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Bioproduction of Hydrogen with the Assistance of Electrochemical Technology

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1. Introduction

The depletion of fossil fuel diverts us to the use of renewable resources as the supplement for fuel. Solar, hydroelectric power and microbial system are known to be abundant renewable resources for fuel production. Hydrogen has a energy yield of 122 kJ/g, which is 2.75 times greater than hydrocarbon fuels (Kapdan & Kargi, 2006). Hydrogen together with oxygen is the key element in the biological energy cycle on the earth. In all organic matter hydrogen atoms are bound to carbon, nitrogen, sulphur and other elements.

Biological processes for the production of hydrogen, which are environment-friendly and less energy intensive, may be categorized into bio-photolysis, photo-fermentation and dark fermentation. Bio-photolysis occurs in organisms such as green algae or cyanobacteria, which carry out plant-type photosynthesis, using captured solar energy to split water. Non-sulphur purple photosynthetic bacteria undergo photo-fermentation to perform an anaerobic photosynthesis. By dark fermentation, a variety of different microbes anaerobically breaks down carbohydrate rich substrates to hydrogen and by-products (Das & Veziroglu, 2001; Hallenbeck & Benemann 2002). Gaseous hydrogen is produced as well as consumed by living microorganisms in the presence or absence of oxygen (under both oxic and anoxic conditions). The anoxic condition is observed during dark fermentation of microbes.

Among the processes, dark fermentation presents a high rate of hydrogen production, using fermentative bacteria, such as *Enterobacter* species (Palazzi et al., 2000; Kumar & Das, 2000; Kumar & Das, 2001; Nakashimada et al., 2002; Kurokawa &Tanisho, 2005; Zhang et al., 2005; Shin et al., 2007), *Clostridium* species (Chin et al., 2003; Lee et al., 2004; Levin et al., 2006; Jo et al., 2008) and *Escherichia coli* (Yoshida et al., 2005). Hydrogen production through bacterial fermentation is currently limited to a maximum of 4 moles of hydrogen per mole of glucose, and under these conditions results in a fermentation end product (acetate; 2 mol/mol glucose) that bacteria were unable to further convert to hydrogen. Thermophiles produced up to 60–80% of the theoretical maximum, demonstrating that higher hydrogen yields can be reached by extremophiles than using mesophilic anaerobes (Chin et al., 2003). The oxidative pentose phosphate pathway as an alternative metabolic route exists for example in microalgae, which can produce stoichiometric amount of H_2 from glucose. However, this pathway is usually not functional for energetic reasons (Lee et al., 2004).

Several problems still remain for the commercial scale production of bio-hydrogen including low hydrogen yield. Alternatively the by-products are to be used by

microorganisms or by bioelectrochemical technology, so that higher moles of hydrogen may be produced.

Electrolysis is a method of separating bonded elements and compounds by passing an electric current through them. One important use of electrolysis is to produce hydrogen, which has been suggested as an energy carrier for powering electric motors and internal combustion engines. All electrolysers work according to a principle of two electrodes separated by an electrolyte. A so-called half cell reaction resulting in the formation of hydrogen and oxygen respectively takes place at each electrode. The role of the electrolyte is to close the electrical circuit by allowing ions (but not electrons) to move between the electrodes.

Bioelectrochemically assisted microbial system has the potential to produce 8-9 mol H_2/mol glucose (Liu et al., 2005). Hence, the hybrid technology is an alternative for the production of hydrogen with higher efficiency.

2. Hydrogen production using microbial systems

Different microorganisms participate in the biological hydrogen generation by using photofermentation or dark fermentation such as green algae, microalgae and bacteria, as shown in Table 1.

2.1 Major enzymes for metabolizing and producing hydrogen

The enzymes catalyzing the formation and the oxidation of hydrogen are collectively called hydrogenases. The enzyme reaction is represented by Equation 1:

$$H_2 \longleftrightarrow 2H^+ + 2e^- \quad (1)$$

In spite of many similarities between the hydrogenases their catalytic and physicochemical properties vary widely. There are three fundamentally different hydrogen producing and metabolizing enzymes found in algae and bacteria (Schlegel & Schneider, 1978):

- reversible or classical hydrogenases,
- membrane-bound hydrogenases, and
- nitrogenase enzymes

Hydrogenase can be differentiated with respect to their position in electron transport systems and their location in the cell. The natural electron donor/acceptor is known only for the soluble, cytoplasmic or loosely bound periplasmic enzymes. For the membrane-bound hydrogenases this information is incomplete or lacking. Details of types and properties of hydrogenases are presented in the literature (Schlegel & Schneider, 1978; Adams et al., 1981). A compilation of papers on function and structure of hydrogenases has been published (Yagi, 1981). Nitrogenase is also responsible for hydrogen evolution by many bacteria. Hence, hydrogenases and nitrogenases possessing microbes can produce hydrogen by their metabolic pathways (Schlegel & Schneider, 1978).

2.1.1 Reversible hydrogenases

The reversible hydrogenase is located at the cytoplasmic membrane (Kentemich, 1991). It has the dual function of catalysing hydrogen evolution and hydrogen uptake (Lambert & Smith, 1981). It has been suggested that this enzyme functions as a valve for low potential electrons generated during the light reaction of photosynthesis, thus preventing the slowing

Broad classification	Microorganisms	Enzymes Involved
Green algae	*Scenedesmus obliquus*	Hydrogenase
	Chlamydomonas reinhardii	
	C. moewusii	
Cyanobacteria Heterocystous	*Anabaena azollae*	Nitrogenase
	Anabaena CA	
	A. variabilis	
	A. cylindrical	
	Nostoc muscorum	
	N. spongiaeforme	
	Westiellopsis prolifica	
Cyanobacteria Nonheterocystous	*Plectonema boryanum*	Nitrogenase
	Oscillotoria Miami BG7	
	O. limnetica	Nitrogenase, Membrane-bound hydrogenase
	Synechococcus sp.	Nitrogenase
	Aphanothece halophytico	
	Mastidocladus laminosus	
	Phormidium valderianum	
Photosynthetic bacteria	*Rhodobater sphaeroides*	Nitrogenase, Membrane-bound hydrogenase
	R. capsulatus	
	R. sulidophilus	
	Rhodopseudomonas sphaeroides	
	R. palustris	
	R. capsulate	
	Rhodospirillum rubnum	
	Chromatium sp. Miami PSB	
	Chlorobium limicola	
	Chloroexu aurantiacus	
	Thiocapsa roseopersicina	
	Halobacterium halobium	
Fermentative bacteria	*Enterobacter aerogenes*	Hydrogenase
	E. cloacae	
	Clostridium butyricum	
	C. pasteurianum	
	Desulfovibrio vulgaris	
	Magashaera elsdenii	
	Citrobacter intermedius	
	Escherichia coli	

Table 1. Microorganisms used for hydrogen generation (Gest, 1954; Das & Veziroglu, 2001)

down of the electron transport chain (Appel, 2000). It is available in the majority of the nitrogen-and non-nitrogen-fixing cyanobacteria (Eisbrenner, 1978). Reversible hydrogenase is a heterotetrameric, NAD-reducing enzyme, consisting of a hydrogenase (encoded by hoxY and hoxH genes) and a diaphorase part (encoded by hoxF and hoxU genes).

2.1.2 Uptake hydrogenases

Uptake hydrogenase is located at the cytoplasmic face of the cell membrane or thylakoid membrane, where it uses hydrogen evolved by nitrogenase. There is a considerable loss of energy through the production of hydrogen during nitrogen fixation. Some of this energy can be regained through the action of uptake hydrogenase. This enzyme splits the hydrogen and feeds the electrons back into the electron-transport chain. The reduction of a substrate with a relatively high redox potential like cytochrome through this hydrogenase seems to be a wasteful process. But since nitrogen-fixing cells maintain a highly reducing environment, it seems necessary to use part of the reductive power of hydrogen and saving reducing equivalents. Hydrogen-using uptake hydrogenase has several functions:

- It serves as one of the mechanisms to protect oxygen-sensitive nitrogenase (Robson & Postgate, 1980).
- It generates ATP in the hydrogen-dependent respiratory oxygen uptake (Knallgas or oxyhydrogen reaction) and
- It provides additional reducing equivalents to photosystem-I.

Uptake hydrogenase has been found in all heterocystous cyanobacteria and in some non-heterocystous cyanobacteria (Peschek, 1979). The structural genes encoding cyanobacterial uptake hydrogenases have been sequenced and characterized in only a few strains (Axelsson, 1999). The large subunit of the enzyme is encoded by hupL genes and small subunit is encoded by hupS genes. In the organisms studied so far, there is a high degree of homology in the gene sequence of hupSL (Tamagnini, 1997). However, the mode or rearrangement of the genes varies from one organism to another (Axelsson, 1999).

2.1.3 Nitrogenase

All nitrogenases studied so far are catalysts for H_2 production as they liberate H_2 during the reduction of nitrogen to ammonia. A minimum of 25% of the electron flux through nitrogenase is used in the reduction of protons to H_2.

$$8H^+ + 8e^- + N_2 + 16\ ATP \longrightarrow 2\ NH_3 + H_2 + 16ADP + 16Pi \quad (2)$$

ATP, reductant and electrons are provided by photosynthesis or by degradation of sugars in cyanobacteria. Nitrogenase is a metalloenzyme complex consisting of dinitrogenase (MoFe protein: $\propto 2\beta 2$) and dinitrogenase reductase (Fe protein: $\gamma 2$). The Mo-Fe protein or component-I is a larger component is responsible for the catalytic reduction of substrate molecules. The Mo-Fe protein from all sources examined are O_2 labile, have molecular weights of approximately 220,000 daltons. Approximately 2 mol of molybdenum and 24±32 mol of iron and sulphide are found per mol of protein (Kim & Rees, 1994). The second protein dinitrogenase reductase or component II accepts electrons from donors such as ferredoxin or flavodoxin, or dithionite and transfers these electrons to dinitrogenase with the concomitant hydrolysis of two molecules of ATP per electron transferred. The six electron reduction of N_2 to $2NH_3$, therefore requires a minimum of 12 ATP molecules making nitrogen fixation an energetically expensive process. The Fe protein is also O_2 labile

and has an average molecular weight of about 60,000 daltons. The protein consists of two subunits of equal weight (Kim & Rees, 1994). In addition to reducing nitrogen to ammonia, dinitrogenase can reduce a number of substrates such as protons, acetylene, cyanide, nitrous oxide and azide. Apart from the conventional molybdenum-based nitrogenase, an alternative vanadium-based nitrogenase has also been reported (Kentemich, 1988). *A. variabilis* can express a third nitrogenase when grown under vanadium and molybdenum deficiency (Kentemich, 1991). This nitrogenase contains vanadium in the prosthetic group. A novel mutant of Azotobacter which has a tungsten-based nitrogenase has also been isolated (Kajii, 1994). In photosynthetic bacteria and cyanobacteria, photohydrogen production is mainly associated with nitrogenase rather than hydrogenase and coupled with ferredoxin or flavodoxin (Kosaric & Lyng, 1988). It requires ATP and is inhibited by N_2 or NH_4. In this case, ferredoxin is reduced (1) directly by a light-driven reaction, (2) indirectly by ATP-driven reversed electron transport, or (3) by dehydrogenation or oxidative de carboxylation reactions of intermediary metabolism not involving electron transport chains (Kosaric & Lyng, 1988). Nitrogenase is an extremely common, if not universal, enzyme in photosynthetic bacteria (Stewart, 1973). It is difficult to ascertain its prevalence in cyanobacteria since oxygenic photosynthesis in these microbes is inherently incompatible with the nitrogenase protein. Cyanobacteria have evolved several mechanisms to overcome the O_2 incompatibility of nitrogenase.

2.2 Genetic engineering aspects of biohydrogen production

Genetic engineering is the transfer of genes of interest from one organism into other known organism for its ease of culturing and its efficient metabolic activity. Usually *E.coli* is considered as the universal host and it is consequently well characterized for harbouring the foreign genes. Especially for hydrogen, *E. coli* possesses different membrane-bound hydrogenases under specific conditions: the two enzymes are hydrogenase 3(Hyd-3) and hydrogenase 4(Hyd-4) responsible for hydrogen gas production as well as hydrogenase 1 (Hyd-1) and hydrogenase 2 (Hyd-2) responsible for hydrogen uptake. The entire gene regulation in *E.coli* for hydrogen production is shown in Fig. 1. *E. coli* cells convert glucose to various organic acids (such as succinate, pyruvate, lactate, formate, and acetate) to synthesize energy and hydrogen from formate by the formate hydrogen-lyase (FHL) system that consists of hydrogenase 3 and formate dehydrogenase-H. Bacterial strain, *E.cloacae* IIT-BT 08 was isolated and characterized shown enhancement in biohydrogen production (Kumar & Das, 2000). The gene [Fe]-hydrogenase encoding gene isolated from *E.cloacae* IIT-BT 08 has been over-expressed in fast growing non-hydrogen producing *E.coli* BL-21 using pGEX 4T-1 vector (Mishra, 2004). Hence genetic engineering helps in the effective production of hydrogen.

2.3 Biohydrogen production using phototrophic microorganisms

Photosynthetic bacteria can use small-chain organic acids as electron donors for the production of hydrogen at the expense of light energy. In such a system, anaerobic fermentation of carbohydrates (or organic wastes) produces intermediates such as low-molecular hydrogen by photosynthetic bacteria in the second step using a photobioreactor (Nath & Das, 2004). Complete degradation of glucose to hydrogen and carbon dioxide is impossible by anaerobic digestion. However, photosynthetic bacteria could use light energy to overcome the positive free energy of the reaction (bacteria can utilize organic acids for

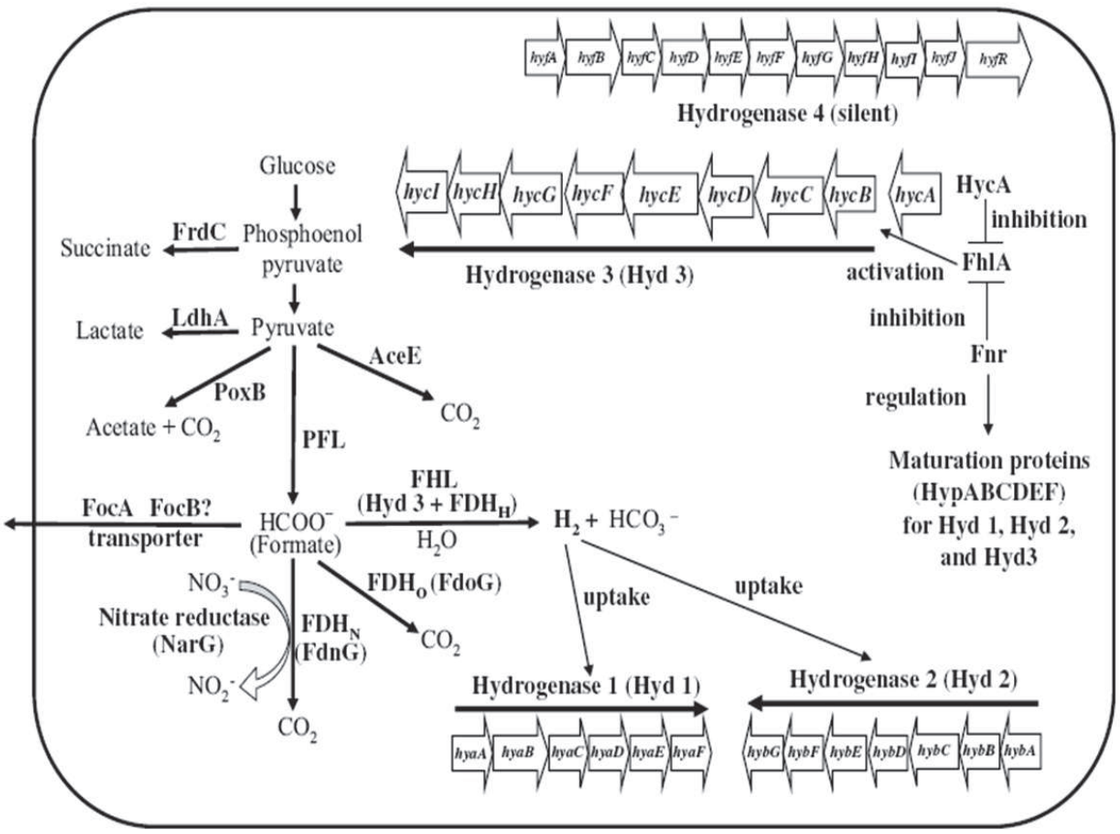


Fig. 1. Schematic of fermentative hydrogen production in E. coli (Vardar-Schara, 2008).

hydrogen production) (Das & Veziroglu, 2001). The conversion of malate and lactate to hydrogen by photosynthetic bacteria (mainly purple non-sulphur bacteria) has been documented (Koku, 2002; Kondo, 2002). Cyanobacteria are using two sets of enzymes to generate hydrogen gas (nitrogenase and hydrogenase). Hydrogen photo evolution catalyzed by nitrogenases or hydrogenases (Wünschiers et al., 2003) can only function under anaerobic conditions due to their extreme sensitivity to oxygen. Since oxygen is a by-product of photosynthesis, organisms have developed the following spatial and temporal strategies to protect the enzyme from inactivation by oxygen (Linus Pauling, 1970; Lopes Pinto, 2002). These factors can be arranged into two categories: environmental factors (light, temperature, atmosphere, nutrient availability) and intrinsic factors (genetic or certain sensitive proteins) (Beral & Zapan, 1977). Genetic engineering has made possible in cyanobacteria for effective hydrogen production (Theil, 1994). The strategies and regulatory studies of enzymes responsible for biohydrogen production in cyanobacteria was well characterized (Hansel & Lindblad, 1998). Cyanobacterial hydrogen production is not rapid which can be circumvented by combining electrochemical technology for higher efficiency of hydrogen production.

3. Hydrogen production by fermentative bacteria using acids

Clostridium diolis JPCC H-3 was obtained from soil and it is capable of producing hydrogen from slurry solution having acetic and lactic acid at higher rates compared with other isolated *clostridium* spp. Maximum hydrogen production by *C.diolis* JPCC H-3 of 6.03±0.15

ml from 5 ml of slurry solution was achieved at pH 6.8 and 40°C (Matsumoto & Nishimura, 2007). *E. coli* produces hydrogen from formic acid with high productivity. Formic acid can be derived from biomass or carbon monoxide plus methanol. Bio-hydrogen production from formic acid by facultative anaerobe is catalyzed by formate hydrogen lyase (FHL) (Das & Veziroglu, 2001; Bagramyan & Trchounian, 2003; Sawers, 2005; Vardar-Schara, 2008). The direct decomposition of formic acid into H_2 and CO_2 by FHL would provide a high hydrogen production rate without the generation of by-products except CO_2. *Enterobacter* species have a higher potential for hydrogen production than *E. coli* (Das & Veziroglu, 2001). However, hydrogen production from formic acid by *Enterobacter* species has not been studied. It was reported that the hydrogen production by FHL-1 system in *E. coli* was also active only at acidic pH and high formic acid concentration (Bagramyan et al., 2002). Although acids are used by bacteria, hydrogen production is not same as that of stoichiometric yield. Hence, this biochemical barrier can be overcome by generating hydrogen gas from acids using electrochemical technology.

4. Electrochemical technology

4.1 Electrolysis

Many different types of electrolysis cells have been proposed and constructed. The different electrolysis cells can be divided into groups based on the electrolyte which capable of using H_2O as reactant to produce H_2. However, only the solid oxide cell is capable of using CO_2 to produce CO (Table 2).

Types	Alkaline	Acid	Polymer electrolyte	Solid oxide
Charge carrier	OH^-	H^+	H^+	O^{2-}
Reactant	Water	Water	Water	Water, CO_2
Electrolyte	Sodium or Potassium hydroxide	Sulphuric or Phosphoric acid	Polymer	Ceramic
Electrodes	Nickel	Graphite with Pt, polymer	Graphite with Pt, polymer	Nickel, ceramics

Table 2. Types of electrolysis cells (Vendt, 1990)

Generally, the electrolysis cell consists of two electrodes and an electrolyte. The electrolyte may be a liquid (alkaline or acid) or a solid (polymer electrolyte or solid oxide). It serves to conduct ions (the charge carrier) produced at one electrode to the other. There has been a great deal of research in splitting water to make hydrogen and oxygen; in fact its commercial uses date back to the 1890s (Norbeck et al., 1996). Water splitting in its simplest form uses an electrical current passing through two electrodes to break water into hydrogen and oxygen. Commercial low temperature electrolyzers have system efficiencies of 56–73% (70.1–53.4 kWh/kg H_2 at 1 atm and 25°C) (Turner et al., 2008). It is essentially the conversion of electrical energy to chemical energy in the form of hydrogen, with oxygen as a useful by-product using proton exchange membrane (PEM) (Grigoriev et al., 2006; Norbeck et., 1996; Pettersson et al., 2006). Currently, electrolysis is more expensive therefore if non-renewable

power generation is used to make the electricity for electrolysis, and results in higher emissions compared to natural gas reforming (Bradley, 2000; Janssen et al., 2004). Several approaches have been addressed these shortcomings. These include using renewable sources of energy such as solar, wind, and hydro, to produce the electricity (Janssen et al., 2004; Koroneos et al., 2004) or excess power from existing generators to produce hydrogen during off-peak times (Yumurtaci & Bilgen, 2004). Since water needs high electrical energy for its electrolysis, use of weak acids or dilute acids which are obtained from wastes or by-products can be electrolyzed for supplementing hydrogen demands using low electrical appliances.

4.2 Electrohydrogenesis

Electrohydrogenesis is a recently developed electrolysis method for directly converting biodegradable material, organic acids into hydrogen using modified microbial fuel cells (MFCs) (Liu et al., 2005; Rozendal et al., 2006; Ditzig et al., 2007; Cheng & Logan, 2007; Rozendal et al., 2008;). In fact, these types of cells are rather versatile and have been shown to be able to generate hydrogen from a variety of substrates, including some wastewaters (Ditzig et al., 2007). The open circuit potential of ~ -300mV is needed for the electrolysis of acetate, if hydrogen is produced at the cathode; the half reactions occurring at the anode and cathode are as follows:

Anode:

$$C_2H_4O_2 + 2H_2O \longrightarrow 2CO_2 + 8e^- + 8H^+ \quad (3)$$

Cathode:

$$8H^+ + 8e^- \longrightarrow 4H_2 \quad (4)$$

Producing hydrogen at the cathode requires a potential of at least E° = -410mV (NHE) at pH 7.0. This voltage is substantially lower than that needed for hydrogen derived from the electrolysis of water, which is theoretically 1210mV at neutral pH. In practice, 1800-2000mV is needed for water hydrolysis (under alkaline solution conditions) due to overpotential at the electrodes (Liu et al., 2005). Hence electrolysis of acids requires less electrical energy compared to electrolysis of water.

4.3 Types of ion exchange membranes

A thin sheet or film of ion-exchange material which may be used to separate ions by allowing the preferential transport or either cations (in the case of a cation-exchange membrane) or anions (in the case of an anion exchange membrane). If the membrane material is made from only ion-exchanging material, it is called a homogeneous ion-exchange membrane. If the ion-exchange material is embedded in an inert binder, it is called a heterogeneous ion-exchange membrane. The difference between anion and cation exchange membrane are summarized in Table 3. The cation exchange membrane based on fluorinated polymer and sulfonic acid group is used as major membrane for PEMFC because of the excellent proton conductivity and durability. On the other hand, AEM based on quaternary ammonium group and hydrocarbon polymer backbone has been considered to have low thermal durability and low OH^- conductivity under the condition of fuel cell (Gasteiger et al., 2008).

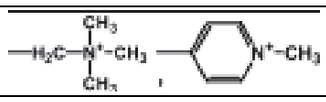
Anion Exchange Membrane	Cation Exchange Membrane
OH^- conductive	H^+ conductive
	$-SO_3^-$, ($-PO_4^-$, $-CO_2^-$)
Pt free catalyst available Advantage for cathode O_2 reduction	High ion conductivity Excellent ionomer solution
Low ion conductivity Low thermostability Influence of CO_2	High cost materials Fuel crossover

Table 3. Differences between ion exchange membranes

4.3.1 Cation exchange membrane electrolyser

PEM electrolyser is a recent advancement in PEM fuel cell technology. PEM-based electrolysers typically use platinum black, iridium, ruthenium, and rhodium for electrode catalysts and a Nafion membrane as the proton exchanger (Pettersson et al., 2006; Turner et al., 2008). The performance that is the hydrogen generation rate can be increased by using efficient electrodes, proton exchange membranes and by reducing electrode spacing (Liu et al., 2005). Proton exchange membranes (PEMs) are one of the most important components in microbial fuel cells (MFCs), since PEMs physically separate the anode and cathode compartments while allowing protons to transport to the cathode in order to sustain an electrical current. The Nafion 117 membrane used in this study is generally regarded as having excellent proton conductivity. Nafion, a sulfonated tetrafluorethylene, consists of a hydrophobic fluorocarbon backbone ($-CF_2-CF_2-$) to which hydrophilic sulfonate groups (SO_3^-) are attached. The presence of negatively charged sulfonate groups in the membrane explains the high level of proton conductivity of Nafion, while also showing a significant undesirable affinity for other cations rather than protons (Chae et al., 2008). Most MFCs are operated at a neutral pH in order to optimize bacterial growth in the anode chamber, while other cations (Na^+, K^+, Ca^+, mg^{2+} and NH_4^+) contained in growth medium are typically present at a 10^5 times higher concentration than protons (Rozendal et al., 2006). Consequently, these cations combine with the sulfonate groups of Nafion and inhibit the migration of protons produced during substrate degradation, causing a decrease in the MFC performance due to the pH reduction in the anode chamber. In addition, the frequent replacement of the buffer solution as a catholyte reduced the economic viability of MFCs. Nafion operated over a period of 50 days was contaminated with biofilm causing adverse effects on mass transport through the membrane (Chae et al., 2008).

4.3.2 Anion exchange membrane electrolyser

Anion exchange membrane fuel cells (AEMFCs) are a viable alternative to PEMFCs and are currently gaining renewed attention. In an AEMFC, an anion exchange membrane (AEM) conducts hydroxide (or carbonate) anions (as opposed to protons) during current flow, which results in several advantages: (1) The oxygen reduction reaction (ORR) is much more facile in alkaline environments than in acidic environments. This could potentially facilitate the use of less expensive non-PGM catalysts with high stability in alkaline environments. (2) The electro-oxidation kinetics for many liquid fuels (including non-conventional choices of importance to the military, such as sodium borohydride) is enhanced in an alkaline

environment. (3) The electroosmotic drag associated with ion transport opposes the crossover of liquid fuel in AEMFCs, thereby permitting the use of more concentrated liquid fuels. This is an advantage for portable applications. (4) The flexibility in terms of fuel and ORR catalyst choice also expands the parameter space for the discovery of highly selective catalysts that are tolerant to crossover fuel. These potential advantages make AEMFCs an attractive future proposition (Christopher et al., 2010).

For a traditional AEMFC with hydrogen fuel and air/oxygen as the oxidant, the half cell and overall chemical reactions are as follows: (Varcoe & Slade, 2005)

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \text{ ; EO, anode} = 0.83 \text{ V} \quad (5)$$

$$\tfrac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ ; EO, cathode} = 0.40 \text{ V} \quad (6)$$

Overall:

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O; \text{ EO, cell} = 1.23 \text{ V} \quad (7)$$

In an AEMFC, hydroxide ions are generated during electrochemical oxygen reduction at the cathode. They are transported from the cathode to the anode through the anion conducting (but electronically insulating) polymer electrolyte, wherein they combine with hydrogen to form water. The electrons generated during H_2 oxidation pass through the external circuit to the cathode, where they participate in the electrochemical reduction of oxygen to produce -OH. Note that in practice, the ideal thermodynamic cell voltage of 1.23 V (at standard conditions) is not realized even at open circuit (zero current) due to myriad irreversibilities that arise during AEMFC operation. The phenomenological sources of irreversibility are very similar to those in PEMFCs and include oxygen and water activities that are less than unity, and gas crossover at open circuit leading to mixed potentials, and activation, ohmic, and mass transfer losses (overpotentials) during current flow. Hence, AEM may be a suitable membrane for electrolysis of acid wastes, waste waters and biomass.

5. Conclusion

In summary, biological hydrogen production may be the environmental pollutant free fuel for future energy needs. This could fulfil the demands of drastic fuel consumption. Some problems for the commercialization of biohydrogen as fuel can be overcome by the electrochemical technology. This review gives the details of the improvement of hydrogen production efficiently through electrochemical technology. The efficiency of hydrogen production from microbial system can be enhanced by the hybrid use of electrohydrogenesis cell. Application of this renewable hydrogen is mainly for transportation and industries. Electrohydrogenesis cell can contribute significantly to these hydrogen demands by producing large quantities of hydrogen from renewable resources and wastes such as biomass, wastewaters and acid wastes. Hence, commercialization of the biohydrogen technology can be possible with the electrochemical technology.

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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