

Solar Hydrogen Fuel Cell Technology, Principle, Applications and Market

Godswill Ofualagba^{1*} Igbinoba Kevwe Charles² Onyan Aaron Okiemute³

- 1. College of Technology, Department of Electrical and Electronics Engineering, Federal University of Petroleum Resources, P.M.B. 1221, Effurun, Delta State, Nigeria.
- 2. Faculty of Engineering, Department of Electrical and Electronics Engineering, University of Benin, Benin City, Edo State, Nigeria.
- 3. Faculty of Engineering, Department of Electrical and Electronics Engineering, University of Benin, Benin City, Edo State, Nigeria.
 - * E-mail of the corresponding author: swillas@ieee.org

Abstract

This paper is designed to provide "The Principle of operation of Solar Hydrogen Energy System" and "Explanation of the Components" and describes "The interaction of the components in detail". Also, it describes its applications and future market.

Keywords: Hydrogen gas, electrolyzer, oxygen gas, electrodes, proton exchange membrane, fuel cell.

1. Introduction

The world is rapidly exhausting the available supply of fuel. The need to reduce pollutant emissions and utililise the world's available energy resources more efficiently has led to increased attention towards new sources of energy. The combination of Solar Energy and Hydrogen is a virtually inexhaustible source of energy.

Our global resources of fossil and nuclear fuels are limited.

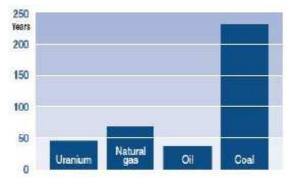


Figure 1. Projected availability of fossil and nuclear fuels (based on today's rate of consumption).

The necessary changes in our energy supply system can be accomplished if we are able to establish regenerative energies like solar, wind and hydroelectric energy as a fundamental part of the energy market.

One issue we are faced with when we use solar panels or wind power plants to produce electricity is that energy supply and demand often do not coincide. For example, a solar panel will provide electricity during the day but we might want to use electricity to power a light in the evening. Or, we might want to use wind-generated electricity in a place far away from the power plant. Hence, when supply and demand do not coincide we need a convenient way to both store and transport regenerative energy. This is where hydrogen



comes into play, as a future storage and transport medium for energy. The combination of solar energy for electricity production and hydrogen for energy transport and storage is called the solar-hydrogen energy cycle. During times when solar panels and wind power plants supply more energy than needed the excess energy is used to produce hydrogen (bottom path on the transparency). This is accomplished with electrolyzers that use electricity to split water into oxygen and hydrogen.

The hydrogen (and potentially the oxygen) can be stored and transported as necessary. When we need electricity, the gas(es) are fed into a fuel cell which converts the chemical energy of the hydrogen (and oxygen) into electricity, water and heat. In this way our energy demands can be met anywhere and anytime.

2. Components of Solar Hydrogen Energy System

In explaining the basic components needed, the general scheme of a stand alone power system based on Solar Hydrogen Energy Technology is shown in fig. 2. The main components of the system includes, PV-generator, a DC/AC inverter, an electrolyzer, a compressor, an hydrogen storage (compressed gas) and a Proton Exchange Membrane (PEM) fuel cell.

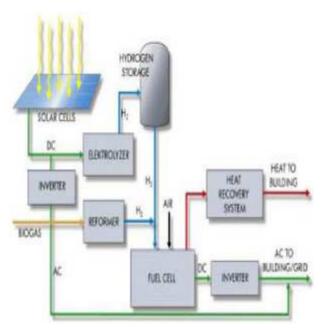


Figure 2. Solar Hydrogen Stand Alone Power System.

2.1 PV-Generator (Solar Panel)

The solar cell is made by doping silicon with phosphorus and boron. Phosphorus is used because it contains five valence electrons (one more than silicon). Four of the phosphorus valence electrons bond to the silicon crystal leaving the fifth valence electrons free. A phosphorus doped region is called N-type silicon because of an excess of negative electrons. Boron is used because it contains only three valence electrons leaving room for a fourth electron and boron doped region is called P-type silicon. When a photon strikes a solar cell its energy is absorbed and transferred to an electron. The excited electrons now flow freely. The flow of electron in a complete circuit gives rise to electricity. The electricity produced is Direct Current (DC).

2.2 The Electrolyzer



Catching the rays of the sun and turning them into electricity is easy with solar cells but storing the energy for use when the sun goes down is another task. The solar energy can be stored as Hydrogen so we make Hydrogen by electrolysis of water. There are two atoms of Hydrogen and one atom of Oxygen in every molecule of water. The Hydrogen is eleven percent by weight of the water. A theoretical electrical potential of 1.23 volts is required to break up the water into Hydrogen gas (H₂) and Oxygen gas (O₂), however, because of transition resistances, somewhat higher voltages are necessary in practice. So an electrolyzer is a device that puts electricity into water to break it apart. Different types of electrolyzers are usually distinguished by their type of electrolyte and/or electrodes.

Higher power electrolyzers are built as stacks in which individual electrolyzers are connected in series and voltages are added.

PEM* electrolyzers have a particularly simple and compact design. The central component is a proton conducting polymer membrane which is coated with a layer of catalyst material on either side. These two layers are the electrodes of the cell.

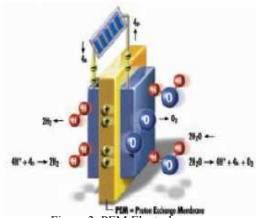


Figure 3. PEM Electrolyzer

2.2.1 How PEM electrolyzers work

Suppose a DC voltage is applied to the PEM electrolyzer electrodes (solar panel on the transparency). At the anode (electrode on the right) water is oxidized, leaving oxygen, protons (H⁺-ions) and free electrons. While the oxygen gas can be collected directly at the anode, the protons (yellow +) migrate through the proton conducting membrane to the cathode where they are reduced to hydrogen (the electrons for this are provided by the external circuit).

Cathode reaction:
$$4H^+ + 4e^- \rightarrow 2H_2$$
 (1)

Anode reaction:
$$2H_2O \rightarrow 4H^+ + 4e^- + O_2$$
 (2)

*PEM electrolyzers are named after their electrolyte material, a proton-conducting polymer membrane. The acronym PEM stands for proton exchange-membrane or polymer-electrolyte membrane. A PEM consists of a teflon-like polymer structure to which sulfonic acid groups (SOH₃) are attached. When the membrane becomes wet the sulfonic acid dissociates, the membrane becomes acidic and thereby proton-conducting. While this allows for an easy transport of protons (H⁺ions), anions (negatively charged ions) cannot pass the membrane.

2.3 Hydrogen Storage

Once the water is broken up, we need to store the Hydrogen if we are going to keep it for later use. Hydrogen



can be stored as a gas in a container, but it is so light weight that a cubic foot weighs just 0.005 lbs. The methods of storage being developed are: Compressed gas, Liquid Hydrogen, Metal Hydride, Raw Iron Pellets and Liquid Carrier Storage. In this paper, the principle of the different methods of hydrogen storage is not explained.

2.4 Fuel Cell

Fuel cells are electrochemical devices converting a fuel's chemical energy directly to electrical energy with high efficiency. With no internal moving parts, fuel cells operate similarly to batteries. An important difference is that batteries store energy, while fuel cells can produce electricity continuously as long as fuel and air are supplied. Fuel cells electrochemically combine a fuel (hydrogen) and oxidant without burning, thereby dispensing with the inefficiencies and pollution of traditional energy conversion systems.

2.4.1 Types of Fuel Cells

A fuel cell essentially consists of two electrodes (cathode and anode) separated by an electrolyte. Usually the type of electrolyte is used to distinguish between different types of fuel cells. However, there are a number of additional characteristics such as operating temperature, efficiency and application which can vary significantly between different fuel cell types.

2.4.1.1 Alkaline Fuel Cell (AFC)

The electrolyte in an Alkaline Fuel Cell is caustic potash solution (KOH). Operating temperatures range from room temperature to $\sim 90^{\circ}$ C (but can be higher depending on electrolyte concentration). AFCs have excellent efficiencies and make use of inexpensive catalysts. The major challenge with AFCs is their incompatibility with carbon dioxide. CO_2 reacts with the electrolyte and forms and insoluble carbonate. This means that AFCs can only be operated with fuels that are extremely pure (highly pure hydrogen and oxygen), but not with air which contains CO_2 .

Applications: military, space exploration.

Cathode reaction:
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH$$
 (3)
Anode reaction: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$ (4)

2.4.1.2 Proton Exchange Membrane Fuel Cell (PEMFC)

The electrolyte in a Proton Exchange Membrane Fuel Cell is a proton-conducting polymer membrane. PEMFCs also operate at low temperatures (room temperature to $\sim 80^{\circ}$ C). They have an excellent cold-start performance and high efficiencies. Moreover, individual cells can easily be stacked (fuel cell stacks) which allows for higher output voltages and makes this type of electrolyzer highly adaptable to a wide variety of applications. The cathode is supplied with oxygen (e.g., from the air) while the anode receives hydrogen. If the hydrogen used was made from carbon-based fuels it must be ensured that the gas no longer contains any carbon monoxide (CO) as this will destroy the PEMFC catalyst. One drawback of PEM fuel cells is the high cost of their catalyst material (platinum).

Applications: Electric motors, e.g. in automobiles, space exploration, mobile electricity supply, battery substitute, block-type thermal power station (electricity-heat-coupling).

2.4.1.2.1 How a PEM fuel cell works

In a PEM fuel cell two electrodes (typically platinum, blue on the transparency) are separated by a proton conducting polymer membrane, the electrolyte (yellow). Hydrogen gas (in red, left side) is supplied to one electrode and oxygen gas (in blue, right side) to the other. The anode is a catalyst for the dissociation of



hydrogen into protons (H⁺-ions) and electrons (yellow + and -).

Both protons and electrons now travel to the cathode side (on the right) but - very importantly on different paths. While the H⁺-ions pass through the cell's proton-conducting membrane the electrons move through the (closed) external circuit and thereby provide the fuel cell's electric power (indicated by light bulb). At the cathode the protons and electrons finally react with the oxygen to form water (in red and blue), the fuel cell's only byproduct.

Cathode reaction:
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 (5)

Anode reaction:
$$2H_2 \rightarrow 4H^+ + 4e^-$$
 (6)

2.4.1.3 Direct Methanol Fuel Cell (DMFC)

The Direct Methanol Fuel Cell is a special case of the PEM fuel cell. DMFCs and PEMFCs have similar structures, two electrodes are separated by an electrolyte consisting of a proton-conducting polymer membrane that is impermeable to electrons.

The difference between a DMFC and a PEMFC is that the DMFC uses methanol (CH₃OH) as fuel, not hydrogen. At ambient pressures (1013 hPa) methanol is liquid at temperatures between - 97° C and 64° C. Thus the major advantage of a DMFC is that its fuel can be handled, stored and transported similarly to conventional liquid fuels like gasoline or diesel. On the other hand, methanol is poisonous and corrosive and DMFCs have low electrical efficiencies compared to most other fuel cell types.

Applications: electric motors, portable electricity supply, battery substitute.

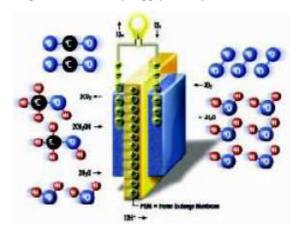


Figure 4. Direct Methanol Fuel Cell

2.4.1.3.1 How a DMFC works

Figure 4 shows a schematic diagram of a DMFC. The electrolyte (PEM) is shown in yellow, the electrodes on either side of it in blue (anode on the left, cathode on the right). The anode is supplied with a methanol/water mixture (red/blue/black and red/blue molecules on the left). Due to the electrode's catalytic effect hydrogen is separated from the mixture and reduced to protons (H⁺⁻ions, yellow +), yielding free electrons (yellow -) to the anode. Both protons and electrons now travel to the cathode side but – very importantly on different paths. While the H⁺⁻ions pass through the cell's proton-conducting membrane the electrons move through the (closed) external circuit and thereby provide the fuel cell's electric power (indicated by light bulb).

At the anode the oxygen and carbon left over from the methanol react with the oxygen from the water and form carbon dioxide (CO₂).

At the cathode the protons that passed through the membrane and electrons from the external circuit react



with the supplied oxygen (blue) to form water (red and blue).

Cathode reaction:
$$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$$
 (7)

Anode reaction:
$$2CH_3OH + 2H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$$
 (8)

2.4.1.4 Molten Carbonate Fuel Cell (MCFC)

The electrolyte in an MCFC is a molten alkali carbonate that is retained in a ceramic matrix of lithium aluminum oxide. MCFCs have high operating temperatures (600 - 700° C) and high efficiencies. They can be operated not only with hydrogen but also with other gases including natural gas and biogas.

Applications: block-type thermal power stations (electricity-heat coupling), utility power plants.

Cathode reaction:
$$O_2 + 2CO_2 + 4e^2 \rightarrow 2CO_3^2$$
 (9)

Anode reaction:
$$2H_2 + 2CO_3^{2-} \rightarrow 2H_2O + 2CO_2 + 4e^{-}$$
 (10)

2.4.1.5 Phosphoric Acid Fuel Cell (PAFC)

The electrolyte in a PAFC is phosphoric acid (H_3PO_4). Operating temperatures range between 160 - 220° C. Compared to other types of fuel cells (except DMFCs), PAFCs have low efficiencies.

Applications: stationary electricity supply, block-type thermal power stations (electricity-heat coupling).

Cathode reaction:
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 (11)

Anode reaction:
$$2H_2 \rightarrow 4H^+ + 4e^-$$
 (12)

2.4.1.6 Solid Oxide Fuel Cell (SOFC)

The electrolyte in this fuel cell is a solid metal oxide, usually yttrium-stabilized zirconium oxide (ZrO₂). SOFCs are high-temperature fuel cells. They can be operated with hydrogen but also other gases including natural gas and biogas.

Applications: block-type thermal power stations (electricity-heat coupling), utility power plants and also home electricity generation.

Cathode reaction:
$$O_2 + 4e^- \rightarrow 2O^{2-}$$
 (13)

Anode reaction:
$$2H_2 + 2O^2 \rightarrow 2H_2O + 4e^2$$
 (14)

2.5 DC/AC Inverter

The DC/AC inverter converts the direct current (DC) voltage given by either solar panel or the fuel cell into alternating current (AC) for applications that requires AC for operations as shown in figure 2 above. There are 3 types of inverters; the square wave, sine wave and quasi-sine wave inverters. In this paper the detail explanation of the 3 types of inverter is not treated.

2.6 Other Components

A complete fuel cell system for generating power and heat consists not only of the fuel cell stack, but also of a number of other components:

1. The Reformer: if the fuel needed to run the fuel cell is of inadequate quality, it has to be conditioned first. This may involve reforming and CO purification as well as desulfurization and the removal of excess oxygen. In some cases, biogas is reformed to produce hydrogen for the fuel cell as shown in figure 2 above.



- 2. Heat exchangers: serve to couple out the heat generated by the cell reaction for external use.
- 3. Other power-generating components: depending on output, these may be expansion turbines, gas turbines or combined gas- and steam turbines.
- 4. Piping, pumps and condensers required for gas and heat management.
- 5. Electrical connections between system units as well as controls and interfaces.

3. Applications of Hydrogen/Fuel Cell Technology

3.1 Fuel cells for portable applications

For portable applications fuel cells are an alternative to typical batteries. Their major advantage is that, unlike batteries, they do not discharge. Batteries are energy storage devices, the electrical energy they can supply is determined by the amount of chemical reactant stored within. When its reactant is used up a battery has to be either recharged (if it is rechargeable) or discarded. Fuel cells, on the other hand, are energy conversion devices and do not store their own fuel. They will provide electrical energy for as long as they are supplied with fuel (hydrogen or methanol).

There is a wide range of possible applications of fuel cell technology for portable devices, for example, fuel cells could provide electricity to low-power devices such as laptops or measuring instruments, or they might even supply power to camping equipment. Low-temperature fuel cells like PEMFCs and DMFCs are the most suited for portable low-power devices because they are operable at low temperatures, work immediately after start-up (i.e. no warm-up phase is required) and allow for a compact design.

The only byproduct of a PEMFC is water while a DMFC - in addition to water - also produces small amounts of carbon dioxide.

3.2 Fuel cells for mobile applications

Mobile applications are dominated by PEM fuel cells. Since they have low operating temperatures PEMFCs can deliver power immediately after start-up. This is particularly important for use in automobiles. Power needs for mobile applications range from a few kilowatts to several megawatts. Small boats typically require onboard power supplies of a few kilowatts while electric power on the order of megawatts is needed to equip a submarine with adequate propulsion as well as on-board electricity and emergency energy supply systems.

Due to their modular character fuel cell stacks can be adapted to meet the most different power requirements imaginable.

The HydroGen3 made by Opel is powered by a fuel cell stack consisting of 200 individual fuel cells that are connected in series. As there are no moving parts in a fuel cell the energy conversion is done noiselessly and without wear and tear.

BMW and DaimlerChrysler, in their research prototypes, use different technologies:

The BMW 745h uses a hydrogen combustion engine instead of a fuel cell stack and an electric motor. This technology is based on the conventional four-stroke internal combustion engine, the difference being that the engine burns hydrogen instead of gasoline. The engine has a capacity of up to 135 kW.

The NECAR5 (NECAR - New Electric Car), DaimlerChrysler's fuel cell car, runs on methanol that is reformed onboard. In a reformer hydrocarbons like methanol are transformed into hydrogen, CO₂ and CO. In this way the hydrogen for the fuel cell is produced directly in the automobile.

3.3 Fuel cells for stationary applications

Stationary applications range from in-home power and heat generation (output starting at 2 KW) to heat and



power supply for entire residential areas by means of heat-and-power block units (with outputs in the MW range).

Conventional block-type thermal power stations, which generate electrical power and heat through coupling rely on combustion engines and gas turbines. In comparison, fuel cells have much higher efficiencies as well as lower emissions and sound pollution.

4. Solar Hydrogen Fuel Cell Market.

The potential of the hydrogen fuel cell market is immense. It is the next fundamental technology change. One estimate by "future perspective on Lithuanian Research in Sustainable Energy Technologies" states that global demand is \in 39 billion in 2011 and the potential for 2021 could exceed \in 2.22 trillion.

Global fuel cell spending -- including research and development funding and investment in fuel cell enterprises, as well as commercial sales -- is forecast to climb 10.9 percent annually to \$10.2 billion in 2015 and then nearly double to\$19.0 billion in 2020. Commercial demand for fuel cell products and services (including revenues associated with prototyping, demonstration and test marketing activities, as well as actual product sales) will more than triple to \$2.9 billion in 2015 and then triple again to \$9.3 billion in 2020. As a result, the share of total fuel cell expenditures accounted for by commercial demand will rise from one-eighth in 2010 to nearly half of all outlays in 2020. Market gains will be driven by continuing technological advances, helping bring costs down to competitive levels in a growing number of applications, and bolstered by improved economies of scale as fuel cell manufacturers increase production. These and other trends are presented in World Fuel Cells, a newstudy from The Freedonia Group, Inc., a Cleveland-based industry market research firm.

US: Industrial activity spreads across all fuel cell and hydrogen technology development areas. The US fuel cell industry covers all technologies and many American companies are world leaders in their particular technology area. In comparison to their European counterparts, they generally have more access to venture capital funds and consequently tend to be the leaders in their fields:

- 1. Praxair is a leading industrial gas and hydrogen supplier.
- 2. Air Products produces hydrogen and equipment for hydrogen separation and purification.
- 3. Fuel Cell Energy has been developing micro fuel cell technology since the 1970s.
- 4. UTC Fuel Cells is presently the leading manufacturer of commercial stationary fuel cell systems.
- 5. Plug Power is a leader in the development of small stationary fuel cell systems.

Together, these companies cover the whole hydrogen economy value chain.

Canada has been a world leader in H₂/FC technology R&D - spanning most fuel cell types, components and systems supply, systems integration, fuelling systems and storage, as well as engineering and financial services. The Canadian fuel cell industry comprises around 80 companies with over 2000 highly-skilled employees. The Canadian fuel cell industry has been leading the world in R&D activities over the last few decades. Revenue generated from the fuel cells in Canada is expected to increase at a CAGR of around 15-20% during 2010-2012. With the increasing number of partnerships, huge investments by both public and private sectors and strategic alliances expected in future, the country is all set to witness technological developments and commercialization in the fuel cell industry.

Canada has also been successful in encouraging H_2/FC cluster development. The Vancouver area has the largest cluster of fuel cell companies, suppliers, infrastructure developers and service providers (possibly the largest concentration of fuel cell expertise in the world). Fuel cell industry clusters are also growing in the Calgary, Toronto, Kingston and Montreal areas.



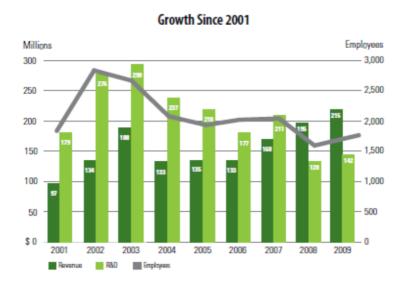


Figure 5. Canada Fuel Cell Technology growth rate from 2001-2009.

In 2003, the following countries established the International Partnership for Hydrogen Economy (IPHE):

Australia, Brazil, Canada, China, European Commission, France, Germany, Iceland, India, Italy, Japan, Norway, Russian Federation, United Kingdom, South Korea, and USA. These countries represent:

- 1. \$35 Trillion, or 85% of world GDP
- 2. ~ 3.5 billion people
- 3. 75% of worldwide electricity used
- 4. 2/3 of energy consumption and CO₂ emissions

The vision of IPHE is that "...consumers will have the practical option of purchasing a competitively priced hydrogen powered vehicle, and be able to refuel it near their homes and places of work, by 2020".

5. Conclusion

It is clear that solar-powered hydrogen energy system is technologically feasible. Several pilot plants were built in the mid-1990.s up till 2011 with solar arrays coupled to electrolyzers, and fuel cell.

It is clear that currently, the technology is far too expensive to compete with cheap fossil fuel based electricity and hydrogen production methods. However, it is also clear that with learning curve based cost-reductions and a steadily growing market for photovoltaic cells that Si solar cell based photovoltaic electricity will very likely be cost-effective by around 2020.

PEM electrolyzer costs will decrease by the same driving forces provided that a market develops in which they can gain significant production volume. It appears that such a market is developing as large-scale hydrogen development projects such as California's Hydrogen Highway are beginning to order PEM electrolyzer systems for refueling stations. This evidence of an emerging market, coupled with the fact that PEM electrolyzer development will benefit in lock-step with inevitable developments in PEM fuel cell technology as the U.S. hydrogen energy economy continues to evolve, bodes extremely well for the future of PEM electrolysis technology, as well as distributed photovoltaic-electrolyzer technology as a whole.



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