

Carbon electrodes for microbial fuel cells

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The high conductivity and active surface area, combined with biocompatibility for working bacteria, is one of the biggest challenges for microbial fuel cells (MFCs). Prospective investigation of electrodes with a foam structure of carbonized polymers with ferrocene catalysts in a regular MFC with *Escherichia coli*, glucose and methylene blue as a mediator is presented. The electrode structures have been characterized by XRD and TEM, and showed a large number of nanotubes with large defects, in a randomly interconnected network. The characteristics of the MFC related to carbon structures and biocompatibility are described.

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1. Introduction

Biofuel cells (BFCs) have recently been reborn due to a series of unusual applications devised for future decades. In general, BFCs operate in two ways, which both encounter obstacles and scientific aspects that need to be overcome [1-4]: 1. by the use of biological catalysts (enzymes), to oxidize fuel molecules at the anode and to enhance oxygen reduction at the cathode - that is enzymatic fuel cells (EFCs); 2. when the complete microorganisms are used to produce electricity via an electron transfer mediator involving a membrane and two electrodes, microbial fuel cells (MFCs). MFCs demonstrate how various microorganisms are able to directly and efficiently convert a substrate such as carbohydrate into an electrical source. The use of microorganisms in fuel cells eliminates the need for the isolation of individual enzymes. Thus, a wide variety of microorganisms with a broad metabolic potential provides an inexhaustible resource for the construction of microbial fuel cells [5-7].

Various bacteria and algae have been tested in both configurations, in terms of efficiency, compatibility to various mediators, coulombic yield, electron transfer rate, and regeneration ability [8-11]. The overall efficiency of the electron-transfer mediators depends on many parameters, particularly on the electrochemical rate constant of the mediator re-oxidation, which is correlated with the electrode materials [12]. In addition to the above-mentioned aspects, there are several, as yet un-studied: the nature of the electrode surface, mediator-electrode interaction, biocompatibility and bacteria-electrode surface.

To bring microorganisms close to an electrode (anode) and to accomplish good aeration at a cathode, we need to pay attention to the electrode geometry, structure, properties and composition. In this work, we studied carbon electrodes with a foam structure and with a nanotube composition, induced in the polymer pyrolysis with a ferrocene catalyst. The idea is to make the anode, or

the cathode chamber, directly into the electrode volume where the pores are supplied with fuel, microorganisms and mediators (anode) and to assure a good aeration (cathode) respectively. Other questions recently raised deal with the microorganism's biocompatibility, that is related to the electrode carbon structure, the accommodation to work in colonies and if there is a cooperative phenomenon which can produce a huge effect.

Two types of carbon materials, derived from pyrolyzed polymers with ferrocene catalysts, have been synthesized. The method induces a large number of carbon nanotubes. The structural properties of the electrode materials have been investigated and the electrodes have been used in a regular MFC with *Escherichia coli*, glucose and with methylene blue as a mediator.

2. Experimental

2.1. Materials for the electrode design

The starting materials were novolac, a resin type phenol-formaldehyde condensation, a cross-linked agent called hexamethylenetetramine (HMTA), polyvinyl alcohol (PVA) and, ferrocene powder (Merck).

HMTA, 10 wt.% novolac-type phenolic resin mixtures and different amounts of ferrocene (the amount of iron from the ferrocene was 2.5% and 5% by weight to novolac) were dissolved in ethanol. After evaporation of the alcohol, drying for 24h at 50°C and mincing, samples were press formed in pellets. The samples were indexing as NH-Fe-x and PVA-Fe-x, respectively, where x (x = 2.5, 5) stands for the iron content (% wt. to novolac or PVA). All pellets were pyrolyzed up to 900°C in three steps: 1. Heat to 180 °C for 1h in an air flow, to produce a cross-linked lattice, 2. Further heated to 300°C for 1h, in an argon atmosphere and maintained for 30 min, 3. Heated to the pyrolysis temperature, at a rate of 200°C/h in an argon flow for a treatment time of 1h. Finally, the samples were free cooled to room temperature.

2.2. Source of the bacteria and activity test

Escherichia coli were grown from a stem on a specific culture media at 37°C for 48h. The colonies were transferred in the buffer solution (pH=7). The density of the bacteria was estimated as 100,000/ml equivalent with 5 mg/ml, sufficient to give a turbid suspension.

Methylene blue (Fluka grade) solution (10 mM) was used to test the bacteria activity. A suspension of the bacteria in the buffer solution was placed in a tube to which 2-3 droplets of methylene blue solution were added. Initially, the medium colour was like blue ink, specific to the oxidized mediator. After 2h, it turned colourless, specific to its reduced form.

2.3. Microbial fuel cell design

The microbial fuel cell (MFC) – (National Center of Biotechnology Education (NCBE) at the University of Reading, United Kingdom) was designed as a two-chamber Plexiglas system with the bacteria that oxidize a substrate (e.g. glucose) in the anode chamber physically separated from the cathode chamber, with the electron acceptor, by a polymeric proton exchange membrane (PEM). The PEM had an available surface area of 12 cm² exposed to either compartment. The electrodes consisted of NH-Fe-x, PVA-Fe-x and carbon fibre tissue as a reference. The working volume of the NCBE microbial fuel cell was 10 cm³ per compartment. The oxidizing solution (catholyte) was a solution of potassium ferricyanide - K₃Fe(CN)₆, 0.02 M, in a potassium phosphate buffer (pH=7). The reducing solution was a mixture of phosphate buffer (pH=7) with the microorganisms (*Escherichia coli*), the mediator methylene blue, and a small amount of glucose (0.5 M solution).

2.4. Investigations

The samples, NH-Fe-x and PVA-Fe-x, were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD patterns of the samples were collected using Bruker D8-Advance powder diffractometer, with CuK α radiation ($\lambda=1.548$ Å) and equipped with a copper target X-ray tube and a diffracted-beam monochromator. A Philips CM120ST (Customized Microscope 120 Super Twin) was used to collect the TEM images.

Experiments with the MFC, that uses NH-Fe-x and PVA-Fe-x as electrodes, were conducted at room temperature. Measurements of the voltage, current and power density were made across a load resistance of 200 Ω , using a data acquisition system. A bumping table was used to ensure that there was a uniform distribution of the methylene blue among the bacteria and that there was an even distribution of the bacterial population across the electrode surface.

3. Results and discussions

The carbon materials identified in the pyrolyzed polymers show combined structures of disordered carbons and a large number of nanotubes. The number of nanotubes increases with the iron content released from the ferrocene catalyst. XRD patterns (Fig. 1) show two types of compound in the carbon materials: multi-walled carbon nanotubes (MWNTs) and Fe₃C.

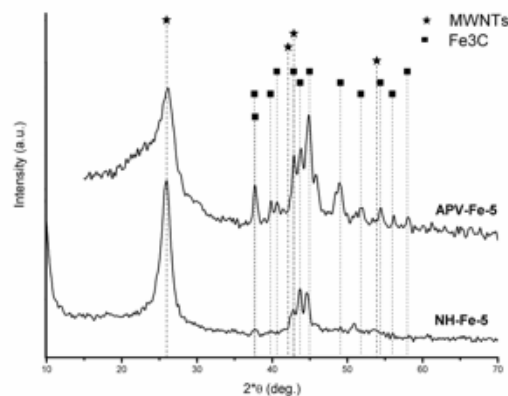


Fig. 1. XRD patterns for NH-Fe-5, and PVA-Fe-5 samples. The peaks corresponding to MWNTs and the second phase Fe₃C are indexed.

TEM images (Fig. 2), of different samples, show a large amount of MWNTs with iron nanoparticles randomly distributed for PVA-Fe-5 (Figs. 2a, 2b). The resulting carbon nanotubes in this system have thick walls (Fig. 2c.) with large variations in the inner diameter.

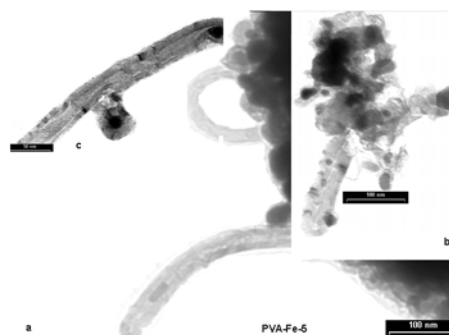


Fig. 2. TEM on PVA-Fe-5, showing thick walled nanotubes (a) and Fe₃C nanoparticles (in the text we refer to these as iron nanoparticles - (b)). A detail at 50 nm (c) shows distinct features with the thick walled nanotubes identified in (a)

In the other composition, NH-Fe-5, there were long and large MWNTs with relatively small defects, ropes and disordered carbon, as shown in Fig. 3. A detail of the ropes is shown in Fig. 3a. Figs. 2 and 3 show the nanoparticle distribution, identified by XRD as Fe₃C. These drive the conversion of the carbon materials from the pyrolyzed polymers into carbon nanotubes. The results are similar to

other reports, which have used nanometer iron instead of ferrocene [13-17]. The nanometric iron has been considered as a by-product and not considered for study. In our case (Fig. 3b), the nanometer iron reaches a maximum diameter of 25 nm. The case in which one of the oxidants in a MFC contains iron for one of electrode (cathode) is beneficial, and not appropriate for the anode in the presence of the mediator. The pore size distribution of the carbon materials was hard to control directly in the pyrolysis process. In general, PVA-Fe-x has shown relatively compact samples, up to micron size.

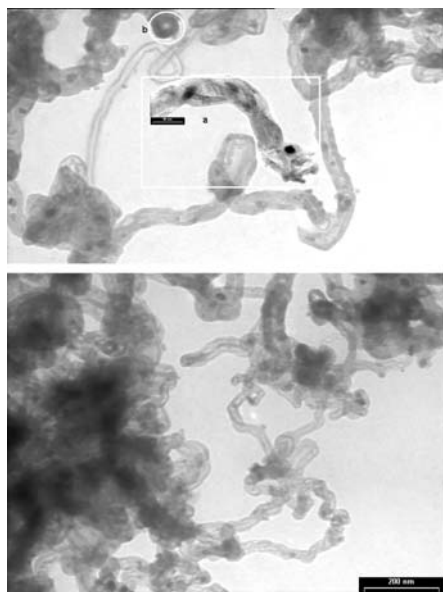


Fig. 3. TEM on NH-Fe-5 with a large number of nanotubes and ropes, randomly intercalated: (a) shows the rope morphology and (b) a Fe_3C nanoparticle ending a nanotube.

Optical micrographs, (Fig. 4), show a size distribution from micron to nanometre size, but the internal porosity is large and determined by a random distribution of nanotubes in the amorphous carbon matrix.

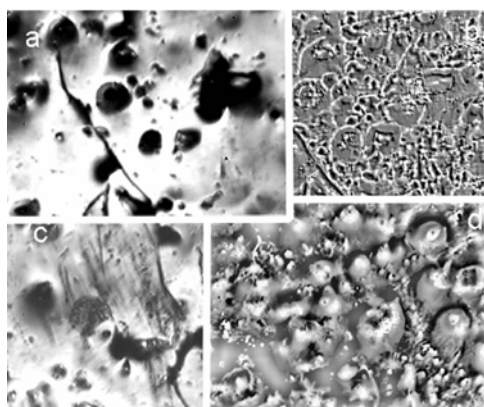


Fig. 4. Optical micrograph (22 x) for NH-Fe-2.5 before and after iron removal: (a) pore size after pyrolysis. (b) pore distribution in bright field (c) after plasma etching (d) after chemical oxidation and iron removal (bright field).

The carbon formed from pyrolysis was used as electrodes in MFC after sterilization. Six series of experiments were performed for electrodes with PVA-Fe-2.5, PVA-Fe-5, NH-Fe-2.5, NH-Fe-5, and carbon fibre tissue, and with NH-Fe-2.5 after iron removal. Fig. 5 shows the specific power density related to carbon electrodes for standard conditions of experimentation with *Escherichia coli*.

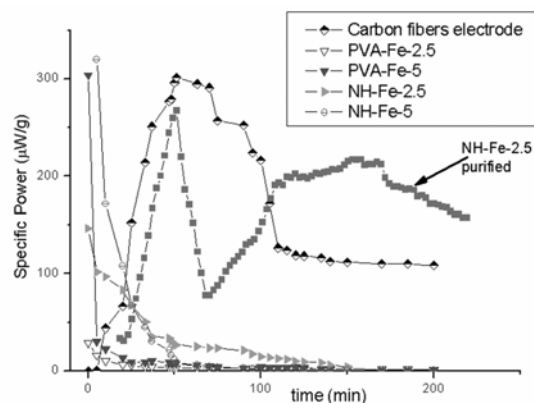


Fig. 5. The specific power generated by MFC with electrodes based on pyrolyzed polymers.

The plots contain all the cell dynamics including processes such as microorganism transport to the electrode (anode), their attachment to the electrode structures, mediator diffusion, electron transfer, oxidation, etc. until a stationary regime is reached. For electrodes made of carbon fibre tissues, a stationary power regime is reached; at around 100 $\mu\text{W/g}$. All samples with PVA-Fe-x and NH-Fe-x have a maximum specific power in the initial stage of the cell operation, which rapidly decrease to low values. It is shown that the iron content in the electrodes causes poisoning of all processes of electron transfer. The iron oxidation and removal from the electrode for sample NH-Fe-2.5 shows a drastically change in the behaviour. Also, the iron content is diminished from the anode when the nanotubes have large open ends and give the possibility to work in a suitable way with the microorganisms. A series of new micro- and nano-pores were opened, but we can see that the nanotubes and microorganisms have a very good biocompatibility, giving rise to an increased specific power up to 200 $\mu\text{W/g}$.

4. Conclusions

The electrode materials are essential components for power production in a MFC. A MFC incorporating *Escherichia coli* as the bacteria and methylene blue as the electron mediator generates electricity and gives a higher specific power when a large number of nanotubes are in the electrode composition. The most important conclusion is that there is a greater biocompatibility with nanotubes than with regular carbon fibres or other carbon forms. This is the first time that a biocompatibility test related to the carbon structures has been done with a biofuel cell.

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References

- [1] E. Katz, A. N. Shipway, I. Willner, in Handbook of Fuel Cells – Fundamentals, Technology and Applications, ed. John Wiley & Sons, Ltd. (2003), **1**, p.1.
- [2] H. Liu, R. Ramnarayanan, B. E. Logan, Environ. Sci. Technol. **38**, 2281 (2004).
- [3] B. Min, B. E. Logan, Environ. Sci. Technol. **38**, 5809 (2004).
- [4] H. P. Bennetto, Biotechnology Education, **1**, 163 (1990).
- [5] H.P. Bennetto, New Scientist, **16**, 36 (1987).
- [6] B. Daviss, Discover Magazine, **16**, 58 (1995).
- [7] R. M. Allen, H. P. Bennetto, Appl. Biochem. Biotechnol. **39/40**, 27 (1993).
- [8] S. B. Roller, H. P. Bennetto, J. Chem. Tech. Biotechnol. **34B**, 3 (1984).
- [9] I. Ardeleanu, D.G. Margineanu, H. Vais, Oxford. Bioelectrochem. Bioenerg. **11**, 273 (1983).
- [10] S. Tanisho, N. Kamiya, N. Wakao, Bioelectrochem. and Bioenerg. **21**, 25 (1989).
- [11] D. R. Bond, D. R. Lovley, Applied and Environmental Microbiology, **69**, 1548 (2003).
- [12] K. Kano, T. Ikeda, Anal. Sci. **16**, 1013 (2000).
- [13] Y. H. Wang, S. C. Chiu, K. M. Lin, Y. Y. Li, Carbon **42**, 2535 (2004).
- [14] H. Nishino, R. Nishida, T. Matsui, N. Kawase, I. Mochida, Carbon **41**, 2819 (2003).
- [15] E. P. Sajitha, V. Prasad, S.V. Subramanyam, S. Eto, Kazuyuki Takai, T. Enoki, Carbon **42**, 2815 (2004).
- [16] L. Pan, M. Zhang, Y. Nakayama, J. Appl. Phys. **91**, 10058 (2002).
- [17] N. Sano, H. Akazawa, T. Kikuchi, T. Kanki, Carbon **41**, 2159 (2003).

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