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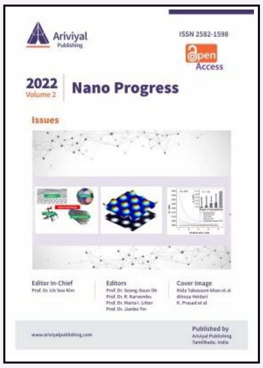

Immobilisation in situ for Electrochemically Active Bacteria on Polypyrrole Polymer Modified Copper Carbon Paste Electrode for Glucose Fuel Cells

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Abstract: In this study we describe a new polypyrrole (PPR) / bacteria (S) composite coating copper carbon paste electrode (Cu-CPE), prepared by electropolymerization of pyrrole (PPR) onto copper carbon paste in an aqueous solution containing staphylococcus bacteria (S). The performances of the prepared microbial electrode (PPR-S/Cu-CPE) were studied for the glucose oxidation in an alkaline medium.

Keywords: Microbial electrode; Electropolymerization; Glucose; Fuel Cells

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1. Introduction

The demand for alternative energy has seen an unexpected increase in recent days due to the threats of strategic wars and also industrial developments which tend to displace non-renewable energy sources, such as fossil fuels and nuclear energy.[1] These conventional energy sources are beginning to become harmful to human life through the very high pollution rate which results from it and which directly impacts the quality of air and water and contributes to global warming.[2-4] The search for reliable alternative sources has become more than ever a demanding priority for respond to the energy problem by relying in particular on renewable energies, such as solar energy, hydraulic energy and wind energy.[5–7] Fuel cells appears attractive for many applications that require much lower power levels, such electric vehicle applications, who use the two most attractive fuel cell options, hydrogen-air alkaline fuel cell and methanol-air acid electrolyte fuel cell.[8,9] These fuel cells use electrodes doped with high-value catalysts, such as the palladium incorporated in the Nafion, which have many advantages such as the absence of emissions of gases polluting the environment, in particular CO_2, CO, NO_x and SO_x, also the absence of disturbing noise. Another generation of fuel cells has recently emerged, microbial fuel cells or bioelectrochemical cells, which invest active bacteria as a biocatalyst for the production of bioenergy in anode compartments.[10,11] In this study we have developed a new method for manufacturing bacterial electrodes, these are polymer-bacteria/copper-carbon paste (PPR-S/Cu-CPE) type electrodes. The initial electrode being a carbon paste electrode modified by copper (Cu-CPE), the polymer (PPR) is developed on the surface of the Cu-CPE electrode, in situ, in an alkaline medium containing the bacteria, these the latter are then incorporated inside the structure of the polymer.

2. Materials and Methods

All electrochemical experiments were conducted by a voltalab-type potentiostat (model PGSTAT100, Eco Chemie B.V., Utrecht, The Netherlands) assisted by general-purpose electrochemical systems data processing software (VoltalabMaster 4 Software). The electrochemical measuring cell is a cuvette with a capacity of 150 cm3 fitted with three electrodes, a reference electrode of the calomel type; the counter-electrode is a platinum plate (1 cm x 1 cm x 0.1 cm); the working electrode is the elaborate electrode (PPR-S/Cu-CPE).

The chemicals used in this study are of high quality. Graphite powder (RWB spectroscopic grade, Ringsdorff-Werke GmbH, Bonn-Bad Godesberg, Germany) was obtained from Aldrich and used without further processing. Staphylococcus type bacteria were obtained from a specialist laboratory, under recognized conditions and ready to use.

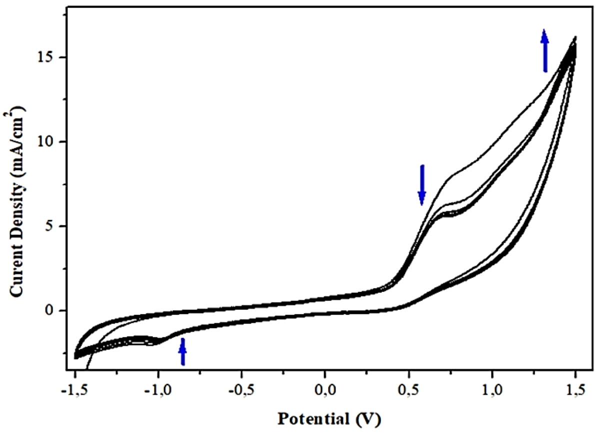

Fig. 1. Electrochemical polymerization of pyrrol by scanning potential scanning (Scan rate: 50 mV/s).

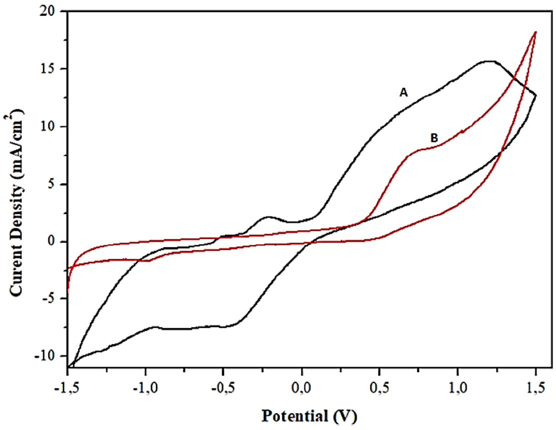

Fig. 2. Cyclic voltammetry of: (A) Cu-CPE electrode; (B) Cu-CPE covered with polypyrrol polymer.

2.1. Preparation of the modified electrode

The initial electrode (CPE) was prepared by mixing carbon powder and liquid paraffin, used as a non-conductive binder. The resulting paste was shaped into a plastic body containing a 0.25 cm^2 area hole. The copper is deposited on the surface of the electrode (CPE) electrochemically at 0.1 A, the electrode (Cu-CPE) is then obtained. This electrode is placed in the electrochemical measuring cell, containing 0.1 M pyrrole monomer and bacteria in an alkaline medium; the electropolymerization is triggered by a series of cyclic voltammetry.

3. Results and Discussions

3.1. Electrochemical polymerization

The polymerization was done by scanning the potential between -1.5 and 1.5 V at a scan rate of 50 mV/s. Fig. 1, shows the growth of the polymer on a Cu-CPE electrode during such polymerization. The growth of the polymer shows two peaks the first one in the direction of the anodic scan; about 0.75 V the second is a cathodic peak at -1 V. However, as the scan number was increased, the oxidation and reduction current peaks decreased rapidly. The voltammograms shown in Fig. 2 indicate that the modification of metallic surface with PPR is successful.

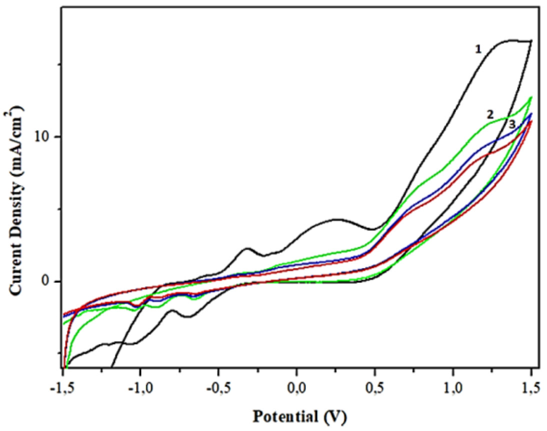

Fig. 3. Superposition of first four cyclic voltammograms obtained during the growth of the polymer in the presence of bacteria.

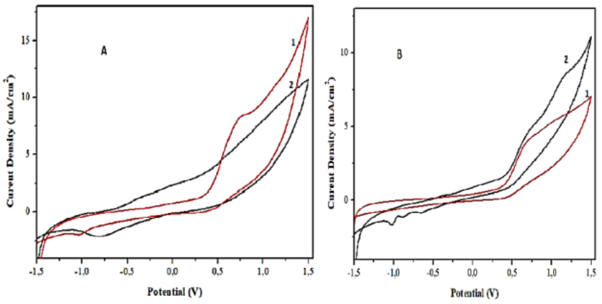

Fig. 4. Cyclic voltammetry of oxidation of glucose (curve 1) at: (A) PPR-S/Cu-CPE electrode; (B) PPR/Cu-CPE electrode. Curve 2 in absence of glucose.

3.2. Electrochemical incorporation of bacteria into the polymer structure

The incorporation of the bacteria into the polymer matrix was carried out simultaneously with the growth of the polymer on the surface of the Cu-CPE electrode. The consecutive cyclic voltammograms results are depicted in Fig. 3. A rapid positive shift of the polymer oxidation potentials (peaks at 0.25 and -0.25 V on the first voltammogram) is observed on consecutive voltammograms, due to increase of the electrical resistance. These observations can be explained by the tendency of bacteria to adhere to the surface of the polymer by the formation of a less conductive biofilm.

3.3. Electro oxidation of glucose at PPR-S/Cu-CPE electrode

Glucose oxidation was carried out on the two electrodes, PPR-S/Cu-CPE (in the presence of bacteria in the polymer) and PPR/Cu-CPE (in the absence of bacteria in the polymer). Cyclic voltammetry (CV) was used in this study. We present in Figs. 4 (A) and 4 (B) the results obtained, respectively on the PPR/Cu-CPE and PPR-S/Cu-CPE electrodes. On the PPR-S/Cu-CPE electrode, the oxidation of glucose is brutal with an onset of 0.3 V, the current densities exceed 15 mA/cm^2 and the activity of this electrode towards the oxidation of glucose is attributed to the connected aspect represented by the polymer, which promotes the adsorption of the electro-active molecule. The presence of bacteria in the polymer structure catalyzes the oxidation of glucose; whereas on the PPR/Cu-CPE electrode, the oxidation of glucose proved difficult to start.

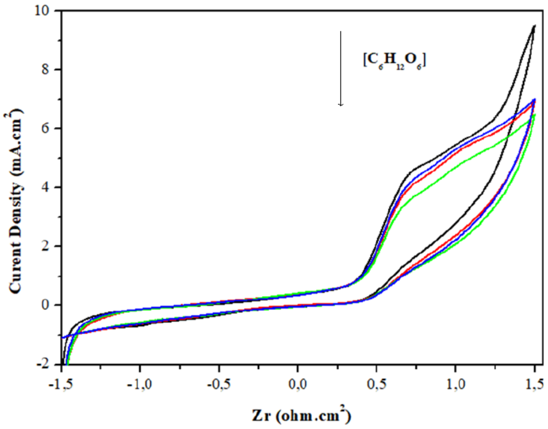

Fig. 5. Evolution of current densities of cyclic voltammetry versus glucose concentration.

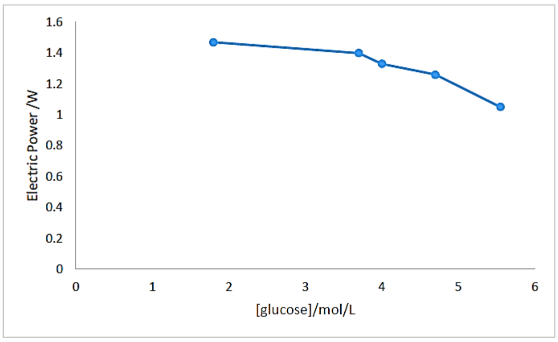

Fig. 6. Evolution of electric power with glucose concentration.

The effect of glucose concentration on the value of the Onset of oxidation was studied by cyclic voltammetry (Fig. 5). We find that the Onset value increases with glucose concentration accompanied by a decrease in oxidation current densities. High fuel concentrations tend to increase electrode resistance. These observations are also encountered in the evolution of the electrical power generated during the oxidation of glucose on the PPR-S/Cu-CPE electrode (Fig. 6). The more the concentration of the fuel increases, the more the electric power decreases.

In Fig. 7 we present three micrographs obtained with optical microscopy. Fig. 7(a) shows an image of Cu-CPE electrode, in which the copper is electrochemically deposited on the surface of the graphic carbon. We can observe the bright copper clusters deposited all over the surface of the carbon paste electrode (CPE), and even at very deep sites. Fig. 7(b) shows the surface of the PPR/Cu-CPE electrode, where the growth of the polypyrrole took place in situ, we can distinguish the film of the polymer covering the entire surface, we continue to see the shiny clumps of copper, which suggests that the polypyrrole is transparent. In Fig. 7(C), we present the micrograph taken for the PPR-S/Cu-CPE electrode where bacteria are deposited during polymer growth. As we can see, the bacteria form regular clusters on the polymer structure at different depths.

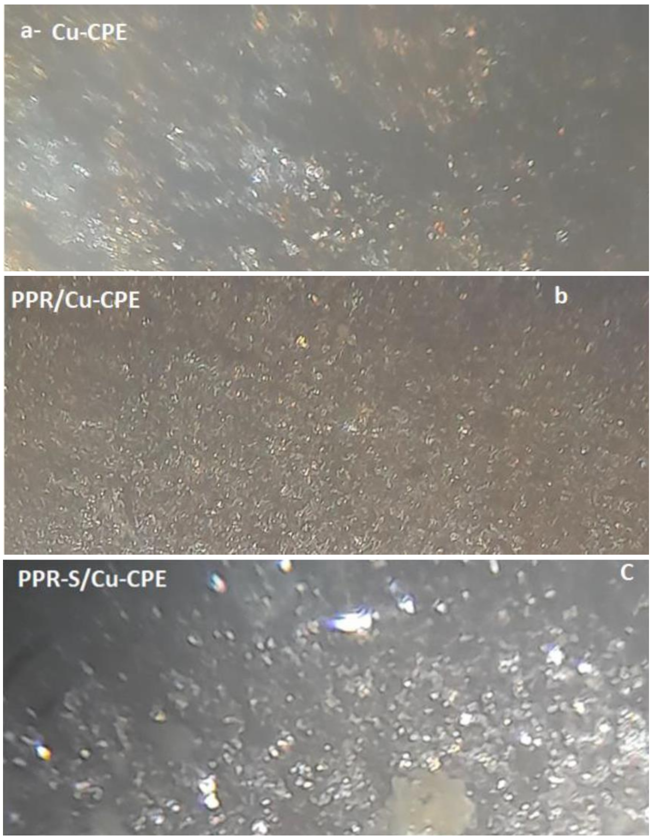

Fig. 7. Micrographs taken by optical microscopy at the surface of the electrodes : (a) Cu/CPE ; (b) PPR/Cu-CPE ; (C) PPR-S/Cu-CPE.

4. Conclusions

The conclusions from this study are as follows:

- The initial electrode is a carbon paste electrode (CPE) prepared according to the protocol previously described;[12]
- The copper is electrochemically deposited on the surface of the initial CPE electrode, it forms shiny clusters scattered over the entire surface of the carbon and also at different depths of the CPE;
- The growth of the polypyrrole takes place in situ on the surface of the Cu-CPE electrode, has led to a polymer that covers the entire surface, its transparent nature allows the copper clusters to appear, the electrode thus produced is denoted PPR/Cu-CPE ;
- The incorporation of bacteria into the polymer matrix was carried out during the electropolymerization of pyrrole, the electrode thus produced will be named PPR-S/Cu-CPE;
- The performance of the engineered PPR-S/Cu-CPE electrode was tested for glucose oxidation;
- The PPR/Cu-CPE electrode exhibits lower activity than the PPR-S/Cu-CPE electrode;
- The PPR-S/Cu-CPE electrode loses activity at high glucose concentrations.

Conflicts of Interest

The authors declare no conflict of interest.

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