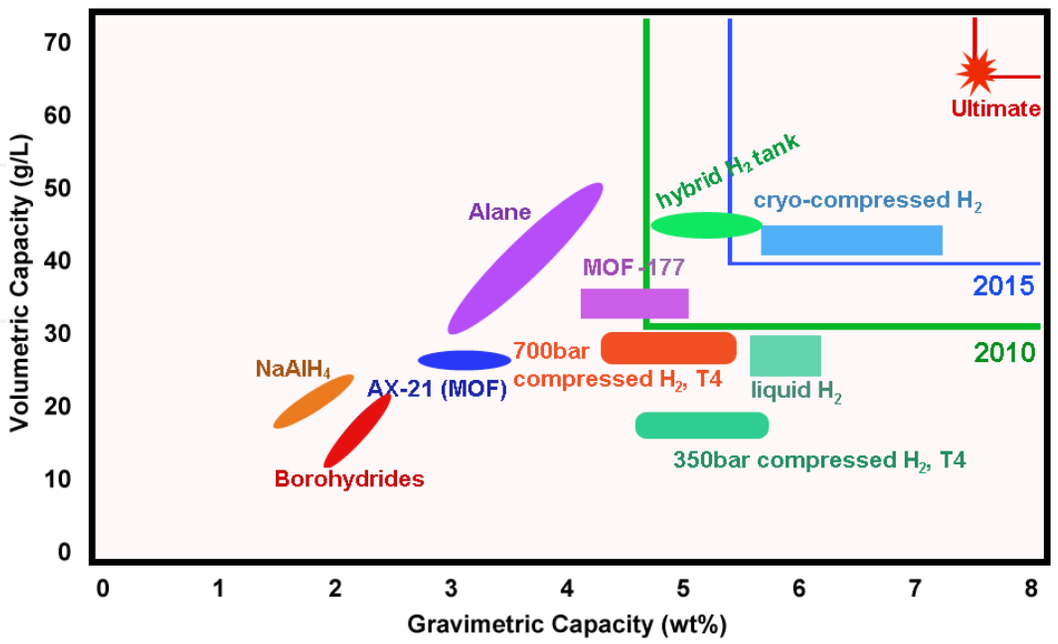

Figure 1. DOE set requirements (solid lines) and overview of existing developed hydrogen storage methods with respect to those requirements

However, pressure in this range makes the relationship between hydrogen pressure and amount non-linear. Therefore, doubling of pressure only leads to an increase of 40-60% more hydrogen, increasing vehicle autonomy to around 500km (Mori & Hirose, 2009).

Tank type	Type 1	Type 2	Type 3	Type 4
composition	all metal (carbon steel)	metal liner + GFRP layer	metal liner + CFRP layer	plastic liner + CFRP layer
thickness ratio (cylinder part)	1.0	0.7	0.32	0.28

Table 1. Different high-pressure (35MPa) tank types for hydrogen storage (GFRP – glass fiber reinforced polymer, CFRP – carbon fiber reinforced polymer)

In order to improve storage capacity of a high-pressure tank, hydrogen absorbing metal alloy is added to the tank to produce a hybrid high-pressure hydrogen absorbing tank system. The alloy increases capacity of the tank from around 3kg per 180L tank to 7-10kg per 180L tank, but hydrogen absorption on charging releases considerable amount of heat, requiring heat exchanger and radiator to be fitted with the tank, resulting in an increase in tank weight from around 100kg to over 400kg. High-pressure (35MPa) hydrogen environment helps metal alloy absorb hydrogen quickly (around 80% charge in 5min) and improves discharge speed, which is a common difficulty of classical metal hydrides, although high hydrogen pressure means that this system has the same safety issues as a regular high-pressure tank system. This system is also capable of operating at temperatures as low as 243K, which is not possible with low-pressure metal hydride systems. These hybrid systems offer a lot of promise offering good charge/discharge performance, but they still don't achieve the required hydrogen capacity and they retain the same safety issues associated with conventional high-pressure systems.

Another improvement of high-pressure system represents the use of cryo-compressed storage, where hybrid high-pressure tank is equipped with heat-transfer system, allowing it to maintain hydrogen gas at temperature around 50K and 0.4MPa pressure (around 6mass%). As the tank is emptied during use, temperature is gradually increased using the heat released during discharge to maintain a minimum 0.4MPa pressure. Figure 2 shows a comparison of gravimetric and volumetric densities of hydrogen for different high-pressure tank systems. Projected capacity of cryo-compressed hybrid system would meet DOE interim requirements for 2015, the first system so far to achieve this. However, this system is still well short of ultimate goals set by DOE.

Liquid hydrogen exists at atmospheric pressure at temperatures below 20K and its density is much higher than compressed gas. From the point of use in vehicles and infrastructure, liquid hydrogen is very attractive, because it offers an opportunity to easily transport and store large amounts of hydrogen. Some studies show that the extra energy consumption of liquefaction process can be compensated by the ease of delivery and storage. However, due to low temperatures involved, liquid hydrogen tanks require double wall construction for

thermal insulation, minimizing heat conductivity with vacuum multi-layer insulation. This consists of a thin metal layer on the spacer material which prevents both radiation and thermal irradiation between individual layers and heat intrusion from irradiation and gaseous convection. The most advanced liquid hydrogen tanks have limited heat flow to a few watts per second, which results in hydrogen evaporation and, therefore, loss of a few percent per day. Further developments in thermal insulation, advanced liquefaction and charge/discharge strategy are necessary in order to make liquid hydrogen a viable commercial alternative to a gasoline tank.

3.2. Carbon materials

There have been a number of studies of use of different carbon materials for hydrogen storage. Although initial reports suggested high hydrogen storage capacity of carbon nanotubes and other related nanostructures, more recent results have shown that the maximum sorption capacity of carbon nanostructures is around 2mass% (Zuettel et al., 2004) and that it is dependent only on the surface area of individual carbon nanostructure. Of those nanostructures, graphene sheets have exhibited the highest surface area and represent the most promising carbon material for hydrogen storage. However, since its capacity in pure form is about 2mass%, recent work has been focused on improving both performance and capacity of graphene. One of the issues that need to be overcome is that binding energy of atomistic hydrogen to carbon is 0.8eV, much lower than the energy of H-H bond in H_2 molecule (2.3eV per hydrogen atom). That is why recent research has been focused on catalyst assisted hydrogen sorption on carbon through spillover effect. Hydrogen spillover refers to transport of an active species generated on one substance (activator) to another (receptor) that would not normally adsorb it. In this case, activator is commonly a metal or a metal oxide, while carbon acts as a receptor, overcoming the energy barrier associated with dissociation of hydrogen molecule. Enhancement of hydrogen adsorption via spillover effect is much more pronounced at lower hydrogen pressure (below 0.5MPa), while it saturates at high pressures. This suggests existence of two distinct mechanisms corresponding to different spillover behavior, which can be controlled by activation of catalyst (Tsao et al., 2010).

Recent first-principle calculations have suggested that use of graphene double-layer and multi-layer structures could increase capacity for hydrogen storage (3-4mass%) (Patchkovskii et al., 2005), while recent experiments of Pd-loaded single-wall carbon nanotubes show improved performance after Pd-loading and thermal treatment at temperatures around 700K (Kocabas et al., 2008). Additional theoretical calculations of spillover on graphene suggests that hydrogen atoms on graphene surface should create compact clusters so that the lowest-energy luster is composed of closed six-hydrogen rings, which would correspond, if entire surface area of graphene is used, to hydrogen storage capacity of about 7.7mass% (Lin et al., 2008). However, recent studies of kinetics of hydrogen adsorption/desorption kinetics in Pd/Pt/Ni/Ru doped ordered mesoporous carbon indicated that there is no difference in the kinetics of doped and pure carbon (Saha & Deng, 2009), suggesting that doping of carbon materials using transition metals might not be able to achieve significant increase in capacity and charge/discharge rates.

Although work on carbon materials is ongoing, it is unlikely that carbon materials will, in the foreseeable future, achieve the necessary performance levels required to replace fossil fuels. These types of materials have exhibited encouraging hydrogen capacity at low temperatures (20-80K), but their performance has regularly diminished at room temperature and this remains the biggest challenge in research of carbon materials for hydrogen storage.

3.3. Zeolites and metal-organic frameworks

Zeolites are crystalline microporous materials, usually alumosilicates or aluminophosphates. They consist of microporous framework, which, in principle, appears highly suitable for hydrogen adsorption, as the adsorption energies in the narrow pores are very low, allowing thermal cycling to be used for adsorption and desorption of hydrogen. Initial reports of their storage capacities (Weitkamp et al., 1992, 1995, 1997) indicated very low capacities at room temperature, but these substantially increased at 77K, to 1.5mass% (Jhung et al., 2007). However, these fall well short of technical requirements. Projected maximum capacities for zeolite systems (assuming hydrogen packing density equal to liquid hydrogen) are a maximal 2.5 mass%, indicating that the currently known systems would not be able to meet the requirements to serve as hydrogen storage materials in mobile applications, although new materials might offer better performance.

Metal-organic framework (MOF) materials are composed of metal ions as vertices connected by organic molecules, often polyvalent carboxylic acids, to create a porous material of exceedingly high surface area (Rowsell & Yaghi, 2005). Reported hydrogen storage capacities of these materials have been encouraging: material MOF-177 was reported to have saturation uptake of 7.5 mass% at 77K and atmospheric pressure (Wong-Foy et al., 2006), although this declines to 1.62 mass% at 0.1MPa pressure (Rowsell et al., 2004). These materials exhibit an interesting feature, which could be of great importance for hydrogen adsorption – the so-called gated adsorption (Kitaura et al., 2003; Zhao et al., 2004). This process relies on flexibility of the framework of some MOFs allowing the structure to expand upon adsorption of guest species and shrink back upon desorption. This leads to a pronounced hysteresis, which can be exploited to load the materials at high pressure and still be able to capture hydrogen at lower pressures or higher temperature. However, these materials have some disadvantages as the loading of the material has to be performed at low temperatures, which consumes additional energy, and the binding of hydrogen to MOF materials is stronger than in carbon materials like graphite and carbon nanotubes (Rosi et al., 2003). However, this is still a new class of materials and most of them have yet to be investigated as hydrogen storage materials. In addition, in the foreseeable future, there should be many more new materials of this type, therefore, this class of materials shows great promise when it comes to hydrogen storage capabilities and offers genuine prospect of a hydrogen storage system that could meet all the requirements necessary for mobile applications.

3.4. Metal hydrides

Many metals and alloys are capable of absorbing considerable amounts of hydrogen according to the reaction (1):

$$Me + \frac{x}{2} H_2 \Leftrightarrow MeH_x \tag{1}$$

Here Me is a metal, a solid solution, or an intermetallic compound and MeH_x is a hydride (x is the ratio of hydrogen to metal H/Me). In most cases this reaction is exothermic and reversible. Heating of the hydride causes hydrogen desorption. Charging can be done using molecular hydrogen gas or hydrogen ions from an electrolyte. If hydrogen is loaded from gas phase, several reaction stages of hydrogen with metal would occur, as shown in Fig.2. The metal is usually in form of powder, and can be amorphous or crystalline (Minić et al., 1996). Repeated thermal treatment during hydrogen absorption and desorption causes structural changes in amorphous metals and intermetallic compounds, leading to crystallization (Minić et al., 1995; Šušić et al., 1996).

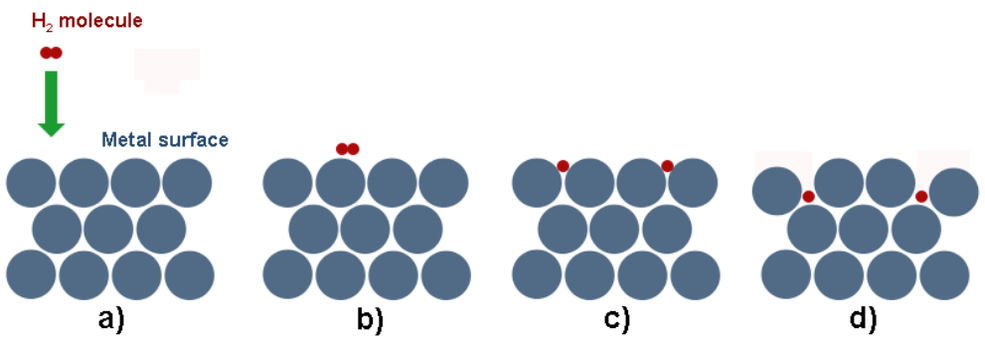

Figure 2. Reaction of H_2 molecule with metal surface: a) H_2 molecule move toward the metal surface. b) physisorbtion of H_2 molecule through Van der Waals interaction with metal surface c) chemisorption of hydrogen after dissociation d) occupation of subsurface sites and diffusion into bulk.

Most of the known metal hydrides exhibit unsatisfactory charge/discharge kinetics, which led to devotion of significant research effort on improving it using surface catalysts and taking advantage of spillover mechanism of hydrogen absorption (Fig. 3). This mechanism includes adsorption and subsequent dissociation of hydrogen molecule on surface catalyst, and migration and subsequent diffusion of adsorbed hydrogen atoms from surface catalyst into the metal (Minić et al., 1997). Since catalyst is a metal or intermetallic compound with superior hydrogen adsorption, it serves as a gateway for hydrogen absorption. This improves charging kinetics of the metal, while using relatively small amounts of catalyst (most commonly Pd) (Šušić, 1997a, 1997b).

The reaction of hydrogen gas with a metal can be described by one-dimensional Lennard-Jones potential curve, Figure 4 (Lennard-Jones, 1932). Far from the metal surface, the potential energy difference of a hydrogen molecule and that of 2 individual hydrogen atoms is equal to dissociation energy ($H_2 \rightarrow 2H$, E_D = 435.99 kJ/molH_2). The molecular hydrogen initially exhibits Van der Waals attractive interaction during approach to metal surface, leading to the physisorbed state ($E_{phys} \approx$ -5 kJ/molH) at a distance from the metal surface approximately equal to hydrogen molecule radius (≈0.2 nm).

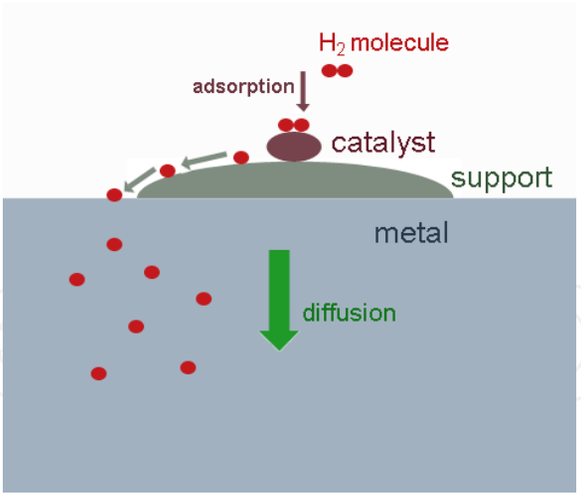

Figure 3. Illustration of spillover mechanism of absorption of hydrogen into a metal using a catalyst

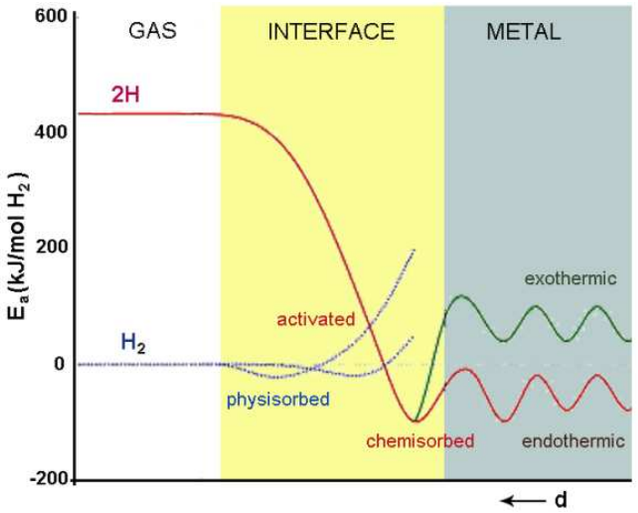

Figure 4. One-dimensional potential energy curve (one-dimensional Lennard-Jones potential for a hydrogen metal system.

Closer to the metal surface, hydrogen has to overcome an activation barrier for dissociation and formation of the hydrogen-metal bond (crossing point of dashed blue and solid red line). The height of the activation barrier depends on the chemical composition of the surface. When hydrogen atom becomes chemisorbed (E_{chem} ≈-50 kJ/molH_2) it shares its electron with the metal atoms at the surface. These hydrogen atoms have high surface mobility, interacting with each other and forming surface phases. In the next step chemisorbed hydrogen atom can migrate into the subsurface layer and, finally, diffuse into the interstitial sites through the host metal lattice, contributing their electrons to the band structure of the metal (Zuettel, 2003).

After dissociation on the metal surface, the H atoms generally diffuse rapidly through the bulk metal even at room temperature to form Me-H solid solution or α-phase. The thermodynamic aspects of hydride formation from gaseous hydrogen are described by pressure–composition isotherms (Fig. 5). After the maximum solubility of hydrogen in the

α-phase is reached, hydride phase (β-phase) will begin to form. Further increase in hydrogen pressure will result in substantial increase in the amount of absorbed hydrogen. This phenomenon can be explained using the Gibbs phase rule (2)

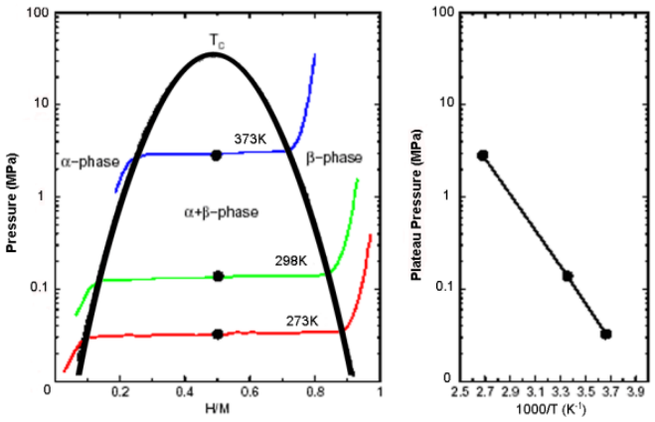

Figure 5. Left: Pressure-Composition-Isotherms (PCI) for a hypothetical metal hydride. Right: Van't Hoff plot for a hypothetical metal hydride derived from the measured pressures at plateau midpoints from the PCI's.

$$F = 2 - \pi + N \tag{2}$$

where F is the degree of freedom, π is the number of phases and N is the number of components.

Hydrogen pressure at which this transformation takes place is called the plateau pressure, where α- and β-phase co-exist. When the stoichiometric hydride is formed, completely depleting the α-phase, an additional degree of freedom is regained and the additional absorption of hydrogen would now require a substantial pressure increase, corresponding to the solid solution of hydrogen in β-phase.

The plateau pressure, described by Van't Hoff equation (3), gives us valuable information about reversible storage capacity. Width of the plateau and the position of the plateau at a given temperature give us a sense of the stability of the hydrides. Stable hydrides (enthalpy of formation, $H_f << 0$) would require higher temperatures than less stable hydrides ($H_f < 0$) to achieve a certain plateau pressure. Recording a series of PCI's at different temperatures makes it possible to construct a phase diagram from the end points of the plateaus in the individual PCI's.

$$\ln p = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{3}$$

where ΔH is enthalpy, ΔS is entropy, R is the gas constant and T is temperature.

Figure 6 represents a Van't Hoff diagram showing the dissociation pressures and temperatures of a number of hydrides. Light elements, such as Mg, have shown promising levels of stored hydrogen (about 7 wt% hydrogen), but require higher temperature for

dehydrogenation. Conventional metal hydrides, which have been well characterized and their capacity for interstitial hydrogen storage is well-established, include type AB, AB_2, AB_5, A_2B (TiFe, $ZrMn_2$, $LaNi_5$, and Mg_2Ni) intermetallic compounds, and body-centered cubic metals. These materials typically store between 1.4 and 3.6 wt% hydrogen. (Table 2). However, the requirements for gravimetric capacity, fast kinetic and high storage capacity is barely satisfied, so development of new lightweight materials presents many scientific and technical challenges. Among metal hydrides, magnesium hydride appears to be the most promising, because of its high storage capacity and relatively low cost.

Type	Intemetallic compound	H/M	H_2 capacity (mass%)	Temperature (K) for 0.1MPa $P_{desorption}$
A_2B	Mg_2Ni	1.33	3.6	528
AB	TiFe	0.975	1.86	265
AB	ZrNi	1.4	1.85	565
AB_2	$ZrMn_2$	1.2	1.77	440
AB_5	$LaNi_5$	1.08	1.49	285
AB_2	$TiV_{0,62}Mn_{1,5}$	1.14	2.15	267

Table 2. Hydrogen storage properties of some intermetallic compounds

3.5. Magnesium hydride

High gravimetric (7.6 wt.%) (Hanada et al., 2004) and volumetric density (130 kg H_2/m^3) and relatively low price make magnesium hydride (MgH_2) an attractive hydrogen storage material. However the wide industrial application is still not feasible, due to its high enthalpy of formation ($\Delta H° = -75$ kJ/molH_2) and dehydrogenation temperature (720 K), as well as slow kinetics of hydrogenation reactions/dehydrogenation reaction. For example, there is no detectable hydrogen desorption at temperature of 573 K, while at 623 K it takes more than 3000s for complete decomposition of MgH_2 (Varin et al., 2009). Furthermore, in order to allow for the formation of MgH_2, it is necessary to perform an activation process of Mg metal by consecutive heating and cooling of metal in vacuum and in hydrogen atmosphere, which makes the material permeable to hydrogen. The efforts to overcome these deficiencies have made MgH_2 one of the most investigated materials in last two decades.

At moderate hydrogen pressure the only hydride phase existing in equilibrium with Mg is magnesium hydride, β-MgH_2. Pure Mg has a hexagonal crystal structure, while its hydride has a tetragonal lattice unit cell (rutile type) (Zeng et al., 1999; Yu & Lam, 1988). Figure 7 shows the crystal structure of β-MgH_2 ($P4_2/mnm$ space group), were each Mg atom is coordinated with six H atoms forming an irregular slightly distorted octahedron (Noritake et al., 2003). Each H atom is coordinated with three planar Mg atoms. Synchrotron X-ray diffraction gives the parameters of crystal a = 0.45180(6) nm and c = 0.30211(4) nm (Lide, 2006; Lide, 2007) while the powder diffraction file (JCPDS 12–0697) provides similar values for a = 0.4517 nm and c = 0.30205 nm. Density of MgH_2 is 1.45 g/cm^3 (Bastide, 1980).

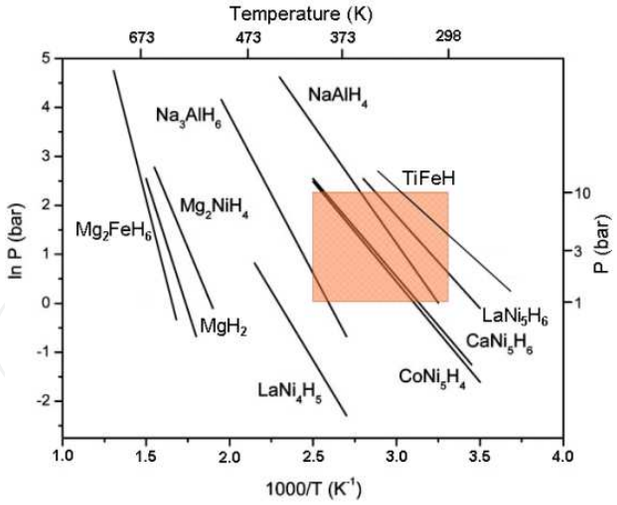

Figure 6. Van't Hoff plots of various metal hydrides, showing hydrogen dissociation pressures and temperatures (red shaded area represents desirable operating conditions).

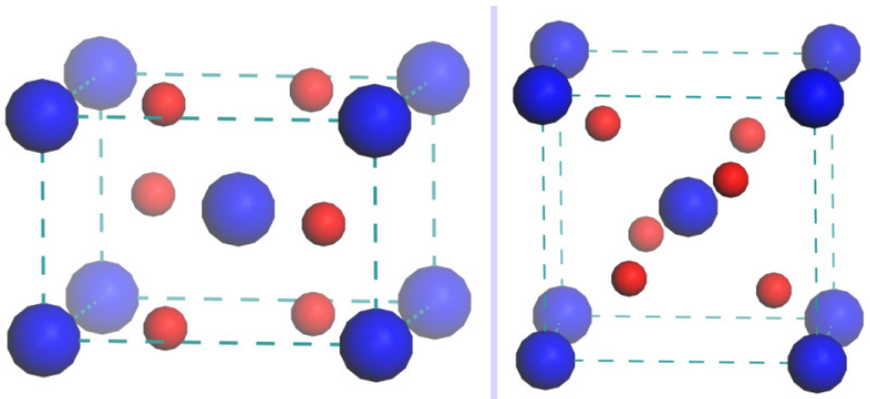

Figure 7. Two perspectives of crystal structure of β-MgH_2 showing the positions of Mg (blue) and H atoms (red)

Although there is considerable literature dealing with structure and properties (Novaković et al., 2009; Schimmel et al., 2004, 2005; Kelkar & Pal, 2009; Basseti et al., 2005) of MgH_2, there are still some uncertainties about H-desorption kinetics, since the Mg–H interaction strongly depends on method of synthesis and presence of additives. For instance, ball milling causes mechanical deformation, surface modification, and metastable phase formation which generally promote the solid–gas reaction. It also introduces defect zones which may accelerate the diffusion of hydrogen (Shan et al., 2004; Jensen et al., 2006; Bobet et al., 2001; Montone et al., 2006, 2007; Aguey-Zinsou et al., 2007). Addition of transition metals, metal oxides or ternary hydrides to mechanically milled MgH_2 decreases its thermal stability and decomposition temperature. It has also been established that nanosized powders provide a possible solution for the problem of hydrogen desorption kinetics (Varin et al., 2006). *Ab initio* DFT calculations (Kurko et al., 2011) have been used to determine possible ways of improving the performance of MgH_2. They have shown that destabilization temperature of MgH_2 reduces with decreasing cluster size, and that a crystallite size of 0.9 nm could result in a desorption temperature below 500 K (Wagemans et al., 2005). However

ball milling can also cause agglomeration and cold welding of particles (Montone et al., 2005), therefore experimentally obtained decrease in hydrogen adsorption temperature in ball-milled samples is relatively low, keeping MgH_2 far from practical application (Milovanović et al., 2008). Based on *ab initio* calculations, Novakovic *et al.* (Novaković et al., 2009) examined the possible pathways for adsorption/desorption of hydrogen from MgH_2, showing that different H-filling patterns influence initial hcp-Mg structure in different ways, qualifying wurtzite MgH as a probable intermediate phase between the hcp-Mg and MgH_2 at 1:1 stoichiometry. Du et al. suggested that surface desorption is rate-determining since the activation barrier computed for H-vacancy diffusion from the surface into sublayer is less than 0.70 eV, much smaller than the activation energy for desorption of hydrogen on the MgH_2(110) surface (1.78-2.80 eV/H_2) (Du et al., 2007). Furthermore, the first principle calculations of MgH_2-*TM* (*TM*=Al, Ti, Fe, Ni, Cu, Nb, Co) were carried out to investigate their influence on the stability of the magnesium hydride (Novaković et al., 2010; Song et al., 2004). It was found that TM-H bonding is stronger than the Mg–H bond, but at the same time it weakens other bonds in the second and third coordination around TM atom, which leads to overall destabilization of the MgH_2 compound. Due to a higher number of d-electrons, this effect is more pronounced in late transition metals. In case of Co doping, spin polarization has an additional stabilizing influence on the compound structure.

3.6. Alanates

Alanates, or aluminohydrides, are a family of compounds containing aluminum and hydrogen, with $NaAlH_4$ being the most popular material in this family (Bogdanović & Schwickardi, 1997; Downs & Pulham, 1994; Fichter et al., 2003; Jain et al., 2010). One of the attractive features of alanates is their easy accessibility, since sodium and lithium alanate are commercially available and magnesium alanate can be easily synthesized. They have relatively high gravimetric hydrogen capacity (5-9 mass%), however, these materials usually undergo multi-step thermal decomposition (Eq. 4) to release hydrogen and these reactions require relatively high temperatures and considerable reaction time ($NaAlH_4$ releases 3.7 mass% H_2 in 3h at 483K).

$$NaAlH_4 \rightarrow NaH + Al + \frac{1}{2}H_2 \tag{4}$$

Additionally, some of the alanates are meta-stable, making their first decomposition (dehydrogenation) step exothermic and irreversible. This makes their direct rehydrogenation impossible, which would rule them out as candidates for on-board hydrogen storage applications.

In order to improve their charge/discharge performance and reduce decomposition temperatures, alanates have been doped with transition metals, with Ti- and Ni-doping exhibiting promising results thus far in improving kinetics and dehydrogenation rates, while preserving very high hydrogen capacity.

Material	H_2 capacity (mass%)	Dehydogenation temperature (K)	Dissociation enthalpy (kJ/mol H_2)
$NaAlH_4$	5.6	480-490 (I step) >525 (II step)	37 (I step, 3.7 mass% H_2) 42 (II step, 1.9 mass% H_2)
$LiAlH_4$	7.9	430-450 (I step) 450-490 (II step)	-10 (I step, 5.3 mass% H_2) 25 (II step, 2.6 mass% H_2)
$Mg(AlH_4)_2$	9.3	380-470 (I step) 510-650 (II step)	41 (I step, 7 mass% H_2) 76 (II step, 2.3 mass% H_2)
$KAlH_4$	5.7	570 (I step) 610 (II step) 650 (III step)	55 (I step, 2.9 mass% H_2) 70 (II step, 1.4 mass% H_2)
$Ca(AlH_4)_2$	5.9	400 (I step) 520 (II step)	-7 (I step, 2.9 mass% H_2) 28 (II step, 2.9 mass% H_2)

Table 3. Overview of characteristics of some of the alanates for hydrogen storage [18]

Alanates exhibit very high hydrogen storage capacity, although they cannot be charged and discharged easily and their working temperatures are too high. There is some hope that doping could alleviate some of these difficulties, but it is clear that if these materials become utilized for hydrogen storage, it will probably be in a hybrid high-pressure system, which could additionally improve their charge/discharge performance and be adapted to account for relatively slow discharge rates, while taking advantage of high hydrogen capacities.

3.7. Borohydrides

Borohydride, or tetrahydroborate, refers to a group of complex hydride compounds in which hydrogen in covalently bonded to the central atom in $[BH_4]^-$ complex anion (Eq. 5).

$$NaBH_4 + (2+x)H_2O \rightarrow 4H_2 + NaBO_2 \cdot xH_2O \tag{5}$$

They exhibit high gravimetric and volumetric hydrogen capacity, making the materials of interest for hydrogen storage research (Schlesinger et al., 1953). One of the issues that would have to be resolved is the fact that they exhibit exothermic desorption reactions (30-300 kJ/mol), making their rehydrogenation more difficult than that of other materials and making direct rehydrogenation thermodynamically impossible. In addition, they exhibit high dehydrogenation temperatures (520-670°C), which practically means that only part of their hydrogen capacity is accessible at normal working temperatures.

Material	H_2 capacity (mass%)	Dehydogenation temperature (K)	Dissociation enthalpy (kJ/mol H_2)
$NaBH_4$	10.8	670	-217 to -270
$LiBH_4$	13.4	650	-177
$Mg(BH_4)_2$	13.7	530-670	-39.3 to -50
$Ca(BH_4)_2$	9.6	620	32

Table 4. Overview of characteristics of some of the borohydrides for hydrogen storage [18]

Therefore, most of the work associated with borohydrates is focused on use of doping and catalysts to improve charge/discharge kinetics, lower dehydrogenation temperature and increase hydrogen discharge capacity and cycling ability of these materials (Soler et al., 2007, Pena-Alonso et al., 2007; Lee et al., 2008; Demirci et al., 2009).

3.8. Amides and imides

Amides and imides have attracted a lot of interest, due to their high hydrogen capacity and relatively low operating temperature (Chen et al., 2003; Hu et al., 2003). However, their poor absorption kinetics limits their current practical application (Eq. 6). Therefore there has been a lot of focus on overcoming this by doping with a catalyst, usually through mechanical ball milling (Liu et al., 2008).

$$LiNH_2 + LiH \rightarrow Li_2NH + H_2 \tag{6}$$

Another direction of research has been combining alkaline metal amides with other hydride materials using ball milling. Although $LiNH_2$ and $LiAlH_4$ mixture released approximately 4 atom equivalents of hydrogen, its rehydrogenation was unsuccessful at H_2 pressures up to 80bar (8MPa) (Xiong et al., 2006).

Metal ion of amide/imide system	H_2 capacity (mass%)	Dehydogenation temperature (K)	Dissociation enthalpy (kJ/mol H_2)
Li	5.4 6.5	 550	148 45
Mg	7.4	470	3.5
Ca	3.5 2.1	620 770	
Li-Mg	4.5	470	39
Li-Al	4 2 2.1	360 440 470	

Table 5. Overview of characteristics of some of the amida/imide systems for hydrogen storage [18]

3.9. Amino borane

Ammonium borane, NH_3BH_3, is considered a promising candidate for chemical storage of hydrogen, due to its low molecular weight and high hydrogen content of 19.6 mass%. Its thermal decomposition occurs in three stages (Eqs. 7 and 8), around 363, 420 and 970K, respectively, with one molar equivalent (6.5 mass%) of hydrogen released during each step (Gutowska et al. 2005; Baitalow et al., 2002).

$$NH_3BH_3 \rightarrow (BN)_n + 3nH_2 \tag{7}$$

$$NH_3BH_3 + H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2 \tag{8}$$

Dehydrogenation rates are very slow due to long induction period (around 200min at 353K) (Chandra & Xu, 2006a, 2006b). The enthalpy is -21 kJ/mol, which is in the range that is suitable for on-board application. Therefore, most of the scientific effort has been focused on overcoming the slow reaction kinetics using additives like silica scaffolds, metal catalysts and ionic liquids (Umegaki et al., 2009).

3.10. Alane

Aluminum hydride (alane, AlH_3) has an average enthalpy of formation of -11.4 kJ/mol and freshly synthesized non-solvated alane is reported to desorb around 10 mass% of H_2 at temperatures below 373K (Graetz & Reilly, 2006). However, while the dehydrogenation reaction occurs readily (Eq. 9), the reverse process does not, requiring 2.5GPa pressure of H_2 to rehydride (Baranowski & Tkacz, 1983).

$$AlH_3 \rightarrow Al + \frac{3}{2}H_2 \tag{9}$$

In addition, dehydrogenation kinetics is too slow for practical applications, as it is limited by nucleation and growth of aluminum particles. Therefore, research has been focused on decreasing the dehydrogenation temperature and improving its kinetics using additives like alkali metal hydride (Sandrock et al., 2006) and particle size reduction using ball milling (Orimo et al., 2006). Best results have been achieved by doping AlH_3 with small amounts of LiH, NaH or KH.

4. Hydrogen power generation – Fuel cells

As early as 1839, William Grove discovered the basic operating principle of a fuel cell by reversing the electrolysis of water to generate electricity from hydrogen and oxygen. This principle remains unchanged today, that a fuel cell is an electrochemical device which continuously converts chemical energy into electric energy (and heat) for as long as fuel and oxidant are supplied. A fuel cell does not need recharging, operates quietly and efficiently and, with hydrogen as fuel, generates only power and water. This is why it is called a zero-emission engine. Unlike thermal engines, it is not limited by the Carnot efficiency; therefore, while thermal engines typically achieve efficiency of 24-32%, fuel cells achieve efficiencies of 35-60% (Minh & Takahashi, 1995).

One of the major obstacles in fuel cell application so far has been their insufficient lifetime: most fuel cells exhibit major performance decay after 1000 hours of operation, while DOE target for 2015 is 5000 hours of operation at 60% efficiency for mobile applications. Additionally, their price per kW is almost twice that of an internal combustion engine (Hoogers, 2003). There is a wide variety of fuel cell types, which can be distinguished by the electrolyte used, but they all function in the same basic way. At the anode a fuel (usually hydrogen) is oxidized into electrons and protons, and at the cathode, oxygen is reduced to

Fuel Cell Type	Electrolyte	Charge Carrier	Operating temperature (K)	Fuel	Electric Efficiency (system)	Power Range (kW)
Alkaline	KOH	OH^-	330-390	H_2	35-55%	<5kW
Proton Exchange Membrane	Solid polymer	H^+	320-373	H_2 (tolerates CO_2)	35-45%	5-250
Phosphoric acid	Phosphoric acid	H^+	~590	H_2 (tolerates CO_2)	40%	200
Molten carbonate	Li and K carbonate	CO_3^{2-}	~1020	H_2, CO, CH_4 (tolerates CO_2)	>50%	200-1000
Solid oxide	Solid oxide electrolyte (Y, Zr)	O^{2-}	~1270	H_2, CO, CH_4 (tolerates CO_2)	>50%	2-1000

Table 6. Overview of different types of fuel cells and their characteristics

oxide species. Depending on the electrolyte, either protons or oxide ions are transported through the electrolyte (ion-conducting, but electronically insulating) to combine with oxide species or protons, respectively, to generate water and electric power. Alkaline fuel cells do not tolerate presence of CO_2 in the system, which forms alkaline carbonates, meaning that they can only use carbon-free fuel.

Of the currently developed types of fuel cells, proton exchange membrane fuel cells (PEMFC) and alkaline fuel cells (AFC) satisfy the required range of operating temperature and provide sufficient current density for mobile applications, although the power range for AFC is sufficient only for specialty applications (like power generation of space crafts). PEMFC, also known as solid polymer fuel cell, takes its name from the special plastic membrane it uses for electrolyte, combining all the key parts (anode, cathode, electrolyte) in a very compact unit, not thicker than few hundreds microns. The membrane requires presence of liquid water, limiting its operating temperature to below 373K, which means that, to achieve a good performance, this fuel cell requires a good catalyst (Wang et al., 2011).

Two high-temperature types of fuel cells (molten carbonate and solid oxide) are mainly considered for large scale stationary power generation. They achieve higher efficiencies than low-temperature systems and high operating temperatures allow for direct internal processing of fuels like natural gas, reducing the system's complexity (Tucker, 2010). However, this also means that they cannot easily be turned off.

In addition to using pure hydrogen of hydrocarbons and carbon monoxide as fuel, in recent times, fuel cells have been coupled with biomass-derived fuel processors. This makes it possible to use biomass-derived fuels, such as ethanol, methanol, biodiesel or biogas, and feed them to a fuel processor as a raw fuel, which would, after reforming, be used by a fuel cell (Xuan et al., 2009).

Although all of types of fuel cells described above operate on gas fuel, recently, PEM fuel cells have been constructed to operate using liquid fuel – methanol (Ismail et al., 2011). This has advantages for mobile applications and fuel transportation, but these direct methanol fuel cells are not yet advanced enough to generate high enough current and power density to compete with gas fuel cells.

5. Conclusion

The limitations of our world's natural resources mean that our civilization has to find an alternative energy source and energy carrier to replace fossil fuels. Taking into account available fossil fuel reserves and that such a conversion of energy source/carrier historically takes 75-100 years, it is clear that this is crucial time for alternative energy research. Hydrogen is the obvious candidate for the renewable energy carrier for the future, due to its availability in form of water, high energy density and lack of negative environmental impact. However, current state of technology is such that significant advances are needed in the next decade in order to make hydrogen economy viable. There is still lack of an effective large-scale hydrogen production process from water, while hydrogen storage still falls well behind the requirements set by gasoline. When it comes to power generation, hydrogen fuel cells are still lagging behind internal combustion engines and conventional batteries in performance and power/weight ratio. On the other hand, significant strides have been made in recent times, which give hope that hydrogen will, in the foreseeable future, be able to challenge fossil fuels as the primary energy carrier, but only through a sustained and focused effort.

Author details

Vladimir A. Blagojević and Dragica M. Minić
University of Belgrade, Faculty for Physical Chemistry, Serbia

Dejan G. Minić
Kontrola LLC, Austin, TX, USA

Jasmina Grbović Novaković
Laboratory for Material Sciences, Institute for Nuclear Science Vinča, University of Belgrade, Belgrade, Serbia

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