"Polyacrinolytrile derived carbon based nanofiber mats as anodes in microbial fuel cells"

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POLYACRINOLYTRILE DERIVED CARBON BASED NANOFIBER MATS AS ANODES IN MICROBIAL FUEL CELLS

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Abstract –**This work aims to enhance the performances of Microbial Fuel Cells. Bundled carbon nanofibers with average diameter from 100 nm to 1 µm were then prepared from polyacrylonitrile through electrospinning process. The spun nanofibers were oxidatively stabilized at 280 °C in air and thermally treated at 600 °C under inert atmosphere for 1 hour. Morphological and physical properties were measured, demonstrating the graphitic character of carbon nanofibers processed at 600 °C. In particular the electrical conductivity of the nanofiber mats is close to $2.47 \cdot 10^{-3}$ S/cm. Cytotoxicity tests were performed demonstrating the suitability of the carbon based nanofibers to host living microorganisms. The formation of a biofilm was finally evaluated through field emission scanning electron microscopy analysis, showing a very good interaction between carbon nanofibers and bacteria, and the development of a densely connected biofilm. These good results open the door to application for anodic electrode in microbial fuel cells.**

Index Terms – **Carbon Nanofibers, cytotoxicity, electrospinning, microbial Fuel Cells, polyacrynolitrile.**

I. NOMENCLATURE

Polyacrinolytrile (PAN); Microbial Fuel Cells (MFCs); N-N dimethylformamide (DMF); commercial felt (CF); Field scanning microscopy (FESEM)

II. INTRODUCTION

MFCs are bio-electrochemical systems that convert chemical energy into electrical energy from the respiratory metabolic profit of electrochemically active bacteria. MFCs are one of the most promising technologies to produce renewable electrical energy. However, it is still necessary to enhance the device performances in order to grant its diffusion. In particular, new anodic electrodes materials, with good electrical properties and able to support microorganisms growth, have to be investigated. For the fabrication of electrodes for energy applications carbon has been found as most promising material in its various forms like powder, fibers and mats. Porous carbon nanofibers have extremely high length to diameter ratio, nanoscale diameter and ultrahigh specific surface area as compared to other carbon materials [1,2]. To generate electricity using bacteria in MFCs, highly conductive non corrosive materials are needed; those materials must have a high specific surface area and an open structure to avoid biofouling [3]. The nanofibers have been obtained through the electrospinning technology. The elettrospinning process produces fibers as a continuous charged polymeric jet by means of an electrical potential applied between the needle of the syringe and a grounded collector. The aim of this work is to evaluate the application of bundled carbon nanofibers as anode in MFCs.

III. EXPERIMENTAL SECTIONS

A. Material and Methods

PAN (average molecular weight Mw=150,000 kDa) and DMF (assay 99.8%) were purchased from Sigma Aldrich. Samples were prepared by electrospinning solutions containing 12wt% PAN in DMF. The electrospinning parameters have been defined as summarized in the TABLE I. The two values of flow rate permit to obtain different morphological properties of the mat of nanofibers and to compare the different interaction between the material and the bacteria growth.

TABLE I
Electrospinning parameters defined during the process.

Samples	Voltage (kV)	Distance (cm)	Time of process (hour)	Flow rate (mL/h)
PAN_0.2	15	15	1	0.2
PAN_0.4	15	15	1	0.4

As spun these nanofibers were stabilized at 280 °C in air and thermally treated at 600°C under inert atmosphere for 1h to obtain conductive carbon nanofibers. The resulting samples are nonwoven mats of graphitic conductive nanofibers with a high surface area. Raman spectroscopy showed the typical G-bands and D-bands of graphitic materials, confirming this feature in the nanofibers, as represented in the Fig. 1.

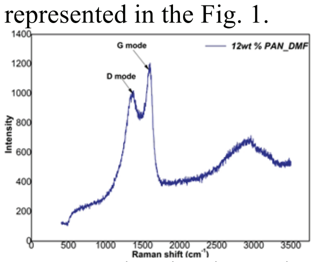

Fig. 1 Raman spectroscopy conducted on the sample PAN_0.2

The morphology of the nonwoven mats of nanofibers was characterized by FESEM: bundled carbon nanofibers were observed in all samples. In particular the mat of PAN_0.2 nanofibers have a diameter smaller , closes to 1 μm, than the diameter of the nanofibers of PAN_0.4, of about 1.5 μm, as shown in the Fig. 2.

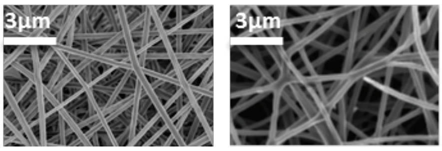

Fig. 2 Fesem characterization of the morphology of the 2 mat of nanofibers respectively PAN_0.2 on left and PAN_0.4 on the right.

Moreover it has been investigated the cytotoxicity and the biofilm interaction with the mat of nanofiber in comparison with commercial electrode material CF. The inclusion of the material within a gel made of agar, sodium acetate, peptone and the microorganism, reveals no cytotoxicity seeing as the bacteria proliferated and spread uniformly in all plates containing the nanofibers of PAN. To investigate the interaction between the bacteria and the material, the samples have been then put in a solution of sodium acetate for 1 month. The formation of biofilm has been finally investigated through a FESEM analysis, showing a very good interaction with a nanofibers of PAN. The development of a densely connected biofilm results better in the mat of PAN_0.2 than the biofilm in CF and in PAN_0.4, as represented in the Fig. 3. In the PAN_0.2 sample, it is possible evaluate the development of a densely connected biofilm.

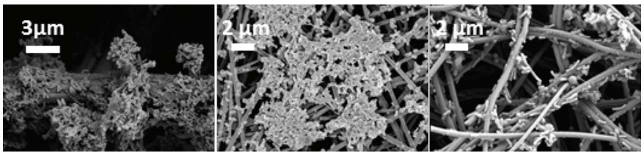

Fig. 3 The comparison of the different biofilms on CF, on left, on PAN_0.2 on the middle and on PAN_0.4 on the right.

Finally the electrical properties of the carbon nanofibers were investigated, showing a value of conductivity equal to $2.47 \cdot 10^{-3}$ S/cm. This value is defined as a function of the resistivity of the sample and its thickness of about 4 μm.

IV. Conclusion

In this work, we demonstrate the biocompatibility and a good conductivity, characterized the mat of carbon nanofibers, obtained from PAN as a polymeric precursor. The graphitic features of nanofibers of PAN, which are pirolysed at 600°C under inert atmosphere, guarantees a good conductivity value that ensure the possible application of the material as an electrode in MFCs. Moreover thanks to the high surface area of nanofibers ratio to volume, we evaluated the formation of deeply connected of biofilm on nanofibers. The bacteria have a better proliferation in the sample of PAN_0.2, than the proliferation on CF, a commercial material used as a reference material. Probably the good proliferation of bacteria on PAN_0.2 is due to an higher porosity of the material and to an higher roughness of nanofibers of PAN than the fibers of CF. In particular the high porosity of nanofibers of PAN_0.2 is due to a lower distribution of diameters, while the roughness is induced by the bundled carbon nanofibers morphology. All these good results open the door to application for anodic electrode in MFCs.

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