BIO CHEMICAL FUEL CELLS - POSSIBILITIES

A brief proposal submitted to the
Ministry Non-conventional Energy sources
For their kind consideration,
to initiate the research activity
in this country

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1. Introduction

Biochemical fuel cells use biocatalysts for the conversion of chemical energy to electrical energy. Most organic substrates undergo combustion with the evolution of energy. In a similar way bio-catalyzed oxidation of organic substrates by oxygen or other oxidizers at two electrode interfaces provides a means for the conversion of chemical energy to electrical energy. A variety of organic raw materials such as methanol, organic acids glucose, cellulose and almost all plant and animal wastes can be used as substrates for the oxidation process and molecular oxygen or hydrogen peroxide can act as the substrate that is reduced.

Biofuel cells can use biocatalysts, enzymes or even whole cell organisms in either of two ways, namely the biocatalysts can generate the fuel substrates for the cell by bio-catalytic transformations or metabolic processes or the biocatalysts may participate in the electron transfer chain between the fuel substrates and the electrode surfaces. However, most of the redox enzymes do not take part in direct electron transfer with conductive supports and therefore many electron mediators (electron relays) are used for the electrical contacting of the biocatalyst and electrode. Another approach would be to functionalize the electrode surfaces with monolayers and multilayers of redox enzymes, thus generate integrated bio-electro-catalysts that stimulate electrochemical transformations at the electrode interfaces.

2.Bio chemical Fuel Cell configurations

In this presentation, the tailoring of conventional microbial based fuel cells as well as methods of integration fuel cell electrodes with bio-catalytic interfaces structures are described with a view to generate new and novel fuel cell configurations. There are three ways a microbial based biofuel cell can be tailored. These include (i) Design of a separate microbial bioreactor providing fuel to the anodic compartment of the fuel cell (ii) Integrated or built-in microbial bioreactor wherein the fuel is generated directly in the anode compartment.(iii)Incorporation of artificial electron transfer relays that can shuttle electrons between the microbial system and the electrode. Various possibilities within these three configurations have been examined, these include (i) various bacteria and algae (example *Escherichia coli, Enterobacter aerogenes, Clostridium butyricum*, etc) have been tried for hydrogen production under anaerobic conditions. The immobilization of *Clostridium butyricum* on polymer matrices have been used to produce hydrogen continuously for weeks while the nonimmobilized baceteria cells were fully deactivated in less than 2 days. Various substrates like glucose and pyruvate can be used with ferredoxin oxidoreductase and *hydrogenase* in the off mode production of fuel for fuel cell application. For the *in situ* operation for fuel production various microorganisms have been tried with nutritional substrates like molasses, lactate, glucose, dextrose and fuel cells have been designed. In the microbial-based biofuel cell configuration, various mediators including thionine, methylene blue, substituted naphthaoquinines, neutral red and Fe EDTA complexes have been employed in the construction of the fuel cells. One of the biofuel cell configurations is shown in Fig.1.

Another important aspect is directly using the oxidative biocatalysts in the anodic compartments for the oxidation of the fuel substrate and transfer of electrons to the anode

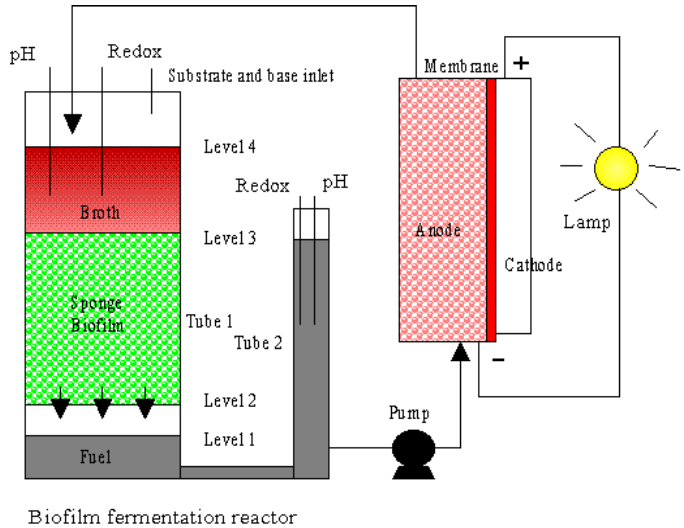

Fig. 1. The schematic diagram of the microbial fuel cell system.

while purified reductive biocatalysts perform similar functions in the cathode compartments. Since redox enzymes lack direct communication with the electrodes due to the insulation of the redox centre from the conductive support by the protein matrices, several methods have been applied to electrically contact redox enzymes and electrode supports. The engineering of the biocatalytic anodes and cathodes is a current activity of intense research.

Various cofactors have been covalently hooked on to the metallic electrodes and these integrated electrode systems have been examined in the fuel cell mode for possible applications. The essences of these studies are:

(i) Various electrochemical techniques have been employed to study the kinetics of bio-transformations occurring at the electrode.
(ii) For the functional electrodes the complex sequence of reactions has to be evaluated in detail.
(iii) Biomaterial engineering has to be done on various redox proteins in order to optimize its electron transfer functionality, that is the elucidating the electrical communication with the electrode and inter-protein electron transfer mediated by the cofactor.

These aspects will be important for developing biochemical fuel cells wherein purified enzymes are used in an integrated fashion to perform the biocatalytic fuel production and also used in the development of electrical energy from the cell reaction.

Another engineering marvel that is conceived is that instead of compartmentalization of the cell with purified enzymes and cofactors, bio-electro-catalytic transformations at the electrodes may be driven efficiently enough that interfacing components do not perturb the cell operation. A typical example of this type of operation of a bio fuel cell is bio-electro-catalyzed reduction of hydrogen peroxide mediated by MP-11 at the cathode and oxidation of NADH to NAD^+ mediated by PQQ(Pyrroloquinoline quinone) at the anode in a single cell operation. Similar single cell operation has also been successfully demonstrated in the oxidation of glucose to gluconic acid mediated by PQQ and FAD and oxygen reduction to water mediated by Cyt-C and Cox functionalized Au electrodes. There are various possibilities for generating either monolayer or multilayer embedded electrode systems for single cell operation.

3. Possibilites – A general outline

Therefore it is clear that the generation of electrical energy from abundant organic substrates can be organized by various approaches as briefly outlined above. The studies that are essential are:

(i) Detailed characterization of the interfacial electron transfer rates
(ii) Determination of the bio-catalytic rate constants
(iii) Reducing the cell resistances
(iv) Establishing suitable communication and identifying appropriate cofactors especially chemical modification of redox enzymes with synthetic units that improve the electrical contact with the electrodes.
(v) The attractive features for this would be site specific modification of redox enzymes and the surface–reconstitution of enzymes. These two routes appear to be available. The development and use of structural mutants of redox proteins may be one way to increase the electrical communication with the electrodes and research in this direction will be beneficial.
(vi) The alteration and adjustment of the redox potentials of the synthetic relays, the output of the bio-fuel cell can be improved. This will be one another area where new knowledge can be created.
(vii) The configurations outlined in this brief write up can be successfully extended to other redox enzymes and fuel substrates thus opening up the possibility of a number of new and useful bio-fuel cells.
(viii) A distinct but definite possibility is to use human body fluids as the electrolyte medium and thus use the potential generated for activating implanted devices like pace makers sensors and prosthetic units. But it must be stated this is a far reaching proposition at present.

This presentation briefly outlines the type of activity that can be generated in a well formed research group in our institute. There are definitely other possibilities which are not covered in this brief write-up but can be outlined if necessary.

4.References (only some key references are given)

1. E.Katz, A.N.Shipway and I Willner, Hand Book Fuel cells, Fundamentals, Technology and Applications, (Ed. Wolf Vielstich, H.A.Gasteiger, A, A.Lamm, John Wiley & Sons (2003) Vol.1 Fundamentals and survey systems.

2.G.T.R.Palmore and G.M.Whitesides, in Microbial and Enzymatic Biofuel cells in Enzymatic Conversion of Biomass for fuels Production,(EDs. M.E.Himmel, J.O.Baker and R.P. Overend, ACS symposium series No.566 ACS, Washington DC pp 271-290 (1994).

3.W.Habermann and E.H.Pommer, Appl.Micobiol.Biotechnol., 35, 128 (1991).

4.B.H.Kim, H.J.Kim, M.S.Hyun and D.H.Park, J.Microbiol Biotechnol., 9, 127, 365 (1999).

5.N.Kim, Y.Choi, S.Jung and S.Kim, Biotechnol.Bioeng., 70, 109 (2000).

6.D.H.Park, S.K.Kim, I.H.Shin and Y.J.Jeong, Biotechnol .Lett., 22, 1301 (2000).

7.A.B.Khstiyonov, L.Alfonta, E.Katz and I .Willner, J.Electroanal.Chem., 487,133 (2000).

8.S.Tsujimura, H.Tatsumi, J.Ogawa, S.Shimizu, K.Kano and T.Ikeda, J.Electroanal.Chem., 496, 69 (2001).

9.I.Willner, E.Katz, E.Patolsky and A.F.Buckmann, JCS Perkin Trans., 2, 1817 (1998).