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BIOCHEMICAL FUEL CELLS - AN OVERVIEW

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The longstanding need for cheap, ubiquitous and reliable source of energy has evoked an interest in fuel cells, inclusive of biochemical fuel cells. The history of development of biochemical fuel cells, inclusive of the substrates and micro-organisms employed, are dealt with in this review. The applications of biochemical fuel cells are reviewed. Scope for further development of biochemical fuel cells is also discussed.

Key words: Biochemical fuel cells, enzymes, micro-organisms

INTRODUCTION

The constant quest for cheaper, ubiquitous and reliable source of energy for some specific applications has evoked an interest in fuel cells, inclusive of the biochemical fuel cells. "Fuel cells are electrochemical cells which continuously change the chemical energy of fuel and oxidant to electrical energy by a process involving an essentially invariable electrode electrolyte system" [1]. In a biochemical fuel cell, electrical energy is derived from biological processes involving micro-organisms, enzymes and the like, the substrates being rich in maltose, glucose etc. Biochemical fuel cells try to mimick the biochemical processes occuring in a living organism. But man has been unable to duplicate the physiological conditions as such, and as a result, no significant break through has been achieved in continuous production of reasonable quantity of electric power, though the research is more than thirty years old. Revival of interest and chances of rapid development are anticipated by these reviewers in view of the rapid progress being made in the allied areas of biosensors and biomolecular electronics currently. Hence, a brief review of this topic has been undertaken.

In biosensors, based on electrochemical transduction, an electrical signal proportional to the concentration of the analyte, is obtained. The electrode, or in other words, the transducer has the immobilized enzyme or micro-organism. Even though biochemical fuel cells and biosensors work on the same principle, biosensors, as an analytical device, have made a significant progress because a weak signal is sufficient for monitoring purposes. The very recently flourishing biomolecular electronics ultimately aims at producing switches in the molecular level and computers with artificial intelligence. In the present stage of development, coenzymes, like NAD and FAD, have been linked to solid supports through polymer chains so as to improve the stability and efficiency. These electrodes will serve a useful purpose in biobatteries [2].

BASIC CONSIDERATIONS

In a biochemical fuel cell, the substrates are usually natural products rich in sugars. Either enzymes or whole micro-organisms are used to initiate the biochemical process. The overall reactions occuring in a biochemical fuel cell are the oxidation of hydrogen rich fuels at the anode

$$SH_2 \rightarrow S + 2H^+ + 2e^-$$

(S = substrate)

The electron transfer through the respiratory chain is interrupted early with the help of a suitable mediator which communicates with the electrode. Oxygen is reduced at the cathode as

$$2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O$$

The biochemical fuel cells can be direct or indirect. In the direct type, the secondary fuel, like hydrogen or formic acid obtained by action of micro-organisms is oxidised with enzymes and coenzymes in the same cell where the micro-organisms are present leading to release of electrons that constitutes the current in the biofuel cell.

It is difficult to maintain favourable conditions for the sustenance of micro-organisms in this case.

In the indirect type, the raw material is converted to secondary fuels by the action of micro-organisms and transferred to a second compartment where electric power is generated by enzyme action.

EARLY DEVELOPMENTS

The early sixties were the first years of investigation into biochemical fuel cells. Two exhaustive reports have been submitted to the US Department of Commerce [3,4].

Extensive studies were carried out on ammonia producers like Bacillus pasteurii, hydrogen producers like Clostridium welchii, Eschirichia coli and formic acid producers like Aeromonas formicans [3,4]. Hydrogen sulphide producing bacteria [5] and micro-organisms acting on inorganic substrates like sulphur compounds [6] also seem to have interested the researchers. Photosynthetic micro-organisms like Rhodopseudomonas spheroides [7] etc. figured in some of these reports. Biochemical fuel cells with Micrococcus cerificans oxidizing n-hexadecane [8], Acetobacter ranscens using ethanol [9] and Pseudomonas ovalis [10] and Saccharomyces cerevesiae [11] metabolizing glucose were some others studied. For the biochemical fuel cells utilizing enzymes, enzyme hydrogenase dominated the study [12].

Current densities obtained from Fuel cells with formic acid as secondary fuel was about 40 $mA.cm^{-2}$ and the coulombic efficiency of the cell approached 100% of the formic acid produced. In the case of hydrogen production, Clostridium welchii was found to be the best organism and glucose or maltose was the best substrate. The hydrogen evolution was maintained at 23 $l.h^{-1}$ [3,4]. In the case of photosynthetic micro-organisms like Rhodopseudomonas spheroides exposed to an electric bulb for 16 days at 301–308K, the current developed was 72–3.5 μA, the volt 7.2–350 mV and the power 0.55 to 1.2 μW [7]. The biochemical fuel with Micrococcus cerificans developed a potential difference of 0.2 V at zero current and the maximum current was 3.5 $\mu A \cdot cm^{-2}$ with fluctuations of $\pm$ 10% [8].

Aspects of cell design [13] and electrochemical nature of biological power producing reactions [14] were typical of subjects that engaged attention on theoretical and practical aspects of biochemical fuel cells [15,16].

RECENT DEVELOPMENTS

Photosynthetic micro-organisms have continued to interest the researchers. Biochemical fuel cells with oxidase enzymes were the subjects of study. Photochemical fuel cells using chloroplasts and Clostridium butyricum, operating under illuminating conditions [17] and those employing marine algae were studied [18]. Glucose enjoyed the preferred substrate status and a fuel cell was developed using Enterobacter aerogenes as the biocatalyst [19]. In the case of biochemical fuel cells employing enzymes, oxidases from carboxydotrophic bacteria [20] and glucose oxidase [21] dominated the study. 2 - hydroxy—1,4 naphthoquinone served as a good electron acceptor [22]. The mediating properties of disulphonated thionines [23], ferric chelate compounds [24] etc were studied and disulphonated thionines were considered to be good mediators for the interruption of electron transport chain in bacteria. Fuel cells with adsorbed enzymes which oxidize C_1 compounds have been developed [24]. Electrodes for regeneration of coenzymes to be used in biochemical fuel cells have been developed [25]. A group of extremely thermophilic bacteria have been identified recently which possess the enzyme hydrogenase which can work at high temperatures and it can be used for the production of hydrogen in large quantities to be used in the indirect type of biochemical fuel cells [26].

The photochemical fuel cell using immobilized chloroplast and Clostridium butyricum which operated under illumination gave a photocurrent of 170 μA for 2.5 hours [17]. In the photobio-electrochemical fuel cell employing marine algae, the current output increased with the illumination intensity and higher current output was observed in the carbon dioxide than in nitrogen atmosphere. A fuel cell containing $\approx$ 50 mg (in dry weight $\approx 5 \times 10^{-7}$ M chlorophyll) of algae and 0.25 mM of the substrate has the highest coulomb output and the longest life [18]. In the case of biochemical fuel cells with Enterobacter aerogenes as the biocatalyst and glucose as the substrate, a current density of $60 \mu A \cdot cm^{-2}$ was obtained during long term operations and the current density was maintained by adding nutrients periodically [19].

Reviews published recently deal, with application of biotechnology for energy conversion [27, 28], use of zeolite catalysts for the production of ethanol from biomass which is used in biochemical fuel cells [29] and also the state of development of biochemical fuel cells [30, 31].

TYPICAL APPLICATIONS OF BIOCHEMICAL FUEL CELLS

Apart from serving as potential sources of energy, the biochemical fuel cells have a wide spectrum of applications, mainly in the medical field. Over the years, the applications of biochemical fuel cells has increased to a great extent.

(1) A major breakthrough was the development of a bioelectric battery for supplying the pace maker. The output current was 200 μA with an available power of 100μW at a stable voltage in the neighbourhood of 0.5 V. The general tolerance by the organism used was good [32]. Alternate fuel cells for increasing the efficiency of the system were also developed [33]. A review is available on the use of implantable bioelectrochemical power sources [34]. However, the fabrication of a practical device to convert the body's own inherent energy into electrical energy for artificial pace makers is considered to be a dead issue [35] and does not seem to have any future [36]. From very recent developments, in implantable power sources, it appears that the output requirements are more, in view of the need for the fully automated pacemakers with computing possibilities. At present, these requirements have already been met by lithium-silver chromate systems, lithium-thionyl chloride system and lithium-bromine type battery [37].

(2) Another significant application oriented development was the glucose diffusion limited fuel cell to monitor the blood glucose levels. Output current proportional to blood glucose levels was converted to an electric signal [10]. Improved electrochemical measurements of the real and simulated body fluids was obtained with a sensor which was useful in the control of diabetes [38] This application has been a stepping stone for the development of biosensors for different analytes like urea or cholesterol, apart from glucose.

(3) An implantable fuel cell was also developed with Hyaluronidase bound membrane as the biomaterial [39] Hyaluronic acid was a contributor to the viscosity of the tissue fluids and it acted as a potential fuel source because of its high sugar content. Hyaluronidase enhances the rate of mass transport of fuel, oxygen and reaction products by reducing the viscosity near the electrode membranes.

(4) Biochemical fuel cells also found an application in the blood and tissue detoxification apparatus [40]. Blood and tissue are detoxified of endogenous substances, such as ethanol or other drugs by an apparatus containing an electrochemical cell, which may be implanted or used in extracorporeal shunt system. The cells converted oxygen and toxic substances in the body fluids to harmless substances which are easily dissipated. The cells have hydrophobic cathodes having membranes, like silicone rubber, which permit the diffusion of oxygen.

(5) The fuel cells were also employed to assay the activity of hydrogenase [41]. Activity is expressed as the current density of the fuel cell composed of a H half cell $H_2 - H^+$ hydrogenase system and a saturated calomel electrode. The principle is based on the fact that the short circuit current density of the cell is proportional to the activity of the enzyme in the anodic half cell.

(6) Biochemical fuel cells can also be applied for the treatment of waste waters. The system used in the study consisted of a waste water packed bed reactor for immobilized Clostridium butyricum, platinum black anode and an ion exchange membrane, a cathode and a continuously stirred tank reactor for immobilized aerobic micro-organisms. Industrial wastes were applied to the system. Hydrogen production and waste water treatment were studied [42]. Simulating criterion has also been developed for the bioconversion of refuse to synthetic fuel and electric power [43]. Fuel cells have been developed for the utilization of kitchen wastes [44] and animal wastes and lactose wastes [45].

(7) Biochemical fuel cells were also developed for specific utilization in space flight [46]. Both urine and carbon dioxide acted as electron donating fuels. A system employing Chlorella pyrenoidosa at the cathode and Micrococcus ureae at the anode produced a maximum density of 5.7 mA. cm^{-2}.

(8) Flavin containing enzymes used in biochemical fuel cells can also be used for the synthesis of biochemicals [47]. A multienzyme system is enclosed. NADH is consumed by 20 β-hydroxy steroid dehydrogenase for reduction. In this system, NADH can be regenerated electrochemically from Lipoamide dehydrogenase in the absence of hydrogen and hydrogenase.

FUTURE PROSPECTS

The report submitted in the early sixties [3,4] stressed on the need for more research in the field of indirect fuel cells. But only very recently, a group of extremely thermophilic bacteria have been identified which can work at high temperatures and can be used for the production of hydrogen to be used in the indirect biochemical fuel cell [26]. Apart from developing much more active enzymes or micro-organisms, applied research would become attractive only if efficient direct electron transfer from the enzyme or the micro-organism to the electrode can take place. Currently, basic researches are pursued vigorously to effect direct electron transfer from enzyme or organism to electrode surface [48].

CONCLUSION

In spite of their inability to produce considerable quantity of power continuously, interest is retained in biochemical fuel cells mainly because of their applications for waste disposal and pollution control. Parallel developments in biosensors and biomolecular electronics can contribute to newer prospects in this area and hasten the progress.

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