Synthesis of an air-working trilayer artificial muscle using a conductive cassava starch biofilm (manihot esculenta, cranz) and polypyrrole (PPy)

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Abstract. In this study, a methodology for obtaining a conductive cassava starch biofilm doped with lithium perchlorate (LiClO4) is shown, as well as the electrochemical technique for the synthesis of polypyrrole films, which are used for developing the trilayer artificial muscle PPy/Biopolymer/PPy designed to operate in air. Furthermore, results from the trilayer movement using chronoamperometric techniques are shown.

1. Introduction
The constant progress of material science has allowed to develop actuators capable of converting chemical reactions into motion by electrical stimulation (reason why are known as electrochemomechanic actuators). Since these devices perform functions of contraction and expansion similar to natural muscles, are also called artificial muscles [1-3]. Nowadays, artificial muscles have been developed in a vast variety of materials. in the laboratory of electrochemistry at the Basque University in San Sebastián, Spain, a bilayer device of polypyrrole (PPy) with another neutral flexible polymer substrate was devised and patented, where the metal electrode, covered with a PPy film electrognerated, was peeled using a commercial nonconductive polymeric adherent film and the peeled bilayer was used then as new electrode in electrolyte solution. The macroscopic result was a remarkable inflection of the bilayer [4]. Actuators based on conducting polymers have become more interesting due to their characteristics such as high mechanical tension, large deflection values, high reversibility and the possibility of precise control using small voltages [5]. However, the reported artificial muscles are made from polymers and most of them work in aqueous media, only a few works reported movements in air [6-8]. Currently, implementation of biopolymers conductors on the generation of artificial muscles has not yet been reported. In this work is presented the development of a polypyrrole/biopolymer conductor/polypyrrole trilayer muscle able to move in air.

2. Experimental procedure
2.1. Preparation of the conductive biofilm
Initially cassava starch (3 g), which was obtained from core operations of washing, peeling, grating, filtering, decanting, drying and grinding was taken. Subsequently, in order to provide flexibility and
conductive properties to the biofilm, it was necessary to use glycerin (3 g), glutaraldehyde (2 g), and LiClO₄ (3 g) [9].

2.2. Synthesis of polypyrrole
To prepare PPy films, electrochemical polymerization techniques were used [10]. In which a solution containing 0.1 M LiClO₄ and 0.2 M pyrrole gauged in 25 ml of acetonitrile was prepared. Using a system consisting of a working electrode (EW) in the center, two counter-electrodes at the ends (EA), and a reference electrode (ER) of calomel saturated with KCl, a potential of 0.8 V was applied by a potentiostat for a time of 2500 s.

2.3. Obtainment of the trilayer
After obtaining the PPy layers, a cut of 4.5 cm² (3 cm x 1.5 cm) conductive biofilm was made, and placed on one of the layers of PPy which was in the steel sheet (EW), due to the adhesion properties acquired by the biofilm, it was possible to detach the layer of PPy. Then, using the same method, the second layer of PPy is removed, thus obtaining the three layers constituent (PPy/conductive biopolymer/PPy).

3. Results and discussion

3.1. Movement of the trilayer actuator
In order to evaluate the movement of the trilayer, potential steps of 2 V and -2 V were set during 20 s and 40 s, for oxidizing and reducing respectively the PPy layers.

Figure 1 shows the chronoamperometric response of the trilayer device, subject to periodic oxidations and reductions. In the first 20 s the movement is from the reference point (0°) to positive angles (see Figure 2), consuming an electrical charge of 95.44 mC, which is higher than in the movement toward negative angles, between 20 s and 40 s, where the electrical charge consumption was 77.17 mC.

Figure 1. Chronoamperometric response of the trilayer actuator.

Figure 2 shows the connection scheme and movement of the trilayer artificial muscle, where is sketched the movement and its relationship to the redox activity of the PPy layers, originating the response of the device. In this case, the oxidation corresponds to the movement of perchlorate ions from the biopolymer layer which acts as conductive solid electrolyte toward the PPy layer, causing an increase in volume, while the other layer of PPy is reduced, implying a reduction in volume of the PPy layer and therefore causing the device to bend towards it.

The record of the movement, is presented in Figure 3. This figure shows the sequential photographs of the movement of the trilayer device operating in air from the position 0° to positive and negative
angles, where it can be noticed the movement due to the increase and decrease in volume of the PPy layers.

![Figure 2. Movement scheme of the trilayer actuator.](image)

![Figure 3. Photo sequence of the trilayer artificial muscle movement: a) to positive angles, b) to negative angles.](image)

4. Conclusions
The developed conductive biopolymer, proved to be very stable physically and in its favorable conductive properties. Which is, the plasticizers in combination with the LiClO$_4$ added, in the aforementioned amounts, granted favorable electrical and mechanical properties for its use as an artificial muscle.

Developing the trilayer actuator (PPy/biopolymer/PPy), showed that the biopolymer was effective when used as solid polymer electrolyte, allowing the successful exchange of perchlorate ions from and towards the PPy layers. Allowing oxidation and reduction of the PPy layers generating a significant change in volume, which allow the smooth flowing movement of the actuator in the air in both directions using currents with the order of milliamps.

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