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Hydrogen fuel generation and storage

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Abstract

We present the various ways by which hydrogen gas is generated and its methods of storing. The future hydrogen economy will feature hydrogen as an energy carrier in a reliable and sustainable energy supply system. Building an infrastructure that allows for easy and cost-effective transportation and delivery of hydrogen energy is a critical step.

Keywords: Fuel cell, hydrogen, electrolysis.

Introduction

At the beginning of the 21st century, fuel cells appear poised to meet the power needs of variety of applications. Fuel cells are electrochemical devices that convert chemical energy to electricity and thermal energy. Electricity made by the conversion of primary energy sources is easily transported and delivered to end-users. Hydrogen is a clean fuel and efficient energy medium for fuel cells and other devices. Building an infrastructure that allows for easy and cost-effective transportation and delivery of hydrogen energy is a critical step toward a future hydrogen economy (NREL, 1995).

Hydrogen can be produced from water, renewable energy sources and from other fuels. A hydrogen life cycle as shown in Fig.1. Hydrogen could be used for a broad range of applications to supplement or substitute the consumption of hydrocarbon fuels and fossil fuels in an environment friendly manner. The large-scale introduction of hydrogen as a fuel would reduce the consumption of fossil fuels and keep the air clean free

from pollution. Hydrogen can be produced from renewable energy sources by various methods. Electrolytic, prototypic/photo biological, photo-electrolysis and thermos-chemical hydrogen production technologies currently under development and use. The selection of production processes/ technologies will depend on the availability of resource, expertise, infrastructure and economical aspect. The aim of the hydrogen program is to expand the role of hydrogen as a fuel for surface transportation. The using of hydrogen initially will be as an additive to conventional fuels. The combination of hydrogen with fossil fuels such as gasoline,

natural gas, ethanol, methanol for fueling IC engines provides less emission, and increase performance.

In this paper we present the various ways by which, the hydrogen gas is generated and methods of storing the hvdroaen.

Sources of hydrogen

Hydrogen does not exist alone in nature. Natural gas contains hydrogen (about 95% of natural gas is methane, CH₄), as does biomass (cellulose) and hydrocarbons, like coal. An equally diverse array of primary energy sources, such as wind, solar, geothermal, nuclear and hydropower, can be used to extract hydrogen from water. Primary energy sources

Primary energy sources in nature includes sunlight, wind, water, nuclear power, geothermal power and potential energy from the Earth's gravity and the stored energy includes biomass, coal, oil and natural gas. **Electrolysis**

Chemical reactions in batteries or galvanic cells provide the driving force for electrons to struggle through

loads. The chemical energy is directly transformed into electric energy. Electrolysis can be carried out in solutions or molten salts (liquid). Because the atoms and ions have to move physically, the medium has to be a fluid. The products, like the reactants in a galvanic cell, can be in a solid, liquid, or gas state.

Electrolysis of water

By providing energy from a battery, water (H₂O) can be dissociated into the diatomic molecules of hydrogen (H₂) and oxygen (O₂). The electrolysis of one mole of water produces a mole of hydrogen gas and a halfmole of oxygen gas in their normal diatomic forms as shown in Fig.2.

Useful Energy Hydrogen Utilization Water Storage Oxygen Enviroment Transport Hydrogen Production Hydrogen Primary Renewable Energy Source

"Hydrogen fuel"

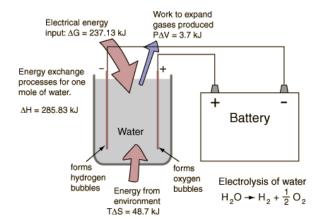
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Fig. 1. Hydrogen life cycle

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Current method of hydrogen production

Currently, there are two widespread applications for production of hydrogen. Hydrogen is also the byproduct of petroleum refining and chemical process.

Hydrogen production by team reforming

In this process hydrogen is derived from fossil fuels such as natural gas ethanol. The aim of the process is to separate hydrogen from carbon component of the fuel. During the first step, fuel decomposes to hydrogen and carbon monoxide by steaming on catalytic surfaces. In the second step, which is called shift reaction, CO and water convert to $\rm CO_2$ and hydrogen. The temperature of reaction is higher than 200 $^{\circ}\rm C$.

Hydrogen production from water

Hydrogen can be produced by dissociation of water. Water splits into its two basic species, oxygen and hydrogen by electrolysis, which is the only practical method currently. In this method an electric current passes through water. The current enters the electrolysis device through the cathode, which is charged negatively and leaves through the anode, which is charged positively. During the process, hydrogen is separated and collected at the cathode: whereas, oxygen is separated and collected at the anode. With this method, hydrogen is very pure and can be used in electronics, food industries and space program.

Advanced hydrogen production

Cost effectiveness in hydrogen production and the selection of the best feedstock are important in hydrogen production. Production technology needs more improvement compared to storage technologies & utilization systems. Research in production is focused on technologies for overcoming cost and energy source barriers (Carl A. Kukkonen & Mordecai Shelef, 1993). There are several technologies bur are in the early research and development stages. These technologies, which use renewable sources of energy, have strong potential for being cost-effective production systems.

Photo conversion production

Solar energy is used in this process as renewable energy resource. Sunlight is used in order to dissociate water into hydrogen and oxygen. The advantage of this process is that there is no need for separate electric

generation step required by electrolysis. There are two main classifications of such systems.

Production using photo-biological technology

There are two approaches available in this technology:

The whole-cell system: It involves certain algae and bacteria and the hydrogen generation from biological systems is generally light dependent. Enzymes in cell (biological system) act as a catalysts to associate water into hydrogen and oxygen by absorbing sunlight. The conversion efficiency of this process, which means the amount of hydrogen energy produced as a percent of sunlight absorbed, is as low as 5 %. This process has potential for near-term production at solar conversion efficiency from 5-10 %.

Cell-free system: It employs hydrogen-producing enzymes, has potential for more long-term technologies that provide efficiency nearly 25 %.

Photo electro chemical production (PEC)

This method helps to convert optical energy into chemical energy by using semi-conducting electrodes in a photochemical cell. There are two systems available: 1) A semiconductor surface has dual purpose. It absorbs solar energy and act as an electrode for dissociation of water. The efficiency in this process is more than 8 % currently. Operating lifetimes of these systems are limited due to the light-induced corrosion of semiconductors and other chemical effects and 2) Dissolved metal complexes are used as a catalyst in the second process. The soluble metal complex absorbs energy and creates an electric charge separation, which causes water-splitting reaction. Although this process is currently less advanced than the semiconductor technology, it has a promise of avoiding corrosion problems.

Gasification production or pyrolysis of biomass

Hydrogen along with different gasses are obtained by applying heat to coal, municipal solid waste, and biomass-wood, grasses and agricultural waste. The composition of the gases depends on the type of the feedstock, the availability of oxygen, the temperature of the reaction and other parameters. There is no CO₂ contribution to the environment during the process. Because the same amount of CO₂ which is consumed by the biomass while growing returns to environment during conversion process. More research needs to be done in this technology in order to have a cost-effective method. Techniques involving selective membranes or catalysts for separating and purifying the hydrogen must be improved to remove of tars and oils from hydrogen.

An alternative method of producing hydrogen from biomass is a combination of pyrolysis and steam reforming process. First step in pyrolysis is to use heat to dissociate complex molecules into simple units. The resultant reactive vapors must be then converted to hydrogen. Although this process is at an early stage, it has potential for being one of the least expensive production methods. Research is focused on improving efficient catalyst and for the steam-reforming step, and



Water passage

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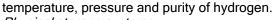
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evaluating economic feasibility and environmental sustainability of total process.

Storage

Currently the on-board storage methods for hydrogen are too expensive and there are some problems in terms of performance requirements for applications due to low

energy density of hydrogen. In other word, energy content per unit of space and lightweight mobile storage are important points for a transportation fuel. At normal temperature and pressure conditions, energy density of hydrogen is about 1/1330 that of gasoline, which is extremely low. The factors that could affect hydrogen storage are: capacity, storage material, total cost and necessary conditions for storage viz.



Physical storage systems

It is possible to store hydrogen in the form of compressed gas and cryogenic liquid, which is as low as 20 K. Energy consumption is significant for liquefaction process but expensive. Compressed gas is stored at . 2000-2500 psi (14-17 mPa) and requires large, heavy containers. Lightweight graphite composite materials which resist high pressure up to 6000 psi (41 mPa) will bring promising results in on-board storage area. This technology requires additional research for developing practical, safe, reliable storage systems using these materials (Walter Peschka & William J.D. Escher, 1993).

Solid-state storage systems

In solid-state storage, gas-on-solids and metal hydrides are options, which are safer technologies, and they provide high storage capacity than physical storage systems. They are more expensive and heavier. Currently, research is progressing on determining the adsorption/desorption properties hydrogen commercially available carbons and zeolites. Basic concept on mechanisms of solid-state storage is essential in order to get more knowledge about high performance storage materials. It includes:

- Storage capacities, rates of charge and discharge, thermal and mechanical effects and costs of available materials.
- Increasing capability of manufacturing conventional solid-state hydrogen storage materials, like magnesiumbased hydrides and high-surface-area activated carbon.
- New materials systems, such as fullerenes, porous silicon, porous metal-silicides, hydrogenated amorphous alloys, metal hydride thin films, new synthetic methods. highly porous and nonstructural materials.
- Working with the geodynamics of underground storage, comp ability with existing natural gas storage facilities and technology to lower the cost of liquefaction such as magnetic refrigeration.

Gas-on-solids adsorption technology

Metal hybrid power

In this method, hydrogen can be stored by being adsorbed onto the surface of activated carbon. This technology provides better volume density compressed gas storage. The adsorption of hydrogen on carbon is realized under 150 K (-190 F). The weight and Fig.3 Metal hydride storage

volume densities of this application Siemer, 1993).

Metal hydride technology

Certain metals (metal hydrides) can be used to absorb and retain specific hydrogen under pressure temperature and conditions. They release hydrogen under different conditions. The application of magnesium is quite

are comparable to liquid hydrogen systems (Herbert Aly & Gunter

common in this process. Although they are safe and highvolume density, they are currently expensive compared with compressed gas or carbon adsorption systems. For low-cost hydrides that can store large amounts of hydrogen, high temperature is necessary to release the hydrogen. On the other hand, hydrides, which release hydrogen at lower temperatures, are expensive and have a less storage capacity. Main components of metal hydride storage system are shown systematically (Fig.3).

The key factors in developing practical, economic hydride systems includes: hydride type which is used, desired operating temperature, desired capacity and costs of various system component like packaging and heat exchangers.

Long life under repeated loading and unloading cycles without significant loss in storage capacity is expected from hydride systems. Impurities in hydrogen can affect capacity negatively. Polyhydride complexes using cobalt and other transition materials have higher storage capacity and faster recycling times than other hydride system tested.

Hydrogen application in vehicles

There are two options for using hydrogen in transportation area.

Hydrogen using in IC engines

Low fuel conversion rates are problem with gaseousfueled engines run with high amounts of excess air. The low guenching distance of hydrogen offers improvement in this matter. Hydrogen flames can easily penetrate into difficult chamber zones and reach the unburnt mixtures than that of fossil fuels. Optimized hydrogen engines can be run at higher compression ratio than that with unleaded gasoline. It makes hydrogen-powered engines 15-25 % more efficient than gasoline engines. Flame speed is one of the fundamental characteristics in combustion process. It identifies the relative motion of flame front respect the unburnt mixture (Karim, 1983). The high flame speed of hydrogen provides efficient cycle similar to constant volume process. On the other hand,

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higher thermal and mechanical loads along increased with combustion temperatures are the of thermal losses. reasons combustion noise and nitric oxide emissions. The wide flammability limit of hydrogen in air provides lean operation, which brings low NOx emission along with higher thermal efficiencies. Diffusion coefficient of hydrogen, which means better homogeneous charge, also affects lean operation positively. High quenching distance provides the flame front to penetrate into smallest crevice without being quenched. With respect to this characteristic, hydrogen flame can reach the unburnt mixtures than flames of

fossil fuels.

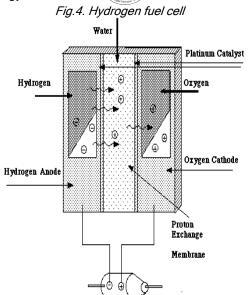
Low ignition energy of hydrogen causes pre ignition and backfiring of hydrogen engines using externally formed hydrogen-air mixtures. The reason is probably hot oil deposits on other hotspots in cylinder. Although, several approaches have been applied in order to solve this problem, none provide satisfactory results. Cooled exhaust gas recirculation, cold gaseous hydrogen, water injection, four-valve schemes are among those methods.

Energy density is related to storage. As a gas, hydrogen has a very low energy density by volume. This causes large fuel tank size even with high-pressure storage and short vehicle range. Exhaust heat is not sufficient for turbo charging application, but supercharger with some efficiency loss can be used to compensate power loss. The energy density by volume of liquid hydrogen is also low (one fourth that of gasoline). Energy density by mass of hydrogen is 3 times that of gasoline, which means that liquid hydrogen system will not suffer a weight penalty compared to gasoline.

Direct high-pressure injection is the most efficient application in IC engines. High-pressure liquid, which is pressurized by a high-pressure pump, is converted to cold high-pressure gas by using a heat exchanger. Injection is provided after the closing of valves, which is similar to diesel engine. Ignition is done with a spark or glow plug. Pre-ignition decreased by using this application. Since hydrogen does not displace air in the cylinder, it provides better volumetric efficiency, which means higher power.

Hydrogen fuel cells

A hydrogen fuel cell is a device as shown in Fig.4 that converts hydrogen gas into low-voltage, direct current electricity by combining hydrogen and oxygen electrochemically. This process is the reverse of the electrolytic method, which splits water into hydrogen and oxygen.



In the fuel cell, the cathode terminal is positively charged and the anode terminal is negatively charged. A membrane is to divide terminals in the proton exchange membrane type of fuel cell. At the anode, hydrogen is split into its electrons and protons (positive hydrogen ions). When protons pass through the membrane, it creates a flow of direct current electricity between the terminals. The only byproduct of this process is water, which is formed by electrons, hydrogen ions and oxygen at the cathode.

The efficiency of a fuel cell is as high as 75 %. There are no NOx, CO emissions, because hydrogen is not burned in air. Pure hydrogen is used

in lower temperature fuel cells. Platinum catalyst is used in the structure. For example a 40 KW fuel cell, which is suitable for automotive applications, needs at least 80 grams of platinum catalyst, which is 30-60 times the platinum in today's catalytic converters (Justin Fulton *et al.*, 1993). It needs further effort to make it cost-effective, practical fuel cell for vehicles.

In the next twenty-five years, the world population is expected to increase by about 2.5 billion, with most of the population growth expected to occur in developing countries. Most of the power plants will bum coal, oil, or natural gas, and contribute to our atmosphere's carbon dioxide content. Soon the effects of the growing CO_2 content in the atmosphere will become obvious, and non-polluting fuel cells for energy conversion will be in great demand. The new concepts being developed can help reduce the cost and pollution from the energy used in transportation, as well as the heating and cooling of buildings.

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