Hydrogen Energy

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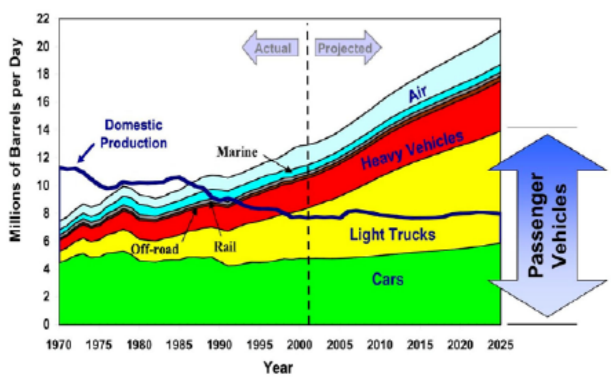
Abstract:

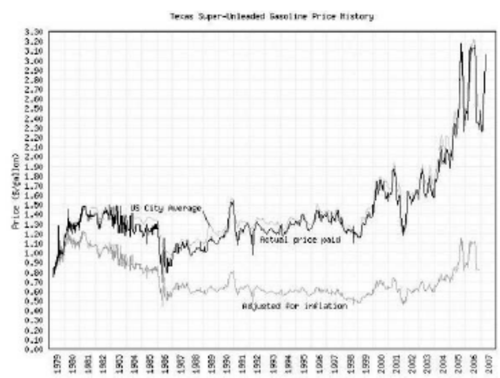
As one of the candidate solutions to the global energy crisis, hydrogen has attracted many people's concern. Compared with traditional fossil fuels, combustion of hydrogen will only lead to the release of water to the atmosphere, which is a successful strategy to tame greenhouse gas emissions. Unfortunately, there are a bunch of hurdles to clear before we could achieve the final goal. Scientific challenges come along within every single process: generation, storage and energy conversion. In this paper, we will briefly introduce the properties of hydrogen as well as the general picture of the three fundamental processes. After that, several specific problems in hydrogen storage (e.g. metal-hydrogen system, carbon nanotubes as storage material, analysis and characterization techniques.) will be discussed. In the end, we will shed light on the current research directions related to hydrogen energy.

Contents:

I. Introduction

Before we jump into the topic of hydrogen energy, a brief review on fossil fuels is quite necessary. Fossil fuels, mostly consist of carbon and hydrocarbons, were the basis of the enormous development during industrial age. Several decades ago, people started to realize that the reserve of fossil was finite and combustion of carbon-based fuel would lead to climate change, see Fig.1. Several alternative renewable energy sources have been brought into public's attention: solar energy, wind power, hydropower, bio-fuels etc. With the large heat of combustion(Hydrogen 141.8 MJ/kg, cf. Gasoline 47.3 MJ/kg) as well as the pollution-free product after reacting with oxygen gas, hydrogen gas is sure on the list of candidate solutions to today's energy challenge and global warming issue. However, as economist said, "There ain't no such thing as a free lunch", quite a lot of scientific and technical problems are waiting ahead. E.g. high cost and low efficiency of hydrogen production (water electrolysis, for instance); desire for new techniques or new materials supporting liquid/solid state storage; research needs on catalysts, electrochemistry and nano-scale behavior to overcome the challenges of energy conversion. In the following sections we will discuss those challenges in detail.





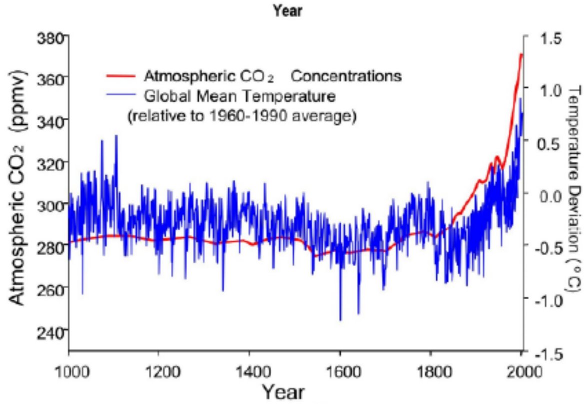


Fig.1

Left Top: U.S. consumption and production of petroleum products trend. [1]

Left Bottom: A rise in global temperature associated with Increased CO_2 Emissions. [2]

Right Top: Texas super-unleaded gasoline price history (1979-2007). [3]

II. Properties of Hydrogen Gas

Hydrogen, as the lightest and most abundant chemical element, has three isotopes (protium, 0 neutrons; deuterium, 1 neutron; tritium, 2 neutrons). Hydrogen gas was first identified by Henry Cavendish in the 18th century and soon named by Antoine Lavoisier ("hydor" in Greek means water former). At standard temperature and pressure, hydrogen is a colorless, odorless, tasteless and highly combustible diatomic gas. Combustion of hydrogen with oxygen will release much energy, which makes it an important energy carrier, but high flammability and wide range of concentrations to burn in air (4%-75% by volume) also bring hydrogen a bad reputation on safety issue (risk of explosion, etc). Hydrogen was liquefied for the first time by James Dewar in 1898 by using regenerative cooling method; Dewar produced the solid hydrogen the next year. [4]

III. Fundamental Procedures in Hydrogen Industry

Generally speaking, scientific research and technologies related to hydrogen energy could be divided into three subareas: Production, storage and use.

A. Hydrogen Production

The "factory" focusing on direct water splitting to hydrogen and oxygen already existed long time ago in nature (e.g. blue-green or green algae). Globally, biological processes more than 250 Mtons/yr of hydrogen and most of this amount comes from anaerobic fermentation of carbon previously fixed by photosynthesis. [5] Much more effective ways are high temperature water splitting using solar concentrators/nuclear energy, as well as electrolytic processes [6], see Fig.2.

Example for High temperature Water Splitting

$$\mathbf{2ZnO + heat \rightarrow 2Zn + O_2}$$

$$\mathbf{2Zn + 2H_2O \rightarrow 2ZnO + 2H_2}$$

Example for High temperature Water Splitting

$$\mathbf{2H_2SO_4 + heat\ at\ 850℃ \rightarrow 2H_2O + 2SO_2 + O_2}$$

$$\mathbf{4H_2O + 2SO_2 + 2I_2 \rightarrow 2H_2SO_4 + 4HI}$$

$$\mathbf{4HI + heat\ at\ 300℃ \rightarrow 2I_2 + 2H_2}$$

Example for Electrolysis Reaction

Anode: $\mathbf{2H_2O \rightarrow O_2 + 4H^+ + 4e^-}$

Cathode Reaction: $\mathbf{4H^+ + 4e^- \rightarrow 2H_2}$

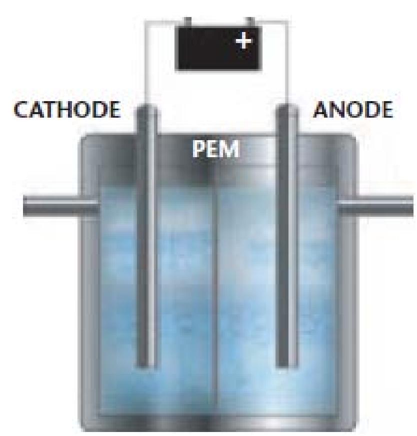


Fig.2
Electrolysis of water

B. Hydrogen Storage/Transportation

With respect to different mobility requirement, hydrogen storage could be classified into stationary storage and portable storage systems. Because two thirds of U.S. oil consumption is used in transportations [5], this sector draws the most concern in practical life. At a glance of the primitive phase diagram for hydrogen (Fig.3), it's easy to understand the difficulty of hydrogen transportation; either very high pressure or very low temperature is required. In the one hand, the density of gaseous hydrogen is too small, which significantly reduces the heat of combustion per unit volume, and, as a price, money on compression of hydrogen gas is needed. In the other hand, liquefaction also consumes quite lot energy during cooling procedure. Besides, the thermal isolation is another headache problem.

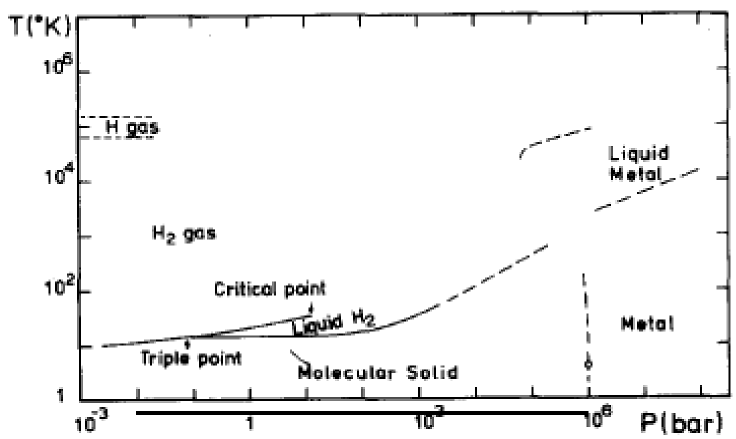


Fig.3
Primitive phase diagram for hydrogen [7]

Another approach to this challenge is solid-state storage (e.g. metal hydrides, nanostructure materials), either reversible (hydrogen is released by raising the temperature at a suitable pressure and can be up-taken by adjusting the temperature, hydrogen pressure and other parameters) or irreversible (hydrogen is released by chemical reaction, but the resulting hydrolysis product cannot be used again without extra reprocessing). Although researchers believe that metal hydrides may be ideal storage materials, none of the well known 2,000+ elements, compounds or alloys (in bulk) which form hydrides has been found to satisfy the commercial standard for hydrogen storage.[8] It seems that our new hope relies on the catalyst and nano-structural behaviors.

C. Energy Conversion (Fuel Cells)

Fuel cell was invented in 1839, by Sir William Grove. It directly converts the chemical energy in hydrogen to electricity and heat, water and heat are the only byproducts. For a typical fuel cell, there are two electrodes (one anode and one cathode) and an electrolyte between them. Usually, series of individual fuel cells are stacked to generate more electricity. Take the Polymer electrolyte membrane fuel cell (PME) for example; a solid polymer (typically plastic wrap) is used as the electrolyte, while the hydrogen gas flows from one side to the anode (porous so that hydrogen could pass through), it will separate into protons and electrons given platinum particles as catalyst. The PEM allows only the protons to pass through it and then conduct those protons to the other side; the electrons will flow along the external circuit and could be used as power source. On the other side, oxygen gas (from air) flows to the cathode and move through it, where reduction reaction will take place. See Fig.4.

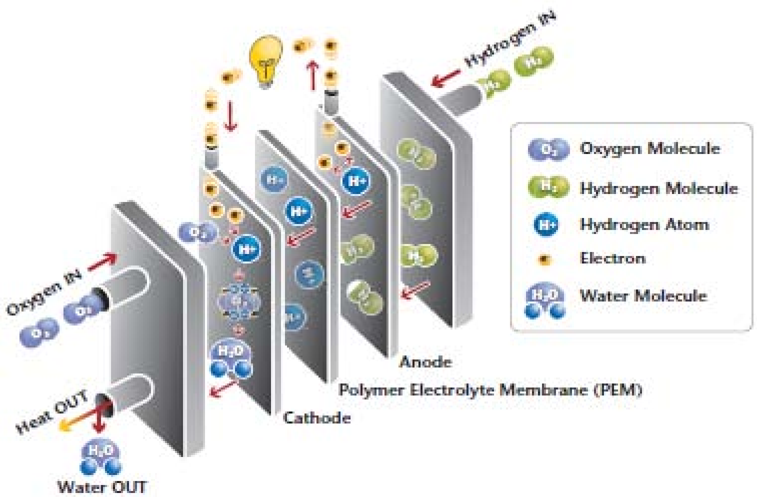


Fig.4
Schematic picture of fuel cell and related chemical reactions [6]

Oxidation half reaction $\mathbf{2H_2 \rightarrow 4H^+ + 4e^-}$
Reduction half reaction $\mathbf{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$
Fuel cell reaction $\mathbf{2H_2 + O_2 \rightarrow 2H_2O}$

IV. Specific Problems in Hydrogen Storage

A. Metal Compound as Storage Material

Several hydrogen- light metal compounds have been identified to have high content of hydrogen on a mass basis, namely sodium, lithium, boron, and aluminum. See Fig.5. [9] However, performance of these metals is limited by the fact that high temperature is required to release hydrogen (in order to desorb hydrogen) and the shortage of reversibility for hydrogen storage.

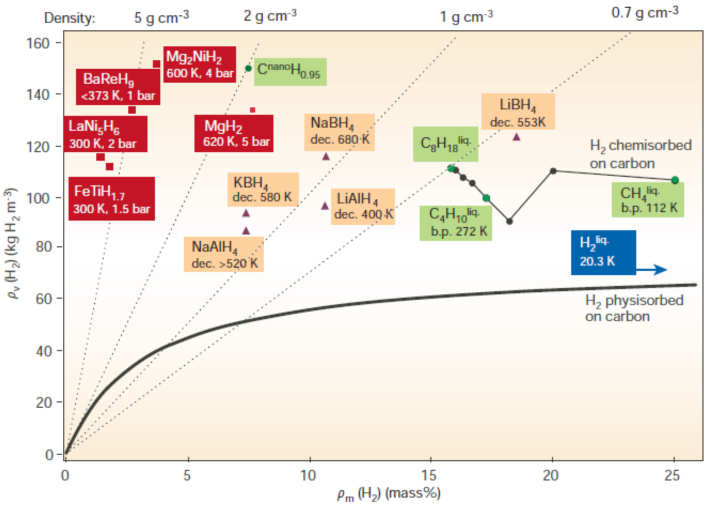


Fig.5
Stored hydrogen per mass and per volume. Comparison of metal hydrides, carbon nanotubes, petrol and other hydrocarbons[9]

In recent years, many researches on nanostructures unveil the fact that low dimensional material may display quite different behaviors, compared with original bulk materials, especially when the size is so enough that the quantum physics takes place. As pointed out in [5], “small amounts of heavier elements could be effective in tuning the lattice spacing or altering the chemical and physical properties of hydrogen storage compounds”, therefore doping light metal with proper dopant may improve the efficiency of absorption or desorption (weaken the relatively strong bond between light metal and hydrogen).

B. Carbon Nanotube as Storage Material

The high surface atoms ratio reminded researchers those nanomaterials as new efficient storage materials which could be employed in hydrogen economy. In 1999, Liu et al. [10] demonstrated that single-walled carbon nanotubes (SWCN) could be a promising direction for hydrogen storage at room temperature, though high pressure (about 10MP) was needed. In another paper published in 2005, Nikitin et al.[11] used core-lever photoelectron spectroscopy and x-ray absorption spectroscopy and tested SWCN and found that C-H bond could be completely broken by heating to 600°C. See Fig.6. To sum up, nanostructure (specifically, carbon nanotubes) provides a promising research direction in hydrogen storage, though there are some drawbacks like high pressure in uptake of hydrogen, or high temperature to release hydrogen, plus the fact that wt% (weight percent) value is still not commercially competent.

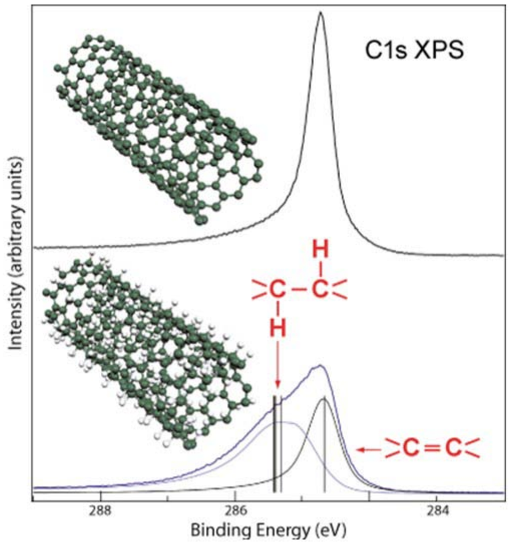


Fig.6
Comparison of x-ray photoelectron spectra carbon 1s peak before uptake (top) and after uptake (bottom) [11]

C. Analysis and Characterization Techniques

Inelastic neutron scattering techniques are very sensitive to hydrogen and deuteriums in bulk, compared with x-ray, see Fig.7. [5]The cross section of H is relatively large so that the intensity of signal is appreciably strong, while the signal of H using X ray or electron probe is rather small. What's more, neutron could distinguish H from isotope D, while x ray is not as powerful as neutron. Another advantage of neutron scattering is that high vacuum condition (which is really a pain) is not necessary. Oak Ridge National Laboratory has very powerful neutron science facilities. High Flux Isotope Reactor (HFIR) can provide continuous beams of neutrons, while the Spallation Neutron Source (SNS), currently under construction at Oak Ridge, has the capability to provide pulsed neutron beams.

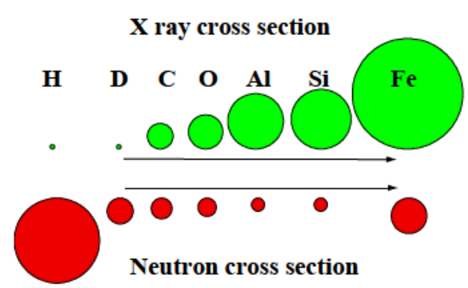


Fig.7
Comparison of cross section of different element using x ray and neutron [5]

Synchrotron radiation is another source for analysis and characterization, which focus more on the surface science and is associated with nanostructures. For example, hydrogen adsorption and release processes on nanotubes, as described in previous section (Fig.6).

V. Conclusion

Starting with the fossil energy crisis and the desire for new alternative energy source, we introduced the properties of hydrogen and basic ideas on hydrogen production, storage and fuel cells. Hydrogen storage is probably the most essential issue, more than 2000 traditional bulk materials(elemental metal, or metal compound) have been tested and none of them could satisfy the commercially acceptable capability (low wt%, need high temperature to release hydrogen). Also, two powerful techniques (inelastic neutron scattering and synchrotron radiation) are discussed. Considering all the advantages and drawbacks, hydrogen economy is not going to see its own boom in the very near future. However, as one of the solutions to the climate change issue, it's still a promising research topic in the long run.

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