Biofuel cells for the energy supply of distributed systems: State-of-the-Art and applications

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Summary / Abstract

Biofuel cells are an attractive possibility to generate electricity for energy-autonomous distributed devices. These fuel cells can tap into a variety of chemical energies available in environments such as the human body, fauna, or aquatic systems. The different biofuel cell concepts can be classified according to the catalyst system that is employed to enable the electrochemical reactions at the electrodes. Here abiotic catalysts (e.g. noble metals), isolated enzymes, or the enzymatic system of whole living microorganisms are used. In our contribution the different approaches and their specific challenges are discussed, and present and future application scenarios are highlighted.

1 Introduction

To convert locally available energies into useful electricity for energy-autonomous distributed devices there are at current a number of “energy harvesting” technologies under development. Besides mechanical and thermoelectric harvesters also biofuel cells are being considered. They are an attractive possibility to tap into the variety of chemical energies available in environments such as the human body (blood sugar), flora (tree-sap), or fresh-, salt-, and waste water systems (biodegradable organic matter). Besides continuous power output independent of motion or temperature gradients, the biofuel cell’s main advantage over thermoelectric or vibrational energy harvesters is its comparably simple design. As key components it demands only two spatially separated electrodes at which the electricity-generating electrochemical reactions take place: the fuel is oxidized at the *anode*, at the *cathode* usually oxygen is reduced to water. An electrical current is generated by the electron flow between the two electrodes (see also Figs. 1-3).

2 Biofuel cell concepts & challenges

The different biofuel cell concepts can be classified according to the catalyst system that is employed to enable the electrochemical reactions at the electrodes. Here abiotic catalysts (e.g. noble metals), isolated enzymes, or the enzymatic system of whole living microorganisms are used. In the following sections the different approaches and their key characteristics are briefly described. For more in-depth descriptions the readers are referred to recent review articles, which are available for abiotically catalyzed glucose fuel cells [1] as well as enzymatic and microbial biofuel cells [2,3] .

2.1 Abiotically catalyzed biofuel cells

Much like conventional hydrogen-oxygen fuel cells, this type of biofuel cell uses abiotic catalysts such as platinum or other noble metals to enable the electro-oxidation of a biofuel, e. g. glucose, methanol, and ethanol (Fig. 1). Abiotic catalysts promise long-term stability and tolerance towards comparably harsh operation conditions, e.g. high temperature during steam sterilization or extreme pH. However, the use of noble metals also translates into comparably high cost, and more complex organic molecules such as glucose can only be electro-oxidized at relatively slow reaction rates and thus low power densities. Furthermore, most noble metals catalysts also catalyze the reduction of oxygen. To prevent mixed potential formation due to fuel-crossover thus an efficient separation of reactants is required [1].

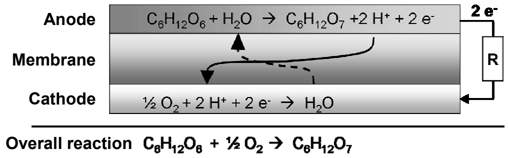

Figure 1 General electrode reactions of an abiotically catalyzed biofuel cell. Glucose is oxidized to gluconic acid at a platinum-based anode catalyst, whereas oxygen is reduced to water at the cathode. Protons are released upon electro-oxidation of the fuel and travel from anode to cathode through a proton-conducting membrane (or electrolyte).

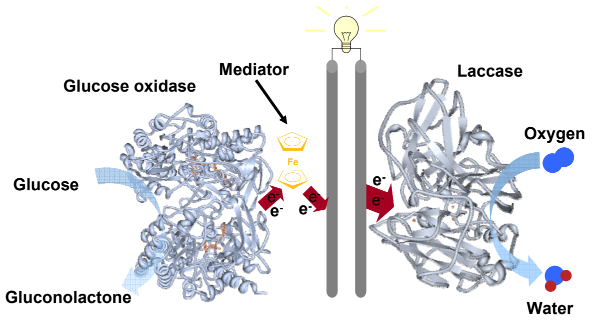

Figure 2 Electrode reactions of an enzymatic biofuel cell. In this example the enzyme glucose oxidase catalyzes the oxidation of glucose to gluconic acid at the anode. The mediator (electron shuttle) ferrocene is necessary to enable the transport of electrons from the active center of the enzyme to the anode. At the cathode the reduction of oxygen to water is facilitated by the enzyme laccase, which exhibits direct electron transfer and thus does not require a mediator.

2.2 Enzymatic biofuel cells

Compared to abiotic catalysts, enzymes offer higher catalytic activity for the oxidation of complex biofuels and thus promise better biofuel cell performance (Fig. 2). Another advantage is their high reactant specificity, which means that the presence of fuel at the cathode or the presence of oxygen at the anode has no negative effect on fuel cell performance. This is particularly desirable when mixed reactant fuels or impure substrate solutions are used, and also facilitates fuel cell construction. However, enzymes are prone to denaturation and thus loose activity over time. In practice, the lifetime of enzymatic biofuel cells is at present limited to a few weeks at best [2], which hinders their long-term application. Currently investigated approaches to extend their lifetime include enzyme stabilization by immobilization e.g. with polymers [4], genetic engineering to optimize the enzyme structure [5], and systems where fresh enzyme is continuously replenished to the electrode [6]. Some enzymes mandate the use of mediators (or electron shuttles) to enable the efficient electron transfer between the enzymes active center and the electrode. These mediators can also lose activity or leach from the system over time.

2.3 Microbial biofuel cells

The short lifetime of enzymatic catalysts can be circumvented when the enzymatic system of living microorganisms [2] is employed as catalyst at the fuel cell electrode (Fig. 3). Their self-regeneration capability renders them particularly well suited for long-term application. With versatile metabolic pathways and the possibility to employ a consortium of different microorganisms in the fuel cell, also complex fuel sources such as waste water become accessible. However, the microbes require some of the biofuel for their own metabolism, which reduces the energy-efficiency of the biofuel cell system. Factors affecting the performance of a microbial fuel cell are its construction, biofilm formation, and the dynamics of microbial communities.

3 Application examples

The potential applications of biofuel cells are as different as their characteristics. In the following sections their application as autonomous power source for medical implants, distributed sensors, and autonomous robots are presented.

3.1 Self-powered medical implants

3.1.1 Abiotically catalyzed glucose fuel cells powering cardiac pacemakers

The most promising application for abiotically catalyzed biofuel cells is the implantable glucose fuel cell [1]. Based on potentially long-term stable catalysts such as platinum or activated carbon, it is intended to generate electrical energy directly within the human body, using glucose (blood sugar) and oxygen from blood or tissue fluid. This way the necessity for regular surgical replacement of spent batteries could be circumvented. Since these fuel cells typically exhibit power densities of 2-4 µW cm^{-2} [1], their range of applications is at present limited to low-power medical implants such as cardiac pacemakers [7]. Since in-series connection of multiple fuel cells within the body would result in a short-circuit a DC-DC converter is required to step up the voltage to the levels required by electronic circuits. Although the feasibility of the concept has already been demonstrated in the 1970s in preliminary *in-vivo* studies [8], the main challenges that have to be further developed are biocompatibility, proper functionality in a body-tissue environment, and long-term stability of the device [1,9]. In Fig. 4 the envisioned integration of such an abiotically catalyzed glucose fuel cell directly on the casing of a medical implant is schematically depicted. With this elegant concept the need for intra-body wire connections or additional surgical procedures to place the fuel cell within the body can be circumvented.

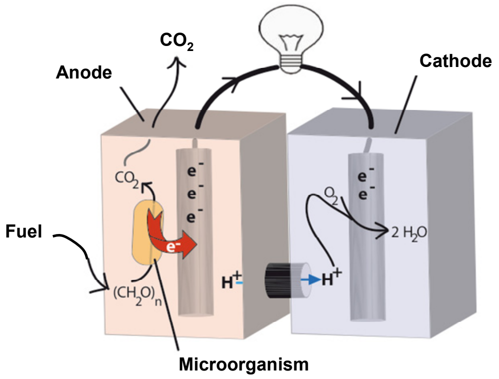

Figure 3 Principle of a microbial biofuel cell. At the anode electro-active microorganisms oxidize the biofuel to carbon dioxide, releasing electrons to the fuel cell anode. At the cathode oxygen is reduced to water, usually with the help of an abiotic catalyst such as platinum or carbon.

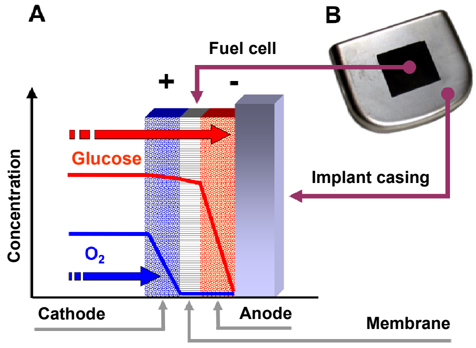

Figure 4 **A:** Schematic representation of an implantable abiotically catalyzed glucose fuel cell, which can be mounted directly on the surface of a medical device. At the cathode oxygen is selectively consumed, resulting in anoxic conditions at the interior anode where glucose is oxidized without oxygen interference. This enables the efficient electricity generation without mixed potential formation although the reactants are fed to the fuel cell as a mixture such as blood or tissue fluid. **B:** Envisioned integration of the glucose fuel cell as coating directly on the surface of a medical implant situated in the body tissue.

3.1.2 Enzymatic glucose fuel cells powering short-term implantable sensors

Another currently considered application for implantable glucose fuel cells is the power supply to short-term implantable glucose sensors. Here glucose fuel cells based on enzymatic catalysts are under investigation. Heller et al. presented a glucose fuel cell, consisting of 2 thin graphite fibers serving as anode and cathode. The device exhibited a power density of ~ 430 µW cm^{-2} under physiological conditions [10]; its projected lifetime is 2 weeks [11]. However, so far no *in-vivo* demonstration of the technology has been reported. One reason may be the instability of the cathode enzyme bilirubin oxidase in human serum [11].

Biofuel cells can also function as sensors. Kakehi et al. have demonstrated that the open circuit voltage of an enzymatic glucose fuel cell can be used to continuously monitor glucose levels [12]. They integrated the fuel cell together with a commercial wireless RF-transmission system and envisioned that with further optimization a subcutaneously implantable continuous glucose monitoring system can be realized.

3.3 Self-powered environmental sensors

3.3.1 Unattended ground sensors

Outside the medical sector the use of biofuels such as tree-sap has been suggested to power e.g. tree-mountable forest fire sensors. Both, abiotically catalyzed and enzymatic glucose fuel cell concepts have been under consideration [13]. However, so far only preliminary studies have been reported, and in particular the poisoning of abiotic catalysts by tree-sap components and the limited lifetime of enzymatic catalysts have been named as main challenges hindering practical application of the concept.

3.3.2 Benthic microbial fuel cell powering a meteorological buoy

A more mature application example is the realization of energy-autonomous senor nodes, powered by a benthic microbial fuel cell embedded within the marine sediment [14-16]. Recently, Tender et al. reported the first demonstration of such a microbial fuel cell in which sufficient electrical power to power a meteorological buoy was generated [16]. Their fuel cell had a total weight of 16 kg and a volume of 30 L. Constructed from graphite-plate anodes embedded in the marine sediment and a graphite brush cathode positioned in the overlying water, the fuel cell delivered 36 mW of continuous electrical energy (16 mW m^{-2} per geometric anode surface). The electrical output was transformed to a voltage of 6 V by means of a DC-DC-converter and supplied a set of sensors (temperature, air pressure, and relative humidity) as well as a low-power line-of-sight RF transceiver, which transmitted the data in 5-min intervals. The current challenges in this technology are the cost and power output. Furthermore, the benthic microbial fuel cell mandates a power management circuit comprising an energy buffer to cover peak power demands during intermittent telemetry and a DC-DC converter to step-up the fuel cell voltage (typically below 500 mV). As with implantable fuel cells, also here the in-series connection of multiple fuel cells is not possible since all fuel cells share the surrounding water as common electrolyte, which would result in a short circuit.

3.4 Energy-autonomous robots

A fascinating application of microbial fuel cells is the realization of autonomous robots that feed from the environment. Kelly et al. [17] first presented their slugbot in 2003 as a robotic predator that autonomically collected snails and carried them to a central fermenter unit. Here the snails were “digested” in a microbial fuel cell, and the generated electricity was in turn used to re-charge the battery packs of the robots. While in this first design the microbial fuel cell had to be stationary due to its size and weight, a later robot called “Eco-BotII” was powered by several on-board microbial fuel cells operating on fuels such as sugar, fruit, and insects [18]. The same research group also suggested the use of microbial fuel cells as power supply for energy-autonomous under-water robots [19].

4 Conclusions & Outlook

In summary, biofuel cells are a promising and versatile concept for the realization of energy-autonomous distributed systems. They are of particular advantage in application areas where solar energy is not available. These may range from inside the human body over pure night-time

operation to submarine environments or even sewerage systems. The only requisite is the availability of usable chemical energy. However, the key challenge for successful commercialization of these concepts will be the improvement of longevity and power output, in particular when implantable biofuel cell systems are considered.
A future application of enzymatic and microbial biofuel cells may be the development of bio-batteries, which can be constructed from fully biodegradable, non-toxic, and low-price materials. Together with advances in biodegradable electronics [20] this may also pave the way for disposable distributed sensors that allow for a truly environmentally friendly “mount-and-forget” approach.

5 Literature

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