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Scope of non conventional energy by formation of hydrogen fuel cell through utilization of microorganisms

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ABSTRACT

Solar energy conversions through the use of photosynthetic microorganisms do not incorporate the use of complex systems or large quantities of factory manufactured products, and indeed have relatively minimal investment and resource requirements. Additionally, these technologies are largely dependent on the use of renewable resources, thereby generating minimal amounts of waste. Although large amounts of solar energy are irradiated to the earth's surface, their actual utilization is pretty less. Algae-baceria biomass, small primitive green plants which abundantly grow in or near aqueous environment and are otherwise notorius and main culprits for causing microbial corrosion of steel structure can produce Hydrogen using sunlight in presence of bacteria during metabolism. Hydrogen thus generated can be utilized in fuel cell where about 548 W.h energy can be obtained out of a liter tank of hydrogen. Thus it would be a novel idea to utilize algae to create energy and simultaneously purifying the global environment by fixing CO_2 cycle of the biosphere.

INTRODUCTION

In recent years research activity in fuel cell technology has increased remarkably due to the (i) Depletion of earth fossil fuel resources (ii) Strict pollution laws for cleaner transportation fuels (iii) Restrict Petroleum import & improve Economy (iv) Reduce global warming, air pollution and offer an environmentally friendly alternative to fossil fuels. Fuel cells promise to help reduce global warming, air pollution They offer an environmentally friendly alternative to fossil fuels. In addition, unlike batteries they do not need to be recharged and consume time from the user's point of view. Approximately 5.7 x 10^{24} J /Year of solar energy are irradiated to the earth's surface but Only 10% of the energy Utilized. Hydrogen can be generated through solar energy conversion by some microorganisms from domestic renewable resources, and usable without pollution. Hydrogen fuel cells are simple, clean and can be regenerative. Algae possess an enzyme called hydrogenase that is capable of splitting water into hydrogen. Hydrogenase, the enzyme responsible for this hydrogen production can be obtained from algae and cynobacteria.

Fuel cell

A fuel cell works similar to a battery. In a battery there are two electrodes, which are separated by an electrolyte. At least one of the electrodes is generally made of a solid metal. This metal is converted to another chemical compound during the production of electricity in the battery. The energy that the battery can produce in one cycle is limited by the amount of this solid metal that can be converted. In the fuel cell an electrode that is not consumed and a fuel that continuously replenishes the fuel cell replace the solid metal. This fuel reacts with an oxidant such as oxygen from the other electrode. A fuel cell can produce electricity as long as more fuel and oxidant are pumped through it. At the anode the hydrogen molecules give up electrons and form hydrogen ions, a process which is made possible by the platinum catalyst. The electrons travel to the cathode through an external circuit, producing electrical current. The proton exchange membrane allows protons to flow through, but stops electrons from passing through it. As a result, while the electrons flow through an external circuit, the hydrogen ions flow directly through the proton exchange membrane to the cathode, where they combine with oxygen molecules and the electrons to form water.

The ideal available electrical work (assuming no losses by heat) from the electrons flowing through the circuit is

$$W_{max} = -nFE$$

where *n* is the number of equivalents, or electrons per molecule of fuel, F is the Faraday (96,493 Coulombs per equivalent) and E is the thermodynamic reversible voltage of the reaction (1.229 for this reaction) Thus,Wmax comes out as 548 W.h. So theoretically 548 W.h of enrgy can be obtained out of a liter tank of hydrogen.

As illustrated in TABLE 1, various kind of fuel cell have been developed but they are prone to problems and limitation. Most applications use expensive metal platinum as catalyst and the reaction conditions are usually harsh: high temperature and pressure, maybe strongly acidic or alkaline solutions.

TABLE 1 : Types of fuel cells

Type	Abbreviation	Operating temp	Uses
Solid Oxide	SOFC	500-1000°C	All sizes of CHP
Direct Alcohol	DAFC	50-100°C	Buses, cars, appliances, small CHP
Polymer Electrolyte	PEFC	50-100°C	Buses, cars
Phosphoric Acid	PAFC	200°C	Medium CHP
Molten Carbonate	MCFC	600°C	Large CHP
Alkaline	AFC	50-250°C	Used in space vehicles

Microbial corrosion

Before we go to the discussion of H_2 fuel cell with the help of microorganisms, it is necessary to have brief idea of corrosion caused by microorganisms. Presences of biological microorganisms aggravate corrosion, in steel structures in and around shore of lake /river or sea. Increasing problems of marine fouling of steel structures are encountered in Oil and Gas platform or hull of a ship or a pile on a jetty. A number of macro and micro-fouling organisms have been identified[1]. Moss[2] pointed that the green and brown algae are the most common ship fouling.

Gall et al. reported cathodic hydrogen consumption by sulphate reducing bacteria such as Desulfovibrio is the factor of anaerobic corrosion of metals in marine environment[3]. Both macroalgae and microalgae interact with bacteria during fouling on steel substrate in sea water[4]. Continual growth and decay of algal and other fouling organisms is a major source of nutrients for bacteria.

Photobiological hydrogen

The above-mentioned microorganisms responsible for accelerated corrosion of steel structures in or near aqueous environment may be effectively utilized to generate H2, using solar energy. Photobiological production of hydrogen involves using sunlight, a biological component, catalysts and an engineered system. Microalgae are primitive microscopic plants living in aqueous environments. Cyanobacteria, formerly known as blue-green algae, are now recognized as bacteria since the anatomical characteristics of their cells are prokaryotic (bacterial type). Algae possess an enzyme called hydrogenase that is capable of splitting water into hydrogen. Hydrogenase, the enzyme responsible for this hydrogen production, catalyses the following reaction. Under certain conditions, *a* few groups of microalgae and Cyanobacteria consume biochemical energy to produce molecular hydrogen

$$12H^+ + 2X_{reduced} \rightarrow 6H_2 + 2X_{oxidized}$$

The electron carrier, X, is thought to be ferredoxin. Since ferredoxin is reduced with water as an electron donor by the photochemical reaction, green alga are theoretically water-splitting microorganisms. Gaffron and Rubin[5] reported that a green alga, *Scenedesmus*, produced molecular hydrogen under light conditions after being kept under anaerobic and dark conditions. Asada and Kawamura[6] determined that cyanobacteria also produce hydrogen gas auto-fermentatively under dark and anaerobic conditions. *Spirulina* species were demonstrated to have the highest activity among cyanobacteria tested.. Hydrogenases have been purified and partially characterized in a few cyanobacteria and microalgae[7]. Miyake et al.[8] proposed the combined use of photosynthetic and anaerobic bacteria for the conversion of organic acids to hydrogen.. *R. Sphaeroides* has been identified as the bacterium having the highest hydrogen-producing rate (260 ml/mg/h)[9], with a photoenergy conversion efficiency (energy yielded by combustion of produced hydrogen/incident solar energy) of 7%, determined using a solar simulator[9,10].). Biological hydrogen production incorporating artificial with chloroplast, ferredoxin, and hydrogenase; a heterocystous cyanobacterial system with oxygen scavengers; and an algal system in a day-and-night cycle, have been studied in Japan[11]. H2-photoproduction depends on low potential electrons supplied to ferredoxin by the photosynthetic electron-transport chain[12,13]. Unfortunately, the reversible hydrogenase in green algae is highly sensitive to O2, (Figure 1) which irreversibly inactivates the enzyme.s activity within minutes[14]. As a consequence, the direct photoproduction of H2 from water in algal cultures is difficult to sustain. To remove O_2 under ambient outdoor conditions[15], extensive research activities are being carried out all over the world. Both chemical and mechanical methods have been developed to remove O2 produced by the photosynthetic activity of the algal cells. These have included the addition of O2 scavengers, the use of added reductants,and the purging the cultures with inert gases. However, all these methods are expensive upon scale-up and realistically may not be applicable to applied systems. To keep the cost of H2 production low, applied systems will have to operateunder ambient outdoor conditions. One of groups[16] is working to generate *Chlamydomonas reinhardtii* mutants that are sufficiently tolerant to O2 to produce H2 under aerobic conditions by means of both classical genetic and molecular biology approaches. By cloning of *Chlamydomonas reinhardtii*, two genes Hyd A and Hyd B clones were produced (Figure 2). The H2 production activity of the mutants showed up to 9 times higher tolerance to O2 when compared to the parental strain (TABLE 2). Another group achieved continuous photoproduction of large volumes of H2 by down-regulating O2 evolution activity in algal cells[17] by temporarily depleting the cells of sulfur. Green algae were subjected to the cultures to sulfur (in the form of sulfate) depleted conditions. Under these conditions, the cells induce the reversible hydrogenase and produce H2 for up to 4 (Figure 2)[18]. A metabolic switch that triggers algae to turn sunlight into large quantities of hydrogen gas, a valuable fuel, is the subject of a new discovery presented by University of California, Berkeley, scientists Dr. T Melis and their Colorado colleagues during a February 21, 2000. The key discovery was that depriving the algae of inorganic sulfur reversibly inactivated the functioning of what's known as photosystem II, which includes the generation of oxygen. Without sulfur, the metabolic pathways change, enabling the algae to function without generating oxygen. After about 24 hours of sulfur deprivation, the plant becomes anaerobic, activating an enzyme that produces hydrogen in the light. Without sulfur, "they're utilizing stored compounds and bleeding hydrogen just to survive," said Melis. "It's probably an alternative form of breathing, an ancient strategy that the organism developed to live in sulfur-poor anaerobic conditions. Normally, algae cells use light's energy to perform photosynthesis which makes sugar, oxygen and the high-energy molecule ATP (adenosine triphospate) from carbon dioxide and water. ATP in turn is a key ingredient in the plant's ability to carry out vital functions, including cellular maintenance, repairs and essential biosynthetic processes in the absence of normal photosynthesis due to the lack of sulfur and absence of respiration due to the lack of oxygen. Under those conditions, every other organism would normally suffocate, explains Melis. These green algae, however, have a trick: they activate the alternative pathways that permit them to generate ATP, giving off hydrogen as the end product of the alternative process. Melis and his colleagues have demonstrated that the hydrogen-producing enzyme stays active for days, producing hydrogen in the light in a sustainable process. The microorganisms helping H2 production through photosynthesis are of two classes Algae and Cynobacteria (TABLE 3). Algae are the photoautotropic, eukarytic soil microorganisms. They habitat in wet soil and shallow water (Figure 3 & 4). They can be separated and cultured in the laboratory. Cynobacteria (blue-green algae) are also photo autotrophic, nitrogen fixing prokaryotes occurring throughout the world and growing in a diversified habitat (Figure 3). They are found in rice field and soil. TABLE- illustrates some of the characteristics of them. We have been studying on formation and characterization of Bioelectrochemical fuel cell using different classes of algaue collected from rural pond and rice field. One of types of algae, known as Chlorophyceae (green algae), found in clean surface pond water gave potential as high as 750 mV in a single cell[19,20].

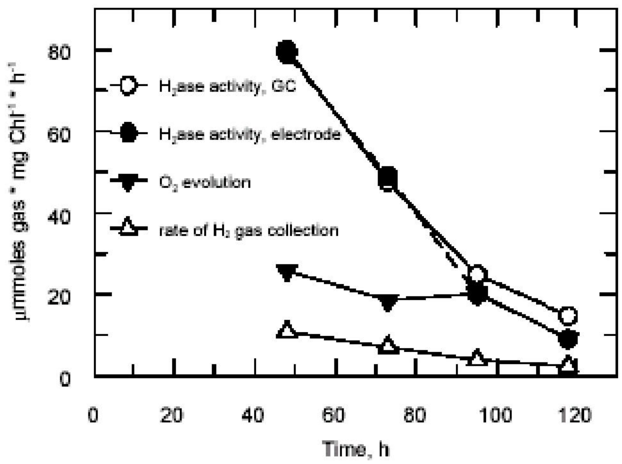

Figure 1 : Measurements of hydrogenase activity, capacity for photosynthetic O2 evolution and the rate of H2 gas collection by algal cells as a function of incubation time under sulfur-depleted conditions.µmmoles gas * mg Chl-1 * h-1

Hydrogen separation & storage

Metal hydrides can absorb hydrogen selectively and reversibly. They are ideal for use in hydrogen separation. A special group of metals and metal alloys can react with hydrogen reversibly under moderate conditions, like room temperature and atmospheric hydrogen pressure. The reaction product is a metal hydride. The term metal hydride has been used loosely to mean both the metal and the product. Examples are palladium and La-Ni-Al alloys. Their reactions may be expressed as follows:

- $\mathbf{Pd + x/2H2 = PdHx + heat (x = 0 to 1)}$
- $\mathbf{LaNi4.25Al0.75 + x/2H2 = LaNi4.25Al0.75Hx}$ $\mathbf{(x = 0 to 6)}$

For hydrogen separation, metal hydrides can be applied in a temperature swing absorption (TSA) process. In a typical TSA process,(Figire 5) the metal hydride is packed in a jacketed column (18). The jacket can be heated and cooled to swing the column temperature. During the absorption phase of a cycle, the column is cooled and the mixture to be separated is fed into one end of the column. Hydrogen in the mixture is absorbed by the metal hydride. The other gases simply pass through the column and can be discharged as waste. When the metal hydride in the column is saturated with hydrogen, the feed is stopped, and the column is heated to discharge the hydrogen. High purity hydrogen can be produced.

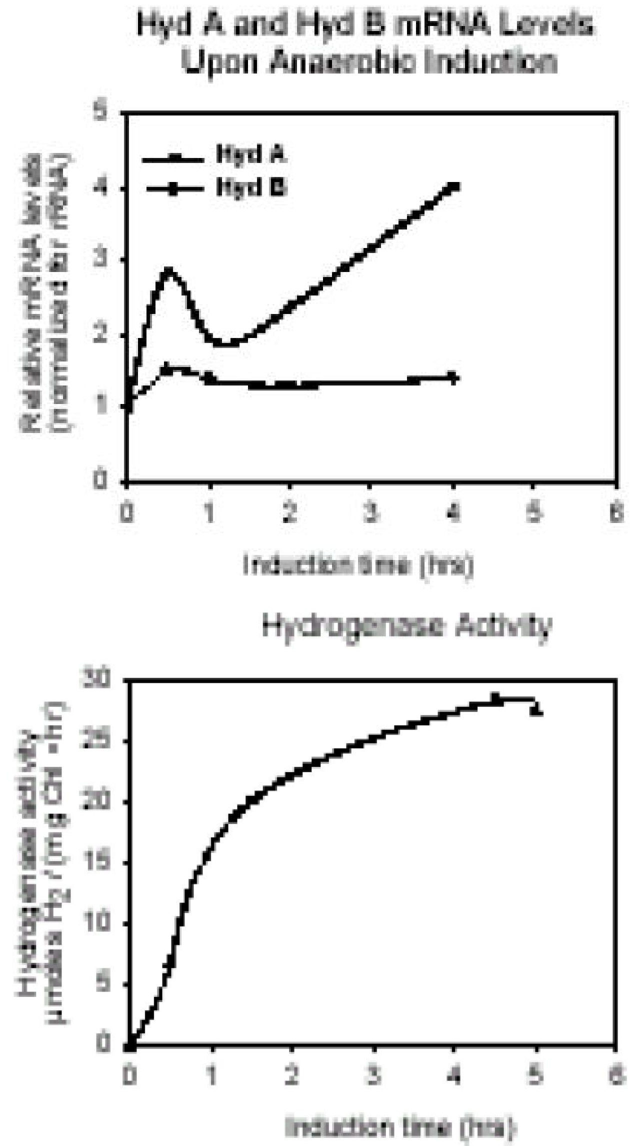

Figure 2 : Quantitation of mRNA levels of Hyd A and Hyd B upon anaerobic induction of *C. reinhardtii* cells (A) and overall hydrogenase activity

The high porosity of these gels (Figure 6) provides many paths for hydrogen gas to reach the encapsulated metal hydride particles. The pore size can also be controlled to screen out impurities other than hydrogen. These possibilities have been studied in an earlier project. Findings of that work have been published (Heung, 1999).

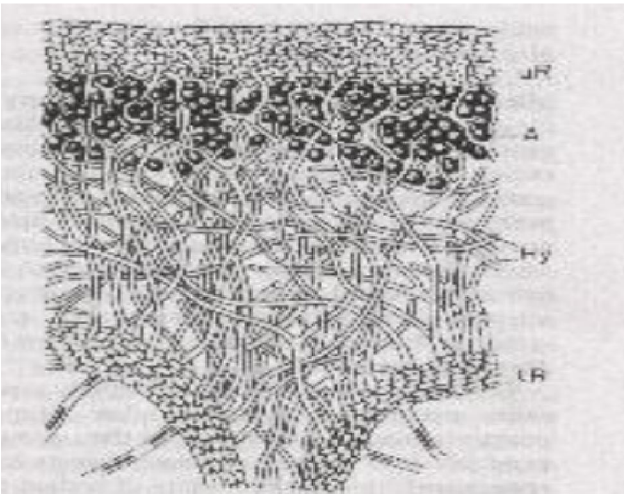

Figure 3 : Algae mixed with other bacteria

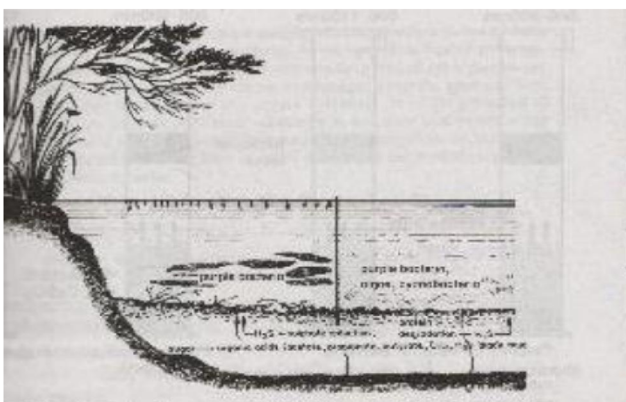

Figure 4 : Algae, cynobacteria at edge of lake

Microboial fuel cell

Having obtained pure hydrogen, it can be used in fuel cell to generate electricity. But here instead of Chemical fuel cell, a biological cell will be more advantageous and economic (TABLE 4). A biological fuel cell is a device that directly converts biochemical energy into electricity. The driving force of a biological fuel cell is the redox reaction of a carbohydrate substrate such as glucose and methanol using a microorganism or an enzyme as catalyst. Working principle is similar to that of chemical fuel cells. The main differences are that catalyst in the biological fuel cell is microorganism or enzyme, therefore noble metal is not needed, and its working conditions are mild: neutral solution and room temperature.

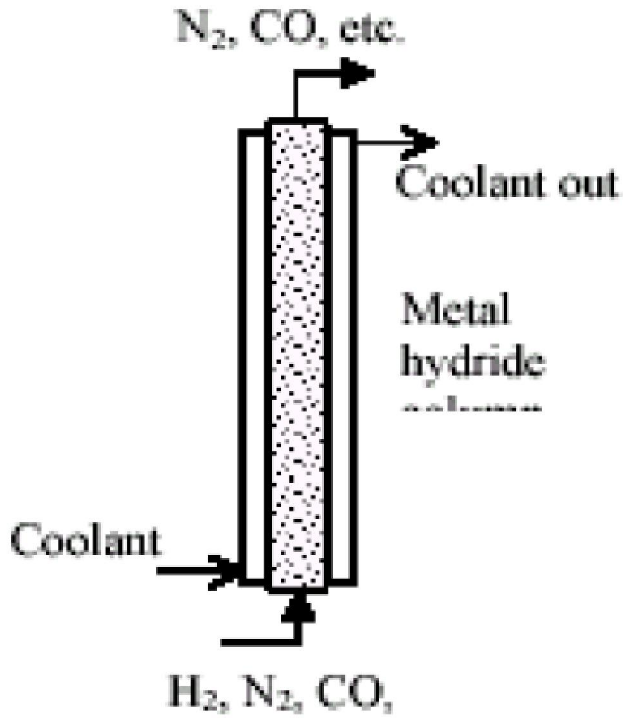

Figure 5 : Hydrogen separation column

Figure 6 : Sol-Gel encapsulation of metal

Finally when three units, photobiological H2 production, its purification and storage and a Biological fuel are assembled together (Figure 7), it produces promising alternative renewable energy from biomass using sunlight. In the future, both small-scale industrial

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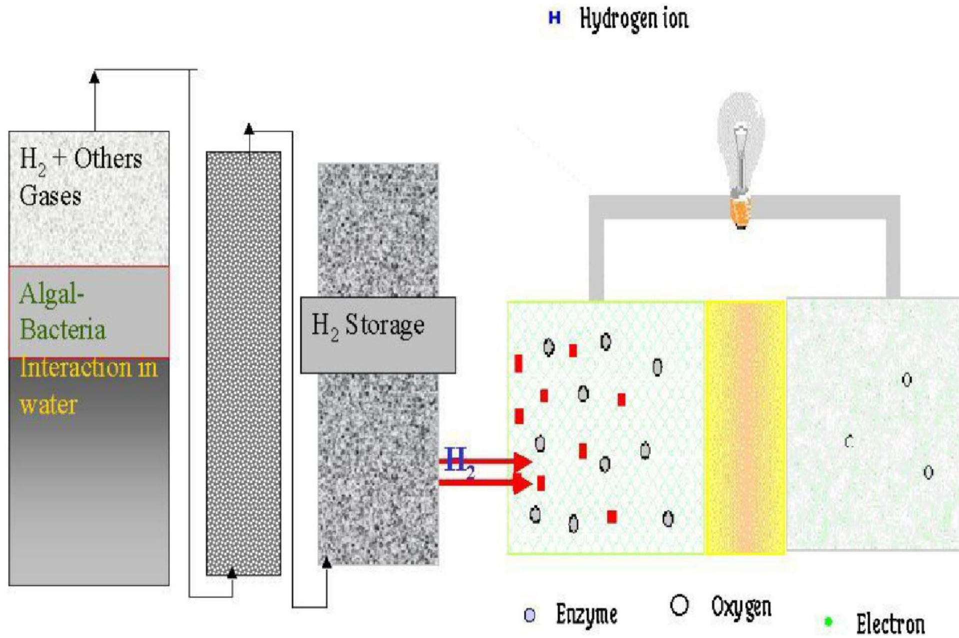

Figure 7 : Photobiological H2 production, its purification and storage and a Biological fuel are assembled together

TABLE 2 : Kinetic parameters for H2 photoproduction by sulfur-depleted algal cells

Sulfur concentrationa, µM	Start of the anaerobic phase, h	Start of H2 the photoproduction, h	Specific initial rate of H2 photo-production[1]	Total yield oh H2 at 140 h
Synchronizaed cultures				
0	25-27	39-43	3.27 ± 0.83[2]	80 ± 31
12.5	35-36	38-39	5.15 ± 0.26	219 ± 43
25	35-38	38-41	5.94 ± 0.56	241 ± 56
50	35-37	39-40	3.96 ± 0.30	109 ± 9
100	-	68[3]	-	56[3]
Unsynchronizaed cultures				
0	31-40	41-49	5.74 ± 0.30	86 ± 19
12.5	30-37	39-47	6.40 ± 0.39	127 ± 14
25	35-37	44-47	5.31 ± 0.16	152 ± 11
50	32-38	43-49	3.99 ± 0.26	191 ± 27
100	-	144[3]	-	43[3]

TABLE 3 : Some of the hydrogen producing microorganisms

Species	Class	Shape	Source
Scenedesmus	Green Algae	Ellipsoidal, fusiform	Ponds & Lakes
Spirulina	Cyanobacteria	Helical screw	Brackish water inland Lakes & Hot springs
Chlamydomonas reinhardtii	Green Algae	Rod shape	Wet soil, marine water, lake
Nostoc	Cyanobacteria	Cylindrical, spherical	Fresh water lake

TABLE 4 : General characteristics of chemical and biological fuel cell

Items	Chemical Fuel Cell	Biological Fuel Cell
Catalyst	Noble Metals	Microorganism / enzyme
pH	Acidic Solution (pH<1)	Neutral Solution pH 7.0-9.0
Temperature	over 200°C	Room Temperature 22-25°C
Electrolyte	Phosphoric-acid	Phosphate Solution
Capacity	High	Low
Efficiency	40 - 60 %	over 40 %
Fuel Type	Natural gas, H_2, etc.	Any Carbohydrates and hydrocarbons

and commercial operations and larger utility photo bioreactor complexes can be envisioned using this process. India being an agriculture based country produces huge biomass, research activities should be directed for further development of this process to minimize expensive petroleum import and upgrade country's economy.

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