Electrochemical Synthesis of Polyaniline/Metal-based Anodes and their Use in Microbial Fuel Cell

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A limited number of metals may be suitable as bioanode material: noble metals, such as gold and platinum, could be the optimum choice being electrochemically inert in the operational potential window of the bio-electrochemical system. However, high costs limit their wide scale application. Even though its antimicrobial nature, copper is being considered as a promising alternative anode material, due to its high conductivity, that allows minimising the electrode material costs. Literature research indicated that high-performing electrochemically active biofilms may be grown on this metal.

In the present work, gold and copper substrates have been coated by a conductive polymer (PANI), using a layer – by – layer procedure: surface grafting by reduction of 4-nitrobenzendiazonium salt was followed by reduction of nitro- to amino-groups; PANI was electrodeposited on this under-layer.

The synthesized anodes were tested as working electrodes (WE) in a microbial fuel cell fed with anaerobic sludge and acetate; to assess the growth of the biofilm on the WE surface, the trend of the bioelectrocatalytic current of acetate oxidation was monitored over time. Cyclic voltammetries reveal the presence of typical redox couples related to the presence of electroactive microorganisms on the electrode surface. Preliminary data show bioelectrochemical activity on polyaniline-coated metal surfaces.

1. Introduction

Nowadays, water and electricity are crucial services in a social-economic system: supplying sufficient clean water and making renewable energy sources available, are becoming pressing issues. In this context, we can understand the recent high interest towards microbial fuel cells (MFCs), a bio-electrochemical system (BES) which exploits the ability of specific microorganisms to produce electricity by the catabolism of an organic substrate. A possible use of MFC can be proposed in water treatment plants, as possible stage in alternative, or complementary to the biological one, allowing a reduction of costs thanks to the lower amount of sludge generated, and the contemporary energy production (Palanisamy et al., 2019) (Verma et al., 2020) (Zhang et al., 2020).

In a typical MFC, the anode material, colonized by a bacteria culture, responsible for the substrate oxidation, is combined with a cathode at which reduction of oxygen generally occurs, while a membrane is adopted to separate the two compartments (Kaur et al., 2020) (Rodríguez et al., 2019). The electrode material is one of the fundamental components of microbial fuel cells and it plays a critical role in the interaction between bacteria and the anode that have to possess some characteristics such as high conductivity, biocompatibility, large surface area for the microorganisms to easily anchor and grow on the surface, resistance to biofouling and cost effectiveness (Yaqoob et al., 2020). Carbon-based materials have been largely considered as the material of choice, since it is biocompatible, chemically and microbially stable and it can be produced at comparatively low costs from biological and chemical polymer precursors via carbonization. Despite these positive properties, carbon possesses a major disadvantage: its electric conductivity lies two to three orders of magnitude below that of most metals. Despite the variety of metals, only a very limited number may appear suitable as bioanode material. The metal should be electrochemically inert in the operational potential window

of the bioelectrochemical system, which means that it should be electrochemically noble or that it can become electrochemically passivated. Inexpensive metals can potentially be used as anode material, provided that a compact oxide layer (passivation layer) protects the metal from further oxidation (Baudler et al., 2015). Copper is known to be natural antimicrobial material due to its antimicrobial action of traces of metal ions liberated from the metal surface upon oxidation. One strategy, therefore, would be to protect the copper with a barrier that allows the retention of its intrinsic properties without interfering with the electrochemical anode processes in the microbial fuel cell (Pan et al., 2016). Conducting polymers might play the role of a protector of the anode materials, such as copper, without compromising their inherent conductivity.

Polyaniline (PANI), a conducting polymer, has been used as a corrosion inhibitor in many applications thanks to its advantages, including facile methods of synthesis and mechanical stability. The ideal protective material must be able to prevent metal corrosion and the poisoning of bacteria while possessing sufficient porosity to allow for bacterial anode interaction and charge transfer (Hindatu et al., 2017).

In the present work, gold and copper substrates have been used as metal anodes and coated by a conductive polymer (PANI), using a layer – by – layer procedure (Vacca et al., 2014): surface grafting by reduction of 4-nitrobenzendiazonium salt was followed by reduction of nitro- to amino-groups; PANI was electrodeposited on this under-layer by galvanostatic runs from aqueous solutions of aniline (0.1 M) and $C_2H_2O_4$ (0.1 M). The corrosion performance of this PANI film against metal corrosion was investigated properly in a Medium buffer solution. The synthesised materials have been inserted in a flow microbial fuel cell and used as working electrodes (WE); the cells were fed with anaerobic sludge and acetate. To assess the growth of the biofilm on the WE surface, the trend of the bioelectrocatalytic current of acetate oxidation was monitored over time.

2. Materials and methods

All electrochemical experiments were performed at room temperature using an AUTOLAB PGSTAT302N (Metrohm, Switzerland) potentiostat/galvanostat equipped with a frequency response analyser controlled with the NOVA software.

A conventional three-electrode cell (V = 10 ml) was used in which working electrodes were prepared from either gold foils (Sigma–Aldrich®, 99.99%) or copper foils (Sigma–Aldrich®, 99.97%), Saturated Calomel Electrode (SCE) was the reference and Pt-grid was used as counter electrode; the exposed geometrical area of the working electrodes was 0.5 cm^2.

Prior to modification, gold electrodes were manually polished with water and acetone and then submitted to 50 voltammetric cycles in 0.2 M phosphate buffer at pH 7 in the potential range between −0.45 V and 1.4 V, at a scan rate of 100 mV s^{-1}; copper electrodes were polished with HNO_3 (30 % v/v) in order to remove the native oxide layer. Afterwards, the metal electrodes have been submitted to a functionalization of the electrode surface with 4-nitrobenzenediazonium performed by cyclic voltammetric runs in the range of potential 0.6 V to -0.4 V (2 cycles, scan rate 100 mV s^{-1}) for gold electrodes and -0.2 V / -1,2 V (4 cycles, scan rate 20 mV s^{-1}) for copper electrodes in acetonitrile solution containing 2 mM of 4-nitrobenzenediazonium tetrafluoroborate and 0.1 M of tetrabutylammonium hexafluorophosfate as supporting electrolyte.

Electrochemical reduction of nitro group to amino group was performed by cyclic voltammetry in water/ethanol solutions (90:10 vol%) containing 0.1 M of KCl; the potential was varied from the open circuit potential to −1.2 V and back to 0.2 V (2 cycles) for gold electrodes and 0.1 V / -1.4 V (4 cycles) for copper electrodes. The scan rate was 100 mV s^{-1}.

Polyaniline was electropolymerized on the phenylamine modified metal electrodes by galvanostatic runs at a constant current density of 20 mA cm^{-2} for 20 minutes from aqueous solutions of aniline (0.1 M) and $C_2H_2O_4$ (0.1 M). The corrosion-resistant properties of the polyaniline-coated samples are evaluated using polarization techniques in a Medium buffer solution. The as-prepared samples were tested as anodes in a bioelectrochemical cell equipped with an air cathode, as described elsewhere (Mateo et al., 2019).

3. Results and discussion

The cyclic voltammograms recorded during the electrodeposition of NBD in acetonitrile containing 2 mM NBD and 0.1 M ($TBAPF_6$) as supporting electrolyte, on bare gold electrode, have been shown in figure 1a. As can be seen, a well-defined peak is present in the first cathodic scan at 0.18 V, which can be attributed to the electroreduction of NBD: a fast and easy reduction of aryl diazonium cations to aryl radicals which can graft onto the clean gold surface occurs in the potential range between 0.6 V and 0 V. In the second cathodic scan, the reduction peak completely disappears: the blocking effect of the layer of NBD progressively hinders the further reduction of NBD cations at the surface.

The reduction of the nitrophenyl group to aminophenyl has been performed by cyclic voltammetry in water/ethanol solution (90:10 vol%) containing 0.1 M of KCl: figure 1b shows the presence of an irreversible

reduction wave around -1 V in the first scan, while, during the second scan, the extent of the reduction peak is drastically diminished, indicating that nearly all the electroactive NO_2 groups are reduced in the first scan.
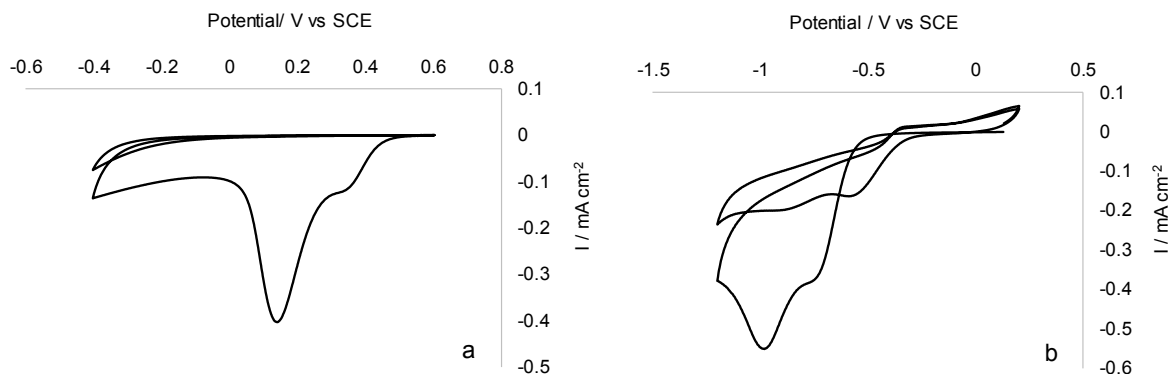

Figure 1: Cyclic voltammograms of functionalization of 4-nitrobenzenediazonium (a) and electrochemical reduction of nitro group to amino (b) on gold electrode.

As the electroreduction of NBD on copper substrates is concerned, cyclic voltammograms have been recorded in the potential range between -1.2 V and -0.2 V with the presence of a single redox wave at -0.95 V in the first scan, that become less evident in the fourth cycle indicating the saturation/blocking of the surface during grafting. The behavior observed on copper electrodes is slightly different compared to that observed on gold, where the reduction peak completely disappears after the first scan: this could be explained by a difference in the film formation conditions due to the different substrate material. The electroreduction of the nitrophenyl group to aminophenyl was performed by cyclic voltammetries in the range from -1.4 V to 0.1 V at 100 mV s^{-1}, with a cathodic reduction peak at -0.75 V (Mooste et al., 2018).
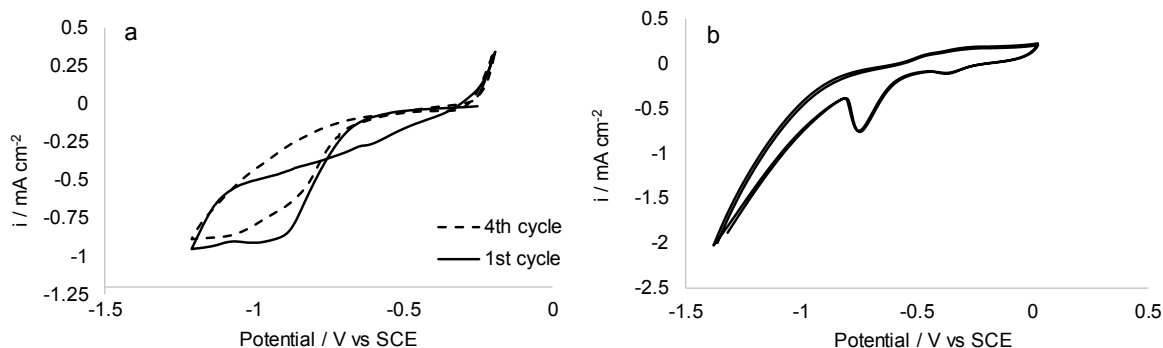

Figure 2: Cyclic voltammograms of functionalization of 4-nitrobenzenediazonium (a) and electrochemical reduction of nitro group to amino (b) on copper electrode.

PANI polymerization was carried out on the phenylamine modified metal electrodes by galvanostatic runs at 20 mA cm^{-2}; as it can be found in the literature, galvanostatic procedure causes the deposition of a dark green coating, which is the characteristic of polyaniline in the emeraldine oxidation state (Shabani-Nooshabadi et al., 2014). If copper electrode is considered, the formation of the PANI coating involves different stages: the first one is related to the electro-adsorption of the monomer and electrolyte and initiation of formation of passive film, followed by the growth of the passive film with subsequent decomposition; the last one is related to the formation of the PANI coating (Shabani-Nooshabadi and Karimian-Taheri, 2015). During the first stage, it is possible to observe a jump in the potential caused by the dissolution of copper, the adsorption anions present in the electrolyte and the initiation of formation of a copper oxalate film. In the second stage, a subsequent increase in the potential, attributed partly to the growth of copper oxalate film, and its subsequent decomposition, is followed by a constancy in potential related to the initiation and formation of the PANI coating (Shabani-Nooshabadi et al., 2014).
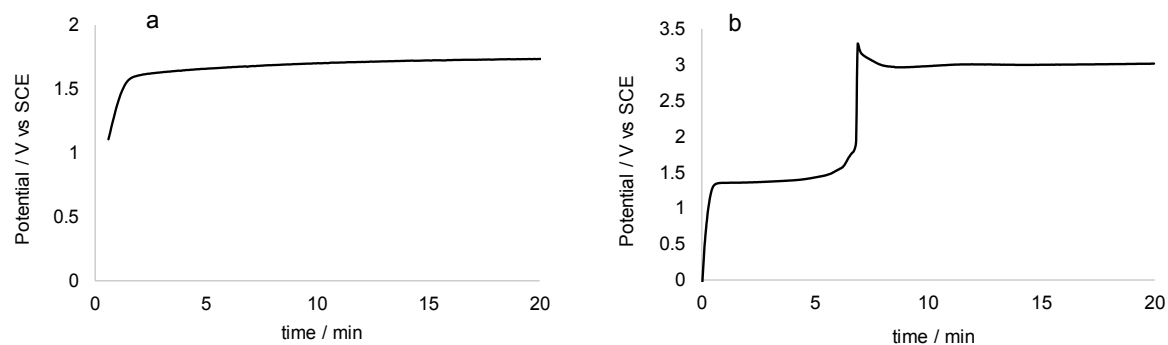
Figure 3: Galvanostatic runs performed at 20 mA cm^{-2} of electropolymerization of PANI on the phenylamine modified gold electrode (a) and copper electrode (b)

Potentiodynamic polarization curves of metal and PANI-metal electrodes have been recorded, in order to derive the polarization parameters (Mansfeld, 2009). Current densities (i_{corr}) at the corrosion potential (E_{corr}) were determined by extrapolating the Tafel lines at E_{corr}: for both metals, the corrosion current density was decreased by the PANI coating. The corrosion potential of Au/PANI and Cu/PANI is shifted to the positive side as compared with the un-coated metal electrodes; the anodic shift of the E_{corr} support the anodic protection of both metals. Moreover, the corrosion rate of both Au and Cu is reduced as a result of the reduction in i_{corr} (Jafari et al., 2016) (Song et al., 2012).

Table 1: Polarization parameters of both gold and copper with and without coating of PANI.

Samples	E_{corr}(mV)	I_{corr}(A cm^{-2})	CR(mm year^{-1})
Au	0.05	1.16×10^{-8}	1.35×10^{-4}
Au/PANI	0.31	5.27×10^{-9}	6.13×10^{-5}
Cu	-0.1	7.07×10^{-7}	8.21×10^{-3}
Cu/PANI	0.26	1.44×10^{-7}	1.61×10^{-3}

In order to derive information on the bioelectrochemical performance of both the Au/PANI and Cu/PANI anodes, the as prepared electrodes have been inserted in a MFC and tested as bioanodes (Mateo et al., 2019). The MFCs was fed with growth medium containing 5% of anaerobic sludge, at a flow rate of 0.6 mL min^{-1}, under continuous recirculation conditions. The MFCs were connected to a fixed external load to polarise the cell (2.2 kΩ), and to a Pico data logger (Pico Technology, UK) to continuously monitor the output voltage. After 15 days of working, cyclic voltammetries (CVs) have been recorded on the bioanodes in order to derive information on the presence of the biofilm grown at the electrode surface. The catalytic CVs were taken during the voltage plateaus with a scan rate of 1 mV s^{-1}. The exchange of charge is the result of the electroactivity of the biofilm already present at the electrode surface. The height of the related voltammetric peaks, may be an indication of the biofilm grown in time: a higher bacterial density, leads to a higher concentration of metabolites in solution, which in turn, influences conductivity and capacity. The potential of the peaks is instead connected to the redox species, i.e. to the specific class of bacteria present in the biofilm. The formal potential (E_f), evaluated as average value between the two potentials of the redox couple, is generally assumed to characterize the bacterial species.

Figure 4 reports the first results obtained by the use of the polymer-coated metal anodes: as it can be observed, a wave is recorded in the cathodic scan on Au/PANI samples at -0.6 V, while in the reverse scan a wave appears at -0.3 V. Two defined peaks, at -0.1 V and -0.2V, appear in the reduction scan of the CV recorded on Cu/PANI electrodes, with two waves at -0.4 V and -0.15 V in the oxidation scan. As it is reported in literature, two major systems (S1 and S2) are individuated with formal potential (E_f) and potential peak distance (ΔV) equal to -0.3 V and 0.2 V, respectively, which may represent the electrochemical activity of microbial species mainly responsible for the charge transfer onto the surface of the electrode. The presence of the electroactive microorganisms could be indicated as corresponding to the formal potential of systems S1 and S2 which are in the range generally reported in literature (Marsili et al., 2010) (Peng et al., 2015). As the formation of biofilm is concerned, further investigation is needed, as the electrochemical activity could be due to both planktonic and adhered microbial species (Pandit and Das, 2018).
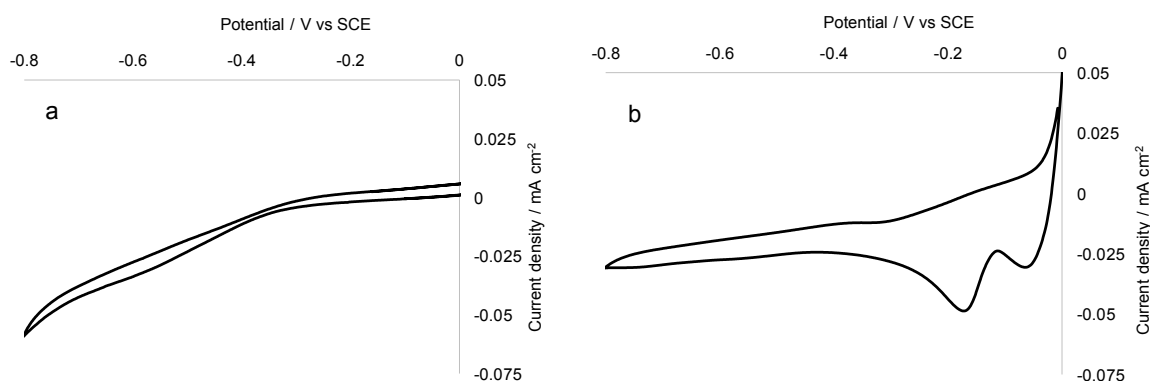
Figure 4: Cyclic voltammetries of the bio-film grown on the Au/PANI (a) and Cu/PANI (b) electrodes, recorded in the Medium solution at pH=7 (scan rate 1 mv s^{-1}).

4. Conclusions

The present work proposes a three steps approach to modify a metal anode (gold and copper) with a conductive polymer (polyaniline): prior to the electropolymerization, the electrodes were functionalized by electrochemical reduction of 4-nitrobenzendiazonium salts followed by the reduction of nitro to amino groups; the conductive layer of PANI was than deposited by galvanostatic runs in the emeraldine form. While in the case of gold anodes it is possible to observe the direct formation of the PANI coating, in the case of copper electrode the formation of the PANI coating involves different stages, starting from the electro-adsorption of the monomer and electrolyte and initiation of formation of passive film, followed by the growth of the passive film with subsequent decomposition; the last one is related to the formation of the PANI coating. Moreover, the synthesized materials have been tested as bioanodes in a microbial fuel cell to obtain electrochemically active biofilm on the surface. Cyclic voltammetric analysis reveals the presence of redox peaks which can be attributed to electroactive bacteria on the electrode surface under the adopted conditions.

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