Preparation of conductive carbon paper based on carbon nanofibers and polypyrrole for biofuel cell application

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Abstract. The development of novel conductive carbon paper has great potential application in biofuel cells (BFC) because it can increase the electrical conductivity. In this work, carbon nanofiber (CNF) was modified with polypyrrole (PPy) to obtain a conductive paper (CNF-PPy) for its application in BFC using lactate as fuel. The anode was prepared from lactate oxidase (LOx) with the FcMe₂-LPEI redox polymer, whereas the cathode was prepared from Laccase (Lc) with MWNT-modified with anthracene, both enzymes were deposited on CNF-PPy. FcMe₂-LPEI/LOx show a pair of redox peaks at 0.27 and 0.16 V (vs. Ag/AgCl) by cyclic voltammetry (CV) in PBS 7.4 and presence of 20 mM lactate the current density increase to 68.12 μA cm⁻². The CV with AnMWCNT/Lc in PBS pH 5.7 presented an oxygen reduction potential of 0.61 V shown a current density of 200.6 μA cm⁻². The evaluation of BFC was carried out in a single compartment in pH 5.7 (0.1 M) obtaining a OCP of 0.59 V a current and power density of 432.5 μA cm⁻² and 71.2 μW cm⁻² respectively using 40 mM lactate. This result showed that CNF-PPy were essential in obtain of a high performance in the BFC that use lactate as fuel.

1. Introduction

Carbon conductive paper (CCP) have great importance for their application in various fields including the detection of elements, electronic components, biomedical systems, among others. CCP has an extensive utility for its versatility as mechanical flexibility, biodegradability, affordability, renewability, mainly [1]; its modification with conductive polymers such as polypyrrole (PPy) gives it a higher electrical conductivity, has a low toxicity, biocompatibility, chemically reactive and economically accessible [2]. CCP has a greater potential for application in the area of alternative sources of energy such as capacitors, fuel and biofuel cells (BFC), the latter being attractive because they can operate at room temperature, possess a high potential in biomedical application systems, such as micro pumps, pacemakers, and so forth. Generally, one of its main challenges of the BFC is to increase its current and power density, so different strategies have been reported as using electrochemical mediators,
metallic materials with a high electrical conductivity, carbon nanoparticles and a higher attention to use CCP that provide greater catalytic stability and electrical conductivity [3]. The importance of lactate as fuel is due to its high energy density and water solubility compared to other biofuels, such as glucose and alcohols. The secondary product of lactate oxidation is pyruvate generating a theoretical energy density of 73 Wh/L and a complete oxidation of pyruvate/air the theoretical maximum current density could be 367 Wh/L [4]. In this study, carbon nanofibers with polypyrrole (CNF-PPy) were modified by the in situ polymerization method to obtain a CCP, which was used for the immobilization of the lactate oxidase enzyme with a conducting polymer in the bioanode and laccase with carbon nanotubes modified with anthracene in the cathode and it was compared with a paper of commercial carbon (Toray carbon) in a BFC of lactate of a single compartment.

2. Experimental

2.1 Preparation of carbon nanofiber modified with polypyrrole in situ (CNF-PPy)

The preparation of CNF-PPy consisted of sonicating the 1 mol CNFs in an acid solution of EtOH bath with H$_2$SO$_4$ (0.5 M) at ratio 1:3 v/v during for 20 min, then 1 mol of pyrrole in H$_2$O$_2$ 30 % was added dropwise in a range of 30 min with the help of a pump keeping the temperature below 25 °C and it was stirred for 45 min dried at 100 °C after the reaction was stopped by adding 30 mL of deionized water (DI), the CNF-PPy were washed three times with DI and centrifuged at 3500 rpm and filtered using waltman paper, after it were dried at 100 °C degrees for 24 h and compressed to 3700 lb (Scheme 1).

2.2 Electrodes preparation

The immobilization of LOx was on CNF-PPy and carbon Toray (Ty) of area 0.25 cm$^2$. The redox polymer was polyethylenimine-modified dimethylferrocene (FcMe$_2$-LPEI) which was prepared as previously reported [5]. The solution was prepared from 10 mg mL$^{-1}$, 100 U mL$^{-1}$ LOx in PBS and 2-6% v/v EGDGE in a ratio of 56/24/3. Finally, 25 μL were deposited on CNF-PPy and Ty and allowed to dry for 24 h. For the immobilization of the biocathode, a solution of Lc 1.5 mg in 75 μL of PBS pH 6.5 with 7.5 mg of anthracene-modified carbon nanotubes AnMWCNT [6] was prepared by vortexing 4 times per 1 min, finally 25 μL of TBAB-nafion solution was added and mixed for 1 min. Finally, 9 mL of the solution was deposited on CNF-PPy and electrode using a brush and allowed to dry for 2 h.

2.3 Electrochemical methods

Electrochemical experiments were performed using a Biologic VSP Potenciostat/ Galvanostat. The FcMe$_2$-LPEI/LOx on Ty and CNF-PPy electrodes were evaluated in a PBS pH 7.4 (0.1 M) solution using an Ag/AgCl electrode and a platinum mesh as reference and counter electrode respectively. Cyclic voltammetry (CV) were performed at a scan rate at 2 mV s$^{-1}$ and a potential range of 0.5 to -0.1 V, while the amperometry experiments were carried out applying a voltage of 0.3 V. While the electrodes with AnMWCNT/Lc were carried out by CV to a potential window of 0.8 to 0 V and a scan rate of 1 mV s$^{-1}$
in PBS pH 5.6 (0.1 M). The polarization curves for the BFC in a single compartment were linear polarization at 2 mV s\(^{-1}\), using FcMe\(_2\)-LPEI/LOx as anode and AnMWCNT/Lc as cathode supported on Ty and CNF-PPy. The supported electrolyte consisted of a solution of PBS (0.1 M) at a pH of 5.6, using different concentrations of lactate 2, 10, 40 mM respectively.

3. Results and discussion
The characterization of FcMe\(_2\)-LPEI/LOx on CNF-Py by VC shows a pair of redox peaks at 0.27 V and 0.16 V (vs. Ag / AgCl) with a formal potential of 0.215 V belonging to the redox polymer FcMe\(_2\) with a current density of 68.12 \(\mu\)A cm\(^{-2}\) measured at 0.26 V in the presence of 20 mM lactate. While FcMe\(_2\)-LPEI/LOx on Ty the pair of redox peaks were found at 0.27 V and 0.21 V (Ep’ 0.24 V) respectively with a current density of 30.62 \(\mu\)A cm\(^{-2}\) (Figure 1A). On the other hand, the amperometric experiments were performed at 0.3 V and found that with the CNF-Py the current increase in the first addition of lactate was 6.03 times higher in comparison to Ty, to both electrodes the linearity range was 1-5 mM but obtaining a higher CNF-Py sensitivity of 29.8 \(\mu\)A mM\(^{-1}\) cm\(^{-2}\) and 5.97 \(\mu\)A mM\(^{-1}\) cm\(^{-2}\) with Ty (Figure 1B).

For AnMWCNT/LC the experiment was performed in PBS (0.1 M) at pH 5.6 saturate in \(\text{N}_2\) and air by CV which are shown in Figure 2. The oxygen reduction reaction (ORR) potential starts at 0.62 V in both materials, which was due to the active site of the copper-containing enzyme T1 which allows the direct electron transfer between the enzyme and its surface [7]. The current density generated with Ty was 122.04 \(\mu\)A cm\(^{-2}\) while with CNF-Py it was 200.63 \(\mu\)A cm\(^{-2}\) 64.4% higher with the latter.

![Figure 1](attachment:Figure1.png)

**Figure 1.** CV comparative of FcMe\(_2\)-LPEI/LOx on Ty (black line) and CNF-PPy (blue line) in the absence (solid line) and the presence (dashed line) of 20 mM lac in pH 7.4 PBS at a scan rate of 2 mV s\(^{-1}\).

![Figure 2](attachment:Figure2.png)

**Figure 2.** Comparative voltammograms of AnMWCNT/Lc on Ty (black line) and CNF-PPy (blue line) in 0.1 M PBS at pH 5.6 at a scan rate of 1 mV s\(^{-1}\).

The BFC evaluation showed for the Ty a higher OCP of 0.47 V and a maximum current and power density of 9.5 \(\mu\)A cm\(^{-2}\) and 2.7 \(\mu\)W cm\(^{-2}\) respectively, using a concentration of 2 mM lactate (Figure 3A), while that at concentrations of 10 and 40 mM the performance decreases considerably (Figure 3 B). While with CNF-PPy the maximum OCP reached was 0.6 V and a maximum current and power density
of 432.5 μA cm⁻² and 71.5 μA cm⁻² using 40 mM lactate, this result is equivalent to 45.5 and 26.5 times greater when compared to Ty and this result is comparable with others reported [8].

![Figure 3](image)

**Figure 3.** (A) Comparison of polarization and power density curves between Ty (black line) and CNF-PPy (blue line) in a BFC single compartment using 10 mM lactate characterized at 2 mV s⁻¹ (B) comparative performance of BFC between TP and CNF-PPy using 2, 10 y 40 mM of lactate.

### 4. Conclusions

This work showed a higher enzymatic catalytic activity of FeMe₂-LPEI/LOx and AnMWCNT/Lc immobilized on CNF-PPy in the oxidation of lactate and ORR respectively, compared to commercial carbon Ty. The application of CNF-PPy in BFC the performance was 45.5 and 26.5 times higher with respect to Ty, exhibit the importance of the CNF polymerizing PPy to increase its electrical conductivity converting them into supports suitable for the immobilization of enzymes and its application in BFC of lactate.

### Acknowledgments

The authors thank the Mexican Council for Science and Technology (CONACYT) for financial support through project Fronteras de la Ciencia 611, Ciencia básica 2015-Grant 256749, LN-280485 and SENER 246079.

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