

Recent Advances in Biofuel Cell and Emerging Hybrid System

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Abstract--*The present paper reviews the recent development of biofuel cell. Due to its renewable nature and milder operating conditions compared to conventional fuel cell, the electrochemical system has been extensively studied. However, major problems associated with this type of electrochemical system remain an intimidating challenge, the utmost being the low power output and stability of biocatalyst being used. Various attempts have been made to overcome these problems, some are reviewed here. The authors suggest a new direction in solving these problems by using hybrid system i.e. metal biofuel cell. The new hybrid system developed is of lower cost, less complex, higher OCV and greater power output.*

Keywords: *Biofuel cell, metal biofuel cell, zinc anode, laccase*

I. INTRODUCTION

Global depletion of non-renewable energy sources has made research and development in alternative power production critical. Recently, researchers are looking into biological world for inspirations. Enzymes and microbes have been explored as catalysts for energy conversions in so called biofuel cells. Biological fuel cells (BFC) are the progeny of two parent technologies: fuel cells and biotechnology. It is capable of directly converting chemical energy to electrical energy through electrochemical reactions involving biochemical pathways [7]. Similar to conventional fuel cells, biofuel cells are made of an anode and a cathode usually separated by a selective membrane that only allows positively charged ions. However, unlike conventional fuel cells, biofuel cells utilize enzymatic catalysts, either as they occur in microorganisms, or as isolated proteins

rather than precious metals. Besides offering clean and renewable energy source, BFC is also capable of utilizing wide variety of fuel choices compared to traditional fuel cell which is limited to simple hydrogen gas, methane or methanol. Much more complex fuels can be utilized in a BFC such as ethanol, propanol, butanol, glycerol, fructose, sucrose, glucose, carbohydrate, fatty acid etc. [16]. Rather than just 2 electrons oxidation in fuel cell, BFC's are capable of doing deeper oxidation which means we can get more energy density out of the fuel.

II. TYPES AND APPLICATIONS BIOFUEL CELLS

In general there are two types of BFC, grouped based on the catalyst being used, microbial biofuel cell (MFC) and enzymatic biofuel cell (EFC) and each has its own advantages and disadvantages. The MFC and EFC are further divided either as direct electron transfer or mediated electron transfer [7],[19], [20]. MFC is based on the oxidation of the fuel through microbial catabolism in the anodic compartment of a fuel cell. The current is generated by redirecting electrons from the microbe membrane respiratory chain to the anode (whole organism is utilized) [23]. Microbial biofuel cell is the most efficient way of utilizing complex fuels, where the oxidation process involves a series of enzyme catalyzed reactions [26]. Meanwhile, EFC's use isolated enzymes as biocatalyst to convert the chemical energy of a fuel into electricity, a good substitute to the platinum catalyst used in conventional fuel cells. The capability of enzymes to oxidize various organic molecules under serene conditions, typically at ambient temperature and pressure offers advantages in fuel cell applications [18]. EFCs have several positive attributes with respect to energy conversion, namely, the use of renewable catalysts, ability to operate at physiological pH and possess much higher power densities as compared to MFC. In addition,

enzymes have the added advantage of catalyzing specific and defined reactions [6]. Due to the advantage of inherent biocatalytic properties that cannot be matched by conventional fuel cell technology, biofuel cells are becoming more popular for various potential applications. Examples of current and potential applications of biofuel cells are briefly described below.

2.1 Medical devices and sensors

Biofuel cells are potential candidate for power source within the living body – in vivo power source. Compared to existing power sources such as lithium-iodine cells [25], biofuel cells are better alternative since the fuel source is derived from the blood stream (glucose or lactate) [4]. This configuration is ideal for implantable power source as the need for surgical procedure to change the battery is mitigated. Biocatalyst used in biofuel cell can efficiently catalyze reactions at physiological pH and temperature as these species generally performs the best at 25-50°C. In addition, there is no tolerance issue of biocatalyst because it produces reaction products that are non-toxic to the host organism.

Other prospective medical applications of BFCs are as biosensor and power source to administer drug delivery system [14],[17]. For example, Katz et al. demonstrated a biosensor for glucose employing a glucose-based anode and cytochrome c cathode [11].

2.2 Bioenergy

Shukla et al., put an estimate that a car could travel 25-30 km with just a liter of concentrated carbohydrate solution [24]. So, a typical sedan car with 50 litre tank capacity should be able to go more than 1200 km. Besides that, the risk associated with transporting large amounts of volatile, flammable fuels (petrol) in the car also eliminated. Atanassov et al. [4] laid down an interesting analogy to describe the potential in harnessing bioenergy,

“After all, there is as much energy in one jelly donut as you can find in 77 cell phone batteries. If you can get that energy out, it could have pretty, ahem, sweet consequences.”

(Atanassov et al., [4]).

Bioenergy harvested from BFCs currently is still in the microwatt range. The energy amount however is suffice to power micro scale electronic sensors for monitoring air quality, plant health or the presence of biohazards. These devices require disconnected and long-term power supply. BFCs fed with ambient fuels which are derived from plants carbohydrates or animal process could be the potential power source to power such devices in the near future [5].

2.3 Wastewater treatment

Waste water engineering utilizing MFCs is one of the emerging applications. Employing MFC, microorganisms' decomposition of domestic wastewater and effluent produces electricity as the by-product. Liu et al. applied a single chamber microbial fuel cell designed with eight graphite electrodes as anodes and a single air cathode. The system operated under continuous flow conditions and was capable to generate a maximum electrical power of 26 mW m⁻² (2.6 μWcm⁻²) while removing up to 80% of the COD of the wastewater [13].

III. PRESENT STATUS AND CHALLENGES

Practical applications of BFCs are currently hampered by two most critical factors i.e. poor power density and short lifetime, which are related to enzyme stability, electron transfer rate, and enzyme loading [12]. Power output of biofuel cells are mostly in the microwatt range which are very much lower compared to other similar technology such as the H₂/air or CH₃OH/air. Many practical applications require a power source with supply range of 10–100 W cm⁻². The key issue in bridging the credibility gap is to establish an effective electron transfer rate between enzymes catalytic site and electrode. As in conventional fuel cells, the electrode design is crucial to obtain an optimum interface between current collector, fuel and catalyst. Therefore, biofuel cell electrodes should be three-dimensional, with optimum surface area, which generally means having smaller pores that increase the reactive surface area and the current generated [15]. Another approach is to employ a mediated electron transfer BFC. The electron mediator employed includes ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)), syringaldazine, PQQ (Pyrroloquinoline quinone), FAD (*Flavin adenine dinucleotide*), NAD⁺ (*Nicotinamide adenine dinucleotide*) etc. [9],[19]. In most cases, the enzyme and electron mediator are immobilized on the electrodes. Besides, since single type of enzyme only capable of partially oxidizing the fuel, a multi-enzyme system could also be employed to completely oxidize the fuel and subsequently generated more power [4].

Stability is another issue that hampers practical applications of BFCs. The service time of biofuel cell is determined by the stability of the biocatalysts used. Most currently developed enzymatic biofuel cells only lasts for few days [11]. The state-of-the-art of present technology is capable to extend the biocatalysts lifetime in the order of months [5],[8]. However, in order to find commercial interest, the lifetime needs to be increased to at least a year.

IV. RECENT ADVANCES IN ENZYMATIC BIOFUEL CELLS

Zebda et al. [27] reported an innovative approach to solve the difficulty of electrical wiring of enzymes to the

electrode. This group produced a mediator less, high power glucose biofuel cells based on compressed carbon nanotube-enzyme electrodes. Laccase and glucose oxidase were integrated in carbon nanotube disks by mechanical compression method. Cellulose film was utilized as separator. It registered an open circuit voltage (OCV) of 0.95 V and delivered a power density up to 1.3 mW cm⁻². The cell remained stable under physiological conditions storage after 30 days and still capable to deliver 1 mWcm⁻² [27].

Researchers from University of New Mexico developed a fully enzymatic biofuel cell that operates under a continuous flow mode [21]. Their system is interesting because it operates in a continuous flow mode by employing two dehydrogenases as anode (malate dehydrogenase, MDH and alcohol dehydrogenase, ADH), against laccase as cathode via direct electron transfer (DET) method. OCV of the MDH-laccase biofuel cell was 0.584 V, while the ADH-laccase biofuel cell's was 0.618 V. Maximum volumetric power density of 20 μW cm⁻³ was reported.

Sakai and his team probably reported among the highest biofuel cell output. They utilized a mediated NAD-dependent glucose dehydrogenase (GDH)-bilirubin oxidase (BOD) biocatalytic system. The enzymes, electron transfer mediators and other components were immobilized on carbon fibre electrodes. The GDH-BOD system gave an OCV of 0.8 V and was able to produce a maximum power density of 1.45 mW cm⁻² at 0.3 V. The key features for the cell's high performance were the densely entrapped enzymes and mediator on carbon-fiber electrodes, retained enzymatic activities, optimized concentration of buffer electrolyte and cathode design structure with efficient O₂ supply [22].

Inspired by the metabolic processes of living cell, Addo and co-researchers worked on rechargeable bio-batteries. In their system: ADH was immobilized into an anodic carbon composite paste with ferrocene as the mediator; Prussian blue (Iron(III) hexacyanoferrate(II)) was used as the cathode; butyl-3 methylimidazolium chloride ionic liquid served as the electrolyte and Nafion 212 was used as the separator. The ability of NAD-dependent ADH to undergo reversible redox process was the key idea. Ethanol served as the fuel in the carbon paste mixture. Under discharge mode, ethanol was oxidized to acetaldehyde and when current was supplied during charging, acetaldehyde was reduced to ethanol. The cell showed a reasonable stability over a 50 discharge-charge cycles [1].

4.1 Noel Hybrid Biofuel Cell

In an attempt to overcome the low power density, low OCV and very complex and delicate nature of enzymes, the authors introduced a new class of biofuel cell by replacing the anodic enzyme with zinc anode [2],[3]. The design is adopted from a well understood and well

characterized zinc-air cell. A hybrid biofuel cell, a zinc-air cell employing laccase as the oxygen reduction catalyst was explored. The bioelectrochemical system combines the well-understood zinc-air cell and an enzymatic biofuel cell - an electropositive zinc element is coupled with the biocatalytic activity of the laccase enzyme. As a result, the biofuel cell design is simplified and its cost is reduced since the anolyte components (enzyme, substrate, electron mediator and buffer solution) are replaced with cheap and abundant metallic zinc. Based on the zinc-air system, an air electrode was utilized in the cell design. The air electrode serves both as the cathodic current collector as well as to feed ambient oxygen continuously into the system through its porous structure. A single chamber, membrane less cell design was utilized. Laccase biocatalyst was left to be freely suspended (i.e. not immobilized) in quasi-neutral potassium dehydrogenate phosphate buffer (pH 6.5) electrolyte. Unlike most biofuel cells, the cell was characterized under open ambient conditions. The hybrid biofuel cell registered an average OCV of 1.2 V and could deliver a maximum power of 3.25 mW at discharge load of 8.5 mA. The highest cell capacity obtained was 7.5 mAh, rated at 0.5 mA.

V. CONCLUSION

Bioelectrochemical energy systems are attractive as they are clean, renewable energy source. They are popularly dubbed as the nature's solution in preserving the environment. However the energy output harvested from such systems are still low and remains as a formidable challenge. One alternative is to employ a hybrid system i.e. metal biofuel cell. The hybrid system reduces the complexity of existing BFCs while extending the energy density. The hybrid zinc-laccase biofuel cell demonstrated attractive features to be further developed.

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