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Electricity Generation in Microbial Fuel Cells as a Function of Air: Cathode Configuration

Blagovesta Midyurova*, Valentin Nenov

Department of Ecology and Environmental Protection, Burgas Asen Zlatarov University, Bulgaria.

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***Corresponding author: Blagovesta Midyurova; Email: blagi77@abv.bg**

Abstract
An inexpensive carbon black and Polytetrafluoroethylene (PTFE) air- cathode was developed as an alternative to an expensive metal catalyst and Nafion electrode for oxygen reduction in microbial fuel cell (MFC). The carbon black (Vulcan) was cold- pressed with PTFE binder to form the cathode around a steel mesh current collector. These constructions avoided the need for expensive metal catalyst and Nafion and produced a cathode with high current densities. Tests with three cathodes with different ratio of PTFE: Vulkan (5: 0.3; 0.2; 0.1g) produced a maximum current value as follows: 291 µA, 283 µA and 12 µA, respectively.
Keywords: Waste water, Air- cathode, Microbial Fuel Cell.

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INTRODUCTION

The microbial fuel cell (MFC) is a system in which conversion of organic matter in the anode compartment takes place by specific anaerobic bacteria to CO_2, electrons and protons. Protons migrate across the membrane and combine with oxygen and received electrons from the external circuit that connected to the anode electrode to form water. The principal scheme of MFC is consisting of two chambers, anode and cathode electrodes, and the two chambers are separated by a proton exchange membrane. Various oxidants have been used as the electron acceptor at the cathode (Logan, 2008; Logan and Regan, 2006), but oxygen is the most promising electron acceptor for MFC applications because it is freely available and sustainable (Santoro *et al*., 2014; Merino- Jiménez *et al*., 2016). Air - cathode MFCs, which have cathodes exposed to air on one side and water on the other, are the most practical approach for designing MFC cathodes due to not having to aerate the water and their ability to generate high power densities (Sun *et al*., 2016).

The key limitations of the use of MFC is the low density and voltage of the power generated. For this reason, many groups tried to increase the power by various modifications of the electrodes, changes in MFC design and addition of mediators (Dai *et al*., 2016; Santoro *et al*., 2016; Hong *et al*., 2009; Rezaei *et al*., 2007; Li *et al*., 2016; Liu *et al*., 2016). The anodes and cathodes can be manufactured from carbon paper, carbon cloth or activated carbon and the membrane can be directly deposited onto the cathode or the cathode can be self-contained without a membrane (Larminie and Dicks, 2000; Rozendal *et al*., 2008; Zhou *et al*., 2016; Wei *et al*., 2012). To increase cathode stability, MFC with air cathodes were developed. Such design was carried out by Park and Zeikus, 2003, who designed a one-chamber MFC with porous air electrode. The protons pass through the cathode to reach the acceptor used (air oxygen) and combine with the electrons to produce a molecule of water (Wang *et al*., 2017).

Initially, the interest in PEM and separators usage was focused on the perfluorosulfonate ionomers implementation as proton exchange membranes. The most thoroughly researched material was of the commercial brand of Nafion® and this is the first one developed by Connolly and Gresham, 1966 and E. I. du Pont de Nemours and Company in 1960. This was the material predominantly used as proton exchange membrane in fuel cells because of its high proton permeability, thermal and chemical stability (Mauritz and Moore, 2004). The main disadvantages of Nafion® which limits its commercial application are its high price ($ 800 per sq. m), its instability in dry state and strong dependence on the transport mechanisms with membrane hydration. For this reasons, Dong et al. (2012) and Zhang et al. (2011) analysed microbial fuel cells using alternative air cathodes instead of using Nafion® 117 as a separator.

In our study we are testing the abilities of different cathodes based on the usage of PTFE and carbon black (Vulcan) in different ratios as elements of MFC, and their

influence on MFCs performance. The attention is focused on testing the effect of different cathodes on the value of current in MFC.

MATERIALS AND METHODS

Fabrication of Air – cathodes

The kind of cathode consists of stainless steel meshes SS 304 McMaster-Carr, IL (projected cross sectional area of 10 cm^2) on which several layers were deposited: 60 wt% solution of PTFE (product of SIGMA ALDRICH, USA) and Vulcan (CABOT VXC72R). The ratios of polymer additive were 5:0.1, 5:0.2 and 5:0.3g. After continuous stirring until homogeneous suspension was obtained, the composite mixture was deposited with brush or putty-knife in a uniformly spread layer onto the entire surface of electrode (Cathodes surface area was $2.8*10^{-3}m^2$ with diameter of 50mm). For better adhesion of the polymer to the metal matrix, the cathode was dried for 24 h at room temperature and then mounted in the cells.

MFC construction and operation

The anodic chamber was a cylindrical PVC tube with 6 cm diameter and 3 cm height; the total capacity of the anode chamber was 48 ml. The anode consisted of a carbon cloth 0.003 m^2 with circular section and activated carbon 13.38 g to provide better biofilm formation. The anodic compartment had one port for input and output flows. The anode and cathode were connected with an external electrical circuit loaded with 100 Ω resistor. During operation of the MFC the potential difference between the electrodes was measured and recorded in 10 minutes intervals by data acquisition system connected to PC equipped with specific software (name of the software). The effect of the increase of catalyst content on the change of the current was studied. The real reactor of the cell used in the investigation is presented in Figure 1.

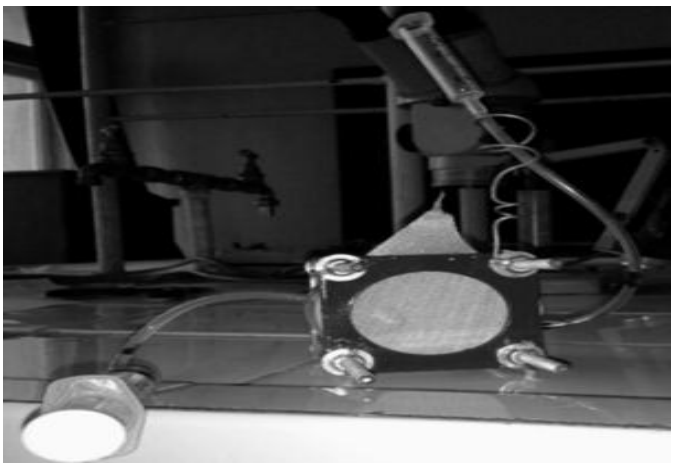


Fig.1. Real reactor of the Microbial Fuel Cell with air cathode

Microorganisms and cultivation conditions

The electrogenic microorganisms were isolated form bottom sediment from „Yasna Polyana" Dam near Burgas, Country. The enrichment of the mixed culture was performed in anaerobic conditions by inoculation of 0.5 ml sediment in 20 ml nutrient medium containing: glucose – 15g/dm^3; tryptone - 10 g/dm^3; yeast extract - 5 g/dm^3 and NaCl – 5 g/l and pH 7. After 96 hours of cell growth the enriched culture was suspended in fresh nutrient medium (LB Broth, Sigma Aldrich) to a microbial concentration of 10^7 CFU/ml and loaded in the anode chamber of the MFC. The temperature on the process was 14-18 ºC.

Analytical methods

Different spectroscopic techniques can be used to identify and study the PTFE-Carbon Vulcan.

Infrared spectroscopy (FT IR) – the analysis was carried out with IR spectrophotometer Nicolet iS 50 FTIR, Thermo Scientific. The IR-spectra of the PTFE layers were registered with tableted samples. All the tablets were prepared from the substance studied and 2 mg KBr.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG)- the two analyses were carried out simultaneously using the thermal analyzer – „STA – TG-DSC/DTA F3 JUPITER" product of Thermal Analyzer Netzsch – Germany, in air at temperature interval from 10°C to 1050 °C at heating rate of 10 ° C/min using α-Al_2O_3 as standard reference.

RESULTS AND DISCUSSION

FT IR and DSC analyses of PTFE

To prove the structure of the different kinds of PTFE, the method of FT IR was used and the thermal characteristics of the polymers were studied by DSC analysis. Sample 1 (PTFE) was white highly viscous product which was 60 wt% solution of PTFE. Sample 2 (VITO 40:60) was PTFE modified by pressing at 15MPa and deposited on metal mesh as substrate (electrode). These aqueous suspensions are quite practical and easy to deposit coatings or impregnation of various substrates (carbon cloth, metal mesh, etc.). The following bands were observed in the FT IR of the different PTFE samples (Figure 2).

Signals corresponding to individual functional groups were observed in the IR spectra; in this case they were from optical isomers with analogous structures:

- Doublet at 1252-1214cm^{-1} corresponding to the valent vibrations of the C–F bonds in the CF_2 group;
- Band at 1154cm^{-1} corresponding to the valent symmetric vibrations of the C–F bonds;
- Bands at 640cm^{-1}, 556cm^{-1}, 504cm^{-1} corresponding to the deformation vibrations of the C–F bonds in the CF_2 group;

Besides, a plateau was observed in the interval 3600cm^{-1} - 3200cm^{-1} corresponding to the valent vibrations of the O–H

bond, as well as a band at 1629cm^{-1} for the deformation vibrations of the O–H bond which probably indicated for the presence of associated moisture in the solidified PTFE.
Bands were registered also at:

- 2975cm^{-1} for the valent asymmetric vibrations of CH_3(methyl group);
- 2925cm^{-1} for the valent asymmetric vibrations of CH_2 (methylene group);
- 2860cm^{-1} for the valent symmetric vibrations of the CH group;
- 1460cm^{-1} for the valent deformation vibrations of the CH_2 group;

All these bands were attributed to the activators and accelerators of the solidification added to the PTFE composition. Similar FTIR spectrum was observed for sample 2 PTFE (VITO Belgium).

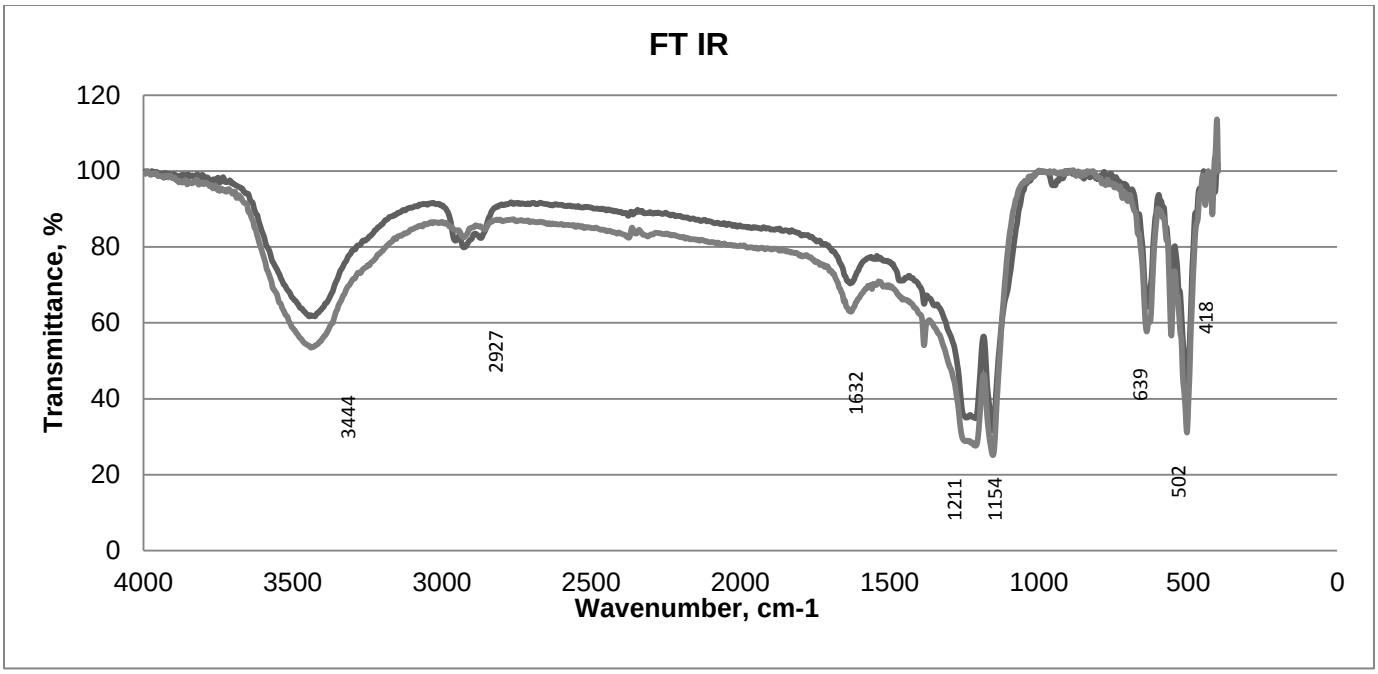
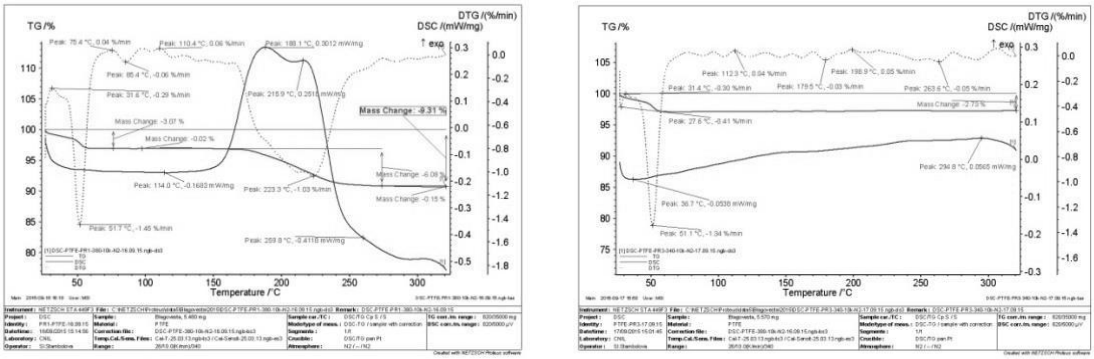


Fig. 2. IR absorption spectra of PTFE: lower – simple 1, upper - sample 2

The thermal characteristics of the polymers were studied by DSC analysis. Using sintering methods of semi-melting of finely dispersed powdery samples or deposition of emulsion layers with thickness comparable to the size of the elementary particles of the dry substance, the distribution by size depends on the microstructural heterogeneity and porosity of the polymer in bulk, as monolithic object, i.e. the final shape and appearance for its service. It defines the gas and water permeability of the model, especially under special conditions or longer exploitation periods. The spectroscopic and thermal methods of analysis provide information on the chemical characteristics and composition of the blends such as these studied here.

The results obtained from the DSC (shown in Figure 3) indicate the structural characteristics of the objects. The TG curve for the first sample showed a mass loss at 51-52^{o}C which was probably due to the removal of the easy volatile fractions (solvents, dispersers, stabilizers, etc.) incorporated in the blend deposited by some physical way. Since the suspension used was 60 wt% PTFE in water, this was probably due to the presence of water included in the micro porous structure.



a b

Fig.3. DSC curves for native PTFE (a) and formed PTFE (b)

In the temperature interval from 60 to 170°C, a rich alternating structure of the DSC curve was observed – alternating endo- and exo- effects. This might be due to the rich composition or great microstructural inhomogeneity of the object. At about 88°C and 216°C, two large overlapping exo-effects were observed, related to a significant mass loss seen on the TG and DTG curves. These effects were probably due to evolving destruction of the complex component composition of the object. Above the temperatures of these exo-effects, no other specific thermo physical (phase, structural transitions) and thermal effects (destruction related to the chemical stability of the phases) were observed.

Using the methods of DSC and FT IR spectroscopy, studies were carried out on the kinetics of the formation of the diffuse layer of PTFE. It was found that the polymer suspension of 60 wt% solution of PTFE had the required characteristics to realize effective diffusion of oxygen (Zhang *et al*., 2011).

Effect of air cathodes on current generation in a microbial fuel cell

The performance of the cathodes was examined in MFC tests following acclimation and steady state performance of the system. Experimental data on the current obtained with air cathode of stainless steel mesh and layer of PTFE and Vulcan in concentrations 0.1g, 0.2g *и* 0.3g are presented in Figure 4. Current production reached a maximum of 12 μA with the air- cathode with 0.1g catalyst, which is 95% less than obtained with the air- cathode with 0.3g catalyst 291 μA. Peak current production for the first and second cathode took 1h, compared to 4h with the third electrode consist 0.3g catalyst. The tendency observed was proportional increase of the current with the increase of the amount of catalysts – 12 μA, 283 μA up to 291 μA, respectively.

Thus appears from this preliminary analysis with air-cathodes that the use of Vulcan with PTFE binder on the cathode will be more useful for current generation in MFCs (Cheng *et al.*, 2006).

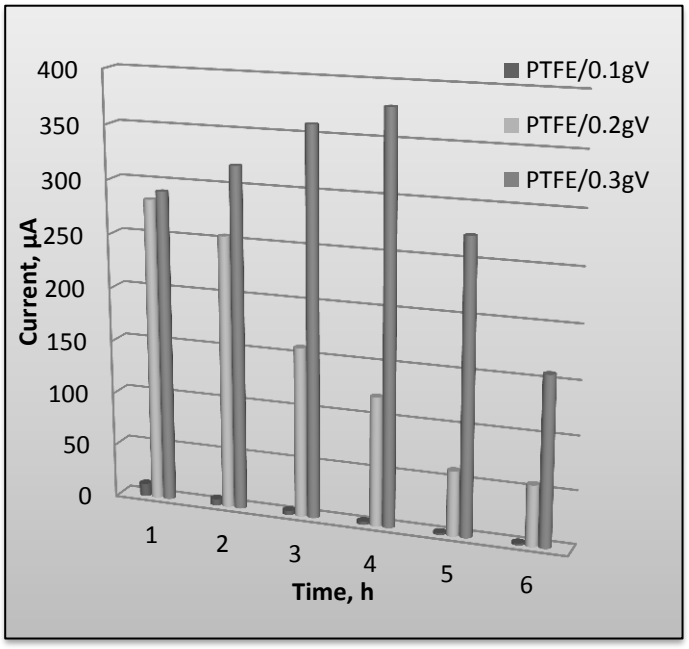


Fig. 4. Current generation in the MFC with three types of cathodes

CONCLUSION

A laboratory MFC was manufactured with air cathode and construction allowing easy change of the air cathode. The anode electrogenic seeding culture was taken from dam sediment. The comparative analyses of two types of

PTFE were tested by FT IR and DSC- TG. The use of finely dispersed polymer suspensions allows controlling the microstructural heterogeneity and the porosity of the composition. It was found here that the application of PTFE and Vulcan (5: 0.3g) produced the best performance of the MFC by increasing the maximum current value to 291 μA.

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CONFLICT OF INTEREST

There is no conflict of interest.

REFERENCES

Connolly, D. J., Gresham, W. F., 1966. U.S. Patent 3, 282, 875.

Dai, Y., Chan, Y., Jiang, B., Wang, L., Zou, J., Pan, K., Fu, H., 2016. Bifunctional Ag/Fe/N/C Catalysts for Enhancing Oxygen Reduction via Cathodic Biofilm Inhibition in Microbial Fuel Cells. ACS Appl. Mater. Inter., 8: 6992-7002.

Dong, H., Yu, H., Wang, X., 2012. Catalysis Kinetics and Porous Analysis of Rolling Activated Carbon-PTFE Air-Cathode in Microbial Fuel Cells. Environ. Sci. Technol., 46 (23): 13009–13015.

Dong, H., Yu, H., Wang, X., Zhou, Q., Feng, J., 2012. A novel structure of scalable air-cathode without Nafion and Pt by rolling activated carbon and PTFE as catalyst layer in microbial fuel cells. Water research, 46: 5777-5787.

Hong, S. W., Chang, I. S., Choi, Y. S., Chung, T. H., 2009. Experimental evaluation of influential factors for electricity harvesting from sediment using microbial fuel cell. Bioresour Technol, 100 (12): 3029-3035.

Larminie, J., Dicks, A., 2000. Fuel cell systems explained, John Wiley & Sons.

Li, R., Dai, Y., Chen, B., Zou, J., Jiang, B., Fu, H., 2016. Nitrogen-doped Co/Co_9S_8/partly-graphitized carbon as durable catalysts for oxygen reduction in microbial fuel cells. J. Power Sources, 307: 1-10.

Liu, Y., Li, K., Ge, B., Pu, L., Liu, Z., 2016. Influence of Micropore and Mesoporous in Activated Carbon Air-cathode Catalysts on Oxygen Reduction Reaction in Microbial Fuel Cells. Electrochim. Acta, 214: 110-118.

Logan, B. E., 2008. Microbial Fuel Cells, John Wiley and Sons: Hoboken, NJ.

Logan, B. E., Regan, J. M., 2006. Microbial fuel cells challenges and applications. Environ. Sci. Technol., 40 (17): 5172–5180.

Mauritz, K., Moore, R., 2004. State of Understanding of Nafion. Chem. Rev., 104: 4535-4586.

Merino- Jiménez, I., Santoro, C., Rojas-Carbonell, S., Greenman, J., Ieropoulos, I., Atanassov, P., 2016. Carbon-Based Air-Breathing Cathodes for Microbial Fuel Cells. Catalysts, 127: 2073- 4344.

Park, D.H., Zeikus, J.G., 2003. Improved fuel cell and electrode designs for producing electricity from microbial degradation. Biotechnol Bioeng, 81: 348–355.

Qiu, Z., Su, M., Wei, L., Han, H., Jia, Q., Shen, J., 2015. Improvement of microbial fuel cell cathodes using cost-effective polyvinylidene fluoride. J. Power Sources, 273: 566-573.

Rezaei, F., Richard, T.L., Brennan, R.A., Logan, B.E., 2007. Substrate-enhanced microbial fuel cells for improved remote power generation from sediment-based systems. Environ SciTechnol, 41(11): 4053-4058.

Rozendal, R.A., Sleutels, T., Hamelers, H.V., Buisman, C.J., 2008. Effect of the type of ion exchange membrane on performance, ion transport, and pH in biocatalyzed electrolysis of wastewater. Water Sci. Technol. 57: 1757–1762.

Santoro, C., Artyushkova, K., Babanova, S., Atanassov, P., Ieropoulos, I., Grattieri, M., Cristiani, P., Trasatti, S., Li, B., Schuler, A.J., 2014. Parameters characterization and optimization of activated carbon (AC) cathodes for microbial fuel cell application. Bioresour. Technol., 163: 54-63.

Santoro, C., Serov, A., Stariha, L., Kodali, M., Gordon, J., Babanova, S., Bretschger, O., Artyushkova, K., Atanassov, P., 2016. Iron based catalysts from novel low-cost organic precursors for enhanced oxygen reduction reaction in neutral media microbial fuel cells. Energy, Environ. Sci., 9: 2346-2353.

Sun, Y., Duan, Y., Hao, L., Xing, Z., Dai, Y., Li, R., Zou, J., 2016. Cornstalk-Derived Nitrogen-Doped Partly Graphitized Carbon as Efficient Metal-Free Catalyst for Oxygen Reduction Reaction in Microbial Fuel Cells. ACS Appl. Mater Inter., 8(39): 25923-25932.

Wang, Z., Mahadevan, G.D., Wu, Y., Zhao F., 2017. Progress of air-breathing cathode in microbial fuel cells. Journal of Power Sources, 356: 245-255.

Wei, B., Tokash, J.C., Chen, G., Hickner, M.A., Logan, B.E., 2012. Development and evaluation of carbon and binder loading in low-cost activated carbon cathodes for air-cathode microbial fuel cells. RSC Adv., 2: 12751-12758.

Zhang, F., Pant, D., Logan, B. E., 2011. Long-term performance of activated carbon air cathodes with different diffusion layer porosities in microbial fuel cells. Biosensors and Bioelectronics, 30: 49–55.

Zhou, L., Fu, P., Cai, X., Zhou, S., Yuan, Y., 2016. Naturally derived carbon nanofibers as sustainable electrocatalysts for microbial energy harvesting: A new application of spider silk. Appl. Catal. B- Environ., 188: 31-38.