

A Review on Electrolytic Method of Hydrogen Production from Water

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Abstract

Generally, renewable energy has a large potential to displace emissions of green house gases from the combustion of fossil fuels and mitigate climate change. Renewable energy source can serve as alternative to non-renewable fossil fuel, which is depleting gradually. However, not all renewable energy source and energy carriers are clean, such as biogas, biodiesel etc. All of these energy carrier which finds major application in transportation and power industries contribute to environmental pollution when burnt. These energy carriers are needed to continually drive the growth rate of a country's economic development. Thus it is more practical to explore on cleaner source of energy and energy carrier such as hydrogen from water. Hydrogen, a clean energy carrier, exists in enormous quantities, but people are unaware of it or its significance in daily life because it maintains a low profile in combination with other elements such as petrol and other hydrocarbon fuels. More than 70% of hydrogen existing in our economy is produced by steam reforming. This method has been considered to be the cheapest means of producing hydrogen however, during production large quantities of green house gases are released into the environment. Based on this fact, this method has become unsuitable for our environment. Producing hydrogen by splitting water using the method of electrolysis can be a simple method to achieve clean hydrogen production. This method has the advantage of being able to produce hydrogen using clean renewable clean energy sources such as wind, solar etc. Common technology of utilizing solar panel as source of electricity for hydrogen production by electrolytic process can be very expensive. This also increases the amount of energy losses in the production process. Thus, to expand the use of hydrogen production by direct water splitting with the method of electrolysis, it is mandatory to reduce energy consumption, cost, and maintenance of current electrolyzers and, on the other hand, to increase their efficiency, durability, and safety. Since the stirling engine can utilize solar energy as source of fuel and has shown to be more efficient than solar pv, thus in our own opinion, utilizing a stirling engine as source for powering electrolyzers to produce hydrogen for expanded use of energy in various engineering system will be a cost effective method in realizing a hydrogen economy. This paper briefly discusses the various points of concern and issues regarding non-renewable energy, hydrogen production from water and hydrogen economy.

Keywords

Hydrogen, Electrolysis, Renewable Energy, Global Warming, Fossil Fuel, Stirling Engine

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1. Introduction

Greenhouse gases (GHGs) which causes climate change and global warming has been recognized as a worldwide issue. These gases (CO, CO₂, SO_x, NO_x, radioactivity, heavy

metals, ashes), are produced majorly from the combustion of fossil fuels such as petroleum, natural gas and coal (Kreuter and Hofmann, 2008). Fossil fuels meets most of the world's energy demand today, however, they are being depleted rapidly (Tester et al, 2005). Therefore, more reliable sources of energy are required for the future energy needs. With the

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rise of the industrial revolution at the turn of the 20th century, the world began to consume fossil fuel energy at a high rate. The electric power generation sector and transportation sector are the major consumers of fossil fuel in the world, accounting for about 82% and 95% respectively. This makes fossil fuel the highest consumed source of energy (USEA, 2011). The availability of these sectors has enabled human civilization to advance technologically at an ever increasing pace with greater standard of living and quality of life. The world energy consumption was reported to be above 10.5 billion tones of fossil fuel in equivalence in 2005 and it was also found that it was increasing due to both the world population growth and the increasing life standards of humans with an average of 2.5% every year since 1960 (BP-WSR, 2014).

According to Hubbert Peak theory it was estimated that the economically accessible fossil fuel resources would finish soon. The theory tells that as the world's energy demand increases, the production rates of fossil fuels are increased. This relationship continues up to a time when there will be no economical fossil fuel reserves available and thus, after this time, the production of primary fuels starts to decrease and according to supply and demand relationship, hence the fuel prices start to increase (Hubbert, 1956).

Recently Nigeria has been having challenges in gas supply to power plants due to shortage in gas supply and breakdown in gas pipelines. This contemporary issue has contributed to some extent the inadequate electricity supply in Nigeria homes and industries. Thus, the current energy crisis urges us to explore a variety of alternate methods to satisfy the economy energy demand. A major market solution for the energy crisis is increasing supply of clean energy source and reducing the demand for crude oil. By increasing the list of feasible clean fuel alternatives, the demand for crude oil reduces. In many ways fossil fuels are an ideal energy source, they are relatively easy to access, efficient, affordable, and their characteristics are widely known. However, it is well established by the scientific community that the use of fossil fuels, including biofuel is resulting in environmental pollution. During fossil fuel combustion, the concentration of CO₂ may seem relatively small in the short term period of a few years, in a long term, CO₂ takes a substantial amount of time to decay and can remain in the atmosphere for hundreds of years. Since 1960, atmospheric CO₂ levels have risen dramatically from near 315 ppm to current levels approaching 400 ppm. CO₂ emissions have been steadily rising since the beginning of the 20th century, during the early 1900's total emissions hovered around 2,500 teragrams of CO₂, they have steadily raised to present levels greater than 30,000 teragrams (BP-WSR, 2014). Recent studies have suggested a strong correlation between the increased

concentration of anthropogenic CO₂ and the increase in the earth's average surface temperature. Global warming can lead to dramatic changes in short-term weather as well as long term effects on climate and ecosystems. Global warming may result in rising sea levels, ocean acidification, changes in precipitation patterns, and the expansion of subtropical deserts. Additional effects may include increase in extreme weather events, species displacement and extinction, and diminished agricultural yields. According to the International Energy Agency (IEA, 2008), coal is currently the dominant fuel in the power sector, whilst natural gas generation becomes the second largest source, surpassing hydro, accounting for 41 % and 20 % of electricity generated respectively. The need to reduce anthropogenic emissions of CO₂ is globally agreed and represents the driving force to reconsider the current technologies used for power generation and transportation.

Since the early 20th Century, the average global temperature has risen to about 0.8^oC. However, limiting this global temperature increase to 2 degrees Celsius is now doubtful (Hugo, Rutter, Pistikopoulos, Amorelli, and Zoia, 2005). To limit global temperature to a hypothetical 2 degrees celsius rise would demand a 75% decline in carbon emissions in industrial countries by 2050, if the population is 10 billion in 2050 (Kesis, 2009).

The World Health Organisation estimates that 7 million premature deaths are caused each year by air pollution caused by green house gases (WHO, 2014). Biomass combustion is a major contributor, even though it is typically counted as renewable in energy statistics (Kreuter and Hofmann, 2008). In addition to producing air pollution like fossil fuel combustion, most biomass has high CO₂ emissions.

Many engineers and scientists agree that the solution to all these global problems would be to replace the existing fossil fuel system with the clean hydrogen energy system (Meurer et al, 2009). Hydrogen is a very efficient and clean fuel which is contained in water and fossil fuel. However, hydrogen produced from fossil fuel does not solve the problem in the reduction of green house gases since during production carbon dioxide and other green house gases are emitted. Hence hydrogen production from water will make a clean energy source. Moreover, water is abundant and ubiquitous in nature. Hydrogen combustion will produce no greenhouse gases, no ozone layer depleting chemicals, and little or no acid rain and environmental pollution. A worldwide conversion from fossil fuels to hydrogen would eliminate many of these environmental problems. This paper aims to provide a conceptual idea for a cost effective electrolytic method of hydrogen production using solar-dish Stirling engine.

2. Hydrogen Economy

Large scale application of hydrogen technology would involve significant changes in the energy system. Decisions on whether and how to promote hydrogen technology are thus strategic choices over different pathways in our energy system today. Despite the fact that hydrogen is an inherent component of conventional hydrocarbon fuels, such as oil, natural gas and coal, the public tends to give hydrogen little attention, perhaps forgetting or not realizing that it is used in large quantities every day to fuel vehicles and power plants. Hydrogen is produced in enormous quantities as an industrial "intermediate" in the production of ammonia, fertilizers, methanol and other chemicals and in the refining of petroleum, but people are unaware of it or its significance in daily life because it maintains a low profile in combination with other elements as gasoline, diesel, natural gas or fertilizer rather than as a free substance in its own name. The range of approaches being investigated for the production of hydrogen covers a wide variety of electrolytic, thermal and photochemical techniques. Hydrogen is more and more often mentioned as a solution to the tremendous challenges resulting from the global warming and depletion of oil and gas. However, hydrogen or subsequent synthetic fuels are only energy carriers, i.e. tools to handle the energy. An energy amount equivalent to at least the energy content of the hydrogen must be supplied by energy sources like e.g. wind, sunshine, biomass or nuclear.

Hydrogen economy advocates hydrogen as a potential fuel for motive power in transportation sector and power sector in the economy. Molecular hydrogen of the sort that can be used as a fuel does not occur naturally in convenient reservoirs; nonetheless it can be generated by steam reformation of hydrocarbons, water electrolysis, solar concentration and biocatalysed production etc. In the current hydrocarbon or fossil fuel economy, transportation is fueled primarily by petroleum. The supply of economically usable hydrocarbon resources in the world is limited, and the demand for hydrocarbon fuels is increasing, particularly in China, India, and other developing countries like Nigeria.

Proponents of a world-scale hydrogen economy argue that hydrogen can be an environmentally cleaner source of energy to end-users, particularly in transportation applications, without release of pollutants (such as particulate matter) or carbon dioxide at the point of end use. A 2004 analysis asserted that most of the hydrogen supply chain pathways would release significantly less carbon dioxide into the atmosphere than would gasoline used in hybrid electric vehicles and that significant reductions in carbon dioxide emissions would be possible if carbon capture or carbon sequestration methods were utilized at the site of energy or

hydrogen production (Alvarez et al, 2009).

Hydrogen has a high energy density by weight but has a low energy density by volume when not highly compressed or liquefied. In automobile vehicles, the combination of fuel cell and electric motor is 2-3 times more efficient than an internal-combustion engine. However, the high capital costs of fuel cells are one of the major obstacles of its development, meaning that the fuel cell is only technically, but not economically, more efficient than an internal-combustion engine (Bennett, 1998). Thus, producing hydrogen for use in conventional internal combustion engine will be much cheaper.

Currently, global hydrogen production is 48% from natural gas, 30% from oil, and 18% from coal; water electrolysis accounts for only 4% (Gabriela, 2007). The distribution of production reflects the effects of thermodynamic constraints on economic choices. The large market and sharply rising prices in fossil fuels have also stimulated great interest in alternate, cheaper means of hydrogen production.

One of the main offerings of a hydrogen economy is that the fuel can replace the fossil fuel burned in internal combustion engines and turbines as the primary way to convert chemical energy into kinetic or electrical energy; hereby eliminating greenhouse gas emissions and pollution from that engine. Although hydrogen can be used in conventional internal combustion engines, fuel cells, being electrochemical and having no moving parts, have an efficiency advantage over heat engines. As stated earlier, fuel cells are more expensive to produce than common internal combustion engines.

Transportation of hydrogen for industrial use has been ongoing since the early part of this century. Storage methods initially consisted of gaseous hydrogen held in steel cylinders, pressurized up to 2,000 pounds per square inch (PSI) (Vries, et al, 2014). After many years of successful use, steel hydrogen tanks show no sign of corrosion or degradation of any kind, as hydrogen is not caustic or toxic. More recently, storage tanks have been reinforced with composite carbon fibers, making them ten times stronger than steel, greatly enhancing the safety with which gaseous hydrogen can be handled. Present technology use composite fiber tanks which can readily resist the impact of a 100-MPH collision. Safety issues surrounding conventional storage and transportation of hydrogen focus on the flammability and explosive qualities of gaseous hydrogen, as any accident involving the exposure of liquid hydrogen to the environment means evaporation into a gaseous state. The possibility also exists of a leak in piping or industrial equipment, presenting problems of detection and fire suppression. As hydrogen ignites in air in very low concentrations, and ignition can be instigated by something as simple and common place as a static electric

spark, these potential problems must be monitored very carefully.

NASA has worked in concert with the International Standards Organization and the U. S. Department of Energy to establish worldwide codes and standards for the safe handling of hydrogen. As the largest consumer of liquid hydrogen, NASA has also led the way toward greater safety by sharing some of its technological developments with industry. This includes enhanced ability to detect hydrogen leaks and fires, which pose a tremendous but hidden threat, as hydrogen burns producing no visible flames. Discussions continue as to whether an odorant should be added to hydrogen gas, as it is to the natural gas we use in our homes so we can smell a gas leak, or whether more work needs to be done on sensing equipment for leak detection. Pipelines carrying natural gas are also capable of delivering hydrogen (NASA, 2015). Natural gas, labeled chemically as methane, has a greater density than hydrogen, which means it takes three times the volume of hydrogen to equal the energy in a given amount of natural gas. But at its lower density, hydrogen can be pumped through a pipeline at three times the flow rate of methane, balancing a delicate energy equation. As long as industrial codes and safety standards are stringently followed, the same should be true of transporting hydrogen.

3. Electrolytic Production of Hydrogen

Molecular hydrogen is not available on earth in convenient natural reservoirs (Alvarez et al, 2009). Hydrogen can be produced using any of the following processes:

(a) Biocatalysed electrolysis

Besides regular electrolysis, electrolysis using microbes is another possibility. With biocatalysed electrolysis, hydrogen is generated after running through the microbial fuel cell and a variety of aquatic plants can be used. These include reed sweet-grass, cord-grass, rice, tomatoes, lupines, and algae (Das and Veziroglu, 2001)

(b) Electrolysis of water

Hydrogen can be made via high pressure electrolysis, low pressure electrolysis or a range of other emerging electrochemical processes such as high temperature electrolysis or carbon assisted electrolysis. High pressure electrolysis is the electrolysis of water by decomposition of water (H_2O) into oxygen (O_2) and hydrogen gas (H_2) by means of an electric current being passed through the water with compressed hydrogen output. The difference with a standard or low pressure electrolysis is the compressed

hydrogen output around 120-200 Bar (1740-2900 psi). The low pressure electrolysis occurs under ambient condition. In high-temperature electrolysis, hydrogen can be generated from energy supplied in the form of heat and electricity. While nuclear-generated electricity could be used for electrolysis, nuclear heat can be directly applied to split hydrogen from water. High temperature (950–1000 °C) gas cooled nuclear reactors have the potential to split hydrogen from water by thermo-chemical means using nuclear heat. Electrolysis of water could offer the cheapest means of hydrogen production only if the source of electricity for decomposing water is relatively cheap. Hence this method is affected by the price of electricity.

(c) Photo-electrochemical water splitting

Water is broken into hydrogen and oxygen by electrolysis of a photoelectrochemical cell (PEC) process which is also named artificial photosynthesis. William Ayers at Energy Conversion Devices demonstrated and patented the first multi-junction high efficiency photo-electrochemical system for direct splitting of water in 1983. This group demonstrated direct water splitting now referred to as an "artificial leaf" or "wireless solar water splitting" with a low cost thin film amorphous silicon multi-junction sheet immersed directly in water. Hydrogen evolved on the front amorphous silicon surface decorated with various catalysts while oxygen evolved off the back metal substrate. A Nafion membrane above the multi-junction cell provided a path for ion transport. Their patent also lists a variety of other semiconductor multi-junction materials for the direct water splitting in addition to amorphous silicon and silicon germanium alloys. Research continues towards developing high-efficiency multi-junction cell technology at universities and the photovoltaic industry. If this process is assisted by photo-catalysts suspended directly in water instead of using photovoltaic and an electrolytic system, the reaction is in just one step, which can improve efficiency (Bard and Faulkner, 2001).

(d) Concentrating solar thermal

Very high temperatures are required to dissociate water into hydrogen and oxygen. A catalyst is required to make the process operate at feasible temperatures. Heating the water can be achieved through the use of concentrating solar power.

(e) Photoelectrocatalytic production

A method studied by Thomas Nann and his team at the University of East Anglia consists of a gold electrode covered in layers of indium phosphide (InP) nanoparticles. They introduced an iron-sulfur complex into the layered arrangement, which when submerged in water and irradiated with light under a small electric current, produced hydrogen

with an efficiency of 60% (Bard and Faulkner, 2001).

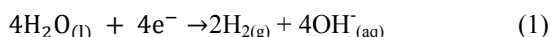
3.1. Electrolytic Cell Technology for Hydrogen Production

Electrolytic cells for hydrogen production can be classified based on the nature of electrolyzers or electrolytic cell used. Some basic design technologies are as follows:

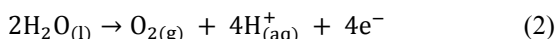
3.1.1. Alkaline Electrolyzers

Alkaline electrolyzers have been in commercial use in industrial application since the 1920s and it is the most mature electrolyzer technology available today (Kai and Zhang, 2010). The anode and cathode electrodes in these systems are typically made of nickel-plated steel and steel respectively. The electrolyte is an aqueous solution containing either potassium hydroxide (KOH) solution or sodium hydroxide (NaOH). Key disadvantage is its inability to produce hydrogen at high pressures. This inability to produce high pressure hydrogen for storage results in the added need for an external compressor, which adds cost to the system. The alkaline basic design consist essentially of anodes and cathode isolated from one another by semi-permeable membrane or separator, usually asbestos, all submerged in electrolyte. Direct current is passed through the cell and water is decomposed to generate hydrogen at the cathode and oxygen at the anode. The two gases are kept away from one another by the separator. The voltage drop across the cell is a measure of its energy efficiency, i.e. the percentage of energy in the electricity that is converted to hydrogen.

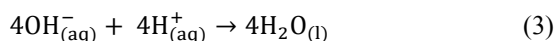
The half-cell reaction at the cathode is:



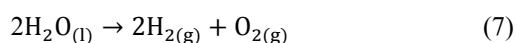
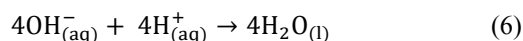
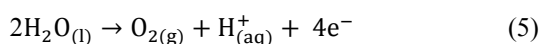
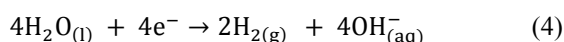
At the anode where oxygen gas is produced:



The OH^- ions and H^+ ions produced by the electrolysis combine to produce water again:



net result is the breakdown of water to hydrogen gas and oxygen gas, with no net change in the concentrations of H^+ and OH^- :



3.1.2. Polymer Electrolyzers

Proton exchange membrane (PEM) water electrolysis technology is frequently presented in literature as a very interesting alternative to the more conventional alkaline water electrolysis. Proton exchange membrane or polymer electrolytic membrane (PEM) water electrolysis systems offers several advantages over traditional alkaline technology including higher energy efficiency, higher production rates, and more compact design (Bard and Faulkner, 2001). A polymer like Nafion is usually used for the membrane. A basic schematic of a PEM electrolysis cell is shown in Figure. The PEM water electrolysis cell consists primarily of a PEM in which the anode and cathode are bonded. These electrodes are normally a composite of electrocatalytic particles and electrolyte polymer.

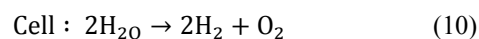
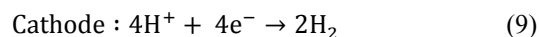
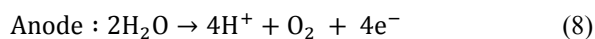
The advantages of the PEM includes:

- The electrolyte membrane or diaphragm can be made very thin, allowing high conductivity without risk of gas crossover.
- The electrolyte is immobilized and cannot be leached out of the cell.

The disadvantages of the PEM cell includes :

- The electrolyte costs more than the conventional alkaline solutions and
- The electrolyte is corrosive and requires more expensive components to be used in the cell. For these reasons,PEMs are usually operated at somewhat higher current densities than cells that use a liquid alkaline electrolyte.

Normally, different electrocatalysts are utilized e.g Platinum. When the electrode layers are bonded to membrane, it is known as the membrane electrode assembly (MEA). The electrical contact and mechanical support is established with porous backings like metallic meshes or sinters. Equations (8) (9) and (10) show the reaction in the electrolytic cell.



3.1.3. Solid Oxide Electrolyzers

Solid oxide electrolyzers use a solid ceramic material as the electrolyte that selectively transmits negatively charged oxygen ions at elevated temperatures (lei, et al, 2014). The way they generate hydrogen is a little different. At the cathode, water combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions. The oxygen ions pass through the membrane and react

at the anode to form oxygen gas and give up the electrons to the external circuit. Solid oxide electrolyzers must operate at temperatures high enough for the solid oxide membranes to function properly (about 500 - 800°C). The solid oxide electrolyzers can effectively use heat available at these elevated temperatures (from various sources, including nuclear energy) to decrease the amount of electrical energy needed to produce hydrogen from water.

4. Stirling Engine as Source of Power for Hydrogen Production

A Stirling engine is an energy efficient system capable of generating electricity for an electrolytic cell. The engine works by the principle of thermal expansion and contraction of gas within a closed system (Kolin, 1991). The heat source for powering the engine could be from solar energy, geothermal energy, nuclear energy, waste heat etc. Practically

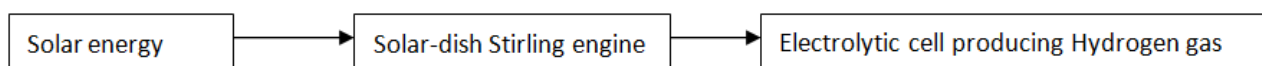


Figure 1. Flow Process for hydrogen gas production.

5. Conclusion

This paper has been able to review the electrolytic processes of hydrogen production and has discussed some contemporary issues relating energy crises. Analysis indicates that utilizing Stirling engine as source of electricity for electrolytic cells can be a more efficient technological approach of producing green hydrogen than solar PV. Stirling engines practically have efficiencies of more than 40%, while the Solar PV cells have efficiencies below 20% of equivalent design capacity. Utilizing the Stirling engine for hydrogen production is perceived to achieve the dividend of a hydrogen economy for the sustainment of the future economy.

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the engine has demonstrated to have more than 40% efficiency for various degree of heat energy sources. The record for heat input to electrical power output is held by Stirling Energy Systems company for one of their solar dish Stirling engines, at 31.25% of solar energy converted to grid-level electricity (Minassians, et al, 2010.). The Stirling engine can be produced from cheaper materials compared to a solar PV of same energy capacity. Also the conversion efficiency of the solar PV is usually less than 20% for most conventional designs (Vejen and Shah, 2010) making it less attractive for hydrogen production. Thus, based on conversion efficiency and cost effective materials for design, the solar Stirling engine system is perceived to be a better option to generate electricity for the production of hydrogen gas. The maintenance cost of a Stirling engine can be as low as that of a solar PV. However, the maintenance cost of the Stirling engine is little higher due to the mechanical motions involved in the system design. The process of production is shown in Figure 1.

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