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Analysis of the possibility of using stainless steel and copper boride alloy as catalyst for microbial fuel cell fuel electrode

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Abstract

Considering the increasing standard of living, the energy consumption increases as well, and so does waste production. However, there is a possibility to combine energy production and wastewater treatment. A device that can accomplish this task is a microbial fuel cell (MFC). In MFC's activated sludge bacteria can be used for electricity production during wastewater treatment. In MFC's the organic material is oxidized on anode, and the product of oxidation is CO_2 and electrons. One of the problems with MFC's is a low current density of those energy sources (lower than 1 mA/cm^2). Nonetheless, it is possible to increase the current density by using the catalyst for fuel electrode (anode) – as long as a low cost catalyst can be found. The possibility of using stainless steel and Cu-B alloy as catalyst for MFC's is presented in this paper. Cu-B alloys were obtained by the method of electrochemical deposition on electrode. The increase of current density with stainless steel is approximately 0.17 mA/cm^{2}and with the Cu-B catalyst is approximately 0.25 mA/cm^{2}at the temperature of 293-303K. Use of stainless steel and Cu-B catalyst will increase the efficiency in the use of microorganisms for the production of electricity. This will contribute to the development of high efficiency green energy sources. This action will also allow to increase the environment protection.

Keywords: fuel cell, microbial fuel cell, renewable energy source, environment protection, clean technology, Cu-B catalyst, stainless steel catalyst

Streszczenie

Analiza możliwości zastosowania stali nierdzewnej oraz stopu Cu-B jako katalizatora elektrody paliwowej mikrobiologicznego ogniwa paliwowego

Rozwój technologii mikrobiologicznych ogniw paliwowych (MFC – *microbial fuel cell*), może stanowić przyszłość zarówno wytwarzania energii elektrycznej z substancji odpadowych, jak i technologii oczyszczania ścieków. Ogniwa te charakteryzują się niskimi kosztami inwestycyjnymi. Ze względu na znakomite własności katalityczne, w wysokowydajnych ogniwach paliwowych (np. wodorowo-tlenowych), jako katalizator stosowana jest platyna. Jednak koszt platyny praktycznie uniemożliwia stosowanie jej w MFC. Z tego względu należy poszukiwać innych katalizatorów nie zawierających metali szlachetnych. W mikrobiologicznych ogniwach paliwowych najczęściej stosuje się elektrody grafitowe. Praca przedstawia analizę możliwości wykorzystania stali nierdzewnej oraz stopu Cu-B jako katalizatora elektrody paliwowej w mikrobiologicznych ogniwach paliwowych. Pomiary objęły elektroutlenianie glukozy na katalizatorze stalowym oraz na stopie Cu-B. Stop Cu-B nanoszono elektrolitycznie na nośnik stalowy. Zakres temperatur pomiarów: 293-303K. Pomiary przeprowadzono przy pomocy potencjostatu w reaktorze szklanym. Uzyskiwana gęstość prądu wynosiła 0,17mA/cm^2 dla katalizatora stalowego oraz 0,25mA/cm^2 w przypadku użycia stopu Cu-B jako katalizatora. Wykazano, że istnieje możliwość wykorzystania stopu Cu-B oraz stali jako katalizatorów mikrobiologicznych ogniw paliwowych. Znalezienie odpowiedniego i taniego katalizatora może przyczynić się do szybkiego rozwoju odnawialnych źródeł energii jakimi są mikrobiologiczne ogniwa paliwowe.

Słowa kluczowe: ogniwo paliwowe, mikrobiologiczne ogniwo paliwowe, odnawialne źródło energii, ochrona środowiska, czyste technologie, katalizator stalowy, katalizator Cu-B

1. Introduction

The energy consumption increases with the increase of the standard of living. Over the last few decades the demand of energy has increased very much. Energy production is generally based on coal, crude oil, natural gas and nuclear energy. Within the recent few years also some alternative energy sources have been developing. They are used with wind turbines, heat pumps, solar panels, photovoltaic cells, heat pumps and more. One of these sources is also high efficiency fuel cell (FCs). Principle of operation of the FC is known from 1839 [1]. The real efficiency varies between 40-80% [2, 3]. In addition, zero or low negative influence on the environment and silent operation is what characterizes fuel cells. Generally, high efficiency FCs are powered by hydrogen [4, 5]. However, problems with storage of hydrogen are the reason for the search of new fuels for FCs [6-8], also using biofuels [9-11]. However, search of the new catalysts for electrodes is also very important [12, 13]. Over the last few decades the use of microbial fuel cells (MFCs) developed very fast [14, 15]. The paper presents the possibility of using stainless steel and copper boride alloy as catalyst for microbial fuel cell fuel electrode.

2. Theory

2.1. Microbial fuel cell

The concept of microbial fuel cell (MFC) was created by Davis and Yarbrough in the 1960's [16]. Bacteria that were identified as capable of creating electricity in fuel cells include a wealth of genera of *Geobacter*, *Shewanella*, *Pseudomonas*, and others [17-21]. So activated sludge is capable of producing electricity. Microbial fuel cells (or biological fuel cell) are bio-electrochemical systems that are devices that use bacteria as catalysts to oxidize organic and inorganic matter and generate current [16, 22, 23]. Stream of electrons produced by the bacteria (most often by the sewage bacteria) from these substrates is transferred from the anode to the cathode through the electric current receiver. By convention, a positive current flows from the positive to the negative terminal, a direction opposite to that of electron flow [14, 24]. Figure 2.1 shows the protons production by the bacteria in microbial fuel cells [15].

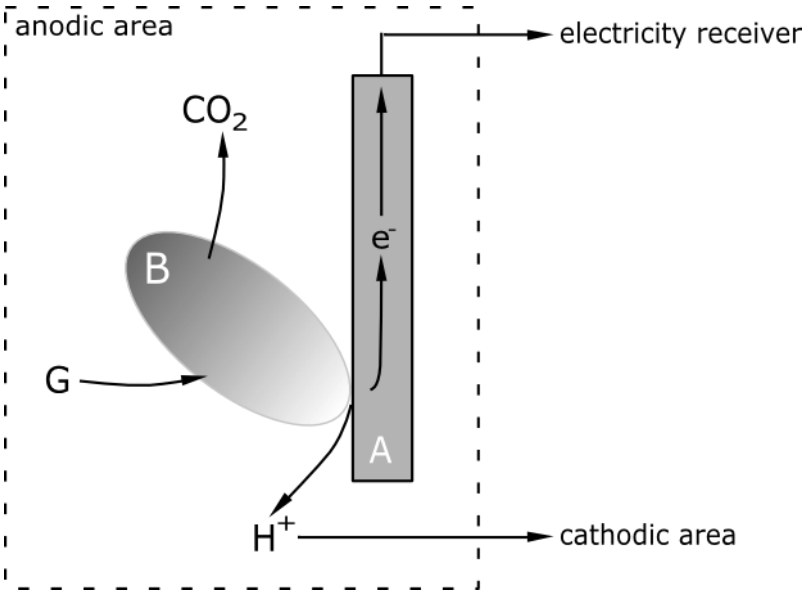

Fig. 2.1.Protons production by the bacteria in microbial fuel cells [15] – figure is not to scale. B – bacterium, A – anode, G – glucose

Graphite is most often used as material of electrode (also as the catalyst). Graphite anodes in the shape of a brush were often used, which constituted the surface for bacterial growth and increased surface of electrode for the increase of current density (Fig.2.2) [25, 26]. Figure 2.2 shows the scheme of a MFC with a graphite anode [15].

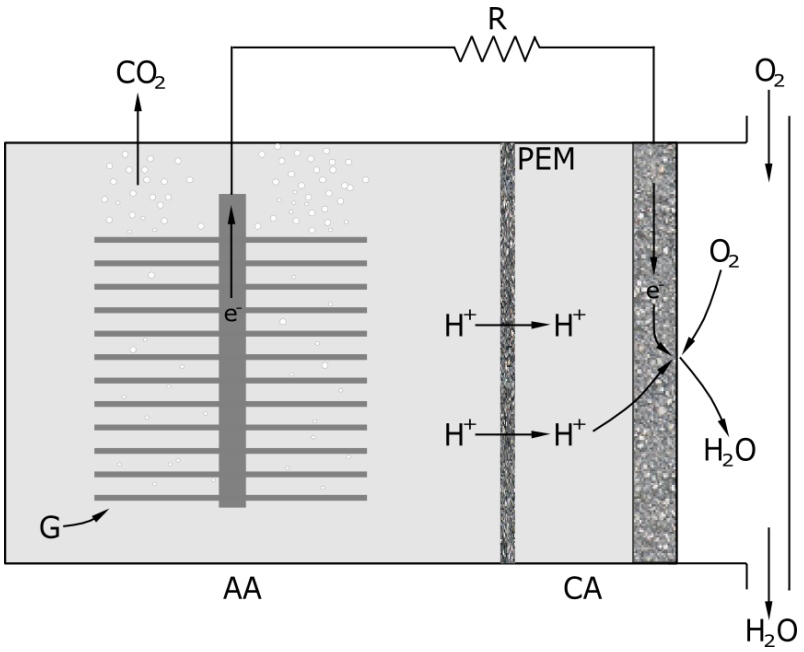

Fig. 2.2. Scheme of a MFC with graphite anode in the shape of brush [15, 25, 26]. G – glucose, R – electricity receiver, PEM – proton exchange membrane, AA – anodic area, CA – cathodic area

Compared with the current density of hydrogen, hydrazine or methanol FC's (1000 mA/cm^2), the current density of MFC is very low (lower than 1 mA/cm^2) [27-31]. The hydrogen or hydrazine FC's are used as high efficiency electricity sources, whereas the MFC's are only additional ecological electricity sources used during wastewater treatment. Thus, the level of current density of MFC's is not that important. In this case, important is the general possibility of obtaining electricity during wastewater treatment process. Obviously, the increase of current density of MFC's allow for wider range of application. Therefore, one should seek every possibility for increasing the current density. One example is the selection of an appropriate catalyst for electrodes. Due to its excellent catalytic properties platinum is most commonly used as the catalyst. However, due to the high price of platinum one should look for other catalysts, that don't contain precious metals. The alloy that could be used as a catalyst in the MFC is stainless steel and Cu-B alloy.

2.1. Efficiency of fuel cell

FCs performs direct conversion of chemical fuel into electrical energy, without combustion. The efficiency of the fuel cell can be calculated from Equation 2.1 [32]:

$$\eta = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \tag{2.1}$$

where: ΔG is the change in Gibbs free energy [kJ/mol], ΔH is the change in enthalpy [J/kg], ΔS is the change in entropy [J/K] and T is the absolute temperature [K].
Electromotive force $E°$ is represented by the relation [32, 33]:

$$E° = \frac{-\Delta G}{n \cdot 96{,}4\ \text{kJ}}\ [\text{V}] \tag{2.2}$$

The current density is described by the Butler–Volmer exponential function [2, 32]:

$$i = A \cdot i_0 \cdot \left(e^{\left[\frac{\alpha_a nF}{RT}(E - E_{eq})\right]} - e^{\left[-\frac{\alpha_c nF}{RT}(E - E_{eq})\right]} \right)\ [\text{mA/cm}^2] \tag{2.3}$$

where: i is the electrode current density [A/m^2], A is the electrode active surface area [m^2], i_0 is the exchange

current density [A/m^2], α_a is the so-called anodic charge transfer coefficient, α_c is the so-called cathodic charge transfer coefficient, E_{eq} is the equilibrium potential [V] and R is the universal gas constant.

The current density is the most important parameter obtained during electrooxidation of fuel in fuel cell. So, it is important to assure high current density of canola oil electrooxidation. But first we need to evaluate basic possibility of glucose electrooxidation with microbes on stainless steel and Cu-B catalyst [32, 34-36].

3. Material and Methods

The stainless steel and copper boride were used as catalysts for MFC. The stainless steel X5CrNi18-10/1.4301 [37] was used as the electrode (catalyst) for measurements. Whereas, Cu-B alloys were obtained by the method of electrochemical deposition. The alloys were deposited on smooth surface of titanium electrode. Attempts of deposition on a nickel support have failed. The alloys were deposited from a mixture of mainly $NaBH_4$ and $CuSO_4$ [12, 13]. The alloys were obtained at temperature of 365K.
Before the deposition of the alloy, copper electrode was prepared in several steps:

- surface was mechanically purified to a shine,
- surface was degreased in 25% aqueous solution of KOH (after the degreasing the surface shall be completely wettable with water),
- electrode was digested in acetic acid,
- electrode was washed with alcohol.

The chemical composition of Cu-B alloys was determined with the X-ray diffraction method (XRD).The alloy selected for measurements was Cu-B alloy with 9% of B.
Researches were done by the method of polarizing curves of bacteria products electrooxidation on stainless steel catalyst and a titanium electrode with Cu-B alloy as a catalyst. Measurements were done in a glass cell with the use of AMEL System 5000 potentiostat. Researches done for three temperatures (293, 298 and 303K) are presented in this paper. The choice of the measurement temperature range was determined by the conditions ensuring intensive development of activated sludge bacteria.
Before each measurement of electrooxidation of activated sludge wastewater pH was measured with the CyberScan 2000 pH-meter, while the conductivity was measured with the use of AquaPro AP-2 conductivity meter. Measurements were made at the temperature of 293K.

4. Results

In the first stage the electrooxidation on graphite electrode was conducted and then measurements were performed for the electrooxidation with stainless steel and Cu-B catalyst. The measurements allowed to evaluate the influence of the stainless steel and Cu-B alloy used as catalyst on change of current density i, compared to current density obtained on graphite electrode.
Conductivity of the wastewater (after initial treatment) with activated sludge was equal to 1.66 mS, and pH was equal to 7.6.
Figures 4.1, 4.2 and 4.3 show the polarization curves of wastewater electrooxidation on graphite, stainless steel and Cu-B alloy electrode with activated sludge bacteria at the temperature of 293 – 303K.

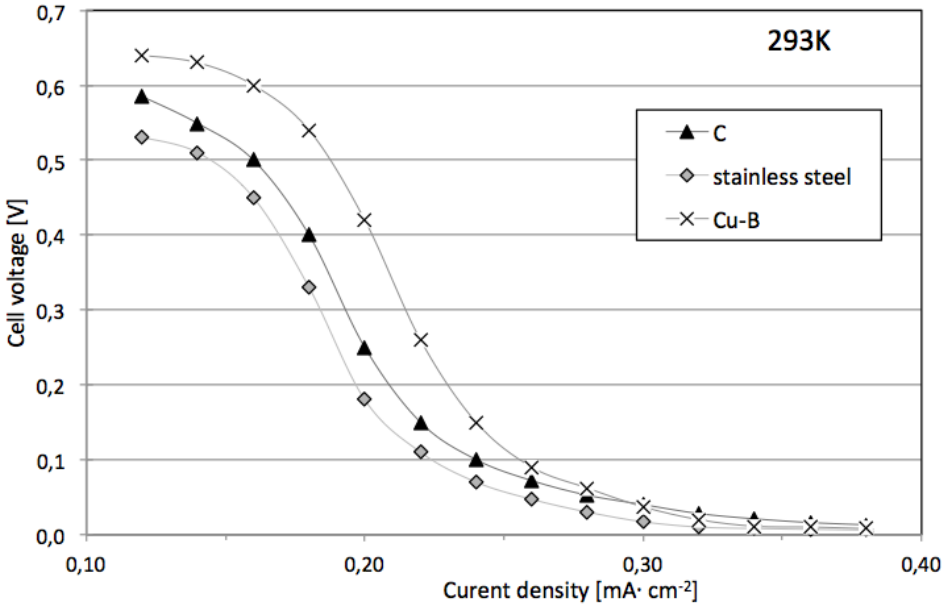

Fig. 4.1. Polarization curves of electrooxidation of wastewater with bacteria from activated sludge with graphite, stainless steel and Cu-B alloy catalyst at the temperature of 293K.

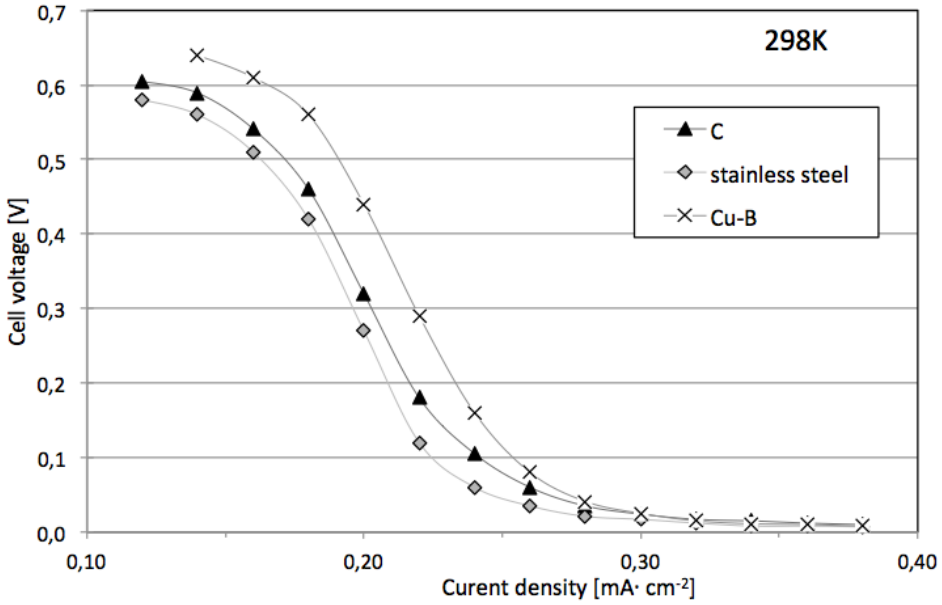

Fig. 4.2. Polarization curves of electrooxidation of wastewater with bacteria from activated sludge with graphite, stainless steel and Cu-B alloy catalyst at the temperature of 298K.

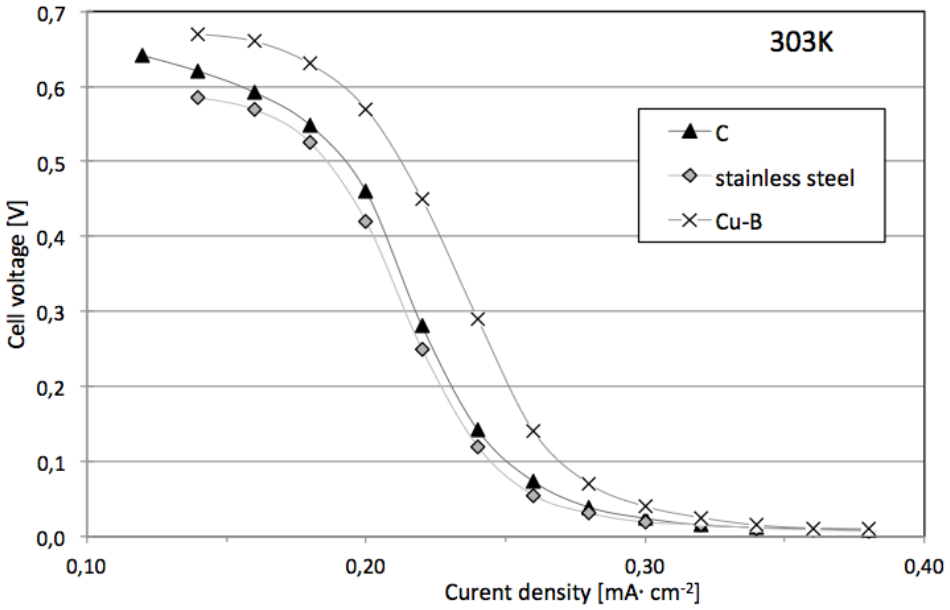

Fig. 4.3. Polarization curves of electrooxidation of wastewater with bacteria from activated sludge with carbon, stainless steel and Cu-B alloy catalyst at the temperature of 303K.

5. Discussion and Conclusions

The measurements for the electrode with Cu-B alloy as catalyst showed an increase of current density compared to the measurements for the graphite electrode, whereas the measurements for the stainless steel electrode showed an slight increase of current density compared to the measurements for the graphite electrode. Polarization curve at the temperature of 293K (Fig. 4.1) shows that current density for graphite electrode is about 0.20 mA/cm^2.In any case (for all temperatures), for the stainless steel the obtained current density was lower than for the graphite electrode (Fig. 4.1, Fig. 4.2 and Fig. 4.3).In any case (for all temperatures), for the Cu-B alloy the obtained current density was higher than for the carbon electrode(Fig. 4.1 – 4.3).Polarization curves for Cu-B alloy (9% of B) as catalyst allow for the increase of current density up to 0.21 mA/cm^2 at the temperature of 293K, and the increase of current density up to 0.25 mA/cm^2 at the temperature of 303K. So, the increase of current density was obtained with temperature increase.

The MFC's are low-density power sources. One of the reasons of low current density is the low electrical conductivity of wastewater. But electrical power generation in MFC's is just an additional process during purification of wastewater. So, slight increase of current density with Cu-B alloy used as the catalyst can allow to develop green energy sources. These sources enable power development, which are additional processes during the ones already existing. The current density obtained with stainless steel, as catalyst is lower than current density obtained with graphite electrode. So, possibility of using stainless steel and Cu-B alloy as catalyst for MFC's was demonstrated in this paper but the use of stainless steel as catalyst does not increase the current density in relation to the graphite electrode.

A fundamental possibility of using stainless steel and Cu-B alloy as a catalyst for fuel electrode in MFC was presented in this paper. Subsequent research should include MFC's operation measurements in real conditions. However, it should be measured how the activated sludge microorganisms develop in the presence of stainless steel and Cu-B alloy. Moreover, it is necessary to perform measurements of MFC's operation in a long time for evaluation of microbial influence on electrodes surface in a long time operation.

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