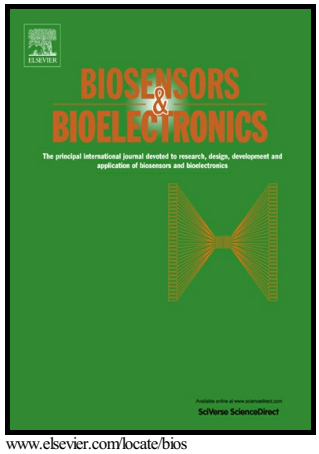

www.elsevier.com/locate/bios

A SELF-POWERED BIOSENSING DEVICE WITH AN INTEGRATED HYBRID BIOFUEL CELL FOR INTERMITTENT MONITORING OF ANALYTES

Dominika Majdecka, Sylwia Draminska, Dariusz Janusek, Paweł Krysinski, Renata Bilewicz

PII: S0956-5663(17)30775-3
DOI: https://doi.org/10.1016/j.bios.2017.11.045
Reference: BIOS10121

To appear in: *Biosensors and Bioelectronic*

Received date: 24 August 2017
Revised date: 11 November 2017
Accepted date: 14 November 2017

Cite this article as: Dominika Majdecka, Sylwia Draminska, Dariusz Janusek, Paweł Krysinski and Renata Bilewicz, A SELF-POWERED BIOSENSING DEVICE WITH AN INTEGRATED HYBRID BIOFUEL CELL FOR INTERMITTENT MONITORING OF ANALYTES, *Biosensors and Bioelectronic,* https://doi.org/10.1016/j.bios.2017.11.045

A SELF-POWERED BIOSENSING DEVICE WITH AN INTEGRATED HYBRID BIOFUEL CELL FOR INTERMITTENT MONITORING OF ANALYTES

Dominika Majdecka[ab#], Sylwia Draminska[a#], Dariusz Janusek[c], Paweł Krysinski[a], Renata Bilewicz[a]*

[a]*Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

[b]*College of Inter-Faculty Individual Studies in Mathematics and Natural Sciences, Banacha 2C, 02-097 Warsaw, Poland*

[c]*SensoriumLab Sp. z o.o., W. H. Lindleya 16, 02-013 Warsaw, Poland*

ABSTRACT

In this work, we propose an integrated self-powered sensing system, driven by a hybrid biofuel cell (HBFC) with carbon paper discs coated with multiwalled carbon nanotubes. The sensing system has a biocathode made from laccase or bilirubin oxidase, and the anode is made from a zinc plate. The system includes a dedicated custom-built electronic control unit for the detection of oxygen and catechol analytes, which are central to medical and environmental applications. Both the HBFC and sensors, operate in a mediatorless direct electron transfer mode. The measured characteristics of the HBFC with externally applied resistance included the power-time dependencies under flow cell conditions, the sensors performance (evaluated by cyclic voltammetry), and chronoamperometry. The HBFC is integrated with analytical devices and operating in a pulse mode form long-run monitoring experiments. The HBFC generated sufficient power for wireless data transmission to a local computer.

Keywords: self-powered biodevice, biofuel cell, biosensor, wireless transmission

[*] Prof. Renata Bilewicz

Faculty of Chemistry, University of Warsaw

ul. Pasteura 1, 02-093 Warsaw, POLAND

e-mail: bilewicz@chem.uw.edu.pl

Tel: +48 225526357

[#] All authors contribute equally to the work

1. Introduction

The progressing industrialization and the rapid growth and development of new technologies associated with the environment call for reduced pollution. Advanced and cost-effective sensing and analytical techniques is required for monitoring and responding to pollution. There is also a need for new solutions in the field of medical diagnostic devices and chemical sensors (Gellett et al., 2010; Newman and Setford, 2006; Rogers et al., 2006; Thevenot et al., 2001; Zhao et al., 2017). Electrochemical biosensors equipped with biofuel cells (BFCs), based on redox enzymes, are becoming an increasingly important devices for solving the emerging requirements for autonomous sensors, which are an important component of the distributed decision-making systems.

All fossil fuel energy sources have impact on the environment, these are typically negative. Therefore, global demand for renewable energy technologies is steadily increasing as the main source of energy production, particularly in developing countries. BFCs are an environmentally safe power source solution, which is becoming increasingly important in energy production for portable electronic devices. BFCs have a unique ability to convert chemical energy stored in non-toxic, biodegradable compounds directly into electricity (Cinquin et al., 2010; Heller, 2006; Stolarczyk et al., 2012; Willner et al., 2009; Zhao et al., 2017; Zhou and Wang, 2012). Interest in biofuel cells results from their ability to operate under mild conditions: at room temperatures and pHs close to neutral. Because of the specificity and selectivity processes occurring at the enzymatic electrodes, they do not require a membrane separating the electrode compartments (Desmaële et al., 2015). The environmentally-friendly products of the catalytic reactions by BFCs and the use of less expensive materials than metallic catalysts used in conventional fuel cells, make the BFCs a desirable alternative power source. The BFCs can work as open–type device, and can be easily miniaturized (Zhou and Wang, 2012). All these unique properties make BFCs more

attractive than conventional fuel cells and more economically effective as a portable energy source, alternative to commercially used batteries. However, because of the low value of the generated voltage and limited current, they impose strong requirements on the design of electronic systems to be powered. There is a need for energy harvester implementation which adjusts the power delivered by BFCs to the electronic requirements of the device, e.g., medical devices, biosensors, cardiac pacemakers and drug delivery systems (such as insulin pumps) (Babadi et al., 2016; Cinquin et al., 2010; Cosnier et al., 2014; Desmaële et al., 2015; Haghighi et al., 2003; Holade et al., 2014; Jensen et al., 2012; Stolarczyk et al., 2014).

Enzymes that show high catalytic activity, have the ability of direct electron transfer (DET), and have a low overvoltage of catalytic reactions are typically used in BFCs studies. Multicopper oxidases such as laccase or bilirubin oxidase (BOx) have been intensively investigated as bioelectrocatalysts of oxygen reduction to water due to their possible applications in the development of biodevices (Shleev et al., 2005). The commercial realization of BFCs requires significant improvement in their performance when immobilized on the electrodes surfaces. This is greatly important to enable DET for more efficient electrical communication between the active site of an enzyme and the electrode (Babadi et al., 2016; Cosnier et al., 2014; Haghighi et al., 2003; Holade et al., 2014; Majdecka and Bilewicz, 2016; Meredith et al., 2011; Poulpiquet et al., 2014; Santoro et al., 2016; Sosna et al., 2010, 2012; Stolarczyk et al., 2014; Yang et al., 2015). The selection of an appropriate electrode material is crucial for high density power production by enzymatic BFCs, justifying their application even in the light of their short life time. There are numerous studies attempting to scale up the power production using different carbon-based materials such as carbon paper, carbon felt, carbon fiber as well as carbon nanotube-based composites as nanostructured materials providing both the electron transfer between enzymes and electrodes, thus creating a suitable microenvironment for the natural catalytic processes of the

enzymes (Babadi et al., 2016; Meredith et al., 2011; Santoro et al., 2016; Stolarczyk et al., 2012, 2014). Previous studies completed by this group notably documented that the biocatalytic current response of these enzymes can be improved by the appropriate design of their adsorption environment on carbon electrodes (Majdecka and Bilewicz, 2016). Properly selected materials, e.g., carbon nanotubes, increase the amount of adsorbed enzyme addressed by the electrode and enhance the enzyme stability and prevent its denaturation (Yang et al., 2015). In addition, the control of the enzyme orientation is not important for their immobilization on such electrodes, because nanostructuring of the electrode surface with carbon nanotubes reduces the distance between the active sites of the redox proteins and the modified electrodes. This results in an efficient electron transfer. It is imperative for the development of biodevices specialized for medical and environmental applications. Monsalve et al. (2015) reported that the H_2/O_2 enzymatic BFC is capable to power a wireless data transmission system. The open circuit potential (OCP) was 1.12 V with a 410 μW maximum power output. The data was sent to the computer every 25 s for 7 hours of continuous BFC operation.

The development of a similar solution was previously reported by our group (Majdecka et al., 2015). As an energy storage unit, a supercapacitor in parallel with a hybrid biofuel cell (HBFC) was used as a source of power for microcontroller with a radio transmitter. The utilization of a supercapacitor as an energy storage unit improves the efficiency of a pulsed-power sourcing from the HBFC (Skunik-Nuckowska et al., 2014). Another solution is the use of lithium-ion batteries, which have a lower leakage current than supercapacitors. In the work by MacVittie et al. (2013), a HBFC was used to power an implantable biomedical device. The HBFC produced electrical power which was sufficient for the operation of the pacemaker for 5 hours. Zhu et al. (2014) reported that they had developed a synthetic high-energy-density

sugar HBFCs which gave a maximum output power density of 0.8 $mWcm^{-2}$ and a maximum current density of 6 $mAcm^{-2}$.

The Cosnier group (Agnès et al., 2014) described a device with a supercapacitor, where redox enzymes of the BFC served for continuous charging of the capacitor. This system can deliver high currents under short pulse discharges and generates 2 mW in every pulse.

MacVittie et al. (2015) produced a wireless electronic system containing a BFC composed of buckypaper electrodes modified with a laccase cathode and a fructose dehydrogenase anode. The open circuit potential, OCP was equal to 0.6 V and the maximum output power was 670 μW. The biodevice was used for environmental parameters monitoring.

A self-powered amperometric biosensor for monitoring acetylcholine was proposed by Moreira et al. (2017). The hybrid biodevice was composed of a metallic cathode for oxygen reduction and an enzymatic anode, which in total generated 4 nW of power at a voltage of 260 mV.

Gai et al. (2015) proposed a BFC device as a portable biomedical sensor which provides a powerful point-of-care tool for early diagnosis of cancer. Bilirubin oxidase, BOx and glucose dehydrogenase were used as biocatalysts for the biocathode and the bioanode, respectively. Recently, Kizling et al. (2015) reported a BFC designed by our group with outstanding long-term performance due to efficient biosupercapacitor properties. The system was used for powering the device for monitoring oxygen levels.

In this study, we aim to design and build the zinc/oxygen HBFC using oxygen and catechol as a perspective analytical tool for medical or environmental applications. Determination of catechol is of importance for monitoring the functioning of central nervous, hormonal, cardiovascular systems since it is a precursor of catecholamine-related neurotransmitters that are secreted in the brain by neurons and relay messages to the target cells. Abnormal level of catecholamines will lead to neurological diseases such as Parkinson's

disease or Schizophrenia (Jackowska and Krysinski, 2013). Novel accurate oxygen biosensors are needed for monitoring life processes, medical diagnostics and chemical applications (Göbel et al., 2009; Gutirres-Sanchez et al., 2015; Mano and Edembe, 2013; Pasternak et al., 2017; Żelechowska et al., 2017).

In the present work, the utilization of carbon paper discs covered with multiwalled carbon nanotubes (MWCNTs) and BOx as a potential cathode is studied. Moreover, the use of a zinc anode covered with a layer of hopeite is evaluated. Lastly, we aim to design and build a custom hand-held, low-power micro sensing device powered by HBFC, which is equipped with a chemical analyte sensor and the ability to wirelessly transmit data.

2. Experimental

2.1 Materials and chemicals

All chemicals were commercially available materials of analytical grade purity. All organic and inorganic reagents were used without further purification. Citric acid ($C_6H_8O_7$), disodium hydrogen phosphate (Na_2HPO_4), potassium chloride (KCl) and ethanol (C_2H_5OH, EtOH) were purchased from POCh (Avantor Performance Materials Poland S.A., Poland). Laccase *Trametes versicolor*, bilirubin oxidase from *Myrothecium verrucaria* and catechol (C9510-100G) were obtained from Sigma-Aldrich (Sigma-Aldrich Sp. z o.o, Poland). Multiwalled carbon nanotubes (MWCNTs), Nanocyl Thin MWCNT 95+% purity, 9.5 nm average diameter, 1.5 μm length were purchased from Nanocyl (Belgium Nanocyl SA, Belgium). The carbon paper (CP) was Toray Teflon Treated (TPG-H-120 Fuel Cell Store). The zinc foil was purchased from Goodfellow (Goodfellow Cambridge Ltd., United Kingdom) and had a purity 99.9% and 0.25 mm thickness. Water was distilled and passed through Milli-Q water purification system. Oxygen gas (99,5%) was obtained from Air Products (Air Products Sp. z.o.o, Poland).

2.2 Electrochemical instrumentation and procedures

Cyclic voltammetry measurements were completed in a three-electrode arrangement with an Ag/AgCl/1M KClaq reference electrode, a platinum foil counter electrode and the carbon paper (CP)/MWCNTs-nanostructured carbonaceous working electrode. The HBFC body is constructed with plexiglass. All current densities and power densities were calculated using geometrical area of the CP/MWCNTs electrode, 3.14 cm^2 area. The HBFC electrical characteristics were completed using a PICOTEST multimeter M3500A (Picotest, USA). The voltammetry and chronoamperometry measurements were performed using a CHI 750E electrochemical analyzer bipotentiostat (CH Instruments, Inc., USA) and an in-house developed electronic system WSPBD-1S (Wireless Self-Powered Biosensing Device with single sensor) was utilized. With regard to the catechol sensor, all measurements were conducted using a commercially available screen-printed three electrode configuration model MAC1.W4.R1, BVT Technologies, Czech Republic (www.bvt.cz). The active region of the sensor is placed in a microcell, 200 µL. These electrodes consisted of a corundum base and graphite layer as working surface, 0.008 cm^2 area and silver/silver chloride reference electrode, also on the corundum base. Catechol sensing was carried out in 0.1 M KCl aerated aqueous supporting electrolyte solution.

All oxygen sensing was carried out in a McIlvaine buffer solution (pH = 5.3) using screen-printed electrodes from DropSens (SPCE, model C110), which consists of a carbon working electrode (4 mm diameter) and a silver reference electrode. The electrode for monitoring the oxygen levels was prepared by adsorbing 10 µL of a MWCNTs suspension onto the electrode surface. After drying, the electrode was kept in 5 mg mL^{-1} BOx solution for 3 hours. All electrochemical measurements were completed at 22 ± 2 °C.

2.3 Preparation of the multilayer biocathode and flow hybrid biofuel cell

The CP multilayer biocathode was composed of 9 modified CP discs (Fig. 1A; for more information please see supplementary material, Fig. S1). The first carbon paper disc (A = 3.14 cm^2) is connected with glassy carbon contact (Fig. 1B) and is modified on a single face with MWCNTs. A MWCNTs suspension (8 mg MWCNTs/ 12 mL EtOH) was applied portion wise (0.5 mL of suspension, 6 times) to one side of the CP disc (2 mg MWCNTs) under reduced pressure using a Büchner funnel, low pressure flask and under pumped pressure. For the other 8 layers, smaller CP discs were used (A = 2.27 cm^2) and 1 mg of the MWCNTs suspension applied to both sides of the disc portion wise (0.5 mL of suspension, 3 times) under reduced pressure. The MWCNTs suspension (1.5 mL) was applied to one side of the CP disc and then dried. The smaller CP discs covered on both sides with MWCNTs and were pressed on the MWCNTs modified side of the larger CP disc (Fig. 1).

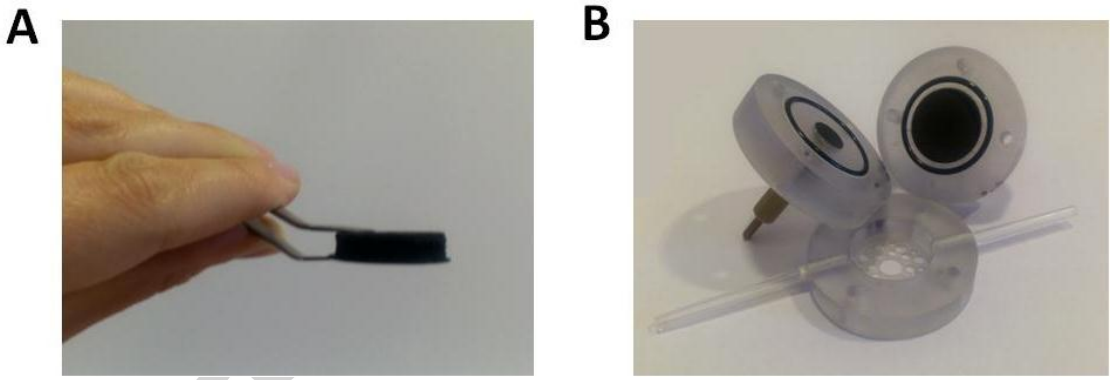

Fig. 1 (A) 9 CP discs biocathode, (B) cathode, anode contact and reaction compartment of hybrid biofuel cell.

BOx was physically adsorbed on MWCNTs covered electrode by incubation in 2 mL of McIlvaine buffer (pH 5.3) solution containing 5 mg mL^{-1} of BOx. Laccase was physically adsorbed onto MWCNTs covered electrode by incubation in 2 mL of McIlvaine buffer (pH 5.3): ethanol (1:1) solution containing 25 mg mL^{-1} laccase as described in the literature

(Majdecka and Bilewicz, 2016). After 15 hours of BOx (or laccase) adsorption, the electrodes were washed thoroughly with water before being used as the biocathode. The biocathodes were prepared using the same procedure together with a zinc/hopeite ($Zn/[Zn_3(PO_4)_2, 4H_2O]$) disc anode and were tested in the HBFC (as shown in supplementary Fig. S1 B). We used the zinc anode to obtain largest possible potential window of HBFC (Jensen et al., 2012).

3. Results and discussion

3.1 Characterization of the enzymatic cathode and hybrid biofuel cell

The reduced pressure procedure allows the anchoring of MWCNTs onto CP surfaces much more efficiently than a simple MWCNT solution method. Previous studies showed how laccase can be prepared for application to a cathode (Majdecka and Bilewicz, 2016). Each CP disc was covered with MWCNT as described in the method. The CP/MWCNT/laccase or CP/MWCNT/BOx discs were arranged to form the multi-CP disc electrodes consisting of varying number of CP discs (Fig 1A). For BOx on a CP electrode (the catalytic oxygen wave with $E_{1/2}$ ca. +0.52 V), the current density was measured at +0.2 V (all potentials are vs. Ag/AgCl/1M KClaq reference electrode) and was 50% higher than for laccase modification (the catalytic wave of oxygen reduction by laccase has $E_{1/2}$ equal to +0.53 V) which achieved 1.2 ± 0,16 mA cm^{-2} (scan rate 1 mV s^{-1}). No mediators were needed to obtain a well-developed reduction curve using either BOx or laccase. It should be noted that the current density for a given mass of MWCNTs on a CP laccase electrode is always larger when the buffer solution contains ethanol, this is due to a favorable enzyme orientation on the carbon nanotubes (Majdecka and Bilewicz, 2016; Wu et al., 2017). BOx is better than laccase for the HBFC, because it is not sensitive towards chloride and larger catalytic oxygen reduction currents are obtained.

The CP/MWCNTs/laccase and CP/MWCNTs/BOx multilayer bioelectrodes were tested in the HBFC's flow mode with a zinc/hopeite anode. The influence of the number of discs (forming the BOx cathode) on the voltage of the HBFC is shown in Fig. 2A. The measurement of voltage was completed after 120 and 240 seconds.

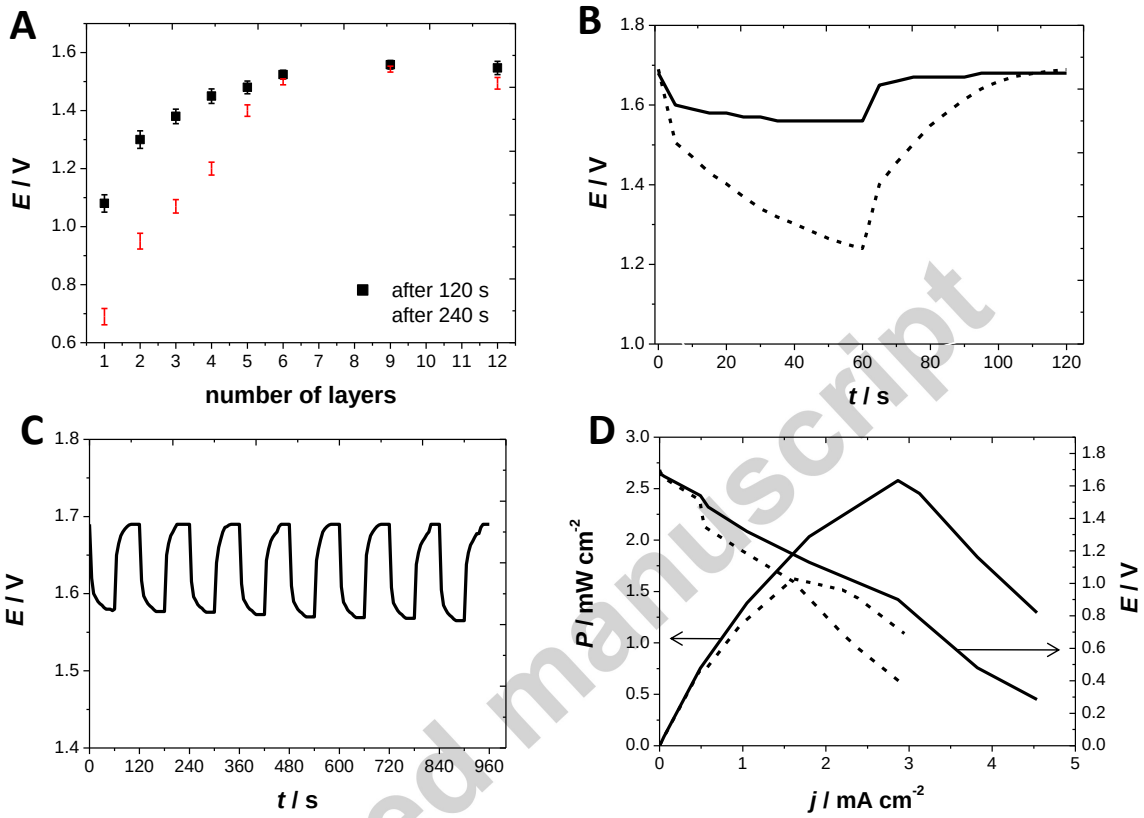

Fig. 2 (A) Discharge, in time, of the HBFC containing different numbers of biocathode after 120 (□) and 240 seconds (■), (B) the voltage-time dependencies of one cycle of discharge/self-recharge of a HBFC composed of nine (solid line) and a single (dashed line) CP BOx cathode at 2 kΩ external resistance, (C) the voltage-time dependencies after 8 cycles of discharge/self-recharge of a HBFC composed of nine CP discs BOx cathode for 2 kΩ switched on and off every 60 seconds and (D) the plots of power density and voltage vs. current density for the HBFC containing nine (solid line) and a single CP disc (dashed line) BOx cathode. Experiments were completed in an aerated McIlvaine buffer solution at pH 5.3, under a flow rate of 10 mL min^{-1}.

The nine CP discs BOx electrode was chosen for further experimentation due to its stable and high voltage obtained. Fig. 2B shows the voltage-time relations at one cycle of discharge/self-recharge of the nine CP discs electrode in the HBFC at 2 kΩ external resistance. For comparison, the behavior of a HBFC with single disc biocathode is also illustrated (Fig. 2B). The HBFC containing a biocathode with nine modified CP discs shows a significantly smaller voltage drop during the operation time compared to that of a single disc biocathode. The latter also requires a much longer time for recharging than when compared to the nine disc cathode. The OCP of nine layer HBFC is achieved shortly after disconnecting the external load resistance. The HBFCs operates efficiently in the pulse mode, comprising of an active phase (first 60 s in Fig. 2B) in which the biofuel cell supplies power with a pre-determined voltage range, and a rest phase (next 60 s in Fig. 2B), where the cells were disconnected from the external load to regenerate to their capacity. The energy of HBFC was harvested and stored, allowing for continuous operation of the detection unit.

The HBFC used in the sensing device was optimized for a 2 kΩ load resistor, that is comparable with the greatest amount most electronic apparatus can supply. Fig. 2C shows a voltage-time dependency of 8 cycles of discharge/self-recharge of HBFC composed of a nine CP discs BOx cathode with the 2 kΩ external load resistors switched on and off every 60 seconds. Following the discharging of the HBFC, the voltage was regenerated within 60s to the initial value, which is equal to the OCP after every discharge/charge sequence and thus proves that the system is stable over that time-frame. The BOx HBFC fulfills the requirement of repeatability in each load cycle, i.e. each successive cycle of the cell is characterized by a similar voltage course over time.

The HBFC power density and voltage vs. output current density, are shown for BOx based system in Fig. 2D. The HBFC yielded the highest power output for the nine CP discs BOx cathode. A maximum power density of ca. 2.5 mW cm^{-2} at 0.88 V output voltage and with a

100 kΩ load was obtained. Similar characteristics for the laccase based HBFC is shown in Fig. S2. In this case, for a single disc laccase HBFC, the voltage is not regenerated within 60 s (Fig. S3A), as opposed to BOx HBFC. The results depicted in Fig. S3 show that BOx is the favorable enzyme from the point of view of regeneration time. When compared to a laccase system, the HBFCs containing BOx generates similar power densities, but voltage drop during the cyclic operation is significantly smaller (Fig. S2).

3.2 The properties of the catechol and oxygen sensing components and of the complete self-powered system

The sensing units were characterized using both the Electrochemical Analyzer CHI 750E instrument and the electronic system specially designed for powering of our device. Full description of the electronic system is provided in the supplementary material and the block diagrams are shown in Figs S4 and S5. The chronoamperometry experiments (CA) were carried out using BVT screen-printed electrode with different catechol concentrations in 0.1 M KCl solution. The catechol is oxidized to ortho-quinone at a potential ca. 0.55 V. The potential used for recording the oxidation current of catechol was set to +0.66 V. Amperometry curves were first recorded using the CHI instrument following additions of 200 μL varying concentration catechol solutions (Fig. 3A). The experiments were repeated five times.

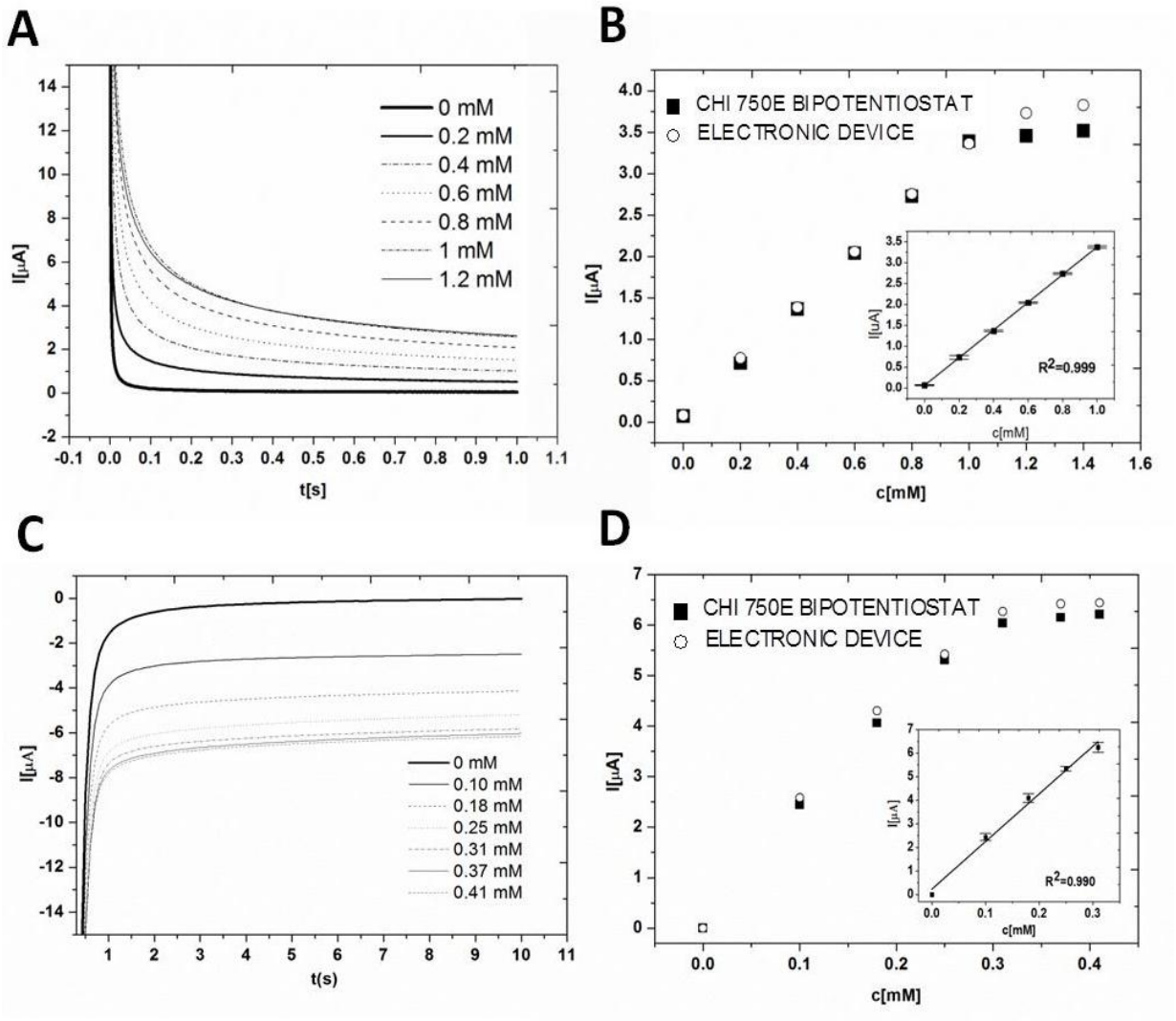

Fig. 3 (A) The CA responses for successive catechol additions recorded using the BVT sensor, in 0.1 M KCl, E=0.66 V, (B) the calibration curve for the system, (C) the current-time curves for the DropSens SPCE sensor in McIlvaine buffer, pH 5.3 with different oxygen concentrations, E=0.1 V, (D) the corresponding calibration curve. Insets (B) and (D) show correlation coefficients for catechol and oxygen sensors, respectively.

The calibration curves recorded with the designed electronic system were in compliance with those obtained using the electrochemical CHI 750E Analyzer . The correlation coefficient was R=0.999 when the catechol oxidation current was sampled 1 second after the application of the sensing voltage (Fig. 3B). The current was measured as a function of the catechol

concentration up to 1.2 mM and showed linearity in the range of 0 to 1 mM. The relative standard deviation of the biosensor response to 1 mM catechol was 2.8 % for the three measurements. The sensitivity and the detection limit for the catechol biosensor were 3.31 µA mM^{-1} and $5x10^{-6}$± 0.02 M, respectively.

The biosensor coated with MWCNTs and adsorbed BOx was utilized for monitoring the oxygen levels. The MWCNTs increased the working surface of the electrode and provided direct contact with the T1 active site of the multicopper enzyme. A constant potential of +0.1 V was selected for the sensing experiments. Fig. 3C shows the chronoamperogram following the repeated additions of 2 mL of oxygen saturated solution (oxygen concentration of 1.1 mM). The relative standard deviation of the biosensor was 6% as determined from the 3 measurements.

The sensor along with the Electrochemical CHI 750E Analyzer and the powered electronic unit gave identical calibration curves with a correlation coefficient of R=0.990 (Fig. 3D).

The current was measured as a function of oxygen concentration up to 0.4 mM and a linear response was found up to 0.3 mM. The sensitivity and the detection limit for biosensor with BOx is 20.19 µA mM^{-1} and $8.28x10^{-6}$ ± 0.04 M, respectively. The analysis of the reciprocals of the steady-state current (1/Iss) against the O_2 concentration (1/C) gave a K_M value of 0.5 ± 0.06 mM. The low values of K_M indicated that the modified electrode exhibited a high affinity for oxygen.

The system consisting of the HBFC composed of nine modified CP discs forming the biocathode and a zinc/hopeite anode, connected with the electronic and sensing units is demonstrated in Fig. 4.

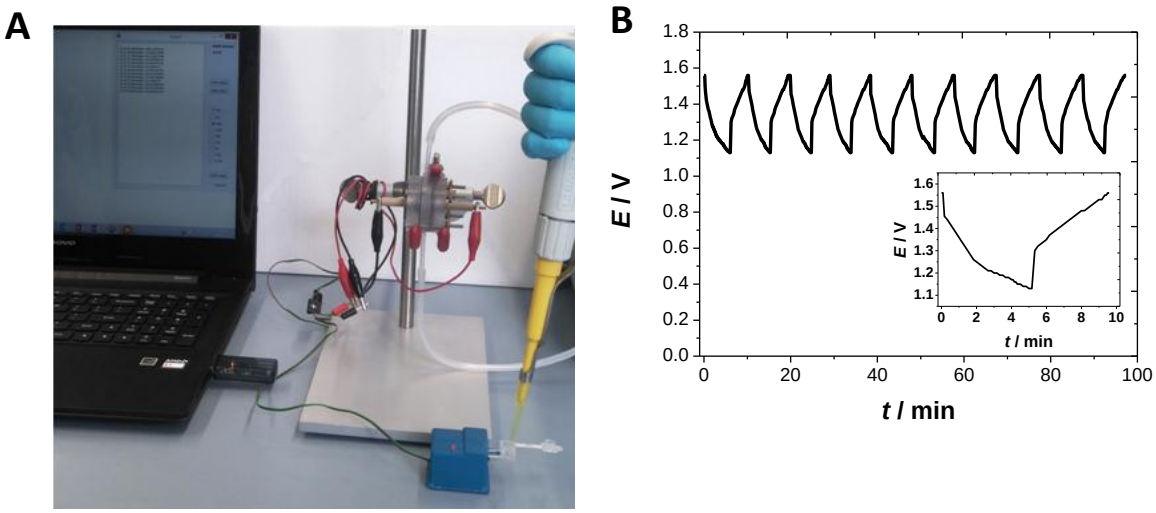

Fig. 4 (A) the HBFC integrated with electronic system and catechol sensor working in a wireless transmission system, (B) the voltage-time dependence of a single HBFC composed of a nine CP discs BOx cathode and zinc/hopeite anode powering the electronic system and catechol sensor in pulse regime. Inset: a single cycle of the discharge/self-recharge of one HBFC composed of nine CP discs BOx cathode. The experiment was completed in an aerated McIlvaine buffer solution (pH 5.3) under 10 mL min^{-1} flow conditions.

The device is not large - electronic and sensor are enclosed in a unit of 30 x 24 x 20 mm. The diameter of HBFC is 30 mm and thickness is 20 mm. The whole system is user-friendly and easy to integrate.

Fig. 4B shows 8 cycles of discharge/recharge of the HFBC working under flow conditions and reflects the stable work of the complete self-powered sensing device. As mentioned previously, the performance of the laccase-based HBFC is not as respectable, as for the case of Box, because it is discharged under the working conditions two times faster (Fig. S6).

The environmental conditions do not affect the performance. Carbon paper, carbon nanotubes, plexi glass, zinc and bilirubin oxidase are stable in the environmental conditions. Laccase can be deactivated in chloride solutions that is why we have chosen BOx which is insensitive to the presence of these ions.

4. Conclusions

The designed self-powered sensing system includes a powering unit – hybrid biofuel cell (HBFC), an electronic management/storage unit, and a small three-electrode sensing device used for catechol and oxygen sensing by chronoamperometry. The optimized HBFC construction in terms of power and stability in time included a zinc anode and a biocathode formed by nine carbon paper discs, which are each modified with carbon nanotubes and bilirubin oxidase or laccase and then pressed together. The power density of such cell was ca. 2.5 ± 0.2 mW cm^{-2} (8 mW) and its OCP was determined to be ca. 1.7 ± 0.4 V. The HBFC operation was tested under an external resistance load. The HBFC operates in a pulse mode with sequential active phase (when sensor measurement is completed) and a rest phase allowing regeneration of the fuel cell to its OCP. The integrated device is suitable for long-run on/off operation of the detection system.

The self-powered three-component analytical biodevice can be a useful alternative application for environmental analysis, medical diagnostics and chemical analysis where a wireless system is desirable.

Acknowledgements

This project was supported by FP7-People-2013-ITN Grant 'Bioenergy, Biofuel Cells: From fundamentals to application of bioelectrochemistry', under grant agreement no. 607793.

References

Agnès, C., Holzinger, M., Le Goff, A., Reuillard, B., Elouarzaki, K., Tingry, S., Cosnier, S., 2014. Energy Environ Sci. 7, 1884–1888.

Babadi, A.A., Bagheri, S., Hamid, B.A., 2016. Biosens. Bioelectron.79, 850–860.

Cinquin, P., Gondran, C., Giroud, F., Mazabrard, S., Pellissier, A., Boucher, F., Alcaraz, J.P., Gorgy, K., Lenouvel, F., Mathe, S., Porcu, P., Cosnier, S., 2010. PLoS ONE 5, 1–7.

Cosnier, S., Le Goff, A., Holzinger, M., 2014. Electrochem. Commun. 38, 19–23.

Desmaële, D., Renaud, L., Tingry, S., 2015. Sensor. Actuat. B Chem. 220, 583–589.

Gai, P., Song, R., Zhu, C., Ji, Y., Wang, W., Zhang, J-R., Zhu, J-J., 2015. Chem. Commun. 51, 16763–16766.

Gellett, W., Kesmez, M., Schumacher, J., Akers, N., Minteer, S.D., 2010. Electroanalysis 22, 727–731.

Göbel, G., Dietz, T., Lisdat, F., 2009. Procedia Chem. 1, 27–276.

Gutierrez-Sanchez, C., Shleev, S., De Lacey, A.L., Pita, M., 2015. Chem. Pap. 69, 37–240.

Haghighi, B., Gorton, L., Ruzgas, T., Jönsson, L.J., 2003. Anal. Chim. Acta 487, 3–14.

Heller, A., 2004. Phys. Chem. Chem. Phys. 6, 209–216.

Holade, Y., MacVittie, K., Conlon, T., Guz, N., Servat, K., Napporn, T.W., Kokoh, K.B., Katz, E., 2014. Electroanalysis 26, 2445–2457.

Jackowska, K., Krysinski, P., 2013. Anal. Bioanal. Chem. 405, 3753–3771.

Jensen, U.B., Lörcher, S., Vagin, M., Chevallier, J., Shipovskov, S., Korelova, O., Besenbacher, F., Ferapontova, E.E., 2012. Electrochim. Acta 62, 218–226.

Kizling, M., Draminska, S., Stolarczyk, K., Tammela, P., Wang, Z., Nyholm, L., Bilewicz, R., 2015. Bioelectrochemistry 106, 34–40.

MacVittie, K., Halámek, J., Halámková, L., Southcott, M., Jemison, W.D., Lobel, R., Katz, E., 2013. Energy Environ Sci. 6, 81–86.

MacVittie, K., Conlon, T., Katz, E., 2015. Bioelectrochemistry 106, 28–33.

Majdecka, D., Draminska, S., Stolarczyk, K., Kizling, M., Krysinski, P., Golimowski, J., Biernat, J.F., Bilewicz, R., 2015. J. Electrochem. Soc. 162, F555–F559.

Majdecka, D., Bilewicz, R., 2016. J. Solid State Electr. 20, 949–955.

Mano, N., Edembe, L., 2013. Biosens. Bioelectron. 50, 478–485.

Meredith, M.T., Minson, M., Hickey, D., Artyushkova, K., Glatzhofer, D.T., Minteer, S.D., 2011. ACS Catal. 1, 1683–1690.

Monsalve, K., Mazurenko, I., Lalaoui, N., Le Goff, A., Holzinger, M., Infossi, P., Nitsche, S., Lojou, J.Y., Giudici-Orticoni, M.T., Cosnier, S., Lojou, E., 2015. Electrochem. Commun. 60, 216–220.

Moreira F.T.C., Sale, M.G.F., Di Lorenzo, M., 2017. Biosens. Bioelectron. 87, 607–614.

Newman, J., Setford, S., 2006. Mol. Biotechnol. 32, 249–268.

Pasternak, G., Greenman, J., Ieropoulos, I., 2017. Sensor. Actuat. B Chem. 244, 815–822.

Patent Application No. P-414079, 2015.

Poulpiquet, A.D., Ciaccafava A., Lojou, E., 2014. Electrochim. Acta, 126, 104–114.

Rogers, K.R., 2006. Anal. Chim. Acta 568, 222–231.

Santoro, C., Babanova, S., Erable, B., Schuler, A., Atanassov, P., 2016. Bioelectrochemistry 108, 1–7.

Shleev, S., Tkac, J., Christenson, A., Ruzgas, T., Yarpolov, A.I., Whittaker, J.W., Gorton, L., 2005. Biosens. Bioelectron. 20, 2517–2554.

Skunik-Nuckowska, M., Grzejszczyk, K., Stolarczyk, K., Bilewicz, R., Kulesza, P.J., 2014. J. Appl. Electrochem. 44, 497–507.

Sosna, M., Chrétien, J.M., Kilburn, J.D., Bartlett, P.N., 2010. Phys. Chem. Chem. Phys. 12, 10018–10026.

Sosna, M., Stoica, L., Wright, E., Kilburn, J.D., Schuhmann, W., Bartlett, P.N., 2012. Phys. Chem. Chem. Phys. 14, 11882–11885.

Stolarczyk, K., Lyp, D., Zelechowska, K., Biernat, J.F., Rogalski, J., Bilewicz, R., 2012. Electrochim. Acta 79, 74–81.

Stolarczyk, K., Kizling, M., Majdecka, D., Zelechowska, K., Biernat, J.F., Rogalski, J., Bilewicz, R., 2014. J. Power Sources 249, 263–269.

Thevenot, D.R., Toth, K., Durst, R.A., Wilson G.S., 2001. Biosens. Bioelectron. 16, 121–131.

Willner, I., Yan, Y.M., Willner, B., Tel-Vered, R., 2009. Fuel Cells 9, 7–24.

Wu, F., Su, L., Yu, P., Mao, L., 2017. J. Am. Chem. Soc. 139, 1565–1574.

Yang, C., Denno, M.E., Pyakurel, P., Venton, B.J., 2015. Anal. Chim. Acta 887, 17–37.

Żelechowska, K., Trawiński, B., Dramińska, S., Majdecka, D., Bilewicz, R., Kusz, B., 2017. Sensor. Actuat. B Chem. 240, 1308–1313.

Zhao, C-e., Gai, P., Song, R., Chen, Y., Zhang, J., Zhu, J-J., 2017. Chem. Soc. Rev. 46, 1545–1564.

Zhou, M., Wang, J., 2012. Electroanalysis 24, 197–209.

Zhu, Z., Kin Tam, T., Sun, F., You, C., Percival Zhang, Y.H., 2014. Nat. Commun. 5, 1–8.

HIGHLIGHTS

- Integrated self-powered sensing system for oxygen and catechol is described
- The biofuel cell operates in pulse mode with sequential active and regenerative phases.
- 9 carbon paper discs with carbon nanotubes and enzyme pressed together form high-performance biocathode