

EE-519 Seminars

Implanted biofuel cells

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Abstract—Biofuel cells are a potential alternative to battery cells as a power source for implanted bioelectronic devices. They generate electricity through chemical reactions, sourcing the reactants directly from the body. They could provide longer life span and higher power density than conventional battery cells although several technical challenges need to be overcome beforehand. This article provides an overview of the technology, explaining its working principle and the challenges of its implementation. It gives examples of priorly conducted in-vivo experiments and presents the current state of the research, the yet-to-be-explored solutions and the possible future of this technology.

I. INTRODUCTION

Implantable bio-electronic devices have been at the forefront of medical research for a number of decades. While certain devices, such as pacemakers, have been developed with great success and are now part of standard healthcare, numerous others are still at the development stage. One of the major roadblocks in the implementation of such devices is the need for a source of energy [1]. Although battery cells give satisfying performance for low-power devices, they need to be replaced periodically and cannot supply the power that artificial organs (for example) would require. The development of an alternative to battery cells could play a pivotal role in the implementation of bio-electronic devices [2]. Biofuel cells (BFCs) are at the core of research on this topic. Fuel cells produce electricity through redox reactions of a fuel and an oxidizing agent, though unlike batteries, they need a supply of reactants. The idea behind implanted BFCs is to use the body as a constant source of reactants, which could make them a source of electricity with infinite lifespan [3].

Various catalyzing agents such as microbial cells, enzymes and inorganic species ("abiotic" catalysts) can be used to provoke the chemical reaction in BFCs. Microbial BFCs are generally better suited for the creation of large scale systems. Therefore, research on implantable BFCs is mostly focused on enzymatic and abiotic catalysts, each having their advantages [4].

The recent research on BFCs has shown promising results though their performance remains largely inferior to conventional battery cells. Increasing their power density and lifespan is the main challenge, while other issues such as biocompatibility and integration with electronic devices need addressing as well [1], [5].

II. HARVESTING POWER FROM BIOLOGICAL SYSTEMS

A broad variety of methods have been investigated to harvest energy from biological systems over the years. Many technologies have been focused on utilizing mechanical energy from walking/running, arm/leg swings, heartbeats, blood flow and so on [6]–[8]. However, since these technologies are dependent on physical activity, the reliability of such methods to harvest constant energy is limited [2]. BFCs tackle this issue by using the more stable physiological activity to harvest energy [2].

Fuel cells are made of two electrodes, the anode and the cathode, separated by a conductive medium (the electrolyte). Semi-permeable membranes may be used to separate the electrode environments from each other or from the environment surrounding the fuel cell. Fuel present at the anode will undergo oxidation, producing ions and electrons. At the cathode, the oxidizing agent is reduced, resulting in byproducts such as water. These oxidation and reduction reactions are triggered by the catalysts. A voltage appears between the electrodes and direct electron current will flow from one to the other via the external circuit connected to them. At the same time, positively charged ions flow through the electrolyte thereby completing the electrical circuit [9], [10].

In BFCs, the most commonly used substrates are glucose as a fuel and oxygen as the oxidizer [10]. They are readily available in living organisms, in the bloodstream for example. The oxidation of glucose to gluconic acid releases two electrons which are transferred to the cathode where oxygen is reduced to water [10], [11]. In enzymatic biofuel cells (EBFCs), these reactions are catalysed by enzymes on the electrode surfaces, see Figure 1 [2], [3], [9], [10]. This process of harvesting power mimics the body's natural metabolic pathway, which means that the environment needed by the EBFC to function efficiently is already supported by the natural regulatory functions of glucose and oxygen levels that exists in the body [10]. The main usable enzymes are glucose oxidase (GluOx) or pyrroloquinoline quinon-dependent glucose dehydrogenase (PQQ-GDH) for the anode and bilirubin oxidase (BOx) or laccase for the cathode [3], [10].

Aside from reactants and catalyst choice, numerous parameters affect the performance of a BFC, some of which are detailed in the next section.

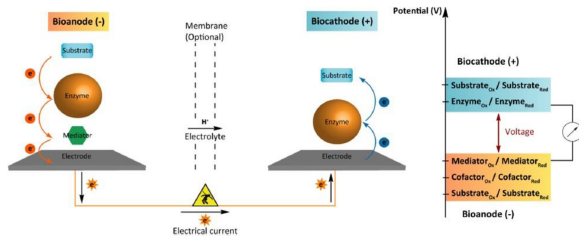


Fig. 1. Overview of an EBFC. The enzyme at the anode catalyses the oxidation of a substrate, usually glucose. The released electrons can be transferred directly to the electrode surface, or with the help of a mediator. These electrons form an electrical current towards the cathode where they are used by another enzyme which catalyses the reduction of another substrate, typically oxygen [10].

III. IMPLEMENTING BIOFUEL CELLS IN LIVING ORGANISMS

The concept of BFCs is promising, but practical implementation *in vivo* remains challenging. Before the technology can be considered a effective solution to power implantable medical devices, issues in the following three areas must be addressed: long-term efficiency, power output and power density, and bio-compatibility.

As of today, the longest continuous operation without voltage drop-off of an EBFC is 15 hours, which was achieved *in vitro* [12]. While EBFCs have shown the ability to recover their function after a period of rest, this is not sufficient for the integration with current medical implants such as pacemakers that require a constant voltage and have a typical operational life-span of 10 years [2], [10], [13]. The lack of longevity is mainly a result of rearrangement, inhibition or loss of the immobilized enzymes from the electrode surface [10]. Proposed solutions to these problems include: using additional enzymes to counteract the inhibition, engineer new enzymes which are resistant to inhibition, protect the enzymes with dialysis membranes or protect the enzymes with porous structures, such as multiwalled carbon nanotubes, buckypaper or gold-nanoparticles [1], [10], [13]–[15].

An additional problem is enzyme degradation over time. In biological systems, this is solved by constant replenishment of the enzyme population, but this involves complex biological machinery and as of now, no solution for EBFCs have been proposed [10].

Abiotic catalysts (usually metals) can be much more stable than enzymes. Raney-platinum electrodes have shown promising results, for example achieving an operational life-span of 140 hours without voltage retention *in vitro* [16]. But abiotic catalysts have several drawbacks as well: platinum is a complete redox-catalyst so the reaction will go in both directions at the same electrode if proper coatings to shield the electrode from its byproducts are not implemented [10], [17]. Abiotic catalysts usually have low activity at *in-vivo* conditions (neutral pH, temperature of 37°). They are only compatible with a small variety of fuels and are negatively affected by the high concentration of biomolecules in biofluids. Their biocompatibility is lower. Finally, they are expensive,

scarce resources obtained only through energy-hungry processes [2], [17]–[19]. Solving these issues could be easier than increasing the lifespan of enzymes to one decade [10]. Therefore, there is active research regarding both enzymatic and abiotic catalysts for BFCs [10].

Long-duration implantable medical devices, such as pacemakers, have a power consumption of 10-100 μW , while rechargeable devices, such as cochlear implants, can require up to 100 mW [10]. In the future, as artificial organs may become a reality, it is plausible that the power consumption will be even higher which requires alternatives to the modern batteries [3], [10]. In theory, the BFC provide a promising solution to this since the substrates needed for energy conversion are constantly renewed by human metabolism. However, the power densities of current BFCs are still insufficient and this depends on a combination of factors [10]. One of those are the number of catalytic sites, which are dependent on the surface area of the electrode. Simply increasing the size of the electrode can potentially cause problems with biocompatibility, which is why research is focused on improving electrode surface area with coatings of nanomaterials [3], [10]. It should be noted that reactant mass transport could also limit the BFC's maximum power output if its operation reduced local concentration significantly [13], [20].

An important factor in the performance of a BFC is the electrical conductivity between the reaction sites and the electrodes. The use of mediators can greatly improve electron transfer but involves a voltage drop that reduces the BFC's effective output voltage. It also poses biocompatibility issues. The use of nano-structured electrodes has been successful in increasing conductivity without requiring mediators ("mediatorless" or "direct" electron transfer) [3], [9], [10]. Here, it is worth noticing that abiotic catalysts are often conductive (e.g. raney-platinum and other metallic catalysts), thereby providing excellent conductivity without mediators [10]. Additionally, reaction velocity, substrate concentration and reaction efficiency also plays an important role [3], [9], [10].

The output voltage of biofuel cells is thermodynamically limited by the redox potentials. It rarely exceeds 0.7V and is much lower than the 2V-3V required by electronics [4]. Two solutions have been considered: using DC-DC converters to increase the voltage [5] and connecting several BFCs in series. The latter approach has proven unsuccessful, as separate flow pathways are necessary to avoid short-circuits between electrodes. Satisfying results were achieved with BFCs implanted each in an electrically separated environment but these conditions are impossible to recreate in a single living organism [2], [21].

Another challenge with BFCs is dealing with infection, rejection and general biocompatibility issues. Firstly, implantable devices need to be sterilized. Conventional sterilization methods involving heat, radiation or chemicals might impact enzymatic catalysts negatively (abiotic catalysts are unaffected). To maintain enzyme performance, the manufacturing process has to be adjusted [3], [10]. Secondly, the implantation location has to be chosen with care. It has to

provide a strong and steady supply of reactants. While the bloodstream is an obvious choice, installation of a cell in a blood vessel presents many drawbacks: it might restrict the blood flow and require the heart to work harder. It also poses a great risk of thrombosis and embolism, which can be deadly. It is therefore favorable to place the BFC out of the bloodstream, but in a highly vascularized area where glucose and oxygen concentrations will be as high as possible [3]. Thirdly, the packaging material of the cell has to fulfill demanding criteria: it should be perfectly biocompatible to avoid inflammation and rejection. In addition, the electrodes need to be wrapped in a membrane that enables diffusion of the reactants (glucose, oxygen) while preventing electrode material as well as enzymes from entering the bloodstream [20]. These aspects need to be carefully studied for maximum device performance as well increased comfort and reduced risks for the patient [3].

IV. EXAMPLE OF PAST RESEARCH

A. EBFC implanted in a snail for 2 months

Halamkova, et.al. demonstrated in 2012 the first well functioning EBFC implanted in a living cell [13]. Their study demonstrated that metabolically regenerated glucose can effectively sustain and "recharge" the living battery, enabling continuous electrical output over several months. For the cathodes, oxygen-reducing laccase was used, while for the anodes the authors utilized PQQ-GDH, chosen because it operates without the need for a soluble cofactor and is not affected by oxygen [13]. Despite a well functioning system, a key drawback continues to be the poor long-term efficiency of the system. More specifically the electrical output of the system decreased rapidly under current extraction, however the metabolic processes in the snail managed to restore the cell voltage within a 30-60 minutes restoration period, where the snail could rest and eat [13]. Although this level of performance would be insufficient for many medical systems, it nevertheless represented a significant advancement, as the EBFC remained operational and reproducible after a two-week implantation period. Another limitation highlighted by the authors is that the performance of the EBFC implanted in a snail cannot be directly transferred to mammals, as the physiology differs significantly. In particular, the oxygen level in snail hemolymph is considerably higher than the oxygen concentration typically found in the blood of mammals [13]. This trend is reflected in the polarization curves in Figure 5, where the snail biofuel cell (curve b) sustains a higher voltage than those measured in mammals such as the rabbit (curve c).

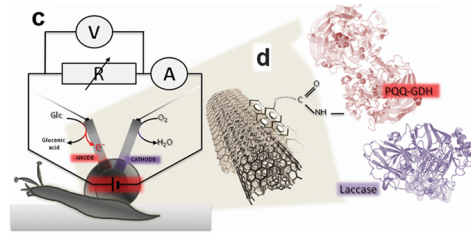


Fig. 2. The illustration to the left shows the circuit for the implanted EBFC in the snail. The diagrams to the right illustrate the coupling of the enzymes with CNTs via the bifunctional linker PBSE [13].

B. EBFC implanted in a rabbit for 2 months

A further advancement in the development of implantable EBFCs was demonstrated by El Ichi-Ribault et al., who implanted an EBFC in a freely moving rabbit for a period of 2 months [20]. The EBFC was coupled with a wireless transmission system, utilizing bluetooth technology. During the first 18 days, the open circuit voltage developed until it reached a stable steady state. Thereafter, the researchers daily discharged the EBFC for 30 minutes, extracting $6 \mu\text{W mL}^{-1}$ for 16 consecutive days [20]. After each discharge, the system required 9 hours to recover to its initial open circuit voltage. This indicates limited diffusion within the implantation environment.

Towards the end of the 2 months, the power output declined, assumedly due to inflammatory processes and biofouling at the electrode interface [20]. This highlights two major drawbacks of long term implemented EBFCs, and suggests the importance of developing electrodes with improved biocompatibility, for example developing more effective coating which minimizes the immune response [20].

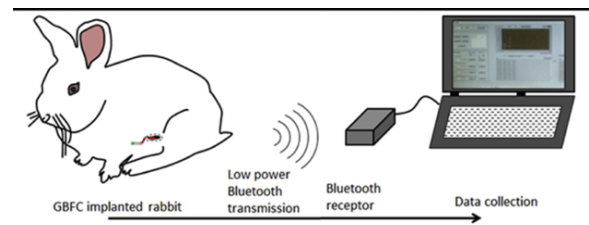


Fig. 3. Illustration of the wireless monitor and control system for the implanted EBFC [20].

C. Pacemaker powered by a single EBFC operating in vitro

To overcome the problem of insufficient power output, Southcote et al investigated the possibility of combining an EBFC with a charge pump [5]. The experiment was performed in vitro to allow larger electrodes, with serum solution mimicking the human circulatory system. The anode was coated with PQQ-GDH and the cathode with laccase. By using an interface consisting of a charge pump and DC/DC converter, the voltage provided by the biofuel cell was increased from 470 mV to the required 3 V. By measurements with a subcutaneous electrocardiographic (ECG) device, it was also shown that the shape of the electrical pulses generated from the pacemaker

was not affected by switching from a standard battery to the EBFC, see Figure 4 [5].

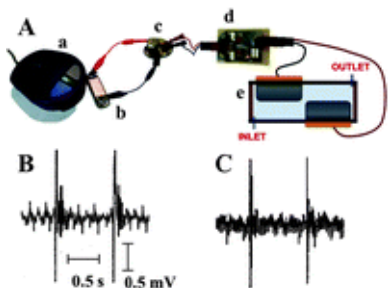


Fig. 4. (A) shows the experimental setup consisting of the EBFC, the charge pump and DC/DC converter, the pacemaker, the ECG device and a sensor to record the electrical pulses. (B) shows the pulse from the pacemaker when powered by a standard battery and (C) when powered by the EBFC [5].

Although this approach successfully powered the pacemaker, the fact that the experiment was done *in vitro* with 6 cm² electrodes has to be taken into account. Since a significant decrease in size is required for *in vivo* implementation, the current would most likely not be high enough to even power the charge pump [2]. This is clearly shown in Figure 5 where the polarization curves for several *in vivo* experiments (b, c and d) show that the current provided by the biofuel cell is below the required threshold to power the charge pump (e) [2]. The generated current from the *in vitro* experiment by Southcott et al (a) is the only one which could successfully power the charge pump and thus utilize its ability to increase the power output [2]. The approach could still be possible in the future, with improved current efficiency, but a more feasible application is to power devices which only require short-time activation, such as biosensors that periodically record and transmit data [2]. This would allow accumulation of electrical energy which could be released in bursts when needed.

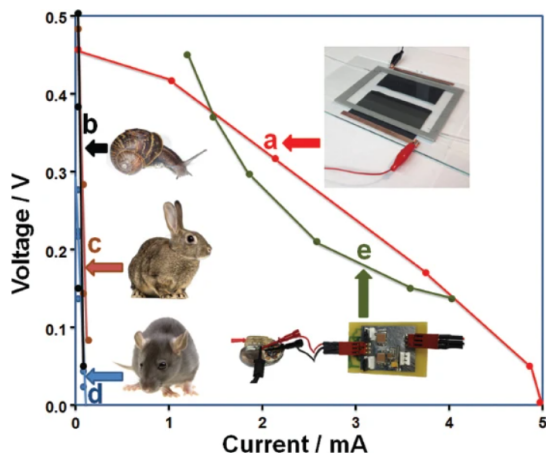


Fig. 5. The polarization curves for *in vivo* experiments of implantable BFCs in snails, rabbits and rats (b, c and d) plotted against the demand curve of a charge pump (e). Only the BFC in the *in vitro* experiment by Southcott et al provided enough current to power the charge pump (a) [2].

V. FUTURE DIRECTIONS

Previous animal studies have shown the potential of implanted EBFCs, yet studies like the one conducted by El Ichi Ribault et al. illustrated the importance of improving the biocompatibility of devices as the delivered power decreased presumably because of inflammation of the rabbit's adjacent tissue [20]. Hence the translation to human implantation would depend upon the development of material science, especially at a nano level [22]. Further research on biocompatible diffusing polymers could be a solution, as they could act as buffering diffusion barriers to reduce the initial inflammatory reaction and decrease the degradation [20].

The nature of energy harvesting from the body is to some extent unpredictable, especially considering fluctuations in glucose level [23]. Hence Sheng et al. proposed the development of hybrid systems that could harvest energy from multiple sources [22]. In a paper from 2018, Katic et al. presented a dual energy harvesting interface consisting of implantable GBFCs and thermoelectric harvesters [23]. This interface enabled the extraction of the maximum power from both simultaneously [23]. Though these hybrid systems require further research, the core idea of gathering energy from multiple sources in parallel could improve the reliability of the system and potentially increase the maximum power output [23].

VI. CONCLUSION

Implanted BFCs are a promising alternative to conventional batteries for powering bioelectronic devices. However, the experiments and analyses presented in this report demonstrate several challenges regarding practical implementation in the human body. Studies performed in living organisms, such as the two-month implantation in snails and the long-term experiment in rabbits, show that metabolic fuels can sustain electrical output. At the same time, these experiments reveal limitations, including low power output, slow recovery after discharge, and progressive performance loss due to inflammation and biofouling at the electrode interface. The *in vitro* demonstration of pacemaker operation further illustrates the concept's potential, yet its reliance on large electrodes highlights the significant gap between *in vitro* experiments and *in vivo* requirements. The combination of the practical studies and theoretical considerations illustrates the practical obstacles for implanted BFCs. Enzyme degradation, limited power density and inflammatory responses remain a challenge, but upcoming nano-material solutions could allow new advancements. Overall, while the development of implanted BFCs has shown considerable progress in the last decade, continued research is necessary before implanted BFCs become a reality in medical implementations.

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