ENERGY HYDROGENATION AND DECARBONIZATION

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INTRODUCTION

From the 1870 book written by Jules Verne, "The Mysterious Island" [1]:

> "And what will they burn instead of coal?" "Water", replied Harding. "Water!" cried Pencroft, "Water as fuel for steamers and engines!" "Water to heat water!" "Yes, but water decomposed into its primitive elements", replied Cyrus Harding, "and decomposed doubtless, by electricity, which will then have become a powerful and manageable force, for all great discoveries, by some inexplicable laws, appear to agree and become complete at the same time. Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. Someday the coal rooms of steamers and the tenders of locomotives will, instead of coal, be stored with these two condensed gases, which will burn in the furnaces with enormous calorific power. There is, therefore, nothing to fear. As long as the Earth is inhabited it will supply the wants of its inhabitants, and there will be no want of either light or heat as long as the productions of the vegetable, mineral or animal kingdoms do not fail us. I believe, then, that when the deposits of coal are exhausted we shall heat and warm ourselves with water. Water will be the coal of the future."

Long before humans came on the scene, nature created revolutionary energy systems on Earth. Chloroplasts and mitochondria in biological cells could make them work continuously, day and night. The process of photosynthesis captures solar radiation and turns water and carbon dioxide into sugars such as glucose, and is the cornerstone of plant life:

$$6CO_2 + 6H_2O \xrightarrow{\;photosynthesis\;} C_6H_{12}O_6 + 6O_2 \qquad (1)$$
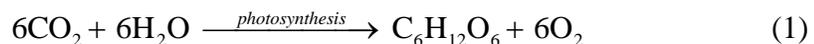
However, all forms of energy have their origin in the transformation of mass to energy. Solar energy, wind energy, hydroelectric power, biomass and fossil fuels energy are all some form of stored energy from the fusion reactions occurring in the sun. Even geothermal energy has a nuclear origin in the radioactivity existing in the Earth's crust, generating volcanic activity.

The capture and control of chemical energy in the form of fire, which is thought to have occurred about 10,000 years ago, was the first major step forward for the human species; the second major step being the release and control of nuclear fission energy. The control of fire protected the early humans from the cold and extended the range of primarily tropical zone mammals into the temperate zones of the earth. It extended the length of their daily activities into the darkest times of night. It protected them against predation by other mammals. It

extended their food supply, allowing them to chemically transform grains into bread and more edible and available foods.

Then the use of solar and animal energy dawned on humanity. The need for an extended food supply lead to the eventual establishment of farming and organized social communities in villages and cities, for mutual protection and shared production. Humans grew foods for themselves and their domesticated animals, which helped them in their work shores, in transportation, in food production, and in protection.

Following the use of solar and animal energy, humans built machines to harness wind and water energy to gather and process energy. This included sailing vessels, harnessing the ocean's fish supply and starting human sea migration and world trade. Mills using wind and flowing water spread over the landscape in Europe. Around 1086, there existed 5,624 wind mills in England. Their number was 100,000 in France around the year 1,700 [3].

HYDROGEN AS AN ENERGY CARRIER AND TRANSPORTATION FUEL

Hydrogen is the most common element in nature. It is a colorless, odorless and tasteless. It packs more energy than gasoline on a weight basis with an energy density three times that of gasoline. The automobile manufacturers have experimented with hydrogen as fuel for decades.

A milestone reached in 2007 is a dual mode hydrogen / gasoline hybrid engine developed by Bayerische Motor Werken (BMW) from Germany which was formerly an airplane engine manufacturer. The 7 series BMW design meets high performance standards while having virtually no emissions. It uses hydrogen as a fuel with gasoline as a backup.

Figure 1. Hydrogen 7, BMW automobile.

The plan for the future is to introduce a car running exclusively on hydrogen as a single fuel. At the same time researchers at the BMW Group are working on fuel cell technology,

seeking to create a highly practical solution for the automobile as an Auxiliary Power Unit (APU) like in airplanes, introducing a far more efficient and powerful replacement to the conventional car battery. This effort by BMW has counterparts in other car manufacturers such as Mercedes-Benz.

Hydrogen poses many problems for engine development. It is too voluminous to use as a gas to fuel cars. Liquefying hydrogen to – 418 degrees F or – 253 degrees Celsius, it can be shrunk to 1/1000 of its original gaseous volume. The BMW automobile uses a liquid hydrogen storage tank designed so that it can maintain the cold temperature of the cryogenic hydrogen but would not injure the passengers in case on an accident. The tank holds 17.5 lbs of liquid hydrogen and is situated between the trunk and the rear passenger seat. It consists of two concentric containers with the inner one insulated with 40 layers of aluminum foil that is equivalent to 56 feet of Styrofoam insulator.

The design uses a 7.6 liter, 12 cylinder engine. Using hydrogen and gasoline, the engine can propel the car to 143 miles per hour (mph) speed. The operator can switch to either hydrogen or gasoline fuel by pressing a button on the steering wheel. The hydrogen tank provides fuel for 125 miles, and the 16 gallon gasoline tank can provide fuel for 425 miles for a total cruising range of 550 miles. When hydrogen alone is used, the only emission consists of water vapor as steam.

Other companies such as Ford, Mazda and General Motors are considering fuel cells as a future engine and a radical development replacing the current internal combustion engine. Ford has devoted a lot of focus to hydrogen internal combustion technology and is developing a market for its hydrogen powered shuttle buses. Mazda champions hydrogen internal combustion through its dual fuel hydrogen rotary RX8 RE sports car development program and concept cars such as the Premacy Hydrogen RE minivan.

HIGHER ENERGY DENSITIES AND EFFICIENT ENERGY USE

Humans, who moved into cold climates before the year 1,000, used dwelling containing open fires in their middle. Most of the heat was carried out with the generated smoke through a louvered roof. Wood gathering occupied a major part of their activity to keep their heat and food preparation source operational.

The first step toward using biomass in the form of wood energy in an efficient way occurred with Benjamin Franklin in the USA designing a smart stove with a chimney, around 1744. Wood and hay remained the main energy sources at the start of the 19th century.

Petroleum
2.21

Exports
4.43

Other[g]
2.23

Coal
22.69

Natural Gas
19.34

Coal
22.39

Residential[l]
21.18

Fossil
Fuels
56.02

Crude Oil[a]
11.53

Natural Gas[h]
22.99

Commercial[l]
17.52

Domestic
Production
70.37

Fossil
Fuels[j]
85.65

NGPL[b] 2.47

Supply
104.17

Consumption[k]
99.74

Nuclear Electric Power 8.23

Industrial[l]
33.25

Renewable Energy[c] 6.12

Petroleum[i]
40.13

Imports
33.00

Petroleum[d]
27.68

Nuclear Electric Power 8.23
Renewable Energy[c] 6.12

Transportation[l]
27.79

Adjustments[f]
0.80

Other[e]
5.33

Figure 2. USA Energy flow chart tracing primary energy resources supply to their end uses in Quads or quadrillion BTUs. Energy Information Administration, EIA, Annual Energy Review, 2004.

As cities started to evolve with high population densities, it became inconvenient to depend on biomass as the bulky and hard to transport wood and hay. With the advent of industry in the cities, the population densities increased. High population densities and the increase in energy per capita consumption lead in turn to a higher energy use per unit area. At higher energy consumption per unit area, energy sources with higher scale economies were needed.

Coal became king as a high energy density fuel source compared with wood and hay. Fossil energy replaced biomass energy, despite its devastating effects on those who mined it as mine accidents and chronic black lung disease. It caused cancer in the lungs of those who used it through its benzo-a-pyrene (bap) content. It fouled-up urban air, and destroyed the rural environment which stripped out of its vegetation during the extraction process.

Coal lead to the invention of the steam engine and lead to a leap in industry and transportation with the invention of the locomotive and rail transportation. However, it remained bulky to be used and hard to store, handle, and mine.

Around the year 1,900, using fossil fuel fluids with still a higher energy density than coal, rather than solids became more convenient. Petroleum from its wellhead to a gas station pump, could flow through pipelines and could be stored in tanks, large and small. Petroleum replaced coal and became the predominant fossil energy source by 1950. The ease of dispensing modest amount of petroleum or its distillates, as kerosene and gasoline, lead to a revolution in land, air and sea transportation. One cannot imagine a modern car or an airplane carrying its supply of coal around.

The presently favored configuration for high energy density spatial consumption of energy is a grid from which it can be fed and bled continuously at variable rates. Natural gas satisfies this condition and is distributed through an efficient system of pipelines, which pervades businesses, industries and even homes. It is safely stored underground in sedimentary geological formations, and can be easily purified leading to complete combustion.

Table 1. Specific energy of different energy supplies.

Fuel	Specific energy [MJ / kg]
Enriched uranium (3-5 % U^{235})	3.7×10^6
Natural uranium (0.72 % U^{235})	5.7×10^5
Natural gas	55.6
Diesel fuel	45.8
Crude petroleum	41.9
Coal	32.5
Ethanol	26.8
Wood	10.0

Electricity produced from primary energy sources such as coal, natural gas, and to a lesser extent from hydroelectric wind, solar, geothermal and nuclear fission processes, is also used in the distributed grid. It can substitute for fossil fuels in the case of space heating, but is primarily used in devices uniquely designed for using electricity. Electricity is cleaner as an energy carrier than natural gas, and its delivery can be easily switched on and off. Its cleanliness at the consumption site is associated with release of pollutants to the environment in a concentrated source manner at the production site, or the power plant, particularly for coal fired power plants. Electricity cannot be stored efficiently, except in minute quantities in batteries. Power plants have to operate continuously to satisfy potential demand. Electricity losses occur when transported over long distances. Electrical power plants are distanced about 100 km in the present configuration, and the economical limit for electrical power transmission is 1,000 km.

Electric motors and generators are very efficient at about 95 percent. It is easy to convert electrical energy into heat: a hair dryer does this with nearly 100 percent efficiency. However, it is more difficult to convert heat back into electricity. A coal fired power plant equipped with pollution control scrubbers achieves only about 30 percent as an overall thermal efficiency. Some natural gas fired gas turbine plants can reach 60 percent thermal efficiency. The inefficiency is here tolerable because electricity is so useful and convenient.

Because of its limited storage capability, electricity cannot be used for distributed uses like in cars, except in the hybrid car concept. The electrical power grid design is controlled by the peak, rather than by the average power demand. Since the peak power demand is typically twice the average demand, power systems are inefficiently large in size and require a large capital cost investment that is not even working at full capacity 24 hours a day, but may sit idle waiting for the times of peak demand. Regardless of these inefficiencies, the share of primary energy used to produce electricity has steadily grown and now has reached the 40 percent level.

ENERGY UNITS

Energy consumption rates are conventionally estimated in the British System of units in terms of the Quad (for Quadrillion) or Q (perhaps for Quintillion) units, where:

$$1 \text{ Quad} = 10^{15} \text{ BTU},$$

or:

$$1 \text{ Q} = 10^{18} \text{ BTU}.$$

Thus:

$$1 \text{ Quad} = 10^{-3} \text{ Q}.$$

In the Système International (SI) system of units, the Trillion GJ unit is commonly used instead, where:

$$
\begin{aligned}
1 \text{ Trillion GJ} \quad &= 10^{12} \text{ GJ} \\
&= 10^{21} \text{ J} \\
&= 0.948 \times 10^{18} \text{ BTU} \\
&= 0.948 \text{ Q}
\end{aligned}
$$

or:
$$1 \text{ Q} \quad = 1.05 \text{ Trillion GJ}$$

The Gigajoule, Terajoule, Exajoule, and Zetajoule units are also commonly used, where:

$$
\begin{aligned}
1 \text{ Gigajoule} &= 10^{9} \text{ Joules} \\
1 \text{ Terajoule} &= 10^{12} \text{ Joules} \\
1 \text{ Exajoule} &= 10^{18} \text{ Joules}
\end{aligned}
$$

In the USA, the utility industry typically consumes 32.8 Quads of primary energy, of which 18.4 Quads were as coal, to produce 10.7 Quads of electricity. The $32.8 - 10.7 = 22.1$ Quads of difference were conversion and plant losses as shown in Fig. 1. This suggests an overall electrical conversion efficiency of:

$$\eta_{electrical} = 10.7 / 32.8 = 0.326,$$

or just 32.6 percent.

The advent of the information age in its Internet realization will further require a reliable and even more extensive global electrical power system. The pervasive spread of the Internet is literally enclosing the globe into an electrical nerve system, moving information from one point to another. The Internet statistics are astounding. There exist about 800 million web pages, with 200 million page entries on the largest Internet index. There are 38 web pages that are created every second, the average number of clicks between two randomly selected web pages is now 19, and 7 is the average number of links to other web sites on each web site.

According to the Center for Energy and Climate Solutions, the Internet economy may have a beneficial impact from the perspective of electrical energy needs. Some 1.5 billion square

feet of retail floor space may be eliminated by electronic commerce. Two million square feet of office space would be saved, or the equivalent of 450 Chicago Sears Towers. Annual operations and maintenance energy savings of 2 billion kilowatt-hours, equal to the output of 21 standard size power plants, and 35 million metric tons of greenhouse gases that are not released to the atmosphere.

Regardless, it appears that for the next 30 to 50 years, we need to reliably operate the gas and electric systems. World wide we shall continue using 50 to 100 billion tons of coal, which are sufficient for 20 to 40 years at the present rate of consumption. Then, the market will make coal all but disappear.

In an analogy given by Jesse Ausubel [3], it is dusk for coal, it is mid-afternoon for oil which is already losing ground in energy markets other than transport, and it is midmorning for natural gas.

THE HYDROGENATION AND DECARBONIZATION TREND

An interesting observation can be made about the trend in using hydrogen and carbon. Starting from 750,000 years ago when cave dwellers used wood fire, 10 carbon atoms per hydrogen atom were burned. Because the combustion of carbon generates soot or CO_2, while hydrogen becomes water, carbon is essentially a dirty element when used as fuel, whereas hydrogen is a clean one as fuel.

Table 2. Hydrogen to Carbon ratio (H/C) for different fuels.

Fuel	Hydrogen to Carbon ratio, (H/C)
Wood	0.1
Coal	0.5-1.0
Oil	0.8-2.0
Light sweet crude oil, $(CH_{1.5})_n$	1.5
Heavy sour crude oil, $(CH_{0.8})_n$	0.8
Clean transport fuel, $(CH_2)_n$	2.0
Cetane, $C_{16}H_{34}$	2.125
Hexane, C_6H_{14}	2.333
Propane, C_3H_8	2.666
Methane, CH_4	4.0
Methanol, methyl alcohol, CH_3OH	4.0
Ethanol, ethyl alcohol, C_2H_5OH	3.0
Hydrogen	Infinity

Table 3. Per capita energy consumption trend for different fuels.

Timescale	Fuel	Per capita consumption in tons of coal equivalent (tce)
1850-1925	Coal	0.3-1.0
1925-2000	Oil	0.8-2.3

2000-2050	Gas	2.0-6.0
2050- …...	Hydrogen	6.0-15.0

In the last 200 years there has been an evolution toward burning less carbon in favor of burning more hydrogen in different fuels as shown by the atomic ratio of hydrogen to carbon (H/C) in Table 2 for different fuels from wood to natural gas or methane: CH_4. The increased per capita energy consumption as estimated by Ausubel [3] is leading to a trend toward using fuels with more hydrogen content as shown in Table 3.

Hydrogen can be produced in different ways. First one needs an energy source and second one needs a hydrogen source. Currently, the cheapest source of hydrogen is methane (CH_4) in natural gas, which is both an energy source and a hydrogen source. A problem is that the resulting hydrogen has only 50 percent of the chemical energy of the original natural gas. Hydrogen can also be produced from oil but the energy efficiency is even worse. If hydrogen is derived from fossil fuel, carbon dioxide, a greenhouse gas, is also released in all cases. For a hydrogen economy, it should thus be contemplated that hydrogen should be produces from a non fuel source: water H_2O.

FUEL CELLS AS HYDROGEN ENGINES

INTRODUCTION

Fuel cells generate electricity through electrochemistry, rather than combustion. They operate in a clean, quiet efficient manner and are compact in size. They are considered as the key to the global energy future, as they become more widely used, promising reduction in global warming, air and water pollution, and world peace in negating the need for the military control of oil resources in the Caspian Sea and the Middle East regions.

Great interest exists in the commercialization and development of fuel cells. A major impediment to commercialization is the high costs of manufacturing and fabrication at $5,000 per kilowatt of electric power, compared with $500-1,000 per kilowatt for energy produced from conventional power plants.

The goal of Fuel Cells technology development is the achievement of high power density cells operating at below 800 ^{0}C. This involves the development of low cost processing techniques for thin films and the optimization of materials and design to increase the power density.

Fuel cells are essentially energy conversion devices that generate electricity by converting the chemical energy of fuels. Heat is generated in the process. They are similar to batteries in that connecting them in series can produce higher additive voltages. Batteries are considered as an energy storage device storing its chemical fuel internally. They can supply only a predetermined amount of energy. In the case of Fuel Cells, the fuel is provided externally. Unlike batteries, Fuel Cells do not possess a limited capacity; they will generate power as long as they are being supplied with fuel and oxygen from the air.

Fuel Cells, with reprocessing and purification, can use practically any type of fuel such as natural gas, coal gas, gaseous decomposition products of biomass as plants or animal manure, and liquid fuels such as gasoline and diesel.

Fuel cells would become the avenue to the adoption initially of natural gas and later hydrogen as the primary source of energy for both transport and electrical power. Fuel cells are essentially continuous batteries that are currently fed by hydrogen extracted from methane gas. In the near future hydrogen would be extracted from water. In replacing the internal combustion engine, they are expected to lead to higher efficiencies and reduced pollution, since the end product of hydrogen burning is water. Fuel cells can be considered as power sources that efficiently convert chemical energy into electricity.

Complex reactions occur at each electrode in the cell. At the anode, hydrogen gas diffuses through tortuous pathways until a platinum catalyst particle is met. The platinum particle catalyzes the dissociation of the hydrogen molecule into two hydrogen atoms bonded to two neighboring platinum atoms. At this point each hydrogen atom releases an electron to form a hydrogen ion in two steps:

Oxidation half reaction: $\qquad 2H_2 \rightarrow 4H^+ + 4e^-$ (2)

Reduction half reaction $\qquad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (3)
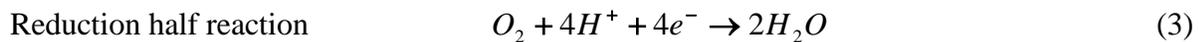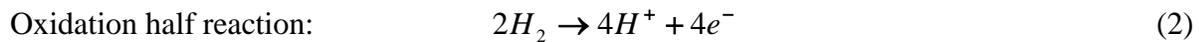
Electrical current flows in the cell as the hydrogen ions are conducted through a membrane to the cathode while the electrons pass from the anode to the outer circuit and then to the cathode. Combining Eqns. 2 and 3 yields the overall reaction:

Cell Reaction $\qquad 2H_2 + O_2 \rightarrow 2H_2O$ (4)

The reaction of one oxygen molecule at the cathode is a 4 electron reduction process occurring in a multi-step sequence. Platinum based catalysts are the only catalysts capable of causing significant rates of oxygen reduction at the low temperature polymer electrolyte fuel cells operate. The oxygen reduction half reaction is 100 times slower than the hydrogen oxidation half reaction. This limits the performance of the polymer electrolyte fuel cell.

The half reactions occurring at the electrodes can occur at a high rate on the surface of a catalyst such as platinum. Electrodes are constructed of porous carbon to which platinum particles 2 nanometers in diameter are bonded. These offer a large surface area for the reactions to occur.

At the anode the platinum sites bond the hydrogen sites according to the reaction:

$$H_2 + 2P_t \rightarrow 2P_tH$$ (5)

These platinum sites then release the hydrogen atoms as hydrogen ions and electrons according to the equation:

$$2P_tH \rightarrow 2P_t + 2H + 2e^-$$ (6)
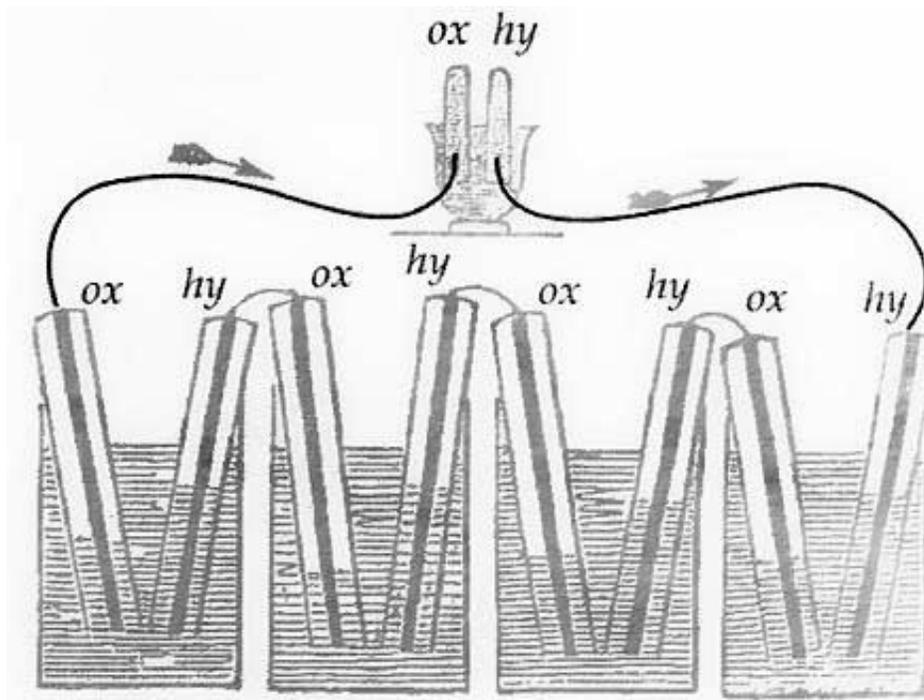
Figure 3. The Grove Fuel Cell consists of four large cells with hydrogen and oxygen, connected in series. The electrical current generated in them is then used to electrolyze the water in the smaller upper cell back into hydrogen and oxygen.

Air and water flow must be carefully managed in the operation of fuel cells. The fuel and the air entering the cell must be humidified to keep the electrodes hydrated. The outgoing air must be enough to carry the formed water and prevent the cathode from flooding.

In his studies in 1839 on reversing the process of water electrolysis, Sir William Grove, a British lawyer with scientific interest, developed an improved wet-cell battery. The "Grove Cell" is capable of generating a current of about 12 amperes at a voltage of 1.8 Volts. This battery was used at the time to power American and British telegraphs. It was abandoned at mid century when it was discovered that it released toxic nitric dioxide NO_2 gas. The Grove Fuel Cell is shown in Fig. 3, and consists of four large cells with hydrogen and oxygen connected in series. The electrical current generated in them is then used to electrolyze the water in the smaller upper cell back into hydrogen and oxygen.

The term "fuel cell" was introduced in 1889 by British chemists Ludwig Mond and Charles Langer. They built the first practical fuel cell using air and industrial coal gas. The introduction of the internal combustion engine within this time frame using the newly discovered petroleum as its fuel source stopped electrochemical research in its track.

Francis Thomas Bacon built a fuel cell using nickel gauze electrodes in the 1930s. It operated at high pressure improving on the one built by Mong and Langer by using hydrogen and oxygen instead of air and industrial coal gas.

A 20 Horse Power (HP) tractor powered by a fuel cell was built by Harry Karl Ihrig of the Allis Chalmers Manufacturing Company in 1959.

The period of 1960-1990 saw fuel cells playing a major role in space exploration with NASA using fuel cells on the Gemini, Apollo and Space Shuttle manned spaced missions.

Recently, using methanol, Robert Hockaday successfully powered a cellular phone for 24 hours using a Microfuel Cell. Time magazine named Geoffrey Ballard founding member of the fuel cell research company, Ballard Power Systems, one of five "Heroes for the Planet," in February 1999. In March 1999, the car company Daimler-Chrysler unveiled the first zero emission fuel cell car having a space for a driver and four passengers. The car had a top speed of 90 miles per hour (mph) with a range of 280 miles. In February of 2001 the United Nations initiated a program to demonstrate clean fuel cell city buses in five developing countries with the worst city air pollution levels. In august of 2001, General Motors unveiled the first fuel cell vehicle powered by hydrogen extracted with a reformer from gasoline. In October of 2001 Motorola laboratories announced the development of miniature direct methanol fuel cells that could be used to power cellular telephones, laptop computers, electronic games and other equipment.

The Patent and License Exchange at the end of the year 2001 named fuel cell technology as the number one automotive and transportation niche market. Fuel cell technology is expected to grow from its 218 million dollar in revenue into a 2.4 billion dollars a year industry.

Space exploration initiated the development of fuel cell technology in the last century. Lately, emission standards are enticing automobile manufacturers to investigate fuel cells with twice the efficiency of an internal combustion engine with negligible harmful emissions. Communication companies are also spending efforts at developing micro power sources for hand held device with the goal of the power source lasting a day to a month without recharge. Government research aims at miniaturizing fuel cells for military applications to power sensors and communication equipment. Some recent applications use fuel cells the size of a pencil's eraser.
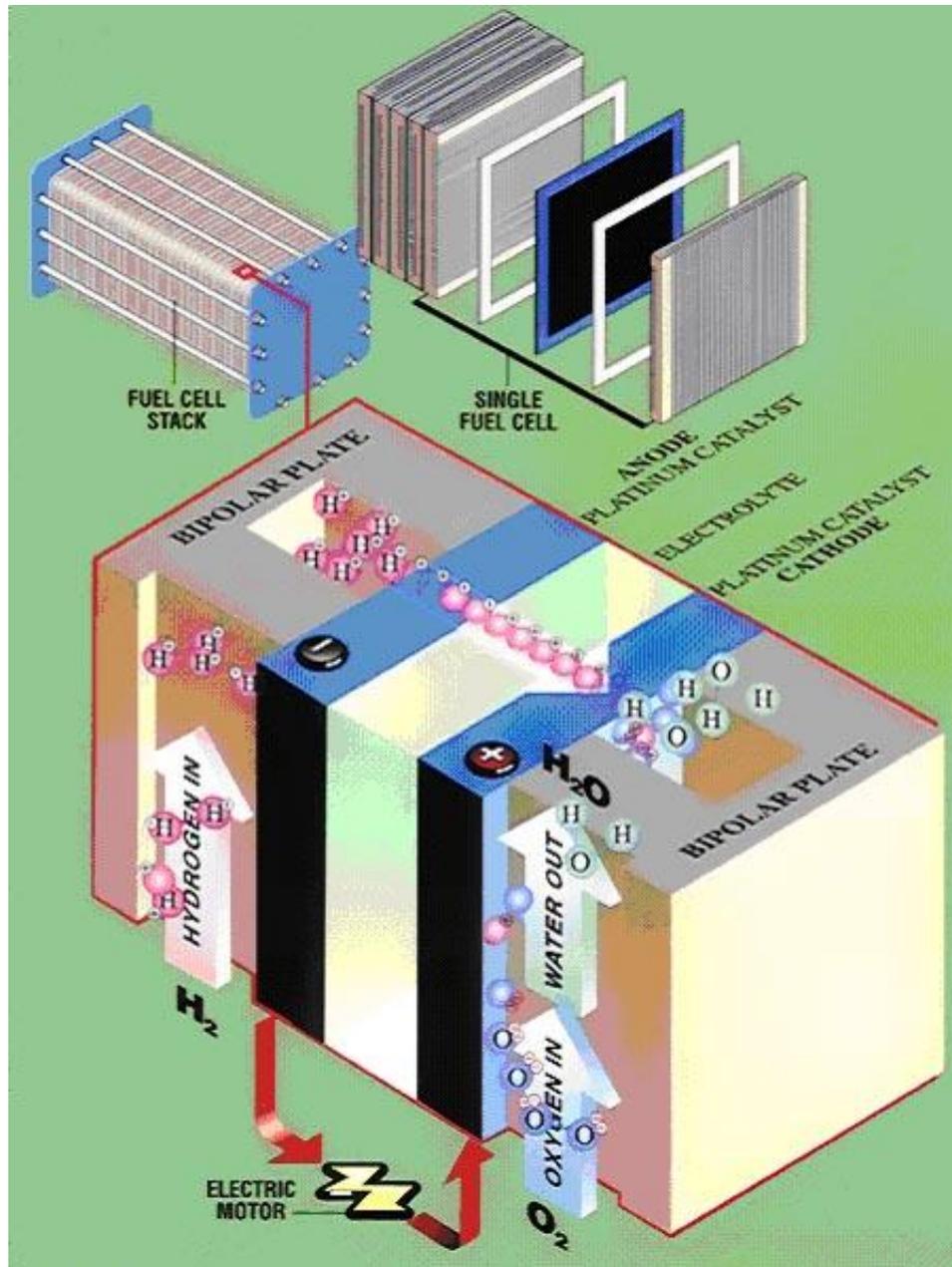
Figure 4. Hydrogen and oxygen are combined in a fuel cell stack producing water and electricity to drive electrical devices.

FUEL CELL TYPES

Numerous types of fuel cells exist, with newer types coming on stream. The main known types of fuel cells are:

1. Phosphoric Acid Fuel Cells (PAFC):

These operate in the range of 175-200 degrees Celsius, and use liquid phosphoric acid soaked in a matrix as an electrolyte. Several fuel cells of this type have been installed in commercial facilities and buildings worldwide. The following reactions occur in this cell:

At the anode: $$H_2 \rightarrow 2H^+ + 2e^- \tag{7}$$

At the Cathode: $$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{8}$$

Overall Reaction: $$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{9}$$
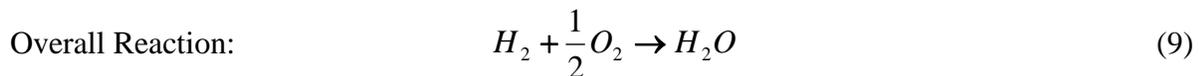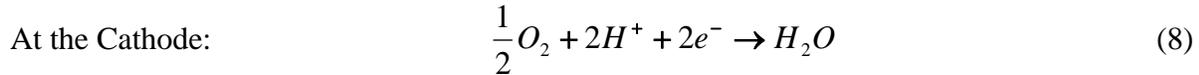
2. Polymer Electrolyte Membranes (PEM) Fuel Cells:

These work with a solid organic polymer electrolyte in the form of thin permeable sheets of poly[perfluorosulfonic] acid. A typical membrane material manufactured by the Dupont Company and designated as Nafion, consists of three distinct regions:

1. A Teflon-like fluorocarbon backbone consisting of hundreds of repeating chemical units:

$$-CF_2—CF-CF_2.$$

2. Side chains connecting the molecular backbone to the third region:

$$-O-CF_2-CF-O-CF_2-CF_2-.$$

3. Ion clusters of sulfonic acid ions:

$$SO_3^- H^+.$$
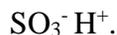
When a membrane becomes hydrated, the hydrogen ions become mobile. They bond to the water molecules and jump from one SO_3 site to another within the molecule.

It operates around a temperature of 60-100 degrees Celsius. The electrochemical reactions are the same as Eqs. 7-9. They possess a high power density and can vary their output quickly to follow the power demand. This makes them suitable for automobile applications.

3. Solid Oxide Fuel Cells (SOFC):

They are made from solid-state materials, particularly ceramic oxides. They use a hard ceramic electrolyte consisting of solid zirconium oxide to which a small amount of ytria stabilizer has been added, instead of a liquid. They operate at a temperature of 600-1,000 degrees Celsius. These are suitable for high power applications including electrical generation stations and motor vehicles.

They consist of three components: a cathode, an anode and an electrolyte positioned between the anode and the electrode, as shown in Fig. 5. Oxygen contained in air is reduced at the cathode and is converted into negatively charged oxygen ions. Those oxygen atoms travel across the electrolyte to the anode. There they react with the fuel that is delivered to the anode. The fuel is oxidized or burned by the oxygen ions and releases electrons to the external circuit, producing an electrical current. These electrons travel back to the cathode where they reduce the oxygen from the air, continuing the cycle in the process.

Several cells can be stacked as a fuel stack in series as a fuel stack to produce higher voltage and power as shown in Fig. 6. The cell are separated in the fuel stack by interconnects called bipolar separator planes.

The relevant reactions in a solid oxide fuel cell are:

At the anode:
$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{10}$$

At the Cathode:
$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \tag{11}$$

Overall Reaction:
$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{12}$$
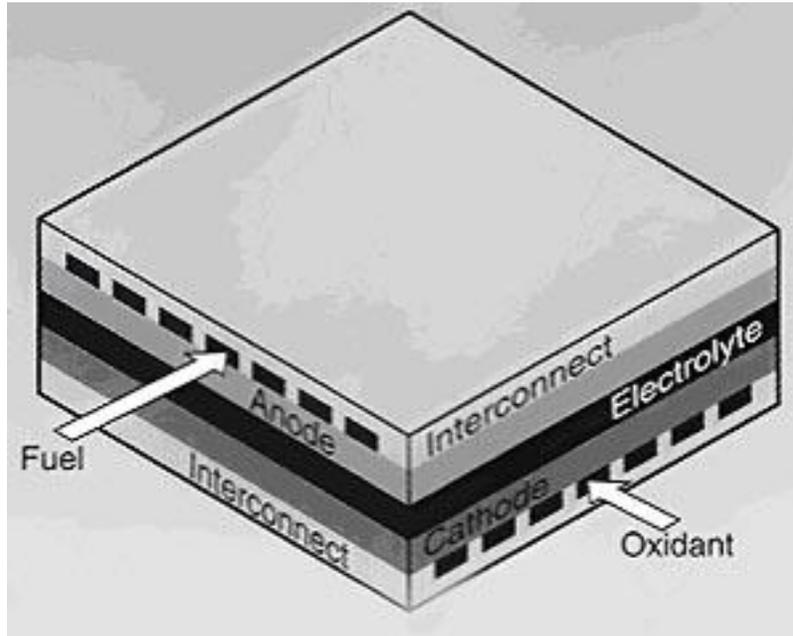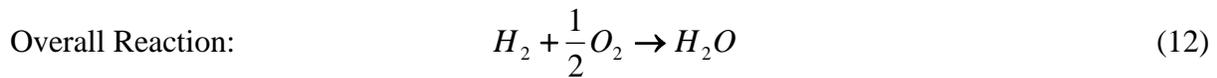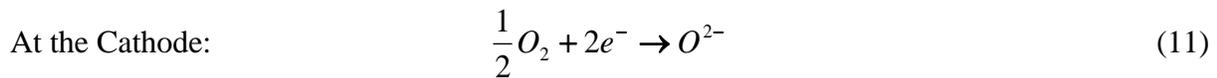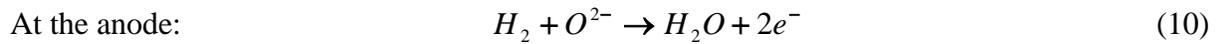
Figure 5. Modular unit of anode, cathode, electrolyte and interconnect layer of a solid oxide fuel cell.
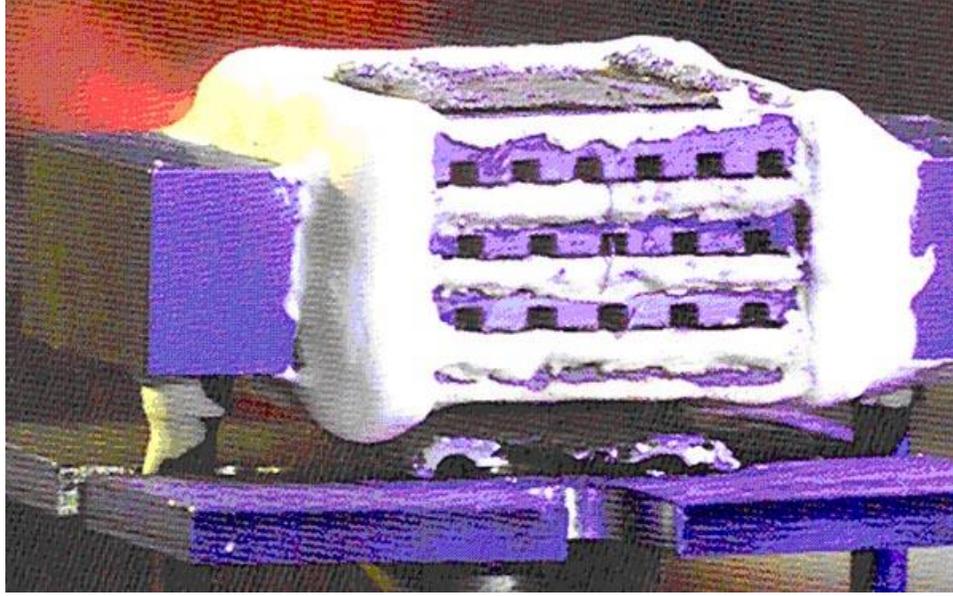
Figure 6. Fuel cell stack of three solid oxide fuel cells modules [9].

4. Direct Methanol Fuel Cells:

These are similar to the PEM fuel cells except that the anode catalyst itself draws the hydrogen from the liquid methanol. These operate between 120 and 190 degrees Celsius. NASA primarily used these in the space program. They have a large potential to be used over a large range of applications from hand held devices to powering whole structures and buildings.

In a direct methanol fuel cell, the following reactions occur:

At the anode:
$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad (13)$$

At the Cathode:
$$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \qquad (14)$$

Overall Reaction:
$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \qquad (15)$$
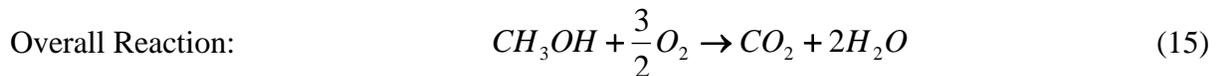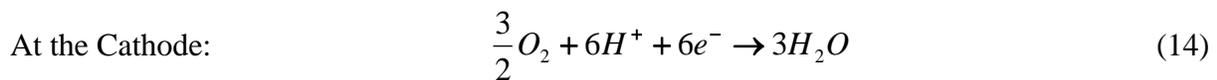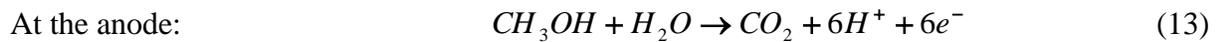
5. Molten Carbonate Fuel Cells (MCFC):

These use molten carbonate salts in the form of a liquid solution of lithium, sodium and/or potassium carbonates as the electrolytes, soaked in a matrix. They operate at a range of 600-1,000 degrees Celsius. The molten salts conduct the carbonate ions from the cathode to the anode. These can be used in power generating stations. The relevant reactions are:

At the anode:
$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \qquad (16)$$

At the Cathode:
$$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$$
(17)

Overall Reaction:
$$H_2 + \frac{1}{2}O_2 + CO_2 \rightarrow H_2O + CO_2$$
(18)
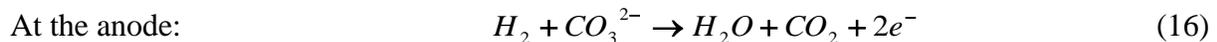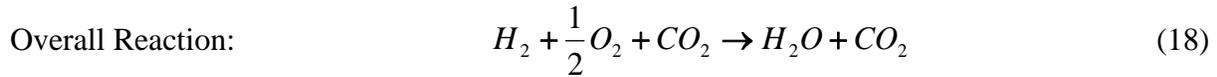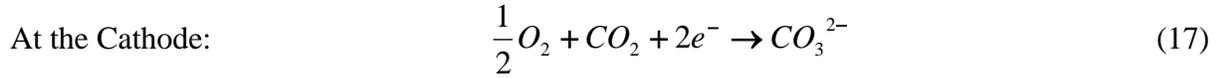
In this type of cell the carbon dioxide is consumed at the cathode and produced at the anode.

6. Alkaline Fuel Cells (AFC):

Use compressed hydrogen and oxygen and use an aqueous solution of potassium hydroxide in water soaked in a matrix as the electrolyte. They operate between 90-100 degrees Celsius. NASA has also used these in the space program. They have been too costly so far for commercial applications. The relevant reactions are:

At the anode:
$$H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$$
(19)

At the Cathode:
$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$$
(20)

Overall Reaction:
$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$
(21)
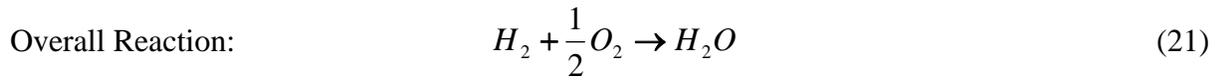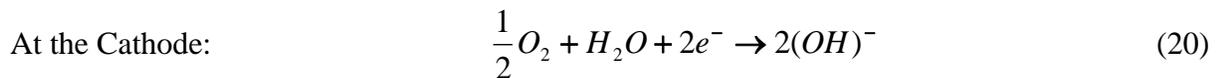
7. Regenerative Fuel Cells:

This is the latest introduction to the family of fuel cells. Water is separated into hydrogen and oxygen by an electrolyzer. Hydrogen is fed into the cell, generating electricity heat and water, which can be recirculated to the cell.

Carbon nanohorns, which are carbon nanotubes tapered at one end, which are manufactured from the soccer ball shaped fullerene molecules, can make excellent electrodes for fuel cells. They are the basis of a new generation of micro fuel cells.

FUEL CELLS OPERATION

Hydrogen fuel produced by wind, nuclear or solar methods stored in palladium, titanium or uranium beds, or in the form of metal hydrides, or hydrogen rich gas produced on board from different hydrogen rich fuels is fed through channels in one bipolar plate. Oxygen from air enters the fuel cell through another bipolar plate. A catalyst such as platinum starts a reaction that strips an electron from the hydrogen. These electrons create an electric current flowing through an electric motor driving a vehicle, or to electric generators producing electricity. The positive hydrogen ions pass through the electrolyte membrane to the platinum catalyst cathode where it combines with oxygen forming water. The only emissions are heat and water.

In a fuel cell an energy balance of chemical energy, electrical energy and heat energy occurs:

Fuel chemical energy = Electrical energy produced + Heat energy released   (22)

The power delivered by a fuel cell in terms of the produced current I in amperes and the terminal voltage V in volts is:

$$P = I.V \ [\text{Watts}]$$ (23)

The power density is the ratio of power to the volume of the cell, and the specific power is the ratio of power to the weight of the cell. These two quantities must be minimized for transportation and hand held applications.

The maximum cell voltage ΔE for the hydrogen air fuel cell reaction is given in terms of the Gibbs free energy change at a given temperature and pressure by the relationship:

$$\Delta E = - \frac{\Delta G}{n.F}$$ (24)

where: n is the number of moles of electrons per moles of H_2 in the reaction,
                F is Farady's constant = 96,487 [Coulombs] or [Joules/Volt], represents the charge transferred per mole of electrons.

At a pressure of one atmosphere, the Gibbs free energy change per mole of hydrogen is given in terms of the reaction temperature T in Kelvins, the enthalpy change ΔH and the entropy change ΔS by:

$$\Delta G = \Delta H - T\Delta S$$ (25)

Combining Eqns. 24 and 25 yields:

$$\Delta E = \frac{T\Delta S - \Delta H}{n.F}$$ (26)

The operational temperature limits the operation of a Fuel Cell. The heat generated by the thermo chemical reaction must be released, or used for cogeneration of thermal energy. We use an example to explore the limitation that temperature imposes on Fuel Cell operation.

EXAMPLE

At room temperature of 298 Kelvins (25 degrees Celsius), and a pressure of 1 atmosphere, the cell voltage according to Eqn. 24 is:

$$\Delta E = \frac{T\Delta S - \Delta H}{n.F}$$

$$= \frac{(298\,K)(-163.2\,J/K)-(-285,800\,J)}{(2)(96,487\,J/V)}$$

$$= \frac{237,166.4\,J}{192,974\,J/V}$$

$$= 1.229\ Volts$$

where: $\Delta S = -163.2\ J/K$,

$\qquad \Delta H = -285,800\,J$.

At the operational temperature of 353 degrees Kelvin or 80 degrees Celsius, assuming negligible changes in the thermodynamic functions, the voltage becomes:

$$\Delta E = \frac{(353\,K)(-163.2\,J/K)-(-285,800\,J)}{(2)(96,487\,J/V)}$$

$$= \frac{228,190.4\,J}{192,974\,J/V}$$

$$= 1.183\ Volts$$

Thus a voltage decrease is observed for higher operational temperatures. Accounting for the use of air instead of pure hydrogen, using humidified air instead of dry gases, further decreases the voltage to 1.16 Volts at atmospheric pressure and 80 degrees Celsius.

MICROBIAL FUEL CELLS
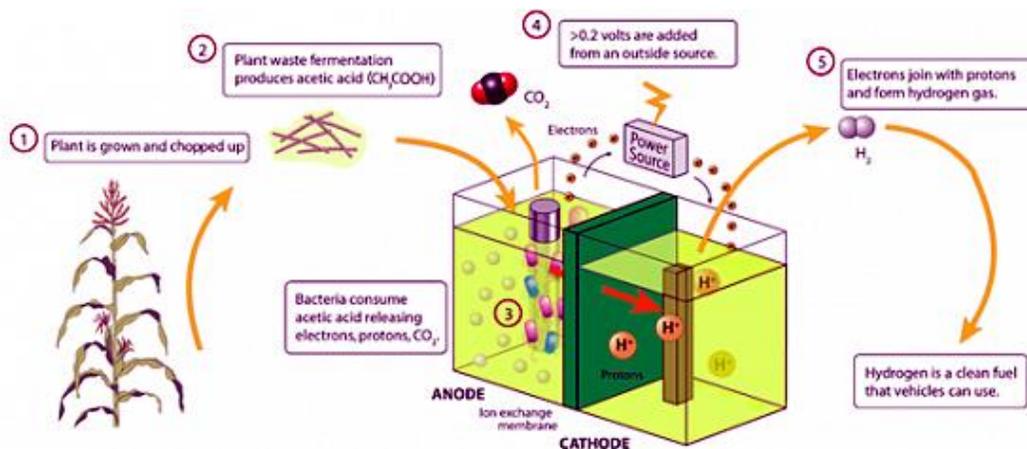
Figure 7. Microbial electrolysis of hydrogen [11].

Microbial Fuel Cells (MFCs) contain bacteria that convert organic material, such as food and bodily waste, into electricity, leaving clean water behind. In addition to being a potential source of renewable energy, MFCs can also provide people in rural areas with sanitary water. An individual MFC is made up of four parts: the anode, which houses the bacteria and organic matter in an oxygen-free environment; the cathode, which contains a conductive saltwater mixture; the proton-exchange membrane, which divides the anode and cathode and allows protons to move between the two chambers; and the circuit, which allows electrons to enter the cathode. Bacteria in the anode chamber turn the wastewater into carbon dioxide, protons and electrons. The protons and electrons move through the fuel cell and merge with the oxygen to make clean water [11].

MFC technology is over a century old. The history of MFCs dates back to University of Durham professor M.C. Potter's successful 1911 experiment to generate electricity from E. coli. Potter made a basic fuel cell, but the biology of bacteria was poorly understood at the time, so there was not much room for improvement. In fact, it was not until the 1980s that further significant developments in the field of MFCs took place [11].

Researchers have been working to take advantage of MFCs as an alternative source of fuel, and for desalination and the treatment of wastewater. In 2012, Indian government officials allocated $20 billion or 1.1 trillion rupees for the treatment and reuse of wastewater over a five-year period [11].

HYDROGEN SAFETY ISSUES

Of great concern in a future hydrogen gas economy is the safety of gas installations as tanks and pipelines, which can be subject to tragic explosions. The Hindenburg dirigible accident is memorable about the reactivity of hydrogen in air.

Figure 8. The Hindenburg using hydrogen burst into flames upon mooring.

However experience exists in the handling of pipelines carrying hydrogen gas among existing oil refineries. Natural gas, which is methane or CH_4, is itself a greenhouse gas. It is also the source of CO_2 greenhouse gas emissions, even though each unit of energy produced by methane yields 2/3 less CO_2 than coal, and 1/3 less than oil. Operation of gas powered power plants at high temperatures and pressures, may allow the sequestration of CO_2 in the form of a liquid with further disposal into porous geological formations.

Hydrogen should be the ultimate fuel since its combustion yields water and energy. From that perspective it can be considered the "immaterial material." Yet, it is not a fuel per se, but rather an "energy carrier ."

Currently, hydrogen is popular as rocket fuel. It is abundant in the Earth's water bodies, but must be extracted from water. Its extraction from water needs a supply of energy that is carbon free. This suggests wind, solar, photovoltaic and nuclear energy routes.

FUEL CELL APPLICATIONS

Numerous applications are envisioned for Fuel Cells. In some of these applications the Fuel Cell is replacing conventional electrical batteries. The difference is that the electrodes in the fuel cell act as catalysts to speed up the reaction, and the reaction takes place in the fuel cell volume, not just at the electrodes like in the case of batteries. This continuous source of electricity needs a continuous source of hydrogen providing electrons at the anode.   The electrolyte transfers the charged particles between the anode and cathode without affecting them. Heat at a temperature ranging from 80 to 1,000 degrees Celsius is normally required, depending

on the type of fuel cell. This range of temperature dictates the possible applications of different types of fuel cells.

1. Space Exploration:

NASA began using Fuel Cells in the 1950s seeking self-contained energy sources on its manned space missions. They are simpler and more compact than solar array sources, and they are more portable than large batteries as a power source for space vehicles instrumentation.

2. Transportation and Specialty Vehicles:

Concerns about costs, availability and environmental pollution are leading to a growing interest in Fuel Cells, as a replacement for the internal combustion engine in automotive and mass transit systems. Less than 15 percent of the energy content in gasoline is utilized in today's cars. Fuel cells can capture up to 85 percent of the energy content of a given fuel. Many fuels have been suggested as a source of hydrogen, including: Ammonia, animal waste gas, biomass gas, ethanol, gasoline, gas to liquid synthetic gas, hydrogen hydride, kerosene, landfill gas, methanol, naphtha, methane or natural gas, propane, and waste treatment gas. The ultimate fuel source is just hydrogen in liquid form or compressed obtained from water through different processes. Fuel cells have been suggested for powering cars as shown in Figs. 9 and 10, trucks, buses, two and three wheeled vehicles, locomotives, surface ships and submarines, specialty vehicles and equipment for construction and mining, and lawn tractors and equipment. Table 4 shows the levels of emissions expected in such vehicles using fuel cells.
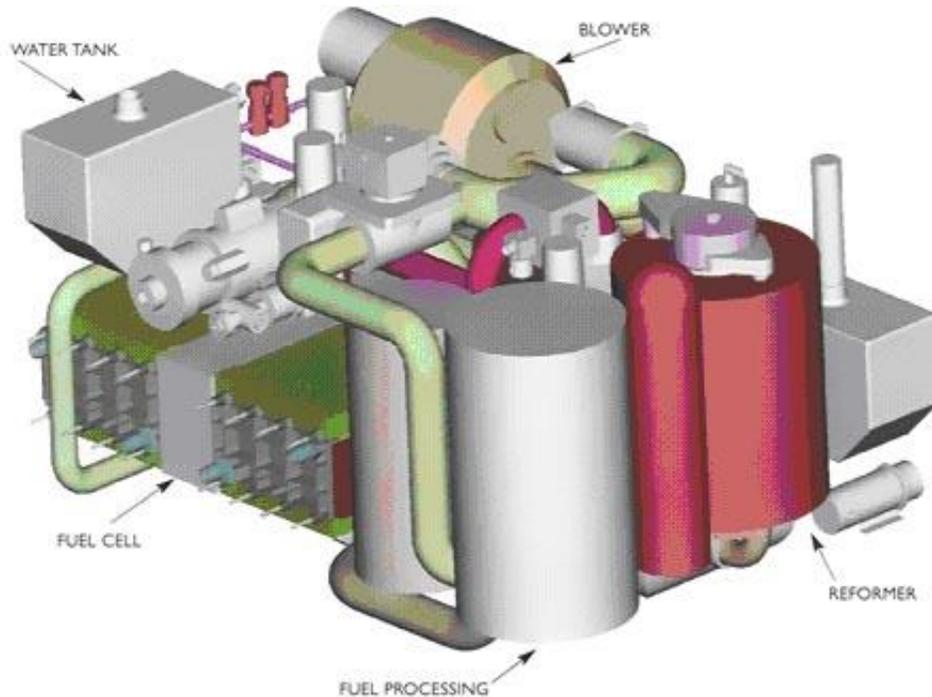
Figure 9. Configuration of a 50 kW Fuel cell Power Plant with a methanol reformer.

3. Residential power:

Fuel cells could become the basis of a distributed system of power generation for homes and commercial installations like hospitals. Hydrogen would be distributed in the existing natural gas distribution system and electricity would be produced at the usage site eliminating the need for cables and avoiding the power lines significant transmission losses over long distances. Figure 9 shows the configuration of a 50 kW power plant using a methane reformer to produce hydrogen.

4. Defense Applications:

Development has been underway of hand-sized fuel cells capable of powering military applications including miniature sensors on the battlefield and armor with camouflage and communication capabilities.

5. Hand held devices:

Fuel cells can power wireless communication devices such as cellular phones and laptop computers for up to 20 hours of uninterrupted use per single charge.

Table 4. Relative pollutants releases from different power sources for transportation vehicles.

Pollutant	Low Emission Vehicle	Super Ultra Low Emission Vehicle	Fuel Cell Vehicle
Hydrocarbons	0.09	0.01	0.005
Carbon Monoxide	4.20	1.00	0.00
Nitrogen Oxides	0.07	0.02	0.00
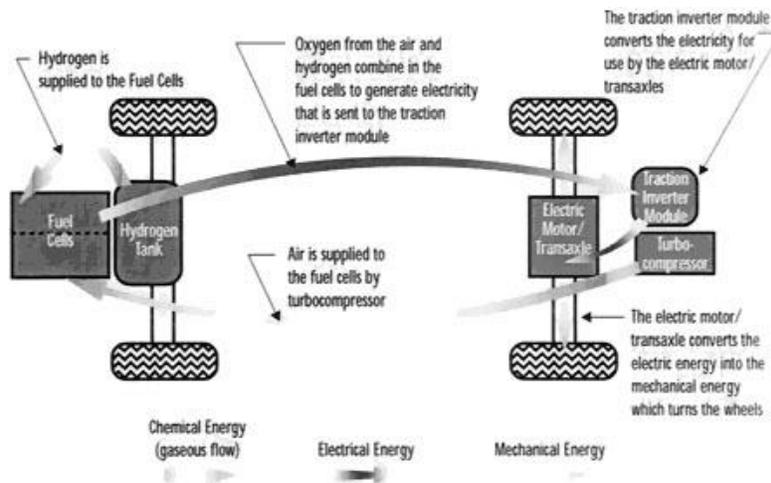
Figure 10. The P2000, a Ford Motor company design of a vehicle using a direct hydrogen polymer electrolyte fuel cell.

THE ENVIRONMENTAL NECESSITY FOR HYDROGENATION AND DECARBONIZATION

Until recently, few questions were asked about the air pollution effects of coal. In 1998 electric power plants in the USA burned 134 percent more coal than in 1973. By the year 2015, coal use is projected to increase by 20 percent. Coal combustion releases to the environment a diverse array of pollutants. These include carbon dioxide as a greenhouse gas, sulfur oxides and nitrogen oxides which act as precursors to acid rain. Radioactivity contained in the coal ore bodies, the benzo-a-pyrene cancer causing compound, polycyclic organic matter, particulate matter in the form of soot, smoke and toxic metals like lead, cadmium, arsenic, beryllium and mercury are also released. These pollutants affect human health and the environment in a pernicious way, leading to asthma, respiratory diseases and premature death.

The first ominous warning about coal burning health effects appeared in the Meuse Valley of Belgium in 1930, when emissions from coal powered factories lead to 60 deaths and 6,000 illnesses. In 1948 in Donora, Pennsylvania, there were 20 deaths versus 2 normally expected in a 4-day period during which 6,000 of the 14,000 people in the valley became sick. There were 8 episodes in London between 1948 and 1962 in each of which hundreds of excess deaths were reported. In 1948 six hundred people in London died from smog linked to open grate coal fires. In December 1952, stagnant air over London trapped smog and soot from millions of chimneys leaving 3,500 of its residents dead. Coal pollution was still killing Londoners in 1956 when the British Parliament passed a law severely restricting the burning of coal in homes. There were three instances in New York City involving over a hundred deaths, one in November 1953 causing 360 deaths, another in January 1963 leading to 500 deaths, and a third in November 1966 leading to 160 deaths.

There are about 50,000 deaths in the USA each year due to air pollution, of which 10,000 to 20,000 are attributable to coal burning. If we conservatively consider the 10,000 deaths per year figure and the 2 million total deaths per year in the USA, this suggests that:

$$\frac{10,000}{2 \times 10^6} = 0.005$$

or 0.5 percent or 1/200 of Americans who die per year are dying prematurely from coal burning air pollution. This estimate is an average value and the uncertainty involved can make it ten times smaller or ten times larger.

The methods used in extracting energy from coal have changed very little in the past 200 years. The USA utility industry runs several hundreds coal units built in the 1950s. In the process they release 6 million tons of Nitrogen oxides (NO_x) per year, which is 1/3 of the annual emissions in the USA. Nitrogen oxides are the major ingredients, which lead to the formation of ozone smog, an odorless, colorless gas that attacks and destroys lung cells. In a given summer, smog triggers 6.2 million asthma attacks. It sends 159,000 people to the emergency rooms, and generates 69,000 hospital admissions.

Coal burning for electrical power generation also releases 13 million tons of sulfur dioxide (SO_2) per year, which is 2/3 of emissions. Combined with fine soot particulates, it forms "sulfate particulates" and is linked to 45,000 premature deaths in the USA annually. The main

sufferers are the elderly and individuals with heart and lung disease, which are at the greatest risk in addition to infants, and those with compromised immune systems.

On top of this, coal-burning utilities emit 2 billion tons of the greenhouse gas carbon dioxide per year, which is 36 percent of all USA emissions. Carbon dioxide added to the atmosphere remains active as a greenhouse gas for about 100 years.

Coal-fired power plants are also the largest mercury polluter in the USA. In the USA, 52 tons of mercury are released per year. In more than 40 states, mercury contamination of the food chain is so severe that health officials have banned consumption of certain fish by pregnant women and children, who are most susceptible to the health effects of mercury. The USA Department of Health now ranks mercury as the third most deadly chemical in our environment. Its toxicity has been long known leading to dementia and irreversible brain damage. Hat makers who used mercury to shape hats in England were noticed to suffer from its toxicity, hence the expression: "mad as a hatter," notoriously expressed in the Alice in Wonderland story.

In other parts of the world, the use of coal is resulting in major health problems, caused by arsenic and fluorine in coal. The use of coal in the Guizhou Province in Southwest China has caused thousands of arsenic poisonings. The symptoms appear as freckled skin or squamous cell carcinomas. Ten million people are afflicted by fluorosis, which can soften and disfigure teeth and bones. Damp and cool autumn weather encourages farmers to use coal indoors in coal burning stoves, for drying their crops such as peppers. Fluorosis is so common because high fluorine coal is combined with high fluorine clay to make coal briquettes.

Chinese coals contain about 35,000 parts per million (ppm) of arsenic, compared with USA coal containing a more tolerable 22 ppm of arsenic. What makes the situation worse in China is that the forests were denuded by the early 1900s, eliminating wood as an energy source, leading people to mine coal from the hillsides. Most homes are designed without chimneys leading to the accumulation of the combustion products indoors. It is estimated that fresh chili peppers contain 1 ppm of arsenic when fresh, increasing to 500 ppm after being dried indoors over coal fires.

Since the cleaning up of coal burning through pollution control technologies remains in large measure an exercise in wishful thinking, adopting hydrogenation effort using wind, nuclear and solar sources becomes the logical way to proceed.

THE HYDROGEN NUCLEAR ECONOMY

Currently nuclear fission energy is used in an inefficient way as an expensive way of boiling water to produce steam and then electricity. Nuclear power plants are operated half the day to satisfy demand at the peak hours. Instead, nuclear power plants can be operated economically ats base load to primarily produce hydrogen for both transportation and as a portable fuel. Neither the power plants nor the produced fuel would generate pollutants. Wind turbines and solar technologies can satisfy part of the demand by billions of people, but the majority of the demand will have to be satisfied by the nuclear approach to hydrogen.

High temperature electrolysis of water can be used to efficiently produce hydrogen for distribution possibly through the existing natural gas distribution pipeline system. Electricity can also be used locally to dissociate water, whenever available, through low temperature electrolysis. For a location that is short on water supplies in arid regions of the world, or with

polluted water supplies from agricultural wastes, the burning of hydrogen will provide both a source of energy and pure unpolluted water.

The ultimate course toward a hydrogen economy would be the development of fusion reactors which themselves burn hydrogen in the form of its isotopes deuterium, produced from heavy water or D_2O electrolysis, and tritium, tritium would be produced from the isotope of lithium: $_3Li^6$, and in the process produce hydrogen from water. They would offer three advantages compared with fission plants:

1. No fission products are produced, requiring geological isolation like in the case of fission reactors, even though some activation products will be produced, and there will be a need to handle tritium which a radioactive isotope of hydrogen.
2. Fusion reactors are not subject to criticality accidents like fission reactors, even though some plasma disruption accidents can occur.
3. The fuel supply in the form of heavy water and lithium are practically unlimited.

FISSION REACTORS FOR HYDROGEN PRODUCTION

The thermo chemical production of hydrogen if fission reactors are used requires operation at high temperatures ranging from 750 to 1,000 degrees Celsius. It also requires the transfer of the process heat from the reactor to the chemical plant at high temperature. The reactor plant and the chemical plant are thus to be isolated from each other. Considering that each has its particular inventory of hazardous materials, the safety design and analysis of the combined configuration has to be addressed. Three fission reactors designs that could operate at the required high temperature can been identified:
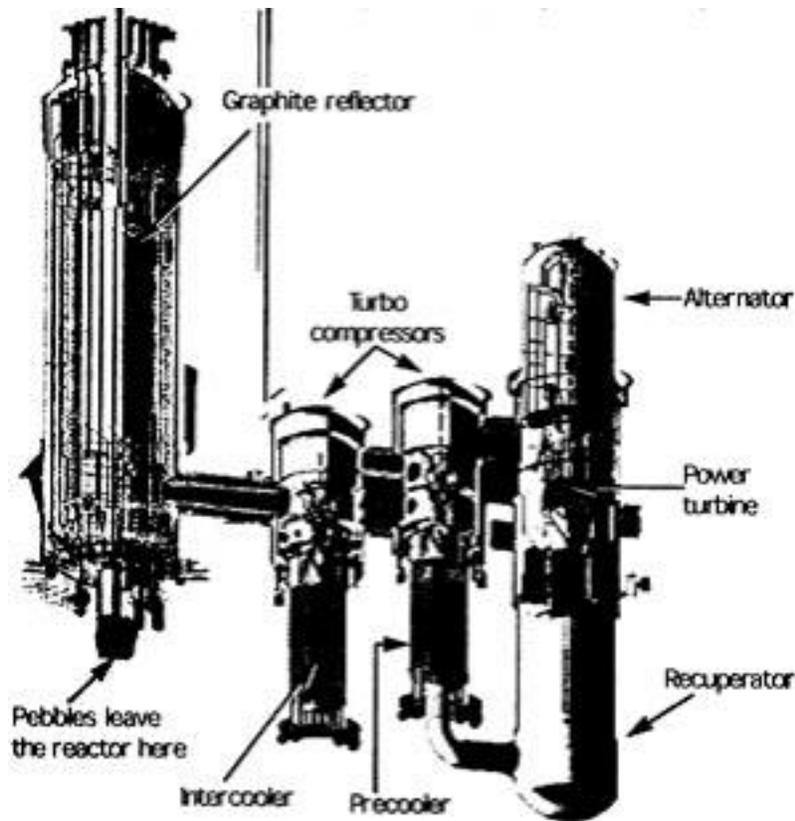
Figure 11. Diagram of the Pebble Bed Modular Reactor (PBMR).

1. The High Temperature Gas Cooled Reactor (HTGR):

Many variant of this reactor exist including the modular HTGR, a hexagonal block core design and a more recent pebble bed configuration using the Brayton gas turbine cycle rather than the Rankine steam turbine cycle. A diagram of the pebble bed reactor under consideration is shown in Fig. 11. Figure 12 shows its process flow diagram, and Fig 13 shows the composition of its spherical fuel elements.

2. Molten Salt Advanced High Temperature Reactor (AHTR):

This is a molten salt cooled reactor, which uses a coated particle graphite matrix. The low-pressure molten salt replaces the high-pressure helium coolant, which eliminates the possibility of the gas coolant depressurization accident. The operation at atmospheric pressure and the higher exit temperature of the coolant are perceived as advantages of this approach. Molten salt cooling has been considered in the past for both fission and fission-fusion hybrid reactors [7].
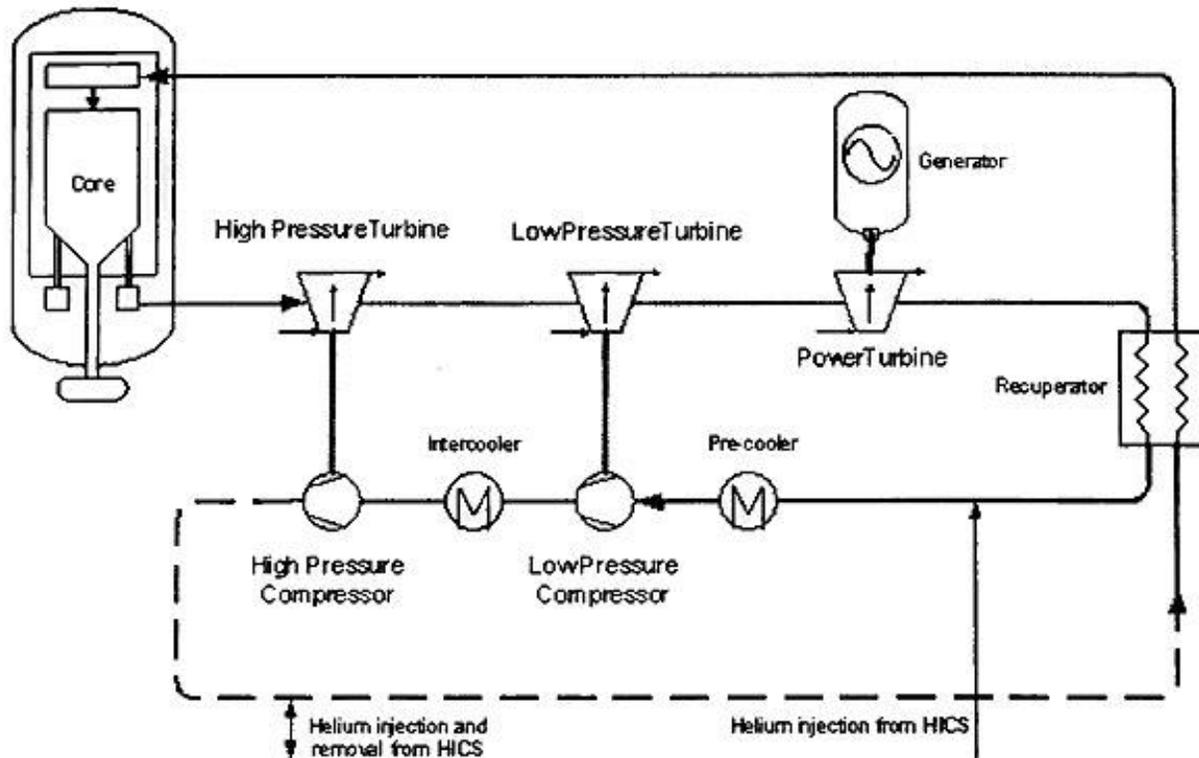
Figure 12. Flow Diagram of the Pebble Bed Modular Reactor (PBMR).

3. Lead Cooled Fast Reactor (LCFR)

Such a reactor would operate with a fast neutron spectrum since lead is not a good neutron moderator. Sodium is precluded as a coolant since it would reach its boiling point at 883 degrees Celsius close to the temperature needed for thermo chemical hydrogen production. With lead as a coolant the operational temperature is lower than that for the gas cooled systems.

HIGH TEMPERATURE ELECTROLYSIS, HTE, FOR HYDROGEN PRODUCTION

OVERVIEW

Ragheb and Salimi [2] considered the use of High Temperature Electrolysis (HTE) from fusion or fission nuclear systems intended for process heat production.

If fusion energy is used, a ceramic, molten metal or a refractory blanket could use the penetrating properties of fusion neutrons as a volumetric heat source. With suitable heat insulation, the first wall and blanket structural components can be kept at a lower temperature than the bulk blanket. Heat can then be extracted from the blanket, achieving high temperatures in the range of 2,000 $^{\circ}$C using inert gas coolants. It is thought possible to develop materials and techniques for use in thermo chemical processes around 1,500 $^{\circ}$K.

In comparison, high temperature gas cooled reactors, steam cycle heat exchangers, and fast breeder reactor material limits are in the range of 1,000 °C.

The interest is substantiated by the fact that there appears to be no shortage of technologies that can meet future electrical needs, but very limited options for supplying portable fuels in the form of hydrogen H_2 or methanol CH_3OH.

Coal conversion is costly and in the long term may be restricted by environmental and supply factors. Conversion to a hydrogen and hydrogen fuel based economy derived from inexhaustible sources has been advocated.

As a transition step, hydrogen produced in fission reactors can be used in conjunction with coal gasification and liquefaction processes. The amount of coal feed can then be reduced by a factor of 2 for liquid, and 3 for gas production, with a 2- to 3- fold reduction in the environmental pollution factors: mining hazards, release of toxic agents, and buildup of CO_2 leading to a possible global greenhouse effect.

HIGH TEMPERATURE ELECTROLYSIS, HTE

Hydrogen can be produced from water by conventional low temperature electrolysis methods, which in fact are the inverse to the fuel cell reactions. The energy required for the reaction is given by:

$$\Delta H = \Delta F + T\Delta S \tag{27}$$

where:
ΔH = energy required for water decomposition,
ΔS = entropy change,
$T\Delta S$ = necessary thermal energy,
ΔF = required electrical energy, which is equivalent to the free energy change.

This equation is plotted in Fig. 13. Note that as the temperature increases, the electrical input needed for the decomposition process decreases. This leads to an increase in the overall efficiency of the process.
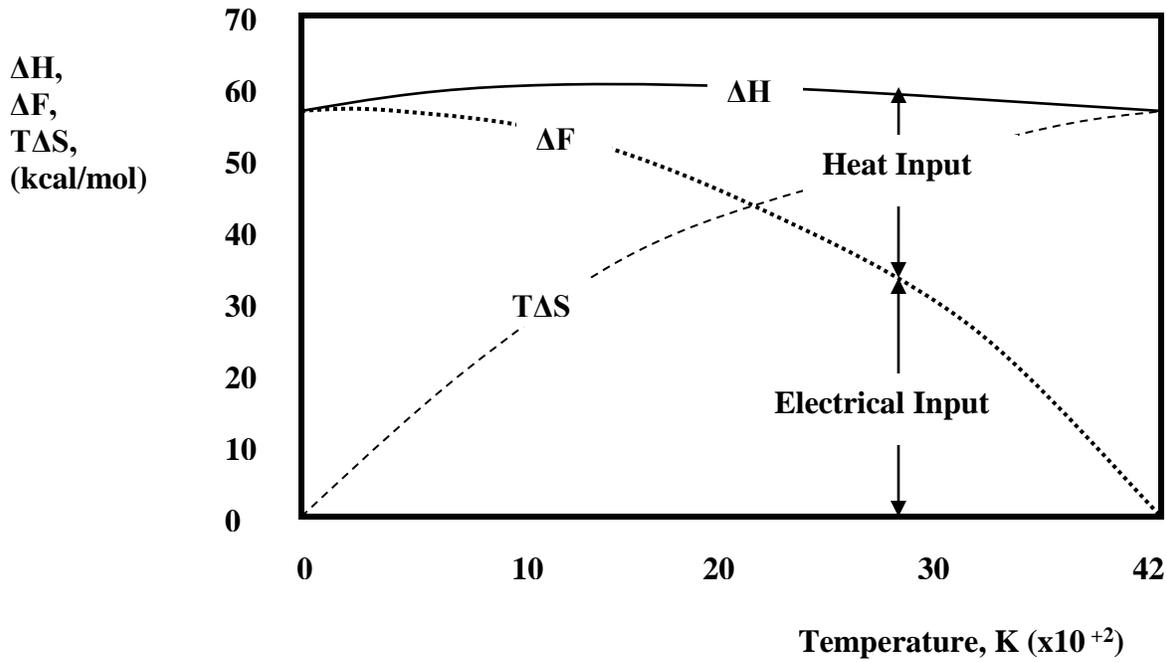
Figure 13. Energy splits for water decomposition as a function of temperature in the High Temperature Electrolysis (HTE) process [2].

Thus, High Temperature Electrolysis (HTE) is a more efficient process for hydrogen production. The electrolysis step itself offers very high efficiencies:

$$\eta_{electrolysis} > 0.90.$$

Even if a conventional electrical generating process having 40 percent efficiency is used with no voltage losses in the electrolyzer, the overall efficiency for hydrogen production at 1,400 ^{o}C can be on the order of:

$$\eta_{hydrogen} = \eta_{electrolysis} \cdot \eta_{electrical}$$
$$= 0.90 \times 0.40$$
$$= 0.36$$
$$= 36 \ percent$$

For a high efficiency electrical generating efficiency around 60 percent, the hydrogen production efficiency would be:

$$\eta_{hydrogen} = 0.90 \times 0.60$$
$$= 0.54$$
$$= 54 \; percent$$

In HTE, a large energy fraction in the range of 30-50 percent is supplied as high temperature heat, and the rest as electricity, which can be produced through a conventional thermal cycle.

THERMOCHEMICAL HYDROGEN PRODUCTION: THE IODINE SULFUR (IS) PROCESS

One can think about using methane reforming as a source of hydrogen, and using wind, solar and nuclear processes as energy sources to what is an inherently energy intensive process. However, this still releases to the environment the carbon contained in methane in the form of carbon dioxide. Achieving the advantage of a hydrogen economy should entail using water as a source of hydrogen instead of hydrocarbons like methane. This has to be set as the goal of hydrogenation, even though the system may be initially started up using methane as a source of hydrogen.
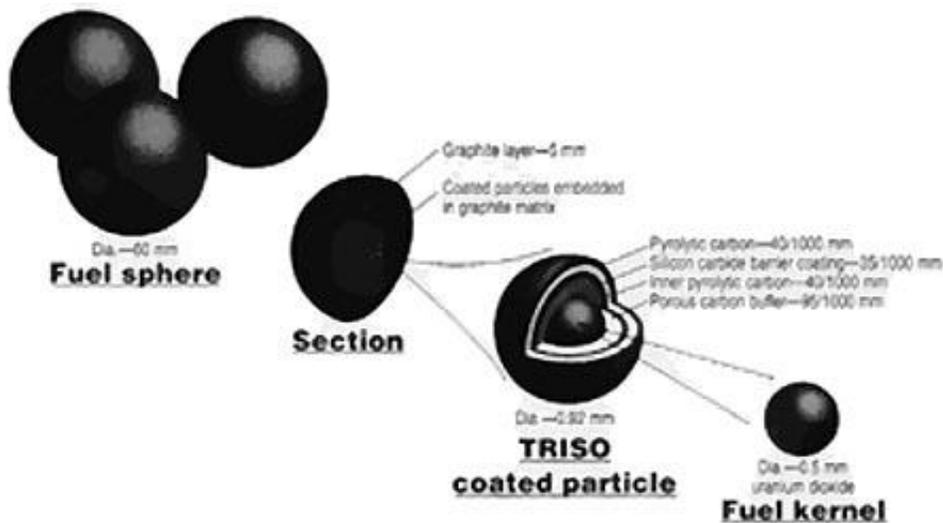
Figure 14. Fuel elements used in the Pebble Bed Modular Reactor (PBMR).

To use water as a source of hydrogen several high temperature thermo chemical processes have been suggested. The leading processes are those using sulfuric acid as a catalyst:

1. The hydrogen sulfide process,
2. The iodine sulfur process,
3. The sulfuric acid methanol process.

High temperature is needed to ensure fast chemical kinetics, resulting in high thermal efficiencies, small plant sizes and low capital costs.

In the last three processes a high temperature low pressure endothermic process involves the decomposition of sulfuric acid to produces water, oxygen and sulfur dioxide:

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2 \tag{28}$$

The last reaction is carried out at about 800-1,000 degrees Celsius for efficient hydrogen production. The oxygen is separated and low and intermediate temperature steps follow.

In the Iodine Sulfur (IS) process, iodine is added in addition to water at low temperature to the sulfur dioxide after removing the oxygen:

$$2I_2 + 2SO_2 + 4H_2O \rightarrow 4HI + 2H_2SO_4 \tag{29}$$
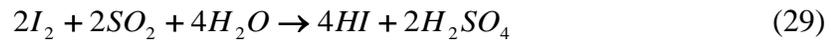
This is followed by an intermediate temperature hydrogen-producing step as:

$$4HI \rightarrow 2H_2 + 2I_2 \tag{30}$$

If we add Eqns. 28-30, we obtain the overall hydrogen producing reaction as:

$$2H_2O \rightarrow 2H_2 + O_2 \tag{31}$$

This identifies sulfuric acid and iodine as catalysts since they appear on both sides of the equations but do not appear in the final overall equation.

Research in Japan at the Japan Atomic Energy Research Institute is demonstrating the production of hydrogen at their High Temperature engineering Test Reactor (HTTR), using steam reforming of methane gas. The iodine sulfur process is under development to be tied up ultimately to the HTTR. Similar research is taking place in the USA.

Currently, thermo chemical hydrogen production processes are favored to water electrolysis which surprisingly has an efficiency of about 80 percent:

$$\eta_{electrolysis} = 0.80 \tag{32}$$

The argument that is presented is that it has to be coupled to a thermal process for the production of electrical energy that would be used in electrolyzing the water. These thermal processes have efficiencies for existing light water reactors of about 34 percent, to 50 percent for advanced gas cooled systems. Thus:

$$\eta_{electricity} = 0.34 - 0.50 \tag{33}$$

The overall hydrogen production efficiency is surmised to be the product of the two efficiencies in Eqns. 32 and 33 as:

$$\eta_{hydrogen} = \eta_{electrolysis}\eta_{electricity} = 0.242 - 0.40, \tag{34}$$

implying an overall hydrogen production efficiency of 24.2-40 percent. So unless the electrical production electricity is increased, thermo chemical processes remain the more efficient process at a projected efficiency of 50 percent. Some suggestions have been advanced of combined cycle hydrogen and electricity plants reaching an efficiency of 60 percent [3].

IMPROVING ENERGY USE EFFICIENCY

In parallel to the movement toward hydrogenation, there is a need to improve the overall efficiency of energy use. The overall efficiency of the energy system advanced from the low value of 1 percent in the year 1,000 to no more than 2 percent in the year 2,000. Current fossil fuel and nuclear electrical power plants using the steam cycle have a thermodynamic efficiency ranging from 30-40 percent. The use of the higher temperature gas turbine cycle can lead to efficiencies in the range of 50 percent. And even better, using fusion fuel cycles producing charged particles would allow the direct conversion of their kinetic energy into electricity, without the intermediate step of the heat cycle at efficiencies that can reach 70 percent.

The hydrogenation of the energy supply is expected to restart the construction of a new generation of safe nuclear fission plants, and eventually encourage the development of even safer fusion systems. This will be in addition to whatever other supplies can be provided with wind and solar energy methods.

REFERENCES

1. Jules Verne, "The Mysterious Island," 1870.
2. Magdi M. Ragheb and Behzad Salimi, "Catalyzed Deuterium-Deuterium and Deuterium-Tritium Fusion Blankets for High Temperature Process Heat Production," Nuclear Technology/Fusion, Vol. 2, pp. 55-72, Jan. 1982.
3. J. H. Ausubel, "Where is Energy Going?" The Industrial Physicist, p. 16, Feb., 2000.
4. C. W. Forsberg and K. L. Peddicord, "Hydrogen Production as a major Nuclear Energy Application," Nuclear News, p.41, Sept. 2001.
5.R. E. Graham, "Fuel cells for Transportation," Fuel Cells, 2000.
6. S. Simpson, "Coal Control," Scientific American, p.20, Feb. 2002.
7. D. Nichols, "The Pebble Bed Modular Reactor," Nuclear News, p. 35, Sept. 2001.
8. M. M. H. Ragheb, R. T. Santoro and J. M. Barnes, "Nuclear Performance of Molten Salt Fusion-Fission Symbiotic Systems for Catalyzed Deuterium-Deuterium and Deuterium-Tritium Reactor," Nuclear Technology, Vol. 48, p.216, May 1980.
9. S. Thomas and M. Zalbowitz, "Fuel Cells- Green Power," LA-UR-99-3231, Los Alamos National Laboratory, 1999.
10. E. Chen, "Solid-Oxide Fuel Cells Stack up to Efficient, Clean Power," Science and Technology Review, National Nuclear Security Administration's Lawrence Livermore National Laboratory, p. 17, Sept. 2002.
11. Jessica Li, "The Magic of MFCs: Generating Electricity from Mucky Wastewater," Science, September 2013.

EXERCISE

1. Compare the voltages generated by a single fuel cell element when it is operated at:
a. 20 °C,
b. 100 °C.
Use: $\Delta S = -163.2 \ J / K$,

   $\Delta H = -285,800 \ J$,

   F (Farady's constant) = 96,487 [Coulombs] or [Joules/Volt].
What is the implication concerning fuel cells operation?