Converter-based accumulation of electric energy generated by microbial biofuel cell

A N Reshetilov¹, A E Kitova¹, A V Dyakov², ³, P M Gotovtsev², R G Vasilov², M A Gutorov³
¹G.K. Skryabin Institute of Biochemistry and Physiology of Microorganisms (IBPM), Russian Academy of Sciences, Pushchino, Moscow Region, Russia
²National Research Centre “Kurchatov Institute”, Moscow, Russia
³Gamma LLC, Zelenograd, Moscow, Russia
E-mail: anatol@ibpm.pushchino.ru

Abstract. Microbial biofuel cell (BFC) was used as a primary energy source for energy storage system. The converter BQ25504 (Texas Instruments) was applied for transformation of electrical energy from microwatt primary sources. The energy storage operation begins if BFC output voltage was higher or equal to 300 mV. In case of stationary operation it was possible to provide energy storage of BFC output voltage equal to 100 mV. The developed system based on converter enables to increase the initial voltage BFC of 0.5 V to 3.1 V; accumulated energy is stored on the various capacitors. Resulting voltage was stable with application of condensers with capacities from 100 μF to 6800 μF. In case of application of 3.1 V and 6800 μF condenser the storage energy was equal to 32.7 mJ. It was enough to provide short time operation of diode L-1154SURDK (2.0 V, 20 mA) and electrical motor M25E-4L (MITSUMI; 3.0 V, 100 mA). Designed system can be applied for energy supply of small electrical devices (for example remote sensors) and autonomous microrobots.

1. Introduction
Recently, increased attention of researchers is paid to development of analytical (biosensor) and energy (biofuel cells) - systems based on biomaterials, which can act as enzymes, cells of warm-blooded organisms or microbial cells. As noted in [1], biosensors and biofuel cells (BFC) devices belong to the same class. In BFC the oxidation of organic compounds that serves as a source of electrical energy; biosensors determine the desired connection and thus can generate current, if applied to their electrodes a potential difference. In both cases the direct conversion chemical energy into electrical energy by biocatalysts.

BFC can be used for electric power low power devices - this point of view is represented in the paper [1]. Low power means enclosed in the range from 10⁻⁷ to 10⁻³ W, extracted from the one square centimetre of electrode area. In this regard, it may be noted that there is a problem of increasing power BFC for their wider use. In this case BFC can be use not only as power sources for remote sensors and devices, but also they may be used in medicine as an electric power source for microdevices such as pacemakers, micropumps, remote sensors etc. It is necessary to mention that operation of all of those devises is operate with its own modes of energy consumption and in some case even periodically, for example based on sensor signal. Additionally, microbial BFC high power can be applied during the municipal wastewater treatment to obtain electricity [2].
The problem of increasing power can be solved by various methods. For example, BFC and biosensors with exoelectrogenic bacteria have the advantage over the cells with intracellular bacteria at equal parameters [3] [4]. Also, series and parallel connection of BFC was used in [5]. Another approach can be based on design of the BFC with application of bacterial cells with exoenzymes on the cell wall [6].

BFC was formed on the basis of living organisms – clams [5]. A set of BFC was connected with a storage capacitor (supercapacitor/ Electric double-layer capacitor) with a capacity of 1 F, who was charged by BFC during about 60 min to 240 mW with stored energy ~ 29 mJ. The stored energy was enough to turn at an angle of 90° to the rotor of the electric motor that has input impedance of 6.5 Ohm. Another example application relates to BFC using them as a source to power biosensor. So, in [7] represent biofuel cell integrated in the contact lens that generates power through the use of glucose, located in the human lacrimal fluid, virtually without changing its contents in the body. BFC generate the open circuit voltage of 0.57 V at develop the power of 1 µw/cm². The authors believe that the use of the diagnostic tool based on the contact lens, containing glucose biosensor would be useful for patients with impaired glucose metabolism. This example can also refer to a regime of periodic use of low-power BFC. In the paper [8] BFC was used for powering up a controller, that sends remote signal trough transmitter. In a review paper [9] attention was paid to the analysis of biofuel cells that have fundamental features - membraneless system that operates without chemical mediator. Many of them have a right to be called micro fuel due to miniature size. A preferred type of enzymes used in these elements - is the cathode compartment - membrane PQQ-dependent dehydrogenases and laccases - in the anode compartment. It seems promising to consider further use BQ25504 type converters to improve and stabilize the voltage in the elements of the type described.

Based on the fact that the BFC is practically useful device whose value would increase significantly in the presence of methods savings generated electricity, in this paper we consider a new approach to the issue of energy storage. Texas Instruments Company manufactures Ultra Low Power Boost Converter with Battery Management for Energy Harvester, designed to work with the micro and milliwatt power sources generated by photovoltaic, thermoelectric, electromagnetic and vibration transducers. Boost Converter based on the chip bq25504; chip transforms received from microwatt power source and transmits it to the storage elements, mainly electrical capacity, including Li-ion batteries, electric double layer capacitors.

The goal of this research was to assess the possibility of applying a voltage converter bq25504 in combination with biofuel cells for energy storage. Despite the development of chips for the unstable power source, accumulation of testing a fuel cell has been described previously. In this work, we examined the accumulation mode, wherein the initial voltage of BFC equal to 350 – 400 mV, the converter rises to the level of 3.1 and stored on the capacitors of various capacities. As a source of electricity has been used microbial BFC with microwatts power output. Developed energy storage system can be used in micropower supply for electronic devices and autonomous micro-robots.

2. Materials and methods

Strain of *Gluconobacter oxydans* VKM B-1280 (All-Russian Collection of Microorganisms) was used in research. Measuring cell were represent by two series-connected BFC with open circuit voltage for each ~ 180 - 250 mV. In series connection the voltage is summed. The volume of the anode chambers was equal and it fits 5 ml. the rods of spectral graphite with diameter of 6 mm were used as the electrodes of the anode and cathode, which are immersed in the solution to a depth of 15 mm. Electrolytic anode and cathode connection ditch single BFC carried out through a hole in the wall of the anode and cathode, a closed membrane MF-4SK (“Plastpolymer”, Saint-Petersburg, Russia) with an area of 1.2 cm². 25 mm of potassium-sodium phosphate buffer (pH 6.0) with addition of 50 mm of sodium chloride were used as the basic solution. 2,6-dichlorophenolindophenol (DGFIP) for the anode compartment and the hexacyanoferrate (III) potassium (GCF) for the cathode (both the mediator procured from Sigma-Aldrich, Co) were used as mediators. Glucose and ethanol were used as substrates for oxidation by *G. oxydans* cells. On external circuit potentiostats (IPCMicro, “Kronas”, 2
Russia and Ametek, Inc., USA) were connected. Registration of cyclic voltammograms was performed at scan rate 3 mV/s. Buffer solution was stirred with a magnetic stirrer. Accumulation mode considered for two BFC connected in series.

Immobilization of microorganisms was accomplished by inclusion in the chitosan gel applied to the surface of the electrode. First of all, 20 µl of biomass diluted 2-fold with a buffer solution, was applied to the electrode. The height occupied by the microbial cells on the electrode was 2 cm. The electrode was dried at room temperature. Then 20 µl was applied to a 2% solution of chitosan in 1% acetic acid [10] over the cells, and dried at room temperature.

Converting complex was presented by controller device bq25504, which is connected to the power source in the form of microbial BFC and a measuring device, paired with a personal computer (PC) equipped with software for data logging (Fig. 1). The authors of this study have developed 4-channel measurement device and the PC software. At Figure 1 the designation Vin corresponds to a measurement channel for electric potential supplied from the BFC to the input of the Converter, Vbat measurement channel corresponds converted voltage supplied to the storage element, Vstor corresponds to a channel voltage measurement output bq25504 chip, Vbat_ok channel is a voltage comparison circuit at the output with a predetermined output voltage. The measuring device has high input impedance in order to prevent the shunting effect on the accumulation mode converter. Energy storage mode was studied on the capacitance of the i1000 100 μF capacitor (SamYoung), as well as the capacity of electric double layer capacitors 1 F (Panasonic brand).

![Figure 1. Block diagram of the complex for electrical energy conversion generated by microbial BFC.](image)

1 – BFC, 2 – converter bq25504, 3 - measuring device, 4- storage element, 5 – Personal Computer. Vin – the voltage supplied from the converter to the BFC, Vbat – the converted voltage to the storage element, Vstor – channel voltage measurement at the output of the chip, Vbat_ok – channel is a voltage comparison circuit at the output with a predetermined output voltage.

### 3. Results and discussion

During first part of research operation of complex with bq25504 converter and chemical energy source was investigated. On the second part bq25504 converter and PV solar cell operation was investigated and in the last part joint operation of bq25504 converter and microbial BFC was provided.

#### 3.1. Chemical energy source “DAEWOO” (AA LR6 1.5 V DAEWOO MEGA ALCALINE).

Processes of energy storage in 1F ionistor are shown at figure 2.

The diagram shows that the input voltage of the converter during the experiment remained constant, thus creating the conditions for rapid conversion. On the drive voltage has reached the value of 3.1 V approximately during 1.5 min and stored on an external capacitor unchanged for 1 min.

Results of experiments with PV solar cell are shown at figure 3. In this case, the solar cell was used as a source with an unstable output voltage varies depending on the lighting. In figure 3 it can be seen exposure uneven the source voltage level due to different levels of light and, as a result, uneven growth of the charge on the capacitor of 1000 μF. After approximately 3 min voltage reaches 3.1 V,
and then cut off the device. It should be noted that when a low initial voltage source (350 mV) the charging time of the integrating capacitor has reached three minutes at 1000 μF capacitance.

![Figure 2. Voltage diagram Vin, Vstor, Vbat_ok and Vbat (explanation in text).](image)

**Figure 2.** Voltage diagram Vin, Vstor, Vbat_ok and Vbat (explanation in text).

![Figure 3. Voltage diagram Vin, Vstor, Vbat_ok and Vbat (experiment with PV solar cell KPS-5130PD7C, Kingbright Electronic).](image)

**Figure 3.** Voltage diagram Vin, Vstor, Vbat_ok and Vbat (experiment with PV solar cell KPS-5130PD7C, Kingbright Electronic).

### 3.2. Converter energy storage from BFC

On figure 4 cyclic voltammograms for single BFC and two BFC connected in series are demonstrated. It can be seen that the series connection enables to measure the voltage source, which provides start-up condition of the converter voltage higher or equal to 330 mV.

Power output curves for single BFC and two BFC connected in series are shown at figure 5. Series connection of power leads to growth due to the growth of the generated voltage.

### 3.3. Operation of “BFC – voltage converter – condenser” investigation.

Condenser with 1000 μF capacity was applied as energy storage device. Results of experiments are presented at figure 6.

Figure 6 shows that the voltage of the capacitor after approximately 30 minutes’ set at 1.2 or more increases; though final potential value is not reached. Hold Time (indicated by two vertical lines) was around 9 min. The resulting voltage is 3.1 V in this case has been reached, it is possible to explain the parameters of BFC - the area of ion-exchange membrane was initially 0.3 cm² and was insufficient to provide the necessary flow of converter input power. This effect is also explained in terms of the value of the internal resistance of the BFC, which in this case was around 3700 Ohms. High internal resistance was due to two factors - the small area of the ion exchange membrane and the initial low
ionic strength buffer (25 mM). The following experiment was increased ionic strength of the buffer solution by the addition of sodium chloride (50 mM) and increased the area of the ion exchange membrane (up to 1.2 cm²), thus reducing the internal resistance of 900 Ohms. Results of this experiment are shown at figure 7. In the experiment, 100 μF capacitor was used as the storage element.

Figure 4. Cyclic voltammograms for single BFC (1) and two BFC connected in series (2).

Figure 5. Power output curves for single BFC (1) and two BFC connected in series (2).

Figure 6. Energy storage experiments results on condenser with 1000 μF capacity.
The accumulation of electrical energy to the integrating capacitance 100 μF.

The diagram shows the voltage rise at the output of the converter Vstor and Vbat on the capacitor. 100 μF capacitor for a time of about 13 minutes to charge up to the value 3.1 V. A tenfold reduction in capacitance and the internal resistance of the BFC possible to raise the voltage on the drive to the desired value for a much shorter time is 13 minutes. Voltage storage time was about 5 hours.

The result of the energy storage in the capacitor 1000 μF using BFC that have an ion exchange membrane area was increased and amounted to 1.2 cm², shown at Figure 8.

The possibility of using the described mode of increase of the output voltage values to the BFC was tested, which may be of practical interest. Integrating capacitance to voltage 3.1 V accumulates, and then it turns the two devices connected - LED (L-1154SURDK, 2.0 V, 20 mA) or electric microengine M25E-4L (MITSUMI; 3.0 V, 100 mA).

Charged to 3.1 μF capacitor with 6800 μF capacity provide stored energy to 32.7 mJ and allowed to short-term operation (around 1 minute) to maintain the LED light or provide a few turns of the rotor rotation electric microengine. Energy storage system designed for BFC can be used in micropower supply for electronic devices and autonomous micro-robots.

4. Conclusion
In conclusion, we can note that operation of "BFC-converter-capacitor" system was shown. The process of accumulation depends on the capacity of the final receiver and in low power BFC
accumulated voltage may not reach the set value. Conversion of the output voltage occurs more slowly than the above internal resistance BFC. Further research plans include assessing and improving system efficiency, increasing power density and stability of the BFC in time that will result in the design of practically important devices.

Acknowledgements
The work was financially supported by RFBR (grant 15-29-01292 ОФИ_М_2015) and by State tusk of Ministry of Education and Science of Russian Federation № 14.2094.2014/K.

References
[1] Bullen R A, Arnot T C, Lakeman J B, Walsh F C 2006 Biofuel cells and their development Biosensors and Bioelectronics 21(15) 2015-45
[2] Du Z, Li H, Gu T 2007 A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy Biotechnol. Adv. 25 464–82. doi:10.1016/j.biotechadv.2007.05.004
[3] Birgit Feketeföldi, Bernd Cermenek, Christina Spirk, Alexander Schenk, Christoph Grimmer, Merit Bodner, Martin Koller, Volker Ribitsch, Viktor Hacker 2016 Chitosan-Based Anion Exchange Membranes for Direct Ethanol Fuel Cells Journal of Membrane Science & Technology http://dx.doi.org/10.4172/2155-9589.1000145
[4] Hendrik duToit, Mirella Di Lorenzo 2015 Continuous power generation from glucose with two different miniature flow-through enzymatic biofuel cells Biosensors and Bioelectronics 69 199–205
[5] Szczupak A, Halamek J, Halamkova L, Bocharova V, Alfonta L, Katz E 2012 Living battery – biofuel cells operating in vivo in clams The Royal Society of Chemistry Energy & Environmental Science DOI: 10.1039/c2ee23209j
[6] Fan Shuqin, Hou Chuantao, Liang Bo, Feng Ruirui, Liu Aihua 2015 Microbial surface displayed enzymes based biofuel cell utilizing degradation products of lignocellulosic biomass for direct electrical energy Bioresource Technology 192 821–825 http://dx.doi.org/10.1016/j.biortech.2015.05.090
[7] Falk M, Andoralov V, Blum Z, Sotres J, Suyatin D B, Ruzgas T, Arnebrant T, Shleev S 2012 Biofuel cell as a power source for electronic contact lenses Biosensors and Bioelectronics 37 38–45
[8] Kevin MacVittie, Tyler Conlon, Evgeny Katz 2014 A wireless transmission system powered by an enzyme biofuel cell implanted in an orange Bioelectrochemistry http://dx.doi.org/10.1016/j.bioelechem.2014.10.005
[9] Magnus Falk, Zoltan Blum, Sergey Shleev 2012 Direct electron transfer based enzymatic fuel cells Electrochimica Acta 82 191–202
[10] Odaci D, Timur S, Telefontu A 2008 Bacterial sensors based on chitosan matrices Sensors and Actuators B: Chemical 134(1) 89–94