Microbial fuel cell based on Ni-tetra sulfonated phthalocyanine cathode and graphene modified bioanode

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A B S T R A C T
A Microbial Fuel Cell (MFC) has been constructed using stainless steel modified with reduced graphene oxide (rGO) by layer by layer (LbL) original method as the bioanode and carbon felt modified with poly[Ni(II)tetrasulfophthalocyanine (poly-NiTSpc) as the cathode. In this work, an easy method is reported to fabricate a MFC with long time life using compost garden leachate as source of micro-organisms for the electroactive biofilm. rGO permitted to obtain stable power density over a period of 40 days (24.8 mW/m² in presence of pure O₂). The cathode presented in this paper allows to obtain a power density 7.5 times higher than using a Pt cathode.

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1. Introduction

Microbial fuel cells (MFCs) are electrochemical devices which convert chemical energy into electricity using micro-organisms as catalyst. Using organic waste for the formation of an electroactive biofilm as well as a source of substrate is really promising due to the fact it will treat wastes and will harvest energy in the same time [1].

Since anode, as the electron acceptor for the electroactive bacteria, directly interacts with the microorganisms, the selection of high-performance anode materials is of crucial importance in the design of an MFC [2–4].

Aside from all the other factors affecting the MFC performance, which include cell design, inoculum, substrate, proton exchange material and electrode surface areas…[5–11], the fabrication materials for the anode plays a profound role in influencing the power generation by determining the actual accessible area for bacteria to anchor and by affecting the interfacial electron transfer resistance.

Therefore, a high-performance anode material is essential to improve the power outputs of MFCs [12]. However, the cathodic electrode plays also an important role. Limitation of oxygen reduction can reduce the performance of MFC. Thus, MFC performance is mainly limited by the cathode [13,14]. Recent works have been focused on the biocathode for enzymatic fuel cell [15,16] as well as for MFC [17,18].

In this paper, a graphene modified bioanode has been combined with a chemical poly-NiTSpc modified carbon felt cathode in the aim to fabricate a MFC. Recently, graphene has been considered as the intriguing material, attracting strong scientific and technological interest with great application potentials in various fields, such as lithium ion batteries [19], solar cells [20] and electrochemical supercapacitors [21], for its unique nanostructure and extraordinary properties (high surface area [22], excellent conductivity [23], passivation of biocorrosion [24] outstanding mechanical strength [25] and extraordinary electrocatalytic activities, etc.). Stainless steel foam has been selected due to its bio-corrosion resistance, its 3-D structure, its porosity (which may facilitate the anchor of micro-organism) and because it was suitable for the LbL method contrary to carbon felt which would have absorb rGO and PEI instead of having a layer deposition. Also, stainless steel foam is a promising material electrode for microbial colonization as report elsewhere [26]. Moreover, the mechanical resistance of stainless steel foam is much higher than that of carbon felt. The influence of supply of oxygen at the cathode has been investigated as well as the long time stability of this microbial fuel cell.

2. Experimental

2.1. Chemicals and materials

Graphene oxide (GO) was synthesized from graphite by a modified Hummers method suspended in MilliQ water [27,28]. Hydrazine and ammonia solution (purchased from Fluka) were used to chemically reduce GO [29]. rGO obtained had a concentration of 0.25 mg/mL. A 1 mg/mL solution of poly(ethyleneimine) (PEI, Aldrich) was prepared in an aqueous solution of 0.5 M NaCl (Fluka).
Compost garden leachate was made with 1 L of commercial garden compost (Botanic, France) and 1 L of 60 mM potassium chloride (Fluka). The mixture was stirred for 48 h and was grossly filtered with a sieve in order to remove all solid compost. Potassium acetate (Fluka) was added to the solution previously filtered to obtain a concentration of 20 mM in the leachate medium. Potassium acetate is thus used as fuel for the fuel cell [30].

Untreated Naion 117® (Dupont USA) was used as proton exchange membrane separator between the two compartments of the biofuel cell.

Stainless steel foams (ASI 316) with a surface area of 10 cm² were used for experiments.

Pt disc electrode with a surface area of 0.78 cm² was used for experiments.

Also, all results have been normalized by the geometric surface area of electrodes in order to compare them.

2.2. Electrochemical measurements

All electrochemical experiments were performed on a SP-50 from Biologic (France) in a three-electrodes set up, including a working electrode, a graphite counter electrode and either an Ag/AgCl (saturated KCl) or SCE reference electrode. An external resistance (1 kΩ) between the anode and the cathode was used to determine the power output during the discharge of the MFC. Data were recorded every 30 min during the beginning of the discharge until stabilization of the system and then it was recorded once a day. All experiments were run at room temperature.

2.3. Field emission gun scanning electron microscopy (FESEM) and Scanning electron microscopy (SEM) experiments

The FESEM equipment used is a JSM-6301F from JEOL (Angers University, France). Before analysis, all samples were washed with
ultra-pure water to remove excess of salts deposited. Carbon felt samples were desiccated and glued to a carbon support. The samples were then attached to steel discs with double side-scotch tape and then covered of an ultra-thin layer of Pt/Pd (4 nm) using an evaporating technique. Beam energy was very low for FESEM analysis (under 3 keV).

The SEM used is a S4800 FEG—HR from Hitachi (Montpellier University, France). Before analysis, all samples were washed with ultra-pure water and attached to steel discs with double side-scotch carbon tape. Then, samples were coated with a thin layer of Pt/Pd (4 nm) using an evaporating technique. Samples with biofilms were pre-treated in order to stabilize bacteria attached to the anode. Sample (cut from the anode) was immersed in 4% glutaraldehyde (Sigma) solution for 4 h. It was then rinsed with de-ionized water for 3 times, followed by dehydration with increasing concentration of ethanol (20%, 40%, 60%, 80% and 98%) for 10 min each times and further rinsed in isoamyl acetate twice (10 min each time). Sample was then dried at CO₂-critical point for 3 h [31].

2.4. Modification and preparation of the anode

Stainless steel foam was modified with rGO by a LbL method [32]. In order to adsorb the rGO (negatively charged) onto the surface of the electrode, it is important to form a positive layer on its surface. The first layer was made with the adsorption of PEI (positively charged polymer) on the surface by soaking the electrode in a solution of PEI (1 mg/mL) for 15 min. The electrode was then washed with distilled water and dried with nitrogen. Thereafter, the electrode was dipped into the solution of rGO for 15 min too, cleaned with distilled water and dried with nitrogen. This process was repeated 5 times in the aim of making 5 bilayers of (PEI/rGO). This electrode is thus named SSF/(PEI/rGO)_5 as shown in Fig. 1.

The growth of an electroactive biofilm was followed by chronoamperometry with a potentiostat (SP 50 Biologic-France). In a three electrodes system, the working electrode (SSF/(PEI/rGO)_5 or SSF) was immersed into a solution composed of compost garden leachate and sodium acetate (1:1). The potential applied to the counter electrode (graphite) was -0.246 V vs Ag/AgCl [26] and was applied for a period of 20 days.

2.5. Cathode elaboration

Carbon felt cathode was first electrochemically pretreated under the following conditions: cyclic voltammetry between 0.0 and 1.2 V vs SCE in 0.1 M NaOH during 10 cycles (scan rate 0.1 V/s). The carbon felt pretreatment is essential to attain a good reproducibility of the poly-NiTSPc film deposition because on one side it helps to eliminate initial impurities and on the other side it prepares the carbon surface to graft oxygen to the surface which is very essential to do O-Ni-O bridges. The electrochemical deposition of poly-NiTSPc was achieved in 0.1 M NaOH and 2 mM NiTSPc aqueous solution by repeated potential scans between 20 and 140 times, between 0.0 and 1.2 V vs SCE (scan rate 0.1 V/s), in order to optimize the poly-NiTSPc deposition.

2.6. Microbial fuel cell set up

The MFC set up is divided into two compartments. One is dedicated to the anode and the other one is for the cathode. Compartments are
separated by a Naflon 117© membrane which allows protons to go through it from the anodic to the cathodic chamber. On one hand, the anode is immersed into a mixture of compost garden’s leachate with sodium acetate (20 mM). On the other hand, the cathode is immersed in a solution of KNO$_3$ 0.1 M and either air or oxygen is provided into the chamber. An external resistance of 1 kΩ is connected to the electrodes [33] in order to shuttle electrons from the anode to the cathode. A voltameter, with a high enter impedance (10 MΩ), is plugged in parallel to observe the evolution of the voltage (Fig. 2).

3. Results and discussion

3.1. Cyclic voltammetry of poly-NiTSPc elaboration: the elaboration of a novel cathode dedicated to O$_2$ reduction

Cyclic voltammetry deposition of poly-NiTSPc film on the pre-treated carbon felt cathode is shown in Fig. 3. Cyclic voltammetry of the modified electrode showed typical electrochemical redox peaks of poly-NiTSPc at 0.2 and 0.75 V vs SCE (Fig. 3b) proving the presence of the film on the carbon felt surface.

The apparent surface coverage of the film electrode by the tetrasulfonated nickel phthalocyanine can be calculated from the cyclic voltammogram of the film after transfer of the film, through careful rinsing, to a fresh alkaline solution containing no monomer. The calculation is based on the charge under the oxidative peak observed at 0.75 V/SCE using Faraday’s law.

The effect of the number of poly-NiTSPc electrodeposition cycle’s number on the oxygen reduction reaction was studied to optimize first the cathode performance. It is expected in modifying carbon felt surface to increase the intensity of oxygen reduction reaction, leading to an increase in fuel cell performances. The study of catalytic oxygen reduction has been carried out by chronoamperometry at $-0.8$ V/SCE to allow the comparison of different electrode materials. Fig. 4 illustrates the evolution of the current density obtained at $-0.8$ V/SCE with the number of poly-NiTSPc cycles of electro-deposition.

A maximum in the current density is observed for 70 cycles of electrochemical deposition, as illustrated in Fig. 4. The nickel-based complex film thickness can be estimated by taking into account the calculation of the electrode surface coverage, based on the charge under the oxidative or reductive peaks observed at 0.4 V/SCE, and the shape and size of the phthalocyanine macrocycle. In our considered case, NITSPc-based films optimized cathode were prepared either by 70 potential scans. This leads to the deposition of $6.1 \times 10^{-8}$ mol/cm$^2$, this corresponds approximately to a film thickness of 884 nm, as reported elsewhere [34–37].

Further experiments have demonstrated a good storage stability of poly-NITSPc film at room temperature during 6 months (results not reported).

Also the poly-NITSPc film enhances electron transfer between O$_2$ and the electrode surface, thus displaying a hypothetic electrocatalytic effect. For more than 70 cycles the intensity at $-0.8$ V/SCE decreased with a minimum observed for 140 cycles. This evolution suggests...
improved kinetics with increase in polymer thickness but the film porosity (nanoporosity suspected) became sufficiently low to limit O₂ diffusion after 100 cycles.

Considering Fig. 5, the ORR intensity increases two times comparing unmodified carbon felt and modified C/p-NiTSPc, we hypothesis an evolution of a two-electrons mechanism to a 4 electrons but none displacement of the OCP shows the absence of electrocatalytic effect. Furthermore, as illustrated in Fig. 6, poly-NITSPc is covering the fibers of the carbon felt increasing the geometrical surface exposed to O₂ reduction and this geometrical effect could explain the increase in the reduction current density observed.

The electrodeposition process must be homogeneous on the surface and the cycling method is the good way to achieve this aim. Thus, the film structure is imposed by the stacking of the complex layers via the interconnecting oxo-bridges, and does not depend on the electrochemical deposition procedure (cyclic voltammetry or controlled potential electrolysis). Ureta-Zanatu et al. [38] reported that poly-NITSPc film elaborated and cycling in NaOH is in the form of β-Ni(OH)₂ very similar to that in nickel hydroxide. A large part of the carbon fibers show matter aggregates deposit (see Fig. 6b), supposed to be β-Ni(OH)₂ clusters and very recent works developed these previous results, see Ref. [39] and references therein.

3.2. Cyclic voltammetry of the anode without biofilm

Blank SSF and SSF/(PEI/rGO)₅ electrodes were both characterized by cyclic voltammetry in a solution of acetate (20 mM) and KCl (60 mM) before and after the growth of the biofilm. As shown in Fig. 7, voltammograms of the SSF/(PEI/rGO)₅ electrode revealed a larger current responses compared to the SSF blank electrode in the potential scan range of −1.0 V to +0.6 V. The increase in the electron transfer efficiency can be attributed to the synergic properties of rGO. In addition, the same behavior is observed with the biofilm onto the surface of electrodes. A current increase is observed for both electrodes when the biofilm is formed although the current is higher for the modified electrode. The oxidation potential is shifted to the right (higher potential) which shows the acetate oxidation by the biofilm.

3.3. Power output of the anode in one compartment

The SSF/(PEI/rGO)₅ electrode was set up in a one compartment cell (compost garden leachate and acetate, 1:1, Fig. 8) with a graphite electrode connected to a resistor of 1 kΩ [33] in a two electrode system. The goal of this experiment was to observe the evolution of the current for a long period in order to know the stability and the lifetime of this
anode, allowed a better stability of the biofilm due to the morphology modification at the surface of the anode. Long time stability of both electrodes strengthens the idea of investigated in these electrodes materials for the realization of a larger size MFCs. Indeed, this novel MFC provided a power output of 24.8 mW/m² in presence of pure O₂ at the cathode and 7.2 mW/m² at ambient air after a period of 40 days.

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