IMPACT OF DIFFERENT TYPES OF SEPARATORS ON THE EFFICIENCY OF A DUAL-CHAMBERED MFC

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ABSTRACT. Microbial fuel cells are an ecofriendly modern technology for production of energy from alternative sources. They provide an opportunity of wastewater or wastes treatment with a simultaneous electricity generation. For the purposes of the present study there was designed an U-shaped two-chambered microbial fuel cell, based on the process of dissimilative microbial sulfate reduction, whereby there was no necessity of mediator addition in the anodic chamber. Graphite electrodes with equal surface areas were used and as a catholyte - a buffered solution of $K_3[Fe(CN)_6]$ with pH 7. Numerous laboratory experiments were carried out with variants of classic salt bridges and recently preferred cation exchange membranes in order to establish the influence of the type of the separator between the two sections, the cathodic and the anodic, on the efficiency of microbial fuel cell. The electrochemical behavior of the fuel element was observed with each one of the separators designs.

Key words: Microbial Fuel Cell, Wastewater Treatment, Alternative energy

ВЛИЯНИЕ НА РАЗЛИЧНИ ВИДОВЕ СЕПАРАТОРИ ВЪРХУ ЕФЕКТИВНОСТТА НА ДВУКАМЕРНА МИКРОБНА ГОРИВНА КЛЕТКА

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РЕЗЮМЕ: Микробните горивни клетки представляват модерна екологощадяща технология за добив на енергия от алтернативни източници. Те дават възможност за третиране на отпадъци или отпадъчни води едновременно с производство на електрическа енергия. За целите на настоящето изследване е конструирана е U-образна двукамерна микробна горивна клетка, базирана на процеса на дисимилативна микробна сулфат редукция, при което отпада необходимостта от добавяне на медиатор в анодната област. Използвани са графитени електроди с еднаква повърхност и буфериран разтвор на $K_3[Fe(CN)_6]$ с pH 7 като католит. Проведени бяха редица лабораторни опити с варианти на класически солеви мостове и предпочитани напоследък катион-обменни мембрани с цел установяване на влиянието на вида на сепаратора между двете секции, катодната и анодната, върху ефективността на микробната горивна клетка. Електрохимичното поведение на горивния елемент е проследено при всеки един дизайн на сепаратора.

Ключови думи: Микробна горивна клетка, пречистване на отпадъчни води, алтернативна енергия

Introduction

Due to the expanding lack of infinite oil and gas reserves there is a severe need of renewable sources of energy. Among the appropriate and well-known alternatives to fossil fuels, such as wind, hydropower, solar energy and biofuels, in the last century (especially last two decades) the scientists have stared and on the microbial fuel elements as a potential for wastewater treatment with electricity production (Wang et al., 2012).

Microbial fuel cells (MFCs) are devices that allow to produce an electric current from the microbial vital activity. MFCs ordinarily consist of two compartments, anodic and cathodic, separated by a membrane, permeable to protons, but not to microbial cells, organic and inorganic compounds. The external circuit connects the anode to the cathode. The anodic chamber is usually fed continuously with fresh wastewater, that supplies the microorganisms with necessary nutrient substrates.

The sulfate-rich wastewaters are widespread around the world (Kosinska, 2009). They occur from mining and industrial processes, but also as a natural reaction. These effluents contain high concentrations of dissolved heavy metals, that can be lethal to the inhabitants of the ecosystems, if they are discharged untreated.

The MFCs based on the process of dissimilative sulfate reduction combine the removal of sulfates from wastewaters with power generation. Under anaerobic conditions the sulfate-reducing bacteria use sulfates as a terminal electron acceptors for the degradation of organic compounds and produce hydrogen sulfide (Angelov, 2012). The bioproduced H_2S serves as a mediator and there is no need of adding another one.

The aim of the present study was to evaluate the type of the separator between the two sections, the cathodic and the anodic, on the efficiency of the fuel element. Numerous laboratory experiments were carried out with variants of classic salt bridges and recently preferred cation exchange membranes. The electrochemical behavior of the fuel element was observed with each one of the separator designs.

Materials and methods

Design of the laboratory scaled MFC

A dual-chambered U-shaped MFC was designed especially for the purpose of these experiments. This design allowed an easy replacement of the separator, a salt bridge (SB) or a membrane, between the two sections, the cathodic and the anodic (Figures 1 and 2).

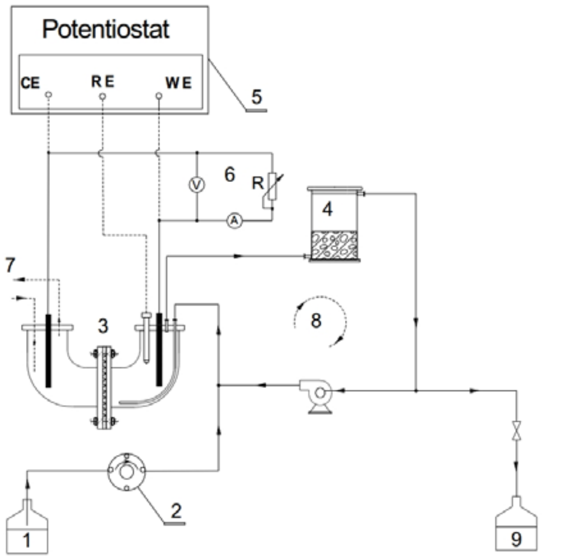

Fig. 1. Laboratory-scaled U-shaped MFC, based on the process of MDSR
1 - Feeding tank, 2 - Dosing peristaltic pump, 3 - MFC, 4 - Buffer tank, 5 - Potentiostat, 6 - Load circuit, 7 - Air, 8 - Recirculating pump, 9 - Collector tank.

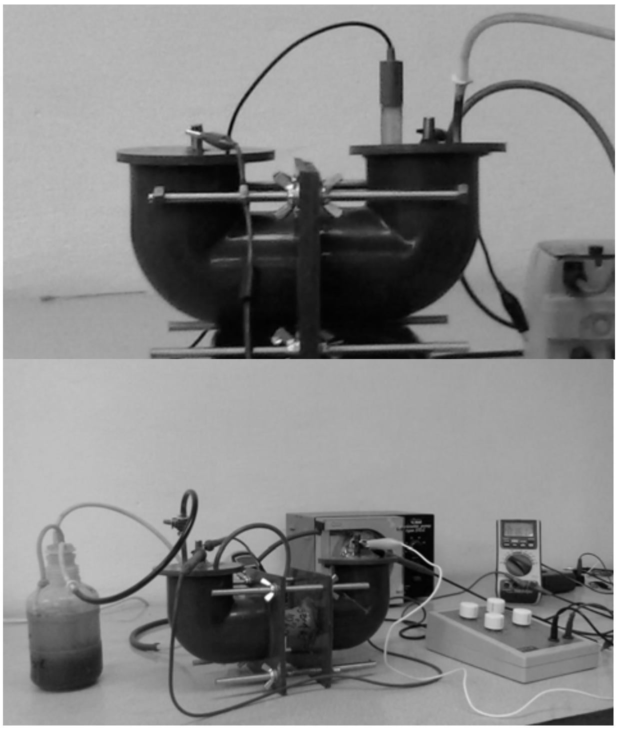

Fig. 2. Two operational modes of the U-shaped MFC, based on the process of MDSR
MFC with a membrane (up), MFC with a salt bridge (down)

The volume of the anodic and cathodic chambers of the MFC itself were of 0.48 dm^3. The volume of anodic section together with the buffer tank was 1.2 dm^3. As electrodes were used graphite rods with a diameter of 8 mm and a length of 9 cm. To separate the two compartments were used different types of separators (Table 1).

Table 1.
Different variants of separators used for different operational modes of the MFC

Variant	Type of separator	Description of the type (composition) of separator
1	Salt bridge	10 % of agar-agar
2	Salt bridge	10 % of agar-agar, 1 M KCl
3	Salt bridge	10 % of agar-agar, 3 M KCl
4	Salt bridge	10 % of agar-agar, 5 M KCl
5	Salt bridge	10 % of agar-agar, 1 M NaCl
6	Salt bridge	10 % of agar-agar, 3 M NaCl
7	Salt bridge	10 % of agar-agar, 5 M NaCl
8	Salt bridge	10 % of agar-agar, 3 M NaCl, 3% graphite powder
9	Membrane	CMI-7000S, cation exchange, Membrane International Inc
10	Membrane	CMI-7000S, covered with a film of Nafion 274704, Sigma-Aldrich
11	Membrane	Nylon membrane, 0,45 µm, covered with a film of Nafion 274704, Sigma-Aldrich

The salt bridges consisted of PVC pipe (diameter - 25 mm, length – 65 mm) filled with electrolyte (KCl or NaCl) and gelified with agar-agar to prevent mixing of anolyte with catholyte. The three types of membranes are also given in Table 1. Each one of them had an area of 0.0012 m^2.

Almost half of the volume of the buffer tank to the anodic chamber was filled up with 0.3 kg modified zeolite with elemental composition as follows: 67.96% SiO_2, 11.23% Al_2O_3, 0.83% Fe_2O_3, 2.85% K_2O, 0.74% Na_2O, 3.01 CaO, 0.06% MgO, 0.90 TiO_2. The zeolite was saturated with NH_4Cl and KH_2PO_4, because these biogenic elements were important for the achievement of high sulfate-reduction rates. The fraction size was 2.5–5.0 mm and the particles were used as a carrier of the electroactive sulfate-reducing biofilm. Cation exchange capacity and the exchanged ions in meq/100 g were respectively: 112.75, K^+ – 33.88, Na^+ – 21.01, Ca^{2+} – 63.48, Mg^{2+} – 2.68. Thus, the reported U-shaped MFC design formed two zones: anodic one, where electroactive biofilm on zeolite derived electrons from organic substrates and produced H_2S and cathodic one, where the oxygen was the terminal electrons acceptor and reacted with the released protons.

The anodic chamber was inoculated with 50 ml mixed culture of sulfate-reducing bacteria. Then, MFC was feeding continuously with culture medium after biofilm formation. The adherence of the biofilm on the carrier took nearly 3 months. The formation of active biofilm was carried out through periodic replacement of 50% of the liquid phase of MFC with fresh medium. Replacement of the liquid phase was performed after sulfate concentration reduced below 0.2 g/l. In the end of this period it was started continuous feeding of the anaerobic reactor with a modified culture medium of Postgate.

Each experiment with a different separator proceeded 24 h. At the end of the cycle the electrochemical behavior of the element was observed. Then the separator was replaced with a new one. The ambient temperature was relatively constant - in the range of 21 – 22 °C.

The catholyte in the cathodic chamber was a solution of 100 mM $K_3[Fe(CN)_6]$ in 67 mM phosphate buffer with pH 7.0. The final electron acceptor was oxygen in air, which in reduction together with the protons located in cathodic space, formed water. The operation of the MFC was implemented under open air mode for the cathodic chamber.

Cultivation of sulfate-reducing bacteria

During these series of laboratory investigations in the anodic area of the installation were treated solutions containing high concentrations of organic compounds and sulfates - synthetic solutions (media for sulfate-reducing bacteria). The culture medium for SRB contained in g/dm³: K_2HPO_4 - 0.5, NH_4Cl - 1.0, Na_2SO_4, anhydrous - 2.0, $CaCl_2$ - 0.1, $MgSO_4.7H_2O$ - 4.0, Na-lactate - 6.0, yeast extract - 0.25 and pH 6.5. The sulfates in the nutrient medium had a concentration of 3 g/dm³, thus the the proportion between organic carbon and the terminal electron acceptor was 0.67.

Analytical methods

Eh, pH and the potential in mV were measured in some certain points of laboratory installation. The same places were sampled for spectrophotometric determination of sulfates. Electric parameters of MCF were monitored with a portable digital multimeter Keithley Model-175. A precise potentiometer with maximum value of 13.5 kΩ was used for measurement of the external resistances. For the establishment of the system electrochemical behavior was used a potentsiostat - ACM 3 connected to PC for reporting and analysis of the accumulated data.

Results and discussions

As Ramya Nair stated in his comparative study, 2013, the 10 % agarose salt bridge (SB) was showing maximum efficiency with a maximum power density. So for the preparation of salt bridges in this study it was chosen this concrete concentration.

The first aim was to investigate the feasibility of using agarose salt bridges for proton transport in Microbial Fuel Cells (MFC). The second aim was to compare the obtained results of classical salt bridges to these of the three design variants with widely used membranes. As the agarose salt bridges are not long resistant to the impact of the two fluids (catholyte and anolyte), the time for implementation of each experiment was specified to 24 h to prevent leakages of one of the liquids into the other.

The chemical composition of the feeding solution is given in Materials and Methods. The initial value of COD was 8.24 gO_2/l, of SO_4 – 3 g/l and pH was adjusted to 7.0. The averages of main operational parameters of the anolyte of MFC in the 24-th hour from the beginning of the experiments for all 11 variants are presented in Table 2.

Comparing the results obtained from the design variants of salt bridge, the highest value of power density was observed when using a SB with 3 M NaCl. This variant was chosen to be modified by adding an extra compound – graphite powder, 3%, to improve the proton transport in the MFC and thus – its efficiency.

Table 2.
MFC performance in the 24-th hour

Parameter	Initial value	Average value (24th hour)
pH	7.0	8.2
Eh, mV	277	-250
TDS, g/l	6.42	5.2
SO_4, g/l	3.08	1.49
H_2S, g/l	0.1	0.25
COD, gO_2/l	8.24	6.48
OCV, mV	354	678
COD reducing rate, %	-	21.3
V_{SR}, gSO_4/l.h	-	0.088

Figure 3 shows the potentials dynamics at different resistances at the 11 different separator designs.

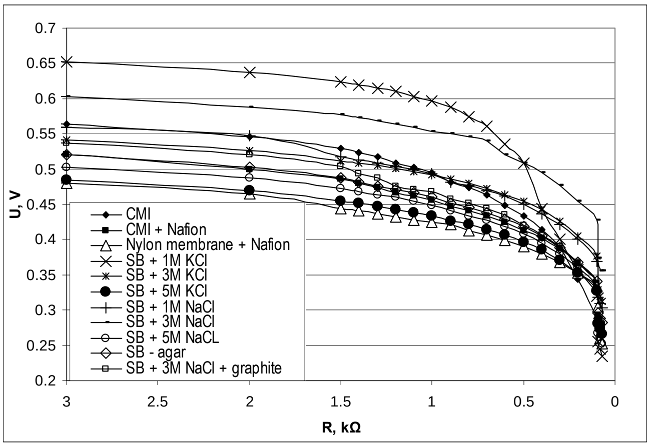

Fig. 3. Drop of potentials at different resistances under 11 different operational modes with different types of separators

At Figure 4 are presented the dynamics of power densities at different resistances at the 11 different separator designs.

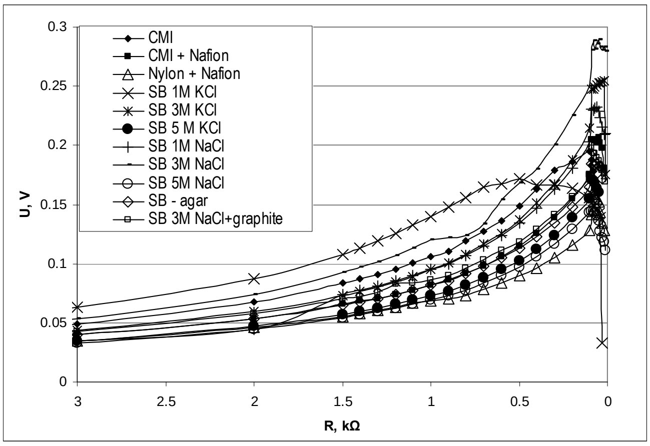

Fig. 4. Dynamics of power densities at different resistances under 11 different operational modes with different types of separators

The effects of different sodium chloride (potassium chloride) concentration on Potential (V) and power density (W/m²) per graphite electrode surface area are presented in Figures 3 and 4. When salt concentration was increased from 1M to 3M the corresponding power densities increased and at the both variants – with KCl and NaCl. The best results were observed when using salt bridges with 3M KCl or 3M NaCl, as with the second one the power density attained to 0.289 W/m².

Increasing the salt concentration facilitated the transfer of more protons from the anode to the cathodic chamber and it also reduced the activation loss. More than 3M salt in the SB had no major effect on the MFC performance, on the contrary, there is a drop in its efficiency.

These outcomes can be set against variants with membranes, especially with the preferred in previous investigations CMI-7000S. This membrane was cationexchange, not selectable to protons. It was possible to conduct variable cations and thus to influence the conductivity of the anolyte and respectively – the electrochemical performance of MFC. The same effect was observed at the variants with SB. The forming of thin film of Nafion on CMI-7000S led to slight increase of the electrochemical parameters of MFC. The maximal power density changed from 0.195 to 0.204 W/m^2.

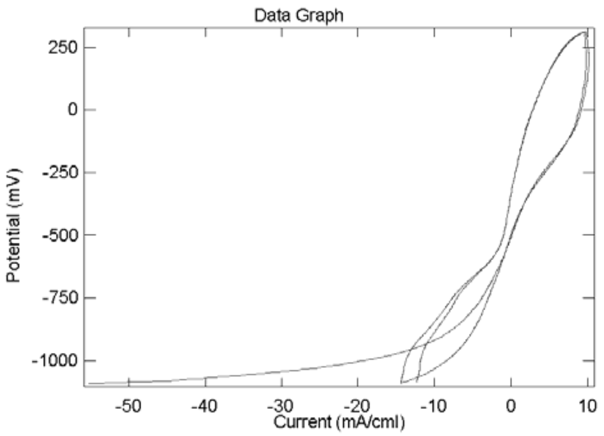

Fig. 5. Cyclic voltammetric characteristic of MFC with 3M NaCl salt bridge

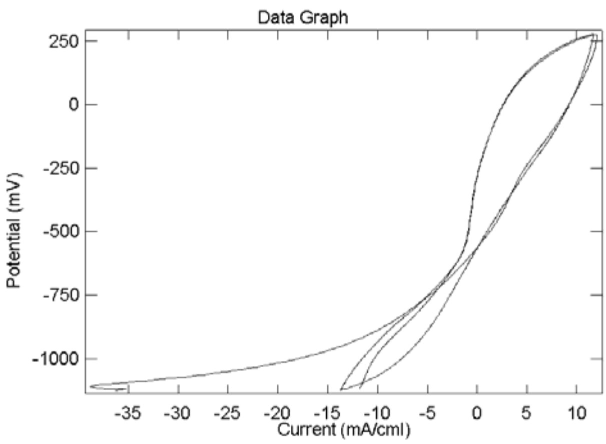

Fig. 6. Cyclic voltammetric characteristic of MFC with 3M NaCl salt bridge with added graphite powder

The addition of graphite powder to the composition of 3M NaCl SB had not a crucial impact. The values of monitored parameters remained in the same range, even the maximum power density decreased slightly in. For this reason subsequent experiments with added graphite to the other options were not carried out. However, there was observed an increase of 18% of the area of CVA at the modified variant of SB (Figures 5 and 6). This was probably due to the facilitated proton transport through the salt bridge.

Conclusions

This study investigated the type of separator affecting the performance of a specially designed dual chambered U-shaped MFC, based on the process of microbial dissimilatve sulfate-reduction. The proton transport was implemented through agarose salt bridges with different molar concentrations of KCl and NaCl. Then this constructive element was replaced with more contemporary one – 3 different variants of exchangeable membranes. The increase of salt concentration in salt-agar bridge (to 3 molar concentration of NaCl or KCl) improved power production, because of the change in electroconductivity of the anolyte and the decrease of its internal resistance. The agarose salt bridges are not long resistant to liquids and although they are easily replaceable and not very expensive they are not convenient for long-term operation of MFC. The higher power production is short-term and does not fulfill their use.

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The article has been reviewed by prof. Yoncho Pelovski and recommended for publication by department "Engineering geoecology".