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Improvements of MFC's Proton Exchange membranes and Cathodes

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Abstract

The microbial fuel cell (MFC) is well known instrument for conversion of chemical energy of organic matter into electrical. This process is driven by the specific biochemical activities of anaerobes. These organisms oxidize the organic substrate into CO_2, electrons and protons in expense of alternative electron acceptors. The classical MFC comprises of anodic and cathodic compartments separated by proton permeable membrane (proton exchange membrane, PEM). The work deals with development of new proton exchange membranes and cathodes. Four types of PEM based on ceramic materials were tested in sedimentation MFC. The values of the voltage are in the range of 15.5 – 20.2 mV. A ceramic membrane with additive of MnO_2 was used in designing of air cathode of a single cell MFC. The behavior of the ceramic-MnO_2 membrane was compared with steel mesh/ Nafion® layer membrane. It was found that the ceramic-MnO_2 membrane is superior with open OCV voltage of 508 mV. Besides, electrochemical analysis (CV) of different air cathodes based electro-conductive polymers and ceramic-MnO_2 powder were studied. In the latter case, the current obtained is highest.

Keywords: Proton exchange membranes, Air cathode, Microbial Fuel Cell.

1. Introduction

Microbial fuel cells are well known as instruments for transformation of chemical energy of organic substrates into electric energy. This process is realized through the specific biochemical activity of certain types of microorganisms. Actually, these microorganisms oxidize organic substrates under anaerobic conditions at the expense of alternative end acceptors of electrons. The electrons and protons are bonded to the acceptor used (oxygen or some chemical reagent) to form water molecules. At the initial stages of the development of MFC, the attention of the researchers was focused on the so called "two-chamber" cells. They are simplified design of an anodic and cathodic chambers divided by a separator (membrane) which allows transportation of protons to the cathode and prevents the exchange of electrolyte between the two chambers. The sedimentation fuel cells (SMFC) are systems where electricity is generated due to biological oxidation of organic substances in sea and lake sediments. The electrons generated in the anode immersed in the sediment are transported through electric circuitry to the cathode where, in presence of O_2, they recombine with protons to give H_2O and the final results is the generation of electric current [1]. Basic components of MFC are the proton-exchange membranes (PEM) and the separators. PEM selectively allow protons through to the cathode. Electrolyte molecules are dissociated to ions during its dissolution in water. Due to the specific structure of the membrane, the positively charged ions which could be Na^+, K^+, Ca^{2+}, H^+, etc., are carried over. The difference with the separators is that they are porous structures or some kind of semi-permeable membranes. Diffusion takes place through the separator so that only solvent molecules are allowed to pass but not the dissolved substance, i.e. it plays the role of a semi-permeable barrier between the anode and cathode chambers in MFC. The most often used materials today are Nafion, Ultrex, composite, ceramic membranes, salt bridge, etc. [2-5]

The main limitations of the use of MFC are the low power density and low voltage. For this reason, methods to increase the power by various electrode modifications, deposition of catalyst layers and changes in electrode design (so called air electrodes) are searched for. In the two-chamber MFCs, an electron acceptor must be present in the cathode chamber (most often chemical reagent, e.g. ferricyanide) but the main disadvantage with it is that it has to be resupplied after its exhaustion. In MFC with air cathode, the electron acceptor is the oxygen in the air. This is an advantage since the atmosphere ensures incessant and stable supply of oxygen [6, 7]. The air cathode is a new kind of electrode consisting of metal collector, catalyst and diffusion layers. When the catalyst (most often activated carbon or carbon black) is deposited onto a metal mesh, it is necessary to use certain binder. The latter is usually a polymer and it is responsible for the good adhesion between the phases; the aim is to reduce the diffusion of oxygen from the air, stable transportation of protons to the aqueous phase and, thus, higher values of the electric energy generated [8]. Various kinds of polymers have been studied as binding substance – Nafion, polytetrafluoroethylene (PTFE), polyaniline (PANI), etc. Interesting studies were reported by other research groups [9-11] who manufactured air cathodes from carbon cloth (CC, 30% wet proofing, Fuel Cell Earth LLC) impregnated with carbon black (Vulcan XC-72) and catalyst (0.5 mg/cm^2 Pt) mixed with Nafion as binding substance. It had four PTFE layers on the air side which are diffusion layers and prevent the loss of water through the cathode surface [12, 13]. The catalytic layer of Vulcan XC-72, Pt and Nafion is necessary for the regulation of oxygen reduction and it is deposited on the aqueous phase side while the diffusion layers are on the air side to provide the diffusion of oxygen [14]. Using composite materials like polyaniline nanofibers (PANI nanofiber) with graphite black as catalyst, mixed with PTFE as binding substance and deposition of the mixture onto carbon cloth, maximum power density of 496 mW/m^2 was achieved which is lower compared to the one with Pt cathode - 604 mW/m^2 but the PANI based composite layer is more cost effective [15]. The industrial air cathode VITO (Belgium) consisting of activated carbon powder (70–90 wt%; Norit SX) and PTFE (70% porosity, 0.13 kg/m^2) obtained by cold pressing onto Ni mesh at pressure of 150 Bar generated maximal power density of 1220 mW / m^2 в сравнение с 1060 mW/m^2 with air cathode made from carbon cloth and Pt catalyst [16]. Dumas, C et al., [17] discussed the problem with the provision of good conductivity through the use of metal electrodes. It was proved that an electrode of stainless steel containing 6% molybdenum (UNS S31254) can be used as anode even in an electrolyte of sea water. Thus, stainless steel can be used as alternative to expensive electrodes. The manufacturing of air electrodes has been discussed also by Zhang, F., et al., 2010. They used activated carbon powder (Norit SX plus, Norit Americas Inc., TX) and PTFE as binder (in 60% solution) at weight ratio AC to PTFE - 9:1. The mixture is stirred until homogeneous paste was obtained which was then deposited with putty-knife on one side of a mesh from stainless steel used further as electrode (50×50, type 304, McMaster-Carr, OH)[18].

Various electrochemical methods are used to determine the characteristics of the MFCs [19]. Polarization curves are powerful tool for analysis and characterization of the cathode. They describe the voltage as function of the current (galvanostatic regime) or the current as function of the voltage (potentiostatic regime) [20]. Using cyclic voltammograms of each cathode, a fast comparative assessment of cathode potential can be done in order to predict how this value will affect the electrochemical processes in the microbial fuel cell. Such experiments were carried out by S. Khilari et al., 2013 [21] who compared different kinds of modified cathodes and their effect on the performance of the MFC. The authors used MnO_2 and Vulcan as catalysts and graphite, carbon nanotubes and graphene as electrodes. The cathode of MnO_2/nanotubes showed maximal power density of 4.68 W m^{-3} compared to the composite cathodes of MnO_2/nanotubes / multiwall carbon nanotubes (MWCNTs) with power density of 3.94 Wm^{-3} and MnO_2/nanotubes /Vulcan XC - 2.2 Wm^{-3} and Pt/C cathode - 5.67 Wm^{-3}. In this respect, the results reported by S. Khilari contribute to the better understanding of the electrochemical processes from the point of view of the cathode potential and the complex reactions occurring due to the different specificity of the cathodes studied.

The aim of the present work is to carry out experiments aiming to compare silicate based PEM incorporated in a SMFC and test different designs of air cathodes.

For this purpose, the following tasks were formulated:

- Compare ceramic membranes of different compositions by using them in the cathode chambers of sedimentation microbial fuel cells
- Developing of new air cathodes using electro conducting materials and their characterization by electrochemical methods

2. Materials and Methods

2.1. Experimental procedure

- *Ceramic proton exchange membranes*

Technological properties of clay minerals depend mainly on their degree of dispersion. Particle size distribution of the clay affects the properties such as density, porosity and etc. For the synthesis of the ceramic membranes, different ratio of raw materials was used [22]. The initial shape of membranes was obtained by pressing the selected composition at 100 MPa and firing at high temperature (950ºC-1100ºC). The temperature was gradually increased with 10 ^{o}C/min and upon reaching the maximal temperature the samples were hold for 60 min. The cooling process was conducted by keeping the heated samples for 24 hours at room temperature and then were incorporated in the SMFC.

- *Air cathode preparation*

This kind of cathode consists of stainless steel mesh with size smaller than 0.25 μm on which several layers were deposited: Nafion®, Polytetrafluoroethylene (PTFE) preparation 60wt.% ; *SIGMA ALDRICH*, USA, Carbon black, VULCAN, CABOT; VXC72R,LOT-3416840, Polyaniline, Polycarbazole and Polynitrotosylcarbazole and Ceramic powder. The ratio polymer: additive was 5:0.3g. The only exception was cathode №8 since three combinations of three concentrations were used. 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 20mm. 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.

Prepared following types of cathodes:

- Reference cathode № 1 - only with a layer Nafion® (perfluorinated resin solution 20wt.%, *SIGMA ALDRICH*, USA);
- Cathode №2 , apply a mixture of Nafion/Vulcan;
- Cathode №3 - Nafion/Polyaniline;
- Cathode №4 - Nafion/ Polycarbazole;
- Cathode №5 - Nafion/ Polynitrotosylcarbazole;
- Cathode №6 - Nafion/ ceramic powder;
- Cathode №7 - This air cathode consists of a ceramic membrane (Trojan clay) impregnated with MnO_2/carbon cloth treated with Nafion® solution and steel mesh with three layers of Nafion®. The structure and the methodology of cathode preparation are given elsewhere [23].
- Cathode №8 - PTFE/ Vulcan, developed are three types of cathodes in different ratios of Vulcan (5:0.1g; 5:0.2g; 5:0.3g);

The synthesis of Polyaniline, Polycarbazole and Polynitrotosylcarbazole is reported in [24, 25, 26, 27], respectively.

Chemical synthesis of polyaniline, polycarbazole and polynitrotosylcarbazole

The certain amount of monomer (one of the aniline, carbazole or our synthesized nitrotosylcarbazole) was dissolved in one of the solvents of HCl, or CH_3CN or acetonitrile. An initiator of ammonium persulfate (APS) was slowly dropped to the monomer solution. After the mixture was stirred for about 6 h in an ice bath, the precipitate product was collected, and washed several times with distilled water until the cleanout fluid was neutral. Finally, polymers were dried in air at 80 °C for 12 h.

Carbazole-based compounds play a very important role in electroactive and photoactive materials. AFM images of Polycarbazole and SEM images of PCz are shown fig.1.

The AFM images reported in this study were obtained with Nanosurf Easy Scan 2™ AFM. SEM images of Polyaniline are shown fig.2.

2.2 Microbial fuel cell design - sedimentation and single MFCs

The sedimentation microbial fuel cell used [22] was cylindrical PVC tube with D=12 cm, H=23 cm, as shown in Fig.3. The total volume of the cell was 1,750 ml. The graphite anode was placed on the bottom and covered with preliminarily homogenized sediments from the Yasna Polyana dam (Burgas district). The chemical analyses of the sediment showed that it contained high concentrations of manganese and iron. Sediment layer was at least 3 cm high, i.e. the thick sediment volume was about 339 cm^3 (0.000339 m^3). The anode used was made of graphite plates and its area was 0.040 m^2. The cathode chamber was a cylindrical PVC tube sized 4.8 x 8 x 6.5 cm with a membrane at the bottom. The chamber was fixed on top of the cell by holders and stayed unmoving. A cathode of carbon fibers with area of 0.176 m^2 was placed on the membrane.

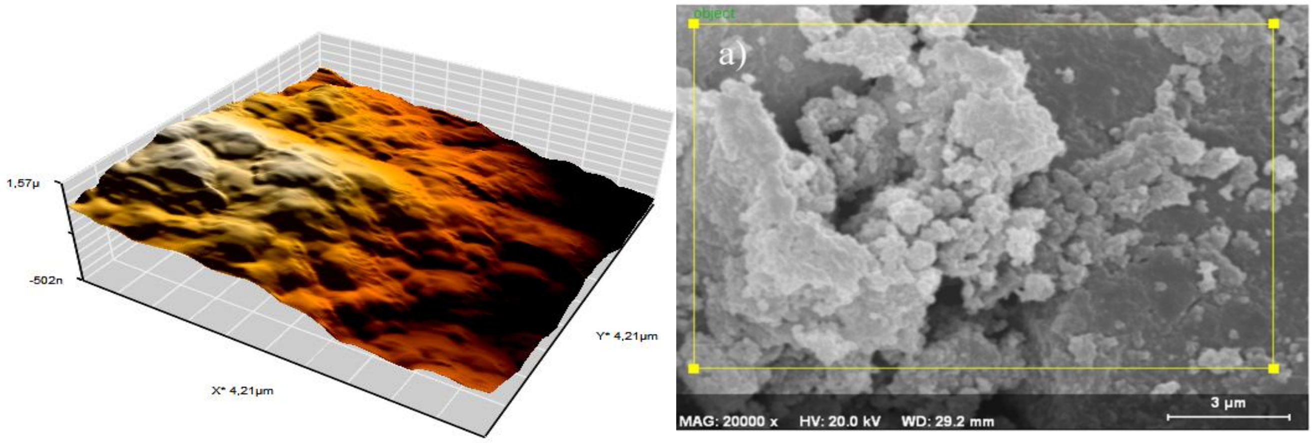

Figure 1: AFM images of PCz and SEM images of PCz was chemically synthesized on stainless steel of SS304.

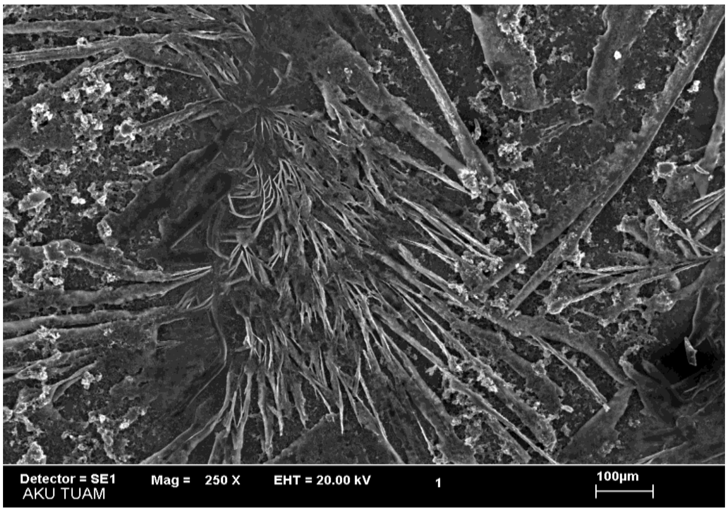

Figure 2: SEM images of PANI was chemically synthesized on stainless steel of SS304.

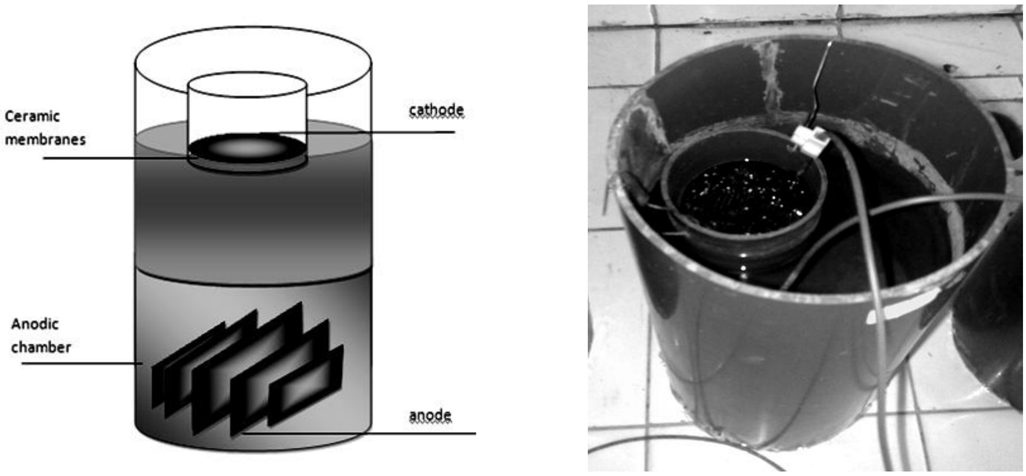

Figure 3: Design of the Sedimentation Microbial Fuel Cell (left) and real reactor (right) used in this study

The above mentioned electrodes were clamped between two PVC elements by using rubber rings. MFCs consisted of a single cylindrical PVC chamber (length - 3cm, diameter- 4.5cm; cell volume- 48 ml) containing carbon cloth (anode) with surface area of 0.0030m^2. The anodic compartment had one port for input and output flows. It is filled with granular activated carbon to provide biofilm formation and electron transduction to the electrode. The anode and cathode were connected with an external electrical circuit with different resistances. The electrogenic microorganisms were isolated from bottom sediment of „Yasna Polyana" Dam near Burgas. 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 of 7. After 96 hours of cell growth the enriched culture was washed and re-suspended in fresh nutrient medium with the same composition but without glucose. Voltage generated was measured and recorded by Auto ranging digital Multimeter Model MY-66. The laboratory MFC with air cathodes is shown in Fig. 4. Particular details of the single chamber MFC is described in our previous studies [23].

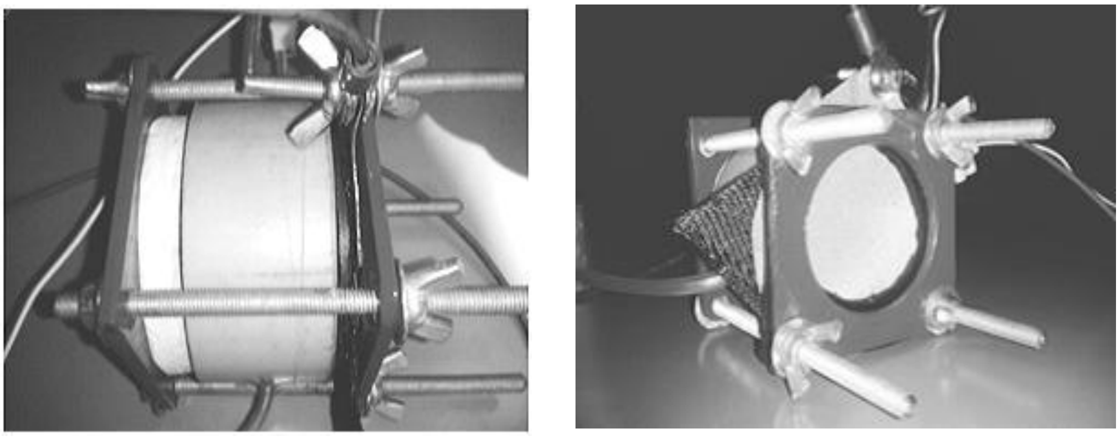

Figure 4: Real reactor of the Microbial Fuel Cell with air cathode used in this study

2.3. Analytic methods and data collection

SEM – The SEM micrographs were taken with a microscope - VEGA3 TESCAN in co-operation with the American university of Sharjah.

Differential thermal analysis and thermogravimetry /DTA и TG/ - the analysis was carried out on an apparatus: „STA – TG-DSC/DTA F3 JUPITER" product of NETZSTH – Germany, in the temperature interval from 10 to 1100 ºC in oxygen medium.

Granulometric analysis – The dispersity of the ceramic masses stipulates the running of the technological processes (mixing, forming, drying, sintering) and, hence, the quality of the ceramic components. After the grinding, the ceramic raw materials and masses are usually a mixture of particles with various sizes, i.e. they are polydispersed materials. Using the method of laser diffreaction and laser granulometer *Analysette 22 Compact, FRITSCH,* the distribution of the particles by size was determined.

Potentiostatic studies – the analysis was carried out on an apparatus: "*AUTOLAB POTENTIOSTAT-GALVANOSTAT*", product of METROHM AUTOLAB B.V.

A three-component configuration was used: *working (indicating) electrode,* in this case the air electrode the half-response of which was measured; *comparative electrode* – carbon cloth with area of 0.004 m^2 was used in an attempt to approximate the conditions of a the real system for which the cathodes of the microbial fuel cells were designated; *the reference electrode* in the three-component configuration was the saturated calomel electrode – silver – silver chloride electrode: Ag/AgCl/KCl (saturated solution) with potential of 0.222 V. The background electrolyte was 250 mM aqueous solution of NaCl. The cyclic voltammograms were registered at 0.00244 steps and scanning rate 0.1Vs^{-1} at room temperature (25 ± 2 ° C).

3. Results and discussion

Granulometric analysis of the samples

All the initial silicate based materials were analyzed. The distribution of the particles by size is given in Table1

Table 1: Granulometric analysis and results by size, µm

№	**10%**	**20%**	**30%**	**40%**	**50%**	**60%**	**70%**	**80%**
Kaolin	≤ 0,442	≤ 1,615	≤ 2,908	≤ 24,9	≤ 30,12	≤ 34,10	≤ 36,15	≤ 38,29
Clinoptilolite	≤ 5,99	≤ 18,505	≤ 33,81	≤ 45,66	≤ 55,17	≤ 64,77	≤ 76,81	≤ 97,64
Montm.clay	≤ 1,745	≤ 6,21	≤ 11,97	≤ 20,80	≤ 35,60	≤ 47,26	≤ 55,86	≤ 64,62
Trojan clays	≤ 0,499	≤ 2,019	≤ 6,027	≤ 10,59	≤ 18,85	≤ 38,52	≤ 49,41	≤ 57,18

In the clinoptilolite sample, the particles size varied from 97.64 µm to 5.99 µm, in kaolin sample – from 38.29 µm to 0.442 µm and in montmorillonite sample – from 64.62 µm to 1.745 µm. The maximum particles size in the Trojan clays was not greater than 57.18µm while the minimum size was not greater than 0.499 µm. With the membranes containing kaolin, clinoptilolite and montmorillonite clay, however, the voltages generated were not sufficiently high so they were not studied in details.
The objects of the SEM observations were the ceramic membranes with highest voltage yield, Table 2.

Table 2: Type of membranes and voltage

№	**Ceramic membrane constituents**	**constituents**	**Ratio**	**Density g/cm^2**	**U, mV**
1	Trojan clay/MnO_2	dicomponent. membrane	50:10	2.00	17.8
2	Trojan clay /electro corundum	dicomponent. membrane	15:15	2.02	20.2
3	Trojan clay	monocomponent membrane	-	1.64	15.5
4	Trojan clay/PAN fiber/carbon/ dextrin	polycomponent membrane	30:1:5:7	1.24	19.6

As illustrated by the micrographs in Figs.5 and 6, pores sized from 20 to 500 µm were observed for the four membranes. The smaller sized pores (within the range mentioned above) were observed in the monocomponent membrane while larger pores were can be seen in the multicomponent membranes.

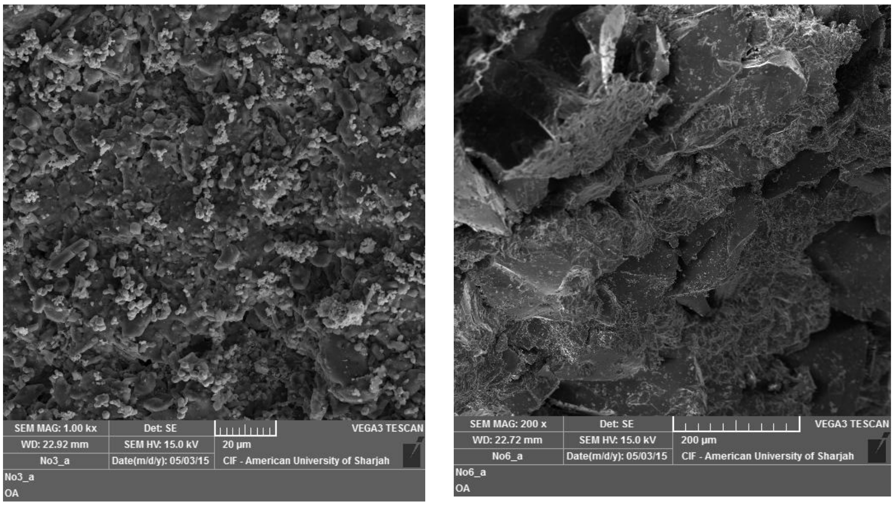

Figure 5: SEM of membranes Trojan clay/MnO_2 and Trojan clay /electro corundum

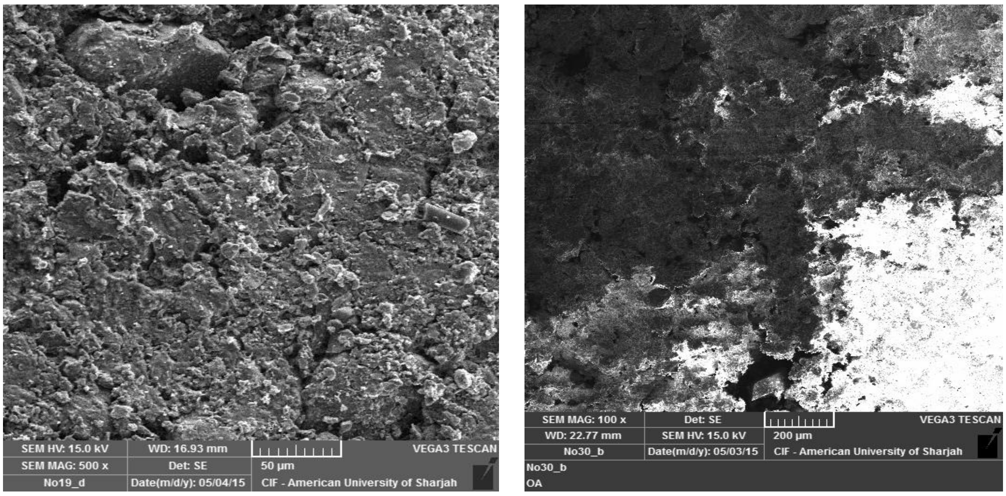

Figure 6: SEM of membranes Trojan clay and Trojan clay/PAN fiber/carbon/ dextrin

The first image in Fig. 5 (membrane 1 with additive MnO_2) shows characteristic morphological forms since MnO_2 crystallizes in various allotropic forms. Elongated structure and needle crystals characteristic for this oxide can be observed. The second image in Fig.5 of membrane 2 reveals the better micro-heterogeneity and the best wholeness and length of the pores. The data obtained from the SEM observations showed good interconnection of the pores which stipulates better debit with respect to the corresponding separator selectivity. The SEM micrograph of membrane 3 (Fig.6, first image) shows small cracks which were most probably due to inhomogeneous pressing of the membrane. For membrane 4 (Fig.6, second image), the micro-heterogeneity observed was good. It was considered enough to suggest that the organic additives and especially electro corundum improved the wholeness of the pores because of the differences in the initial dispersities of the fillers, as well as the way and degree of the homogenization by mixing. The structural rearrangements were also affected by various phase (polymorphous) and other transitions and effects.

Differential thermal (DTA) and thermogravimetric (TG) analyses

The DTA and TG curves of the proton-exchange membranes are presented in Figs.7 and 8. They can be analyzed as follows: under heating to 1000 ^{o}C, the mass loss of membrane 1 was about 8-9%, for membrane 3 they were about 7-8%, for membrane 2 – 4-5% while for membrane 4 the mass loss was about 37-38%. This means that when the membrane contained organic additives (fibers and dextrin) the thermal stability of the composition sharply deteriorayed.

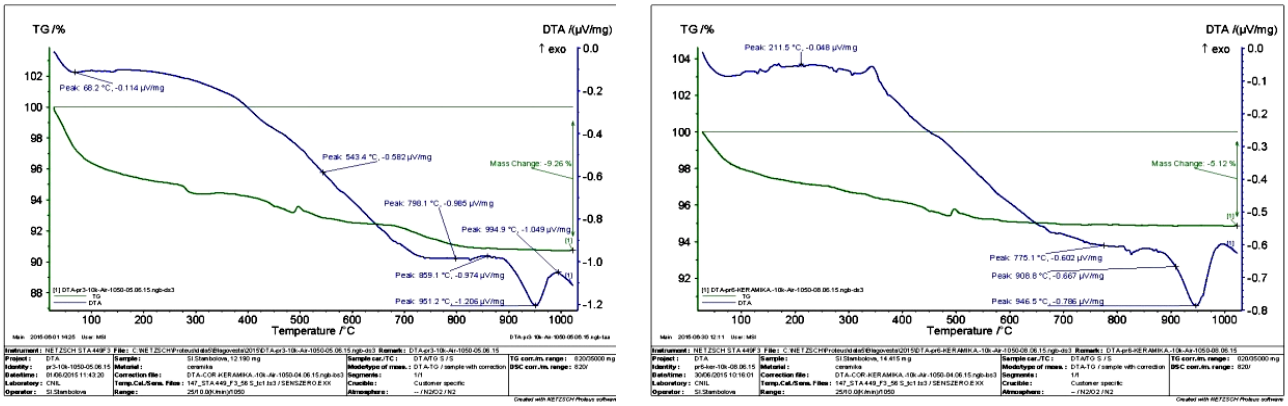

Figure 7: DTA and TG diagrams of membranes Trojan clay/MnO_2 and Trojan clay /electro corundum

The addition of manganese dioxide had almost no effect on the thermal stability of the sample. The addition of electro corundum even improved composition stability which correlates well with the highest value of the working voltage achieved in the MFC.

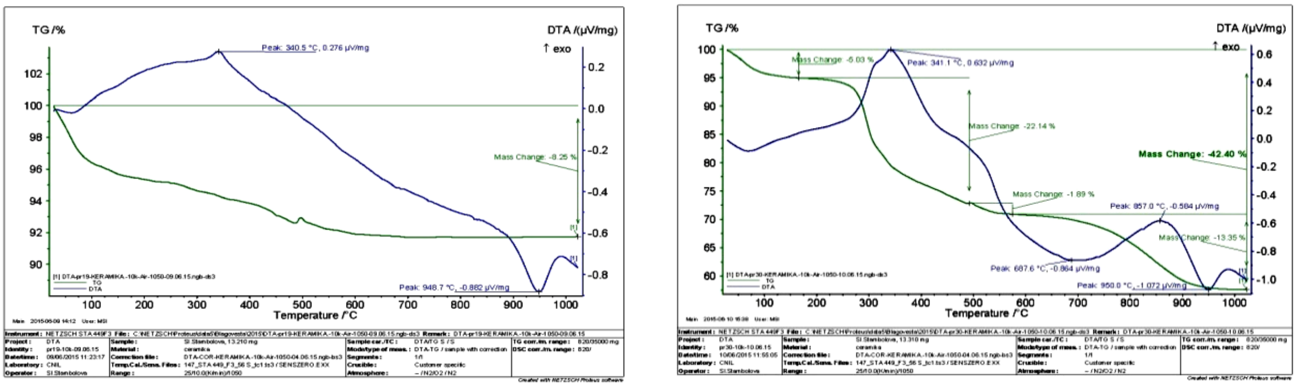

Figure 8: DTA and TG diagrams of membranes Trojan clay and Trojan clay/PAN fiber/carbon/ dextrin

All the for DTA curves showed comparatively large endo effect (significant energy absorbance by the objects) which was supposed to be related to a phase transition in the alumnosilicate matrix (Trojan clay). Three samples showed an exo effects at about 350 ^{o}C but with different intensities. Only for membrane 4, a number of exo effects were observed, most probably due to destruction of the organic components in the matrix.

Voltage and electrochemical analyses

Further experiments were done with membrane 1 loaded with MnO_2. The membrane was used in the single chambers MFC as a component of an air cathode. The membrane was selected because the promising results were reported in the special literature with similar (Mn loaded) membranes. Several sources show that the use of manganese oxides additives can be considered as an alternative of the more expensive catalysts like Platinum [21].

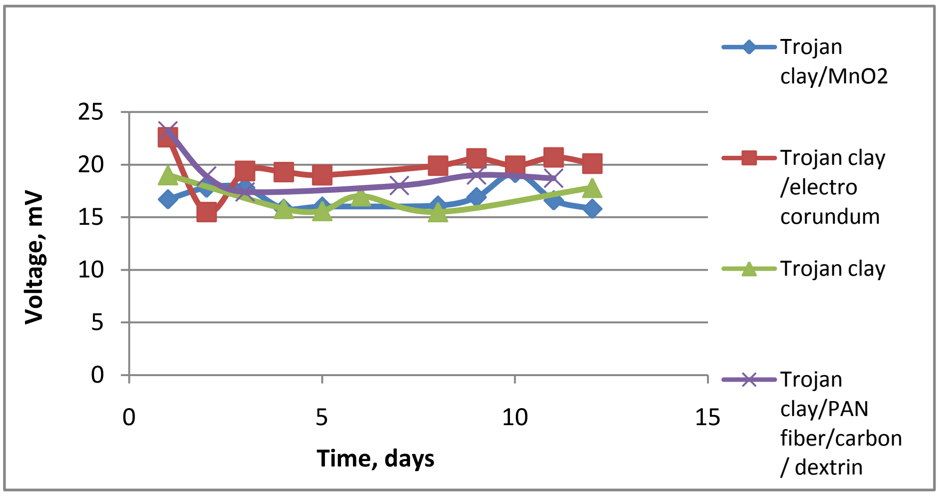

Figure 9. Voltages measured in the SMFC with ceramic membranes

The main purpose to use a MnO_2 catalyst as a component included in the ceramic membrane is to avoid these effects which can occur after a contact between the manganese ions and the anodic solution containing the electrogenic microorganisms. The inorganic matrix of the ceramic membrane "holds" the catalyst particles and thus it cannot express a negative influence on the biology and electrochemistry of the anode. The results obtained show that the modification-cathode N7 applied is successful and we observe 66 % higher OCV (508 mV). Since the anode design and the content of the anodic solution (growth medium and the microbial culture) is not changed during this experiment it is obvious that the improvement observed is a result of the increased cathodic potential [23].

Another kind of air electrode №8 was developed by combining metal mesh and polymeric film. For this purpose, the so called substitute of Nafion® - Teflon (Polytetrafluoroethylene) was used. The effect of the increase of catalyst content on the change of the voltage was studied. Experimental data on the voltages obtained with air cathode of steel mesh < 0.25μm and layer of Polytetrafluoroethylene and Vulcan in concentrations 0.1g, 0.2g и 0.3g are presented in Fig.10. The tendency observed was proportional increase of the voltage with the increase of the amount of catalysts – 1.2 mV, 28.3 mV up to 29.1 mV, respectively - Fig.10.

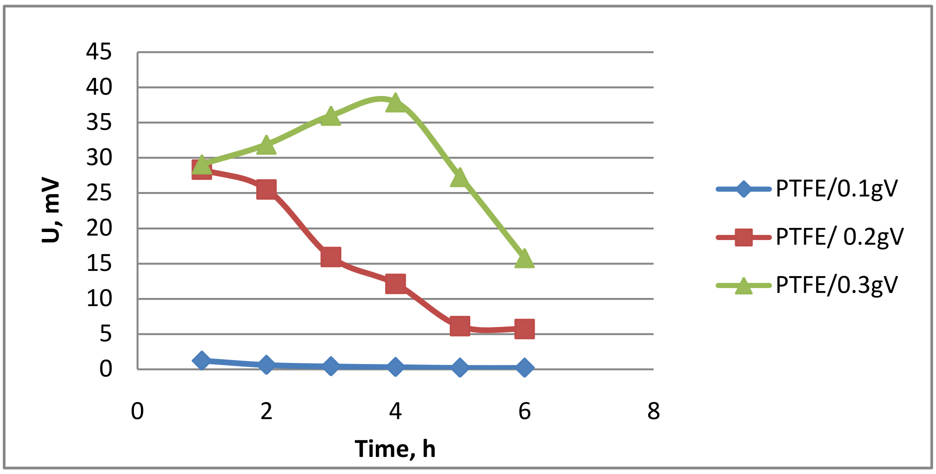

Figure 10: Voltages measured in the MFC with air cathodes modified with Polytetrafluoroethylene

Cathodes N7 and N8 were applied in a single cell MFC and their generated voltage was analyzed. It was found that the electrochemical processes can be controlled by the experimental parameters of reduction charge of the polymer layer and the concentration of the catalyst incorporated in it.

The next stage of the studies involved comparative analysis by cyclic voltammetry of air cathodes containing new layers of electro conductive polymers – Polyaniline, Polycarbazole and Polynitrotosylcarbazole. Fig.11 shows the comparison between modified cathodes 1-6 (see the sub-chapter 2.1) which had close values of the current and the working range was from -0.5V to 0.5V. Differences in the potential ranges of the curves were observed due to the different modifications applied.

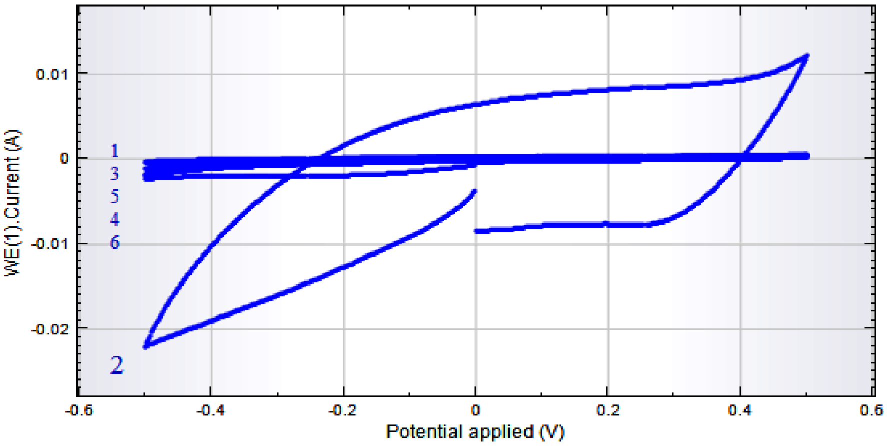

Figure 11 : Cyclic voltammetry of modified electrodes N1- reference electrode with Nafion; Cathode N2 - Nafion/Vulcan; Cathode N3 - Nafion/PANI; Cathode N4 - Nafion/ Polycarbazole; cathode N5 - Nafion/ Polynitrotosylcarbazole; cathode N6- Nafion/ ceramic powder.

The voltammograms studies show that the voltammogram of cathode N2 (Nafion/Vulcan) is substantially different from the other ones by its width, i.e. the process is reversible and the current produced was I_2= -0.22mA. This result is was most probably due to the strong catalytic effect of the carbon black and the activation of cathodic reactions. Such behavior defined good expectations in applying the cathode N2 as a MFC electrode. Since the anode behavior is the same in all cases, the current measured under constant potential was as follows: I_1= -0.4mA; I_3= -1mA; I_4= -2mA; I_5= -1.8mA; I_6= -2.4mA; Better results were obtained with cathode N2 apply a mixture of Nafion/Vulcan and cathode № 6 on which a layer of Nafion containing MnO_2 dispersed ceramic powder was deposited during the synthesis of the ceramic separators.

Similar comparison between modified air cathodes was reported by other authors where voltage peaks with cathodes of MnO_2/nanotubes, MnO_2/nanotubes /Vulcan XC, MnO_2/ nanotubes/multiwall carbon nanotubes (MWCNTs) and MnO_2/nanotubes/graphene were observed. The reported peak shifts in the voltammogram [21] is related to the improved reduction of oxygen resulting from the presence of the corresponding catalysts. Positive response of electrodes modified with Mn salts is also observed in other studies [28] which show maximum power density similar to electrodes based on Pt.

Conclusions

The study on the conditions of synthesis and characterization of several ceramic membranes based on natural clay materials show that some of them (the combinations Trojan clay/MnO_2, Trojan clay /electro corundum and Trojan clay/PAN fiber/carbon/ dextrin) implemented in sedimentation microbial fuel cell (SMFC) have promising technological behavior. The SMFC voltage obtained in applying these membranes varies within 17.8-20.2mV. The comparative tests of different air-cathodes in single cell MFC show positive results in implementing the membrane with the MnO_2 additive in respect of its good electrochemical characteristics.

Through the CV tests performed with modified cathodes it was shown that besides the strong catalytic effect of the carbon black (Nafion/Vulcan layer) the layers based on Trojan clay/MnO_2 powder, Polyaniline, polycarbazole and polynitrotosylcarbazole also possessed positive properties. The studied π- conjugated polymers (conducting polymers) are continuously in scope based on their good electronic conductive properties due to the substantial π-electron delocalization along their backbones. The technique of their synthesis in-situ on cathodes is highly prospective and such experiments are currently under way.

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