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ESTABLISHMENT THE IMPACT OF ANODIC TYPE ON THE PERFORMANCE OF MFC WITH H_2S AS A MEDIATOR

Katerina Nikolova, Anatoliy Angelov, Svetlana Bratkova, Petia Genova

University of Mining and Geology “St. Ivan Rilski”, Department of Engineering Geoecology, 1700 Sofia, nikolova_kat@yahoo.com

ABSTRACT. In order to establish the impact of the type of electrode in the anodic chamber of an MFC, based on microbial sulfate reduction, a series of laboratory experiments is performed with the same U-shaped design of the fuel element and identical experimental conditions. Each time the anodic surface area is the same. The cathode at the five variants is a graphite rod. It was found that the aluminium anode allows a transfer of a larger electron flow and the generation of higher maximum power density rates - more than three times higher than those obtained with the graphite. The lowest value of coulombic efficiency is that of the lead anode.

Keywords: Microbial Fuel Cell, Wastewater Treatment, Alternative energy

УСТАНОВЯВАНЕ НА ВЛИЯНИЕТО НА ВИДА НА АНОДА ВЪРХУ РАБОТАТА НА МГК С МЕДИАТОР СЕРОВОДОРОД

Катерина Николова, Анатолий Ангелов, Светлана Браткова, Петя Генова
Минно-геоложки университет “Св. Иван Рилски”, катедра “Инженерна геоекология”, 1700 София, nikolova_kat@yahoo.com

РЕЗЮМЕ. С цел установяване на влиянието на вида на електрода в анодната област на МГК, базирана на микробна сулфат редукция, е извършена серия от лабораторни опити с една и съща U-образна конструкция на горивния елемент и идентични условия за провеждане на експеримента. Площта на анода всеки път е еднаква. Катодът и при петте варианта е графитна пръчка. Установи се, че алуминиевият анод позволява трансферирането на по-голям електронен поток и генерирането на по-високи стойности на максималната плътност на мощността – над три пъти по-високи от тези, получени с графит. Най-ниската стойност на кулонова ефективност е при оловния анод.

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

Introduction

The long-term ensuring with cheap, accessible and eco-friendly energy and the complex answer to energetical and environmental problems is a prospective new strategy that can be summarized as a conversion of "energy for waste disposal" to "energy from waste". Mine and industrial wastewaters formed during mining and ore processing cause a serious impact on the environment. A common problem is the formation of acid mine waters with low pH and high concentrations of heavy metals and sulphates as a result of the exposure of fresh surface of the sulfide minerals to air and fluids. The sulfates are highly mobile and can migrate easily on large distances and in depths. These cases can lead to damages of ecosystems (Krishnakumar et al., 2005), with a number of negative effects on surface and groundwater basins (Johnson and Hallberg, 2005).

The idea of microbial fuel cells (MFCs) is relatively new - it provides the possibility of consideration of wastewater as a resource, not only for an economic and an environmental problem (Logan and Regan, 2006; Wang et al., 2012). MFCs enable the treatment of waste or wastewater with a simultaneous production of electricity through the vital activity of microorganisms.

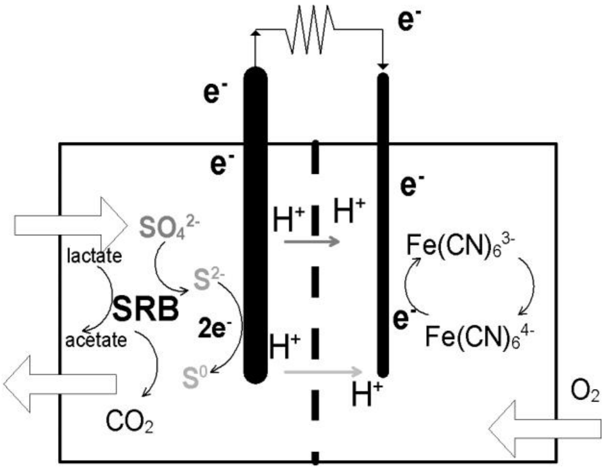

Fig. 1. A schematic diagram of MFC, based on the process of DMSR

…The MFCs, based on the process of dissimilatory microbial sulfate reduction (DMSR) in the anodic chamber (fig. 1), are capable of simultaneous removal of sulfate via sulfide (Angelov et al., 2013; Habermann and Pommer, 1991). The biogenic H_2S serves as a mediator and ease the electron transfer onto the anodic surface (Nikolova et al., 2013; Kleinjan et al., 2005; Ateya et al., 2003).

Materials and methods

Design of the laboratory scaled U-shaped MFC, based on the vital activity of sulfatereducing bacteria

The scope of the present article is to study the role of one of the main constructive and technological parameters, the anode, on the efficiency of MFC, based on the process of dissimilatory microbial sulfate reduction. It was found in previous studies that the anodic surface area has no significant impact on the generation of maximum power densites - they remain in the same range with the increase of the anodic surface. So the attention was focused on the material of anode, which determines its conductivity, adhesion, potential and respectively the electrochemical parameters of the fuel element.

For this purpose a series of laboratory tests is carried out with the same U-shaped design of the fuel element (Nikolova et al., 2015), presented at Figure 2, and identical conditions for the experiment. It should be borne in mind that the cathode each time remains the same (graphite rod with a surface area of 0.0024 m^2). The area of the anode is 0.0048 m^2 for each one of the experiments. The five various options of the anodes are presented at Table 1 and Figure 3. The electrochemical behavior of the MFC was observed with each one of the used anodes.

…The volume of the anodic and cathodic chambers of the MFC were of 0.48 dm^3. The volume of anodic section together with the buffer tank was 1.2 dm^3. To separate the two compartments was used a cationexchange membrane CMI-7000S. It was preferred in previous studies for its wear resistant properties and the attainment of high potentials.

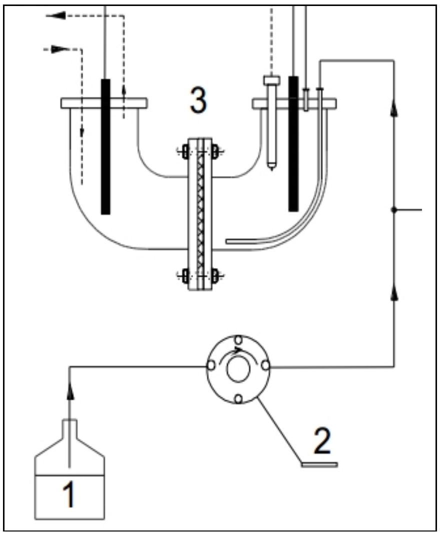

Fig. 2. Laboratory-scaled U-shaped MFC, based on the process of MDSR
1 - Feeding tank, 2 - Dosing peristaltic pump, 3 – MFC

…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.

The buffer tank to the anodic chamber was filled up with 0.3 kg clinoptilolite zeolite from “Beli plast” deposit with fraction size 2.5–5.0 mm. The particles were used as a carrier of the electroactive sulfatereducing biofilm. The elemental composition is given in Table 2. The zeolite was modified by saturation with NH_4Cl and KH_2PO_4 in course of the availability of the biogenic elements for the achievement of high sulfatereduction rates. The 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.

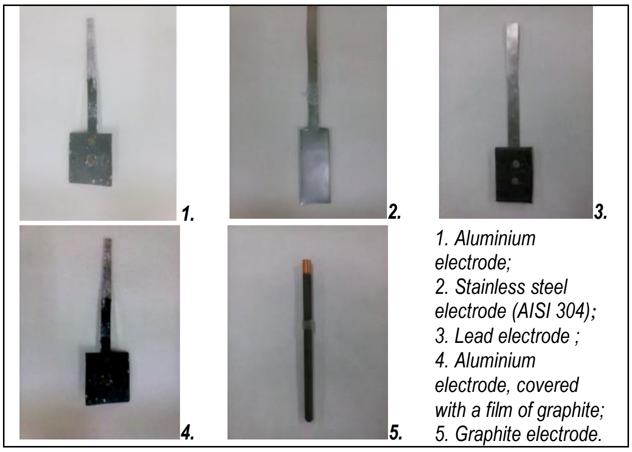

Fig. 3. Different variants of anodes of the MFC

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

Variant	Type of anode - description
1	Aluminium electrode - type “plate”
2	Stainless steel electrode (AISI 304) - type “plate”
3	Lead electrode - type “plate”
4	Aluminium electrode, covered with a film of graphite - type “plate”
5	Graphite electrode - type “rod” (3 pcs.)

Table 2.
Elemental composition of the clinoptilolite used as a carrier of consortium of sulfatereducing bacteria and other microorganisms in the anodic chamber of MFC

Oxides	Percentage, wt %	Oxides	Percentage, wt %
SiO_2	67.96	Na_2O	0.74
Al_2O_3	11.23	CaO	3.01
Fe_2O_3	0.83	MgO	0.06
K_2O	2.85	TiO_2	0.90

The anodic chamber was inoculated with 50 ml mixed culture of sulfatereducing 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.

Thus, two zones were formed in the U-shaped MFC: 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.

During these series of laboratory investigations in the anodic area of the installation were treated with solutions containing high concentrations of organic compounds and sulfates - synthetic solutions (modified Postgate medium for sulfatereducing bacteria). The culture medium for SRB contained in g/dm^3: 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 3.0 g/dm^3, thus the proportion between organic carbon and the terminal electron acceptor was 0.67.

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 potentiostat - ACM 3 connected to PC for reporting and analysis of the accumulated data.

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

Results and discussions

Regarding the behavior of the MFC major electrochemical parameters in Figures 4 and 5 is presented data on voltage drop and the dynamics of power density, summarizing the operation of the fuel cell with different load resistance (consumption), that ranges from 0 to 11 kΩ. The oxidation products accumulate on the anodic surface during continuous operation. Carbon materials are highly prevalent because of their developed surface area, providing space for the immobilization of electroactive microbial biofilm. Thereon respectively accumulates and elemental sulfur, produced by the oxidation of hydrogen sulphide on the anodic surface, and thus passivate the anodic surface.

…In this series of laboratory experiments it is found that the aluminium anode allows a transfer of larger electron flow and the generation of higher levels of maximum power density - more than three times higher than those, obtained with the graphite. The probable reason except the difference in electrode potentials is much weaker adhesion of sulfur formed on the surface of the electrode. The graphite film applied on the aluminium electrode is proved to be perishable, after 24 hours in the aquatic medium there are observed faults of the structure of the film. The monitored characteristics are observed in the 24th hour from the beginning of the experiment and the improvement of the performance of MFC is due to the free "fresh" surfaces of the aluminium base of the electrode.

The steel anode provides relatively high power density due to differences in electrode potential and higher values of the rate of the generated electricity at different resistances.

…For the variant with the lead electrode it should be taken into consideration its toxicity to organisms whose vital activity could be negatively affected or even inhibited by chronic use. At low and neutral pH values the lead, however, is practically insoluble. In an acidic medium, it is dissolved and oxidized, but quickly passivated by forming a thin oxide film that prevents it from its further oxidation. The formed oxide layer is the reason for the bad behavior of microbial fuel cell in the variant with the lead anode.

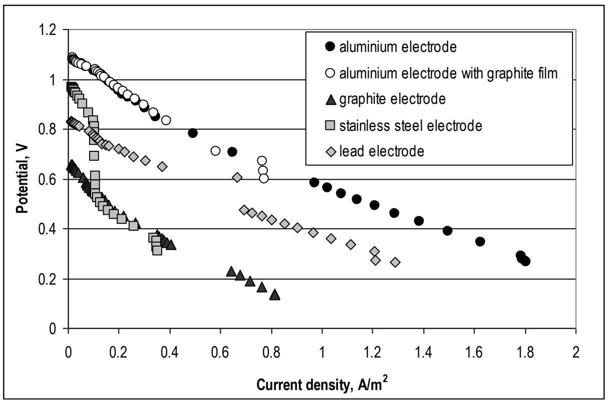

Fig. 4. Potential drops with different electrodes of U-shaped MFC, based on the process of DMSR

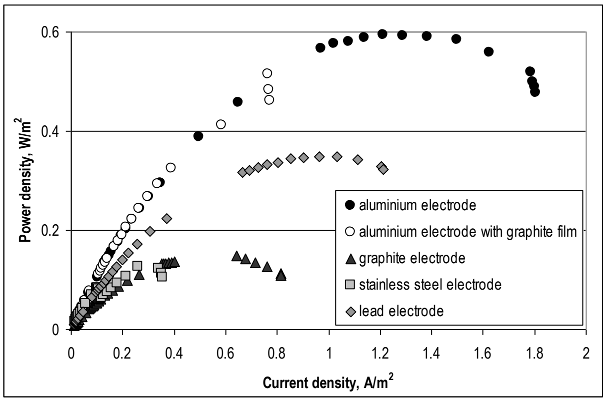

Fig. 5. Dynamics of power densities with different electrodes of U-shaped MFC, based on the process of DMSR

These conclusions are confirmed by the calculated values of coulombic efficiency for all variants with different anodes, presented at Table 3 and Figure 6.

The chemical oxygen demand (COD) removal rates are calculated using the equation 1.

$$€_{COD} = [(€_0 - €_t)/ €_0].100, \% \quad (1)$$

where: $€_0$ is the initial value of COD (mgO_2/L);
$€_t$ is the COD at any time (mgO_2/L).

Table 3.
Percentages of COD removal rates in the anodic chamber and of coulombic efficiencies for U-shaped MFC, based on the process of DMSR, with different types of electrodes

Anode	$€_{cb}$, %	$€_{COD}$, %
aluminium electrode	77.18	20.90
aluminium electrode with graphite film	77.27	20.86
graphite electrode	50.35	20.86
stainless steel electrode	61.64	21.79
lead electrode	45.30	21.43

For continuous flow through the system, the Coulombic efficiency is calculated on the basis of current generated under steady conditions (equation 2).

$$€_{Cb} = [M.I/ (F.b.q.\Delta COD)].100, \% \qquad (2)$$

where: M = 32 is the molecular weight of oxygen;
F is Faraday's constant;
b = 4 is the number of electrons exchanged per mole of oxygen, q is the volumetric influent flow rate;
ΔCOD is the difference in the influent and effluent COD.

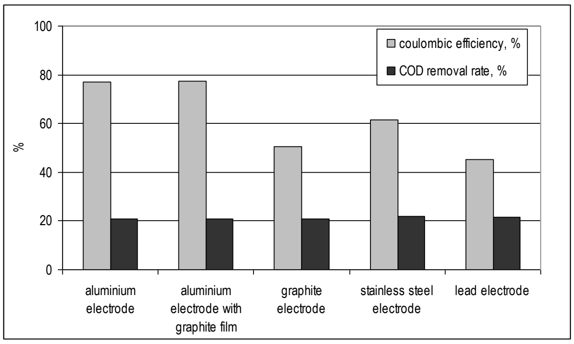

Fig. 6. COD removal rates in the anodic chamber and coulombic efficiencies of U-shaped MFC, based on the process of DMSR, with different types of electrodes

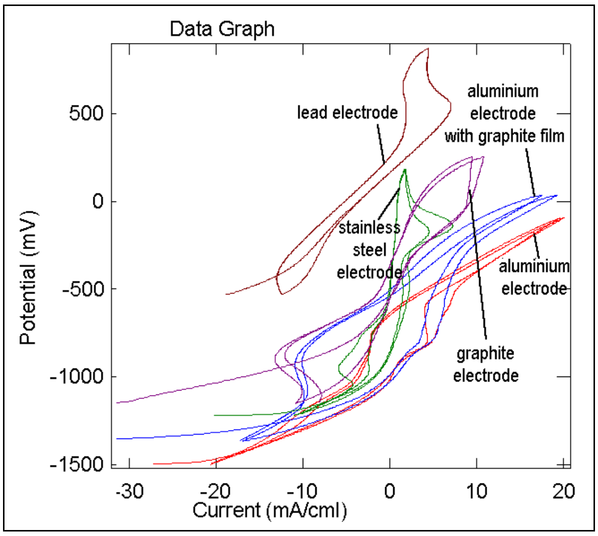

Fig. 7. CVAs of U-shaped MFC, based on the process of DMSR with different types of electrodes

…The shapes of CVAs for the two variants with aluminium electrodes (with or without graphite film) are identical (fig. 7). The difference in the hysteresis for the other three variants (fig. 7) and the reduction of voltage ranges are probably as results of different electrode potentials and prevalence of various Red-Ox processes in the anodic chamber.

Conclusions

The aluminium and the aluminium covered with graphite anodes give the best results - 77% of coulombic efficiemcy. Aluminium allows the transfer of larger electron flow and the generation of higher levels of maximum power density - more than three times higher than those obtained with the graphite. The probable reason except the difference in electrode potentials is much weaker adhesion of sulfur formed on the surface of the electrode.The lowest calculated rates of this parameter are for the lead anode, due to its passivation with oxide film. There is a necessity of further study of the potential for use of aluminium anodes in MFCs to replace more preferred graphite products.

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