

Research Article

Synthesis and Electrochemical Characterization of Polypyrrole/Sodium p-Toluenesulfonate Biofilms Supported on Cassava Starch Conductive Polymers for Applications in Electrical Charge Accumulators

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Abstract: The aim of this study is to evaluate how the number of dopants in the cassava starch polymer and the oxidation potential of the cathode influence the electrical energy accumulation properties. Materials are synthesized by two stages: In the stage I, synthesis of the conductive polymer was performed from cassava starch, plasticizers and lithium perchlorate; later, in the stage II, salt-doped polypyrrole was electrochemically synthesized. Sodium p-toluenesulfonate and lithium perchlorate were used as doping salts. Characterization of materials were performed by Electrochemical Impedance Spectroscopy (EIS) and cyclic voltammetry. The best results were obtained for assays 1 and 4 constituted by 1.5 g of starch and 0.5 V for the cathode and 3 g of starch and 0.7 V for the cathode, respectively. Respective specific charge capacities and specific energies were 3.765×10^{-4} Ah/kg and 3.477×10^{-5} Wh/kg for the assay 1 and 2.234×10^{-4} Ah/kg and 9.095×10^{-5} Wh/kg for the assay 4. These responses are associated with a higher values of electrical conductivity for the assay 1 and 4 by EIS, favoring the mobility of the charges within the materials; Finally, the stability of assay voltammograms indicates how their properties can be maintained at the time.

Keywords: Accumulator charge, conductive biopolymer, cyclic voltammetry, *Manihot esculenta* Crantz, polypyrrole

INTRODUCTION

The interest for the development of clean technologies with a different origin to those generated from hydrocarbons has increased in recent years (Sultana *et al.*, 2012), in consequence, the number of researches aimed at the synthesis of environmentally friendly materials and the development of electricity storage systems has enormously increased; some materials recently proposed are based on composites of conductive biopolymers, low molecular weight substances and doping agents (Arrieta *et al.*, 2010; Hu *et al.*, 2010).

Conductive polymers have been of particular interest in the field of electrochemistry, being much the antecedents related with the study of these materials (Deep *et al.*, 2012); thus, by instance, Polymers as Polypyrrole (PPy) and PPy doped with lithium salts have been described as materials with promissory applications (Venugopal *et al.*, 2014; Arrieta *et al.*, 2014). In particular, these materials are great interest

for applications as electric charge accumulator systems because they are capable to experiment reversible redox reactions by the exchanging of electrons without any change of their original structure and therefore, they have important electrochemical properties useful for specific charge storage (Otero *et al.*, 2010; Wu *et al.*, 2013).

The aim of this study is to determine how different experimental variables, amount of dopant in cassava starch polymer and oxidation potential, influence both the production and electrochemical properties of PPy/Sodium p-Toluenesulfonate (PTS) films supported on starch conducting polymers doped with Lithium Perchlorate (PL).

MATERIALS AND METHODS

Chemical synthesis of cassava starch-conducting polymer films: For the extraction of the cassava starch, the starch-rich white tissue of cassava was extracted using the traditional method which consists in

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Table 1: Factors of each assay studied

Assay	Salt (g)	Oxidation potential (V)
1	1.5	0.5
2	1.5	0.7
3	3.0	0.5
4	3.0	0.7

Polymerization potential 0.8 V; Salt type PL; Counterion PTS; Reduction potential -1.5 V

sequential stages of washing, peeling, grating, decanting, filtering, drying and maceration. The obtained starch had a particle size of 60 μm in order to ensure its homogeneous mixing. Glycerol (GLY), Glutaraldehyde (GLU), Polyethylene Glycol (PEG) and Lithium Perchlorate (LP) were purchased from Sigma-Aldrich; these were added in an aqueous dissolution of starch previously obtained and which was prepared using Milli-Q Millipore grade ultra-pure water. Synthesis of the starch conductive polymer was performed at pH 9.0, at room temperature and constant stirring.

Solutions were temperature-controlled heated of $75 \pm 1.0^\circ\text{C}$ for 15 min, poured into opened Petri dishes and finally, brought to an oven at a temperature of 70°C for 48 h (Arrieta *et al.*, 2017).

Electrochemical synthesis of PPy/PTS by chronoamperometry: For the electrochemical synthesis of the PPy/PTS biopolymer, 0.1 M solutions of pyrrole and PTS were prepared and placed in a batch-type glass reactor. Electrochemical polymerization was performed on a stainless steel working electrode, using a saturated calomel electrode as reference electrode and a platinum sheet as auxiliary electrode; working parameters were a time of 5000 sec and a potential polymerization of 0.8 V.

For the polarization of the cathode and anode, a 0.1 M aqueous solution of LiClO_4 was prepared applying a polarization time of 600 sec. In this time, a potential oxidation to the cathode of 0.5 or 0.7 V was implemented; anyways, these are factors under study, where as a constant reduction potential of -1.5 V was used for the anode.

Characterization of the energy accumulator system:

For the electrochemical characterization of each of the assays (Table 1), a solid sample cell was made up of two 2×2 cm stainless steel sheets, fitted on an acrylic support, which were closed with a system of press type nuts. This assembly was required for the application of Electrochemical Impedance Spectroscopy (EIS) technique. For the EIS study, a frequency range from 100 to 100 MHz and an amplitude of 10 mV RMS were used.

The characterization of the components of the energy storage system, as well as of complete system was performed by means of the Cyclic Voltammetry (VC) technique, for it, a potential range of 1.0 to -1.5 V, a scanning rate of 100 mV/sec and 30 voltammetry cycles were used.



Fig. 1: Charge accumulator systems

RESULTS AND DISCUSSION

The factors of each of the assay for the energy accumulator are shown in the Table 1.

During the process, the pyrrole was deposited on the electrode forming long polymer chains. Thus, the working electrode is coated on both sides by PPy layers. After the polymerization was completed, the working electrode was removed from the cell and rinsed with Milli-Q water to remove residues that might have remained on its surface, finally, electrode was dried at room temperature.

Subsequently, the resulting PPy/PTS polymer was polarized and placed on the cassava starch conductive polymer, with an area of 2×2 cm^2 where the energy accumulator was finally assembled with cathode and anode (Fig. 1).

The electrical charge storage system was assembled with cathode + starch polymer + anode (Fig. 1), the exposed faces of the medium were the conductive PPy/PTS polymer and was put in contact with the cassava starch conducting biopolymer, previously pressed with the cell for solid samples, where the new material was later characterized.

Voltammograms of the different assays are shown in the Fig. 2a to 2d.

The voltammograms showed the characteristic cycles of redox reactions, as well as the peaks that are expected for PPy doped with PTS, which were evidenced clearly in the potentials close to 0.3 and -1.0 V both for reduction and oxidation potentials (Fig. 2).

It was also possible to evidence how each of the voltammetric cycles tended to overlap in each charge and discharging of the PPy/PTS supported on the cassava starch conductive biopolymer, which is of particular interest in the study of the electrical properties of electric charge accumulators.

It is noteworthy to point out that the material that makes up the accumulator does not change its morphology when subjected to charge and discharge conditions, which is very important because the material thus accumulating the charge maintains its electrical properties, which is basically related to the useful lifetime of the accumulator.

When conductivity calculations were performed, from EIS and using the equation $C = L/RA$, where C is the conductivity, L is the thickness of the biofilm, R is the resistance and A is the area (Table 2), the biodegradable batteries synthesized from cassava starch

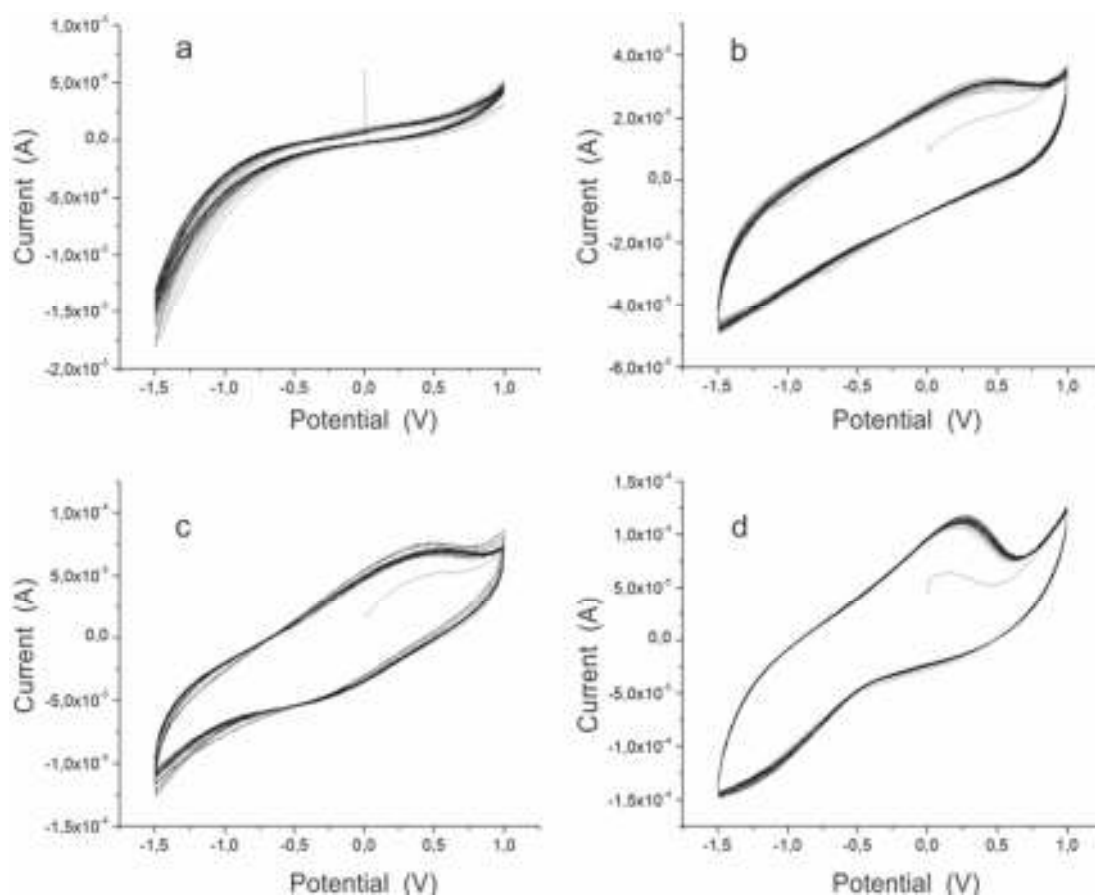


Fig. 2: Voltammograms of the charge accumulators a) Assay 1, b) Assay 2, c) Assay 3, d) Assay 4

Table 2: Conductivity and resistance of charge accumulator

Assay	Resistance (Ω)	Conductivity (sec/cm)
1	123.52	5.984×10^{-5}
2	16.49	7.651×10^{-5}
3	428.64	1.143×10^{-6}
4	37.79	37.351×10^{-5}

Table 3: Response variables for charge accumulator systems

Assay	Charge accumulator systems weight (g)	Specific capacity (Ah/kg)	Specific energy (Wh/kg)	Specific power (W/kg)
1	0.764	3.765×10^{-4}	3.477×10^{-5}	4.462×10^{-3}
2	0.681	1.233×10^{-5}	1.594×10^{-6}	1.835×10^{-4}
3	0.877	1.149×10^{-5}	1.357×10^{-6}	1.571×10^{-4}
4	0.908	2.234×10^{-4}	9.095×10^{-5}	1.364×10^{-2}

Had high values of electrical conduction; therefore, these can be classified as conductive material.

The values concerning to electrochemical properties such as specific charge capacity, specific energy and specific power, of the energy accumulators are showed in the Table 3, as well as the amounts in grams of the organic accumulator; being observed like this type of organic materials is able to store charge when hybrid systems based on cassava starch and PPy conducting polymers are made.

From results, it can be seen that there were high conductivity data (Table 2) associated with low resistance values of the electrochemical accumulators,

possibly attributed to the oxidation potentials of 0.7 V in the synthesis of these materials. This may be due to a higher polarization of the cathode of the conductive biofilm that would increase that conductivity, as a result of the greater insertion of lithium cations confined in the chemical structure of the PPy.

Results correlate with the previous studies related with PPy/PTS polymers and supported on cassava starch, in terms of electrical conductivity and resistance (2.22×10^{-4} sec/cm and 5.397Ω , respectively) (Arrieta *et al.*, 2010) with similar values to those reported in the present work (7.651×10^{-5} sec/cm and $16,49 \Omega$ in the same order). Jointly with the data of both

investigations, the responses of the voltages of PPy/PTS evidenced, in both works of the presentation in -0.5 and -0.9 V, the assignment of the processes of reduction PPy, which is an object of interest due to its accumulative properties of electric charge.

CONCLUSION

The voltammograms presented responses in the stability of the different synthesized materials, due to the overlapping of the voltammetric cycles, which corroborates that by applying successive charge and discharging to the material, it maintains its electrochemical structure and consequently the response variables obtained in said work.

On the other hand, good values of conductivity were observed in the charge accumulator systems, which place them within the group of semiconductors; it was also observed that the conductivity values associated with the lowest resistance values relate to the oxidation potential of 0.7 V that will be optimized in future works.

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CONFLICT OF INTEREST

Authors have no conflict of interest.

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