

Polypyrrole/Cassava Starch/Polypyrrole Electrochemical Accumulator

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Abstract: Currently there is a need to develop new devices capable of storing energy which should be lightweight, flexible and friendly to the environment. The aim of this research was to present the synthesis and characterization of cassava starch conducting polymer and polypyrrole films which were used in the development of an electrochemical accumulator. The starch films were chemically synthesized from native cassava starch adding plasticizers and lithium perchlorate. Moreover, polypyrrole films were electrochemically synthesized and doped with p-toluenesulfonic acid and indigo carmin. The characterization was carried out using electrochemical techniques of cyclic voltammetry and electrochemical impedance spectroscopy. The results indicate excellent electrochemical behavior of cassava starch films and polypyrrole films and good redox activity which allow the accumulation of charge in the electrochemical accumulator device. This opens the possibility of using these organic devices as an electrochemical charge accumulators.

Key words: Cassava starch, polypyrrole, electrochemical accumulator, conducting polymers, organic, charge

INTRODUCTION

In order to contribute to the development of clean technologies and independent from petrochemical sources are carrying out investigations into the production and storage of energy from alternative sources and using new biodegradable materials in order to improve the future of energy and pollution problems that cause their production (Klein *et al.*, 2017; Martinez, 2010). In this sense, the accumulator and battery technology has a promising future on the path to sustainability, being the development of polymer accumulator and batteries which have recently gained great interest in the scientific community and industry, mainly by the possibility of making devices flexible and friendly to the environment, since, the electrode materials used for processing they may be more suitable than metal substrates with electrodes (Guerfi *et al.*, 2016; Jeong *et al.*, 2018; Sultana *et al.*, 2012a-c).

It is very common to use the starch in the development of biofilms for food packaging (García-Tejeda *et al.*, 2011) but have also, emerged research aimed at the study and development of conducting properties in this biopolymer (Arrieta *et al.*, 2011). In most studies done, starch films are not conductive but the new developments that have been done to generate starch conducting biopolymers (solid

ionic conductor) have attracted attention because favorable electrical and mechanical properties are obtained and also because the starch is a natural, abundant, renewable, economical and biodegradable polymer.

Electrical conduction in this biopolymer is ion mobility, namely, takes place by hopping of ions (positively or negatively charged atoms) at affordable neighboring positions in the structure of the material. To take place, therefore, the transport or diffusion of ions in these materials must meet certain characteristics. Solid ionic conductors must have a structure that mechanically hold the material but which in turn has the ions accessible positions that are empty, to allow movement of ions carry charge through the material structure (Zheng *et al.*, 2018; Gray, 1991).

The ability to conduct electricity through ionic conduction, making a very attractive biopolymers leads to the development of new technologies it is the case of electrochemical charging batteries which require a medium for ion transport operation (Jacob *et al.*, 1997).

Conducting polymers such as Polypyrrole (PPy), Polyaniline (Pani), Polythiophene (PTph) etc. have also, been studied extensively in the last three decades due to their potential applications in sensors, optical devices and rechargeable batteries. Since, these are undergoing a reduction/oxidation as ion exchange medium (Eramo and

Otero, 2000). Many studies have shown that the polypyrrole is an excellent material for use as an electrode of the charge storage devices with lithium electrolyte (Rao *et al.*, 2017; Duan *et al.*, 2016).

The principal purpose for which it has carried out this work is to develop an electrochemical accumulator charging from a cassava starch biopolymer which was used as solid electrolyte medium. Initially cassava starch films were synthesized by the method of chemical synthesis. Biodegradable polymers generally require constituents provide wetting properties, plasticity, lubrication, spreading, conductivity and resistance, etc., therefore it was necessary to synthesize starch films through the addition of some plasticizers agents (glutaraldehyde, glycerol and polyethylene glycol) and lithium perchlorate. Moreover, the films of polypyrrole with against anions (pTS) and (IC) were synthesized and electrochemical characterization of each of these materials was carried out using the electrochemical techniques of Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) to evaluate their performance as materials with potential use in an electrochemical accumulator.

MATERIALS AND METHODS

Chemical synthesis of cassava starch conducting polymer films: Cassava starch was extracted using the traditional method, comprising the basic operations of washing, peeling, grating, decanting, drying and grinding. Product quality was evaluated by the technical Standard ISO 6647. Glycerol (GLY), Glutaraldehyde (GLU), Polyethylene Glycol (PEG) and Lithium Perchlorate (LP) were purchased from Sigma-Aldrich.

The synthesis of cassava starch conducting biopolymer was carried out in 100 mL of ultra-pure water (milli-Q), 3 g of cassava starch was dissolved and GLY (1.99 g), GLU (5.31 g), PEG (0.99 g) and LP (1.5 g) were added at room temperature and constant stirring.

The solution was heated at a controlled temperature of $75.0 \pm 1.0^\circ\text{C}$ for 15 min and then were poured into Teflon tray to heat them in an oven at 70°C for 48 h. A cassava starch films was prepared by a method similar to that described above but without any additive (plasticizers) added.

Electrochemical synthesis of polypyrrole films: For the electrochemical synthesis of polypyrrole (electrodes for the accumulator), chronoamperometry on a stainless steel polished 2×2 cm dimension was used. Polymer films were electrodeposited on these sheet. The films of PPy/pTS were synthesized from a solution of 0.1 mol/L^{-1} pyrrole

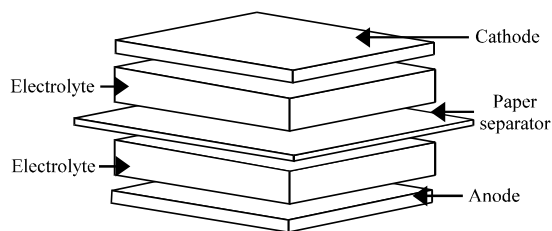


Fig. 1: Electrochemical accumulator: cathode (PPy/pTS), electrolyte (cassava starch polymer conducting), paper separator (recycled cellulose based paper) and anode (PPy/IC)

and 0.1 mol/L^{-1} pTS. The polymerization process was carried out at room temperature at a potential of 0.8 V for 5000 sec using a reference electrode saturated calomel KCl and as counter electrode were used stainless steel sheet of 2×2 cm.

Once synthesized PPy films these were washed with ultrapure water (Milli-Q) and then introduced in a 0.1 mol/L^{-1} LiClO_4 solution to the electrode polarization. This process was carried out at a potential of 0.5 V for a time of 600 sec, converting Ppy/pTS film in a completely oxidized film (cathode). Moreover, the films of PPy and indigo carmine (PPy/IC) were synthesized by a method similar to that described for the films of Ppy/pTS with the only difference that for these films, the polarization was carried out at -1.3 V for a period of 600 sec which allowed us to have a fully reduced film (anode).

Assembly electrochemical charge accumulator: In the first instance, the polymer cassava starch film to the same dimension of polypyrrole films (anode and cathode) 2×2 cm was cut. Also, there was no need to use any adhesive, since, the film of starch is this property that enables it to adhere to each of the components used. The configuration was developed sandwich type. The separator used was elaborated from recycled cellulose-based paper, since, it requires that they are made mainly of non-conductive material with good wettability with a low porosity, low electrical conductivity and good mechanical strength and flexibility (Broussely, 2017; Hu *et al.*, 2010). The architecture of electrochemical accumulator is represented in the Fig. 1. In addition, it aim was to build an organic accumulator, so that, the separator must also comply with this condition.

The cyclic voltammetry and electrochemical impedance spectroscopy was used to study the behavior and electrochemical properties of the polypyrrole and cassava starch films and armed electrochemical accumulator device. The electrochemical characterization

was carried out with a Potentiostat/Galvanostat Model 2263 SYS, EG&G from Princeton Applied Research and Powersuite Software.

RESULTS AND DISCUSSION

Synthesis of starch conducting polymer and polypyrrole films:

During the synthesis of starch films was observed that the environmental humidity, significantly affecting the stability of the films making them more flexible to increased moisture in the first 3 days. At the time that starch films are synthesized presented a flexible behavior which is attributed to the addition of plasticizers, due to this ability to reduce the hydrogen bonds between the chains of glucose from starch and increase the space between molecules (Myllarinen *et al.*, 2002; Georges *et al.*, 2018; Forssell *et al.*, 1999). Once synthesized, biofilms exhibit a completely transparent appearance but after the third day these take a yellowish opaque color, also they exude a liquid on its surface this is perhaps due to excess concentration of plasticizer which causes phase separation and physical exclusion of the substance.

During the electropolymerization of PPy films, chronoamperometric curves were generated which were showed a typical behavior of these processes. The thicknesses for the films of polypyrrole doped with pTS was approximately 48.5 μm whereas the films of polypyrrole doped IC, thicknesses were approximately 47.68 μm . The thickness (τ) was determined from the following Eq. 1, corresponding to the derivative of the first law of Faraday:

$$\tau = \frac{QM}{2F\delta_M} \quad (1)$$

Where:

- Q = The charge per unit area specified polymerised
- M = The molar mass of polypyrrole ($67 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$)
- F = The Faraday constant
- δ_M = The polypyrrole mass density ($1500 \text{ kg} \cdot \text{m}^{-3}$)

This implies a direct proportionality between the charge consumed and the amount of polymer deposited, assuming that in the process it is meant a 2-electron mechanism of the monomer molecule and that the current efficiency is 100% (Almorio and Tarazona, 2009).

The polypyrrole electroactive material can be oxidized or reduced, reaching different redox states. This property is important in the application of this material as an electrode because it allows to oxidize or reduce it can be used as anode or cathode. By keeping the polypyrrole film is a negative potential is reduced in the case of using positive potential is oxidized. Therefore, by applying negative potentials to PPy/IC films, the chronoamperograms begin with negative currents and

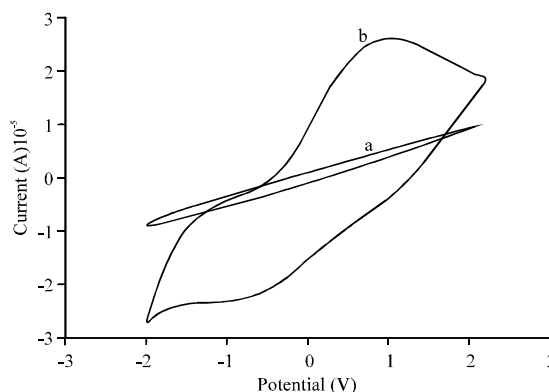


Fig. 2: Voltammograms of cassava starch films: a) Without plasticizers and b) With plasticizers

currents evolve toward zero at which indicates that the film has been fully reduced. In the PPy/pTS case the chronoamperograms begin with positive currents and decreased to a zero current, indicating a state of complete oxidation of the film.

Electrochemical properties of conductive films from cassava starch and polypyrrole:

The electrochemical analysis of starch films was carried out for unplasticized (without plasticizers) and plasticized (with plasticizers) starch films and the pure substances used in the starch polymer synthesis (starch, glycerol, glutaraldehyde, polyethylene glycol and lithium perchlorate).

As a result of this study, absence of electroactivity with no faradaic charge movement was observed in the pure substances and the film synthesized only with starch (Fig. 2a). When starch films were prepared with plasticizers the voltammetric responses recorded showed a redox process on the films (Fig. 2b).

The response consisted in a broad anodic peak at ca. 0.18 V and a cathodic peak at ca. -0.09 V. However, when the same analysis on each of the components separately was not any kind of electrochemical activity was observed. This behavior may be due to the addition of components in starch films generates a rearrangement of the polymer chains resulting in possible changes in the structure and hence, on their electrochemical properties.

To evaluate the electrochemical stability of the films their voltammetric behavior was evaluated for 10 days straight and behavioral changes were observed until the 6th day. The voltammograms recorded in the 1st day show broad peaks and poorly defined while the 6th day, the peaks appear better defined and more intense. This phenomenon may be due to newly synthesized films undergo a rearrangement process fillers in the polymer

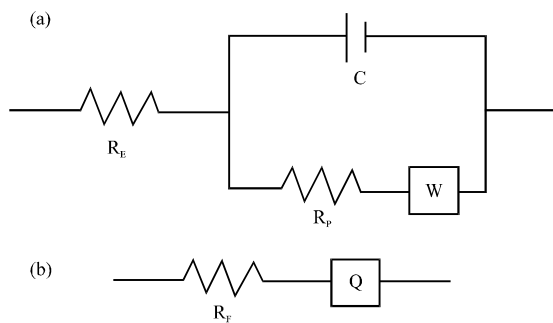


Fig. 3: Equivalent circuit of cassava starch films: a) Without plasticizers and b) With plasticizers

matrix which leads to greater efficiency in transporting them which explains the higher intensity signals and changing the electroactivity.

The EIS of the films synthesized without plasticizers showed high electrical resistance (6.50 MΩ). While films synthesized with plasticizers showed a low electrical resistance with four orders of magnitude (0.159 kΩ) compared to the film containing only starch which represents a high conductivity (8.61 × 10⁻⁴ S cm⁻¹).

This significant change in electrical conductivity is due to the additives improve charge transport properties in the polymer matrix and the ionic nature of lithium perchlorate allows to increase the electrical conductivity dramatically.

Additionally, EIS analysis showed a change in freight mechanisms. The determined equivalent circuit mechanism of the films synthesized only with starch has a typical mechanism comprised of a resistance due to passage of electrons from the substrate to the film (R_e) to a series Capacitor system (C) with a Resistor (R_p) and resistor Warberg (W), produced by resistors loads passing through the polymeric matrix (Fig. 3a).

However, the films synthesized with plasticizers showed a drastically different behavior, showing a resistive mechanism, composed of a Resistance (R_e) due to passage of electrons from the substrate to the film and a constant phase element (Q), possibly forming product of capacitance generated by roughness or non-uniform surfaces in the film (Fig. 3b).

This change in the transport mechanism is evidence that the addition of plasticizers increases the conductivity and the kinetic motion of charges in the polymer matrix. For analysis of CV polypyrrole electrodes made in 0.1 mol/L⁻¹ LiClO₄ solution showed clearly two redox processes for both PPy films, PPy/pTS and PPy/IC. The oxidation and reduction potentials are resumed in the Table 1.

Also the nature of the electrochemical processes that occur during the oxidation/reduction of polypyrrole films are interpreted with the model of polaron/bipolaron

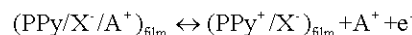
Table 1: Peak potentials of polypyrrole electrodes

Process	Variable	PPy/IC	PPy/pTS
Redox process 1	Oxidation	0.11	0.55
	Reduction	-0.12	-0.19
Redox process 2	Oxidation	0.03	0.23
	Reduction	-0.51	-0.92

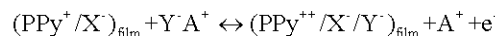
whereby the partial oxidation of the polymer chain leads to the formation of a polaron (PPy⁺), a combination of an electron and a positive charge no localized.

By removing a second electron (second oxidation) of the same section of polymer chain, may form a second independent polaron of existing or it may be that the delocalized electron is removed to form a dication or bipolaron (PPy²⁺) (Sultana *et al.*, 2012a-c; Almario and Tarazona, 2009; Appel *et al.*, 1999). In the first process of oxidation/reduction which occurs at lower potential, anion dopant is trapped in the polymer matrix, so that, to maintain electroneutrality, the cation exchange polymer in the medium. In the second process of oxidation/reduction of the film, the anion exchange polymer matrix with the environment and thus maintains its electroneutrality.

Process 1:



Process 2:



EIS results for the films carried out in polypyrrole described a transfer mechanism equivalent to a capacitive resistive circuit with the PPy/pTS and more capacitive tendency for the PPy/IC film. Proving that both materials are suitable for use as accumulator and battery electrodes. The conductivity values shown in the electrodes used in the assembly of the electrochemical charge accumulator were calculated from the resistance values obtained of the EIS graphs. The conductivity of these materials is similar to that reported in the literature (Lopes *et al.*, 2003) showing a higher conductivity to the cathode, compared to the anode. The PPy/pTS films presented a resistance of about 5.39Ω (2.22 × 10⁻⁴ S cm⁻¹) and the PPy/IC films of 7.01Ω (1.71 × 10⁻⁴ S cm⁻¹).

Assembly and analysis of the electrochemical charge accumulator:

For the accumulator assembly, electrode materials prepared with polypyrrole doped with pTS and IC were used which had a stable and flexible appearance with a completely homogeneous morphology. The main feature that the separator must meet is that this is fabricated of a nonconductive material, the study being the most suitable material for being made of cellulose in

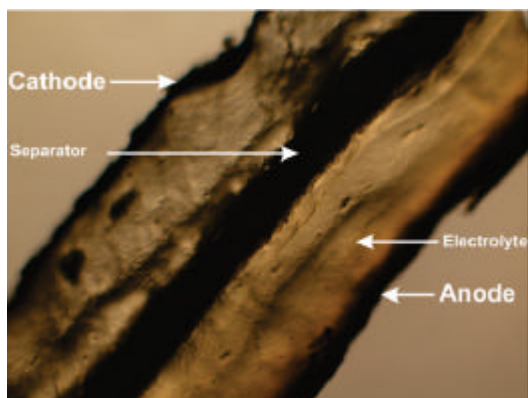


Fig. 4: Image of interface electrochemical accumulator

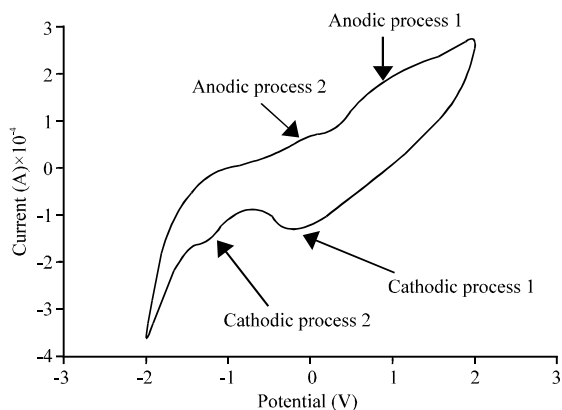


Fig. 5: Voltammograms of electrochemical accumulator

addition, to having low porosity in the microstructure, low electric conductivity and good mechanical strength and flexibility, thus, preventing the short circuit may occur arising from contact between the other components.

Figure 4 shows the microstructure of the interface and accumulator assembly seen in an optical microscope at a magnification of 100x in this image can be seen the good adhesion having each components. This is important because a good contact between these components for the transfer or flow of loads is required.

Besides, the EIS analyzes showed than the electrochemical behavior of the electrochemical accumulator was a transfer mechanisms purely resistive capacitive in the same way as with the analysis of the EIS in the conducting films that make it up.

In the voltammograms of the electrochemical accumulator can be detailed two redox processes (oxidation and reduction) with less defined peak (Fig. 5).

The voltammogram has two anodic peaks at 0.05 and -0.89 V. In the corresponding reverse scan, the cathodic wave of the first redox couple was observed at about

-0.31 V whereas that of the second redox process appeared at -1.81 V. It can be seen that the composition does not influence directly in the voltammetric response of the electrochemical accumulator device, since, graphs are very similar with little variation to the voltammetric response of PPy and starch films combined.

CONCLUSION

It was obtained cassava starch films with conductive properties ($8.61 \times 10^{-4} \text{ S cm}^{-1}$) classifying as a semiconductor materials. Moreover, showed stable behavior and homogeneous appearance.

The cassava starch films CV response presented a redox processes (oxidation and reduction) well defined. The CV response was more defined and stable at 10 days of starch films preparation. This ensured a good functionality of these films as solid polymer electrolyte and allowed him to be considered a good candidate for the accumulation of charge in the assembly of electrochemical accumulator.

The load transfer mechanism change resistive-capacitive to a resistive with constant phase, according biopolymer composition due to plasticizers and lithium ion mobility in the polymer matrix.

Polypyrrole electrodes doped with pTS and IC exhibit redox properties that allow reversible oxidation and reduction which shows its excellent performance as electrodes. The electrochemical accumulator of polypyrrole and cassava starch films with configuration of sandwich type was easily armed due an adhesive properties of starch polymer. The accumulator showed a reversible redox process with two oxidation/reduction peaks and a capacitive behavior. This opens the possibility of using these devices as an electrochemical charge accumulators. In summary, the cassava starch conducting polymer and polypyrrole electrodes have been shown to be perspective elements for the development of charge accumulators organic.

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