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EVALUATION OF ELABORATION PARAMETERS OF A SOLID BIOPOLYMER ELECTROLYTE OF CASSAVA STARCH ON THEIR PERFORMANCE IN AN ELECTROCHEMICAL ACCUMULATOR

EVALUACIÓN DE PARÁMETROS DE ELABORACIÓN DE UN ELECTROLITO SOLIDO BIOPOLIMÉRICO DE ALMIDON DE CASSAVA SOBRE SU DESEMPEÑO EN UN ACUMULADOR ELECTROQUÍMICO

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Abstract

This work presents the evaluation of the performance of a solid biopolymer electrolyte elaborated from cassava starch according to its composition, humidity and thickness in an electrochemical accumulator made with polypyrrole electrodes. An experiment design was carried out with the composition, humidity and thickness of the films. The response was evaluated in terms of specific capacity and specific energy density of the accumulators. In addition, the electrochemical behavior was evaluated by impedance spectroscopy. The results showed that the studied factors did not modify the electrochemistry response model of the films, therefore these factors did not influence the conduction mechanisms of the solid electrolyte. However, the values of capacitance and resistance obtained from the equivalent models in the different films showed marked differences in their values. On the other hand, it was observed that one of the most influential factors in the performance of the accumulators was the composition of the films and the one that had the least influence was the humidity of the same. It was possible to conclude that although the elaboration parameters of the solid electrolyte did not have an effect on the conduction mechanisms, they did affect their electrochemical performance in a charge accumulator.

Keywords: solid biopolymer electrolyte, cassava, polypyrrole, electrochemistry accumulator.

Resumen

En este trabajo se presenta la evaluación del comportamiento de un electrolito sólido biopolímérico elaborado a partir de almidón de cassava en función de su composición, la humedad y el espesor en un acumulador electroquímico realizado con electrodos de polipirrol. Se realizó un diseño de experimento con la composición, humedad y espesor del electrolito sólido. La respuesta fue evaluada en términos de capacidad y energía específicas de los acumuladores. Además, se evaluó su comportamiento electroquímico mediante espectroscopia de impedancia. Los resultados mostraron que los factores evaluados no modifican el modelo de respuesta electroquímica, por tanto, estos factores no influyeron en el mecanismo de conducción del electrolito sólido. Sin embargo, los valores de capacitancia y resistencia obtenidos de los modelos equivalentes en los diferentes ensayos, presentaron diferencias marcadas en sus valores. Por otra parte, se observó que uno de los factores más influyentes en el desempeño de los acumuladores, fue la composición de las películas y el que menos influyó fue la humedad de las mismas. Se pudo concluir que, aunque los parámetros de elaboración del electrolito solido no tuvieron un efecto en los mecanismos de conducción, éstos si afectaron su desempeño electroquímico en un acumulador de carga.

Palabras clave: electrolito sólido biopolímero, cassava, polipirrol, acumulador electroquímico.

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1 Introduction

In recent years, solid polymer electrolytes (SPEs) have attracted the attention of industry and research centers due to their high potential in technological applications such as solar cells, batteries, capacitors, light-emitting diodes (LEDs), fuel cells, among others (Zhang *et al*, 2019; Jiang *et al*, 2017; Cebollero *et al*., 2017; Foong *et al*., 2018; Lee-Sie *et al*., 2017). The advantage of these materials lies in their good stability, high energy density, easy processing, high conductivity and excellent electrochemical properties. However, SPEs are commonly of synthetic origin and made from petrochemical pressurizers, so they retain the characteristics contaminants of traditional polymers made from petroleum.

Due to pollution problems generated by polymers, biopolymers have recently attracted the attention of research centers because they have some desirable characteristics such as biodegradability, renewability, low cost, easy accessibility, environmentally friendly, among others. In this sense, multiple investigations have been carried out aimed at the development of new biopolymers from sources or resources of natural origin such as chitosan extracted from shrimp exoskeleton, starch extracted from corn, cassava and other vegetables, alginate extracted from algae, among others (Zargar *et al*., 2015; Khlestkin *et al*., 2018; Shanura *et al*., 2019; Rocha-Pino *et al*., 2008).

Starch is one of the most abundant biopolymers in nature and is one of the most widely studied and used in the industry as an additive for textiles, stationery, food, packaging, adhesives, among others (Khlestkin *et al*., 2018; Ogunsona *et al*., 2018; Lopez-Vidal *et al*., 2014). Recently, this biopolymer has expanded its application possibilities to be used to develop a new type of solid biopolymer electrolyte (Teoh *et al*., 2014; Arrieta *et al*., 2011; Ning *et al*., 2009). In addition, some research has been conducted on the mechanical and electrical properties of ionic conductive starch biopolymers (Teoh *et al*., 2014; Arrieta *et al*., 2017). Also, this conductive biopolymer has been combined with other types of compounds to generate new materials with improved or novel properties. The starch biopolymer has been combined with, polypyrrole, polyvinyl alcohol, nanosilicon oxide particles, among others (Chatterjee *et al*., 2016; Arrieta *et al*., 2016; Lin *et al*., 2017; Yao *et al*., 2011).

SPEs are materials that can conduct electrical current by moving ions through a polymer matrix and in the case of solid starch electrolyte, the conductivity is due to ion mobility, commonly coming from lithium salts, in the matrix of biopolymer chains of amylose and amylopeptin. Corn starch is the most commonly used material in most research on the development of solid biopolymer electrolytes, however some research has integrated cassava starch into the development of this type of new materials (Pawlicka *et al*., 2008; Arrieta *et al*., 2011; Ismanto *et al*., 2010; Arrieta *et al*., 2017).

The SPEs used in the development of electrochemical accumulators are mostly of synthetic origin, because the SPEs based on biopolymers or solid biopolymer electrolytes (SBPEs) have been recently reported. Although the SBPEs are of recent development, a large number of this type of materials based on different biopolymer matrices have been reported (Sudhakar *et al*., 2018; Rasali *et al*., 2018; Guo *et al*., 2018; Singh *et al*., 2017). However, there are few reports on the study of SBPEs based on cassava starch biopolymer and even less on their application and performance in the development of charge electrochemical accumulators.

On the other hand, intrinsically conducting polymers (ICPs), such as polyacetylene, polypyrrole, polyaniline and poly 3-methylthiophene, among others, which conduct electricity through the movement of electrons or charges (polarons and bipolarons) along the chain polymeric, have shown to be materials with technological potential for the development of electrodes and electrochemical devices (Perez-Rodríguez *et al*., 2018; Aydinli *et al*., 2018; Arrieta *et al*., 2018).

Polypyrrole is one of the most used due to its good stability, easy processability and excellent electrochemical properties. This intrinsically conductive polymer has been used successfully as an electrode in secondary batteries and capacitors (Zhao *et al*., 2018; Canobre *et al*., 2013).

In this paper we present the evaluation of the effect of the composition, humidity and thickness of plasticized starch films on their performance as SBPE in an electrochemical charge accumulator from polypyrrole.

2 Materials and methods

All the reagents used were of analytical quality. The solutions were prepared using milli-Q grade ultra pure water. The cassava starch was extracted in our

laboratory from the *Manihot esculenta* Crantz variety. The extraction process was carried out by mechanical extraction, which consisted of washing the roots (500 g) with abundant water, then these were peeled, again washed and liquefied to break the cells and extract the starch. To the resulting mass obtained during the liquefy process was added 1 L of water and stirred for 3 min, this mixture was filtered with a mesh of 200 μm and the filtrate was left to decant, the decanted water was removed and washed again. This washing procedure was repeated three times. Finally, the decant was dried in the oven at 45 ° C. The resulting starch was a bright white powder. The purity was evaluated by the technical standard ISO 6647 (International Organization for Standardization, 2015).

2.1 Preparation of SBPE films

For the preparation of the solid biopolymer electrolyte films, 3 g of cassava starch were dispersed in 0.1 L of ultrapure water pH 9.0 (the pH was adjusted by addition of NaOH). The dispersion of starch in water was heated to 75 °C for 15 min and the plasticizers glycerol, sorbitol and polyethylene glycol were added, in addition the lithium salt $LiClO_4$ was added to the mixture. This mixture was heated at 70 °C for 15 min under constant stirring, then poured into Teflon Petri dishes and taken to an oven for 48 hours at 70 °C.

Plasticizers and salt were added in different proportions to evaluate the effect of the composition on the behavior of solid electrolyte. Three types of films with different compositions were prepared; the films type 1 (composition 1) were prepared with 1.5 g of glycerol, 4.5 g of glutaraldehyde, 1.0 g of polyethylene glycol and 3.0 g of lithium perchlorate; the films type 2 (composition 2) were prepared with 1.5 g of glycerol, 3.0 g of glutaraldehyde, 0 g of polyethylene glycol and 1.5 g of lithium perchlorate. The films type 3 (composition 3) were prepared with 2.5 g of glycerol, 4.5 g of glutaraldehyde, 2.0 g of polyethylene glycol and 0 g of lithium perchlorate. In addition, three types of thickness (0.3, 0.6 and 1.2 mm) and three percentages of humidity (20, 30 and 45%) were used in the films. In this way, 3 factors (composition, thickness and humidity) were evaluated, with three levels each (33), yielding a response surface experiment design with a total of 27 trials. The thickness of the films was controlled by the amount of substance (mixture) and were measured with a digital micrometer Mitutoyo, reference 293.

2.2 Polypyrrole electrodes

The polypyrrole electrodes were made from films generated by electrochemical polymerization of pyrrole on a 2 x 2 cm stainless steel sheet as a substrate. The polymerization was carried out by chronoamperometry at 0.8 V and for 500 s in a three electrode electrochemical cell; a saturated calomel reference electrode, a platinum sheet as auxiliary electrode and as working electrode the stainless steel sheet (substrate).

For the generation of the anode electrodes (accumulator anode), a solution of 0.1 M pyrrole and 0.1 M carmine indium (IC) was used. Once the films were generated (PPy/IC), they were polarized at -1.3 V for 600 s in a solution of 0.1 M $LiClO_4$. The elaboration of the cathode was carried out in a solution of 0.1 M pyrrole and p-toluenesulfonate (pTS) 0.1 M. The PPy/pTS films were subjected to polarization in 0.1 M $LiClO_4$ for 600 s. V to convert them into cathodes.

2.3 Arming of the charge cumulators and electrochemical characterization

The electrochemical characterization was carried out on the accumulators, which were elaborated with a sandwich configuration using the polypyrrole films, anode (PPy/IC) and cathode (PPy/pTS), the conductive starch films and recyclable paper was used as a separator (PPy/IC-SBPE-recyclable paper-SBPE-PPy/pTS). Figure 1 shows a schematic representation of the configuration used to assemble the accumulators.

The characterization was performed by electrochemical impedance spectroscopy and galvanostatic charging and discharging cycles, using a PAR (Princeton Applied Research) 2263 potentiostat / galvanostat controlled by the PowerSuite software. The measurements were carried out at room temperature and a sandwich cell with two finely polished stainless steel electrodes was used. Impedance spectroscopy was analyzed using the ZSimWin software. The potentials were referred to the open circuit potential which had a value of 0.19 V.

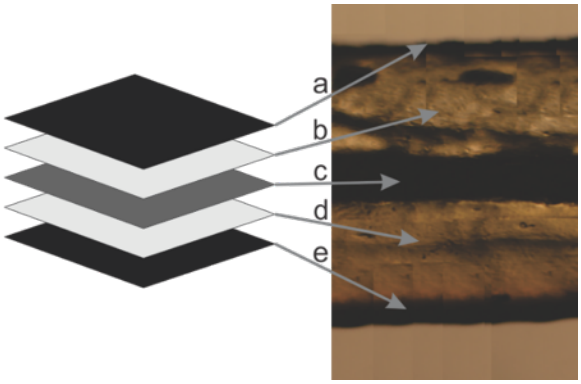

Fig. 1. Electrochemical accumulator configuration: a) PPy/IC, b) Starch SBPE, c) recyclable paper, d) Starch SBPE and e) PPy/pTS.

3 Results and discussion

During the assembly of the accumulators, an excellent adherence of each of the layers of the system could be observed, due mainly to the adhesion properties of the starch. In this way, the accumulators could be assembled without the need for any additional procedure to prevent the detachment of the components.

Once assured the good quality and mechanical stability of the accumulators, we proceeded to conduct the study of the behavior of the SBPE films through the electrochemical impedance measurements. To do this, the impedance spectra were recorded in a frequency range of 10 Hz to 1 MHz with an amplitude of 10 mV (rms), in each of the films. The resulting spectra, consisted in all cases, of a semicircle accompanied by a line with an approximate angle of 45 °. In figure 2, the Cole-Cole graph obtained with the SBPE films made with different composition and the same humidity and thickness of 45% and 0.6 mm, respectively, is presented as example.

Figure 2 clearly shows a semicircle, which in these processes is related to two phenomena; the resistance of the electrolyte movement in the polymer matrix and the capacitance generated by the charge of the electrolytes with the polymer chains. In Figure 3 an illustration of the interaction phenomenon between the starch polymer and the ions of the medium is presented. Additionally, the line contiguous to the semicircle is attributed to the polarization of the electrodes and the process of charge diffusion in the matrix.

In general, the electrochemical behavior of all the films under study was similar in terms of the shape of the impedance spectrum obtained. However, the values of resistance and capacitance were different in each case, which is reflected in the differences observed in the heights of the semicircles and the length of the straight line contiguous to the semicircle. This result was corroborated with the determination of the equivalent circuit of the recorded impedance spectra. In all cases, the equivalent circuit consisted of a Randles circuit: R1(C [R2W], consisting of a resistor (R1) in series with a system consisting of a capacitor (C) in parallel with a resistor (R2) and a Warburg impedance (W).

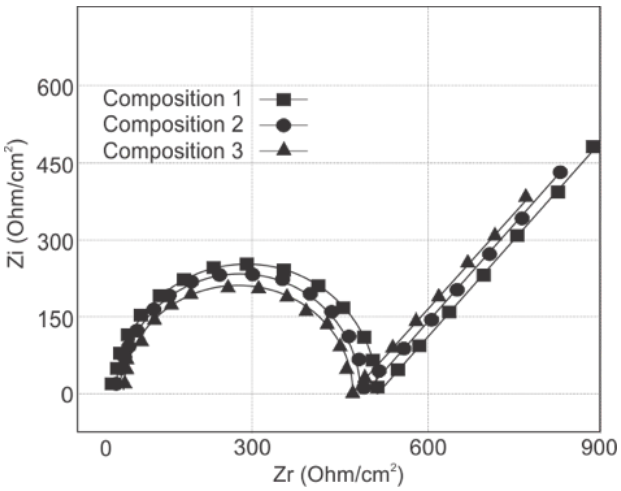

Fig. 2. Cole-Cole graph obtained from films made of SBPEs with different compositions.

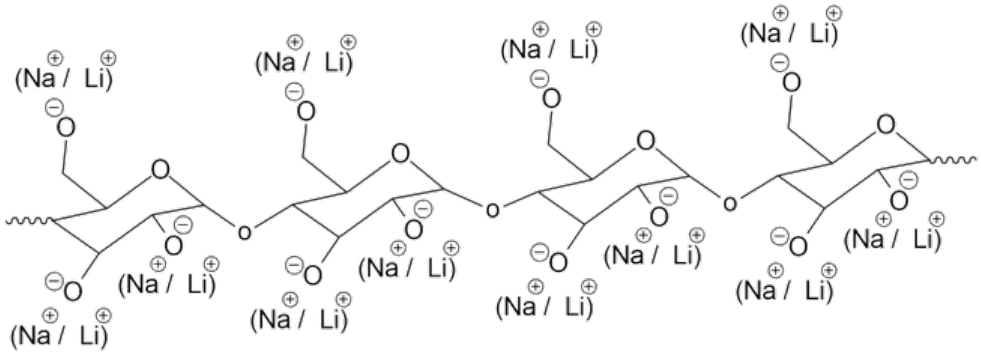

Fig. 3. Schematic representation of the polymer chain of charged starch and its interaction with lithium and sodium ions.

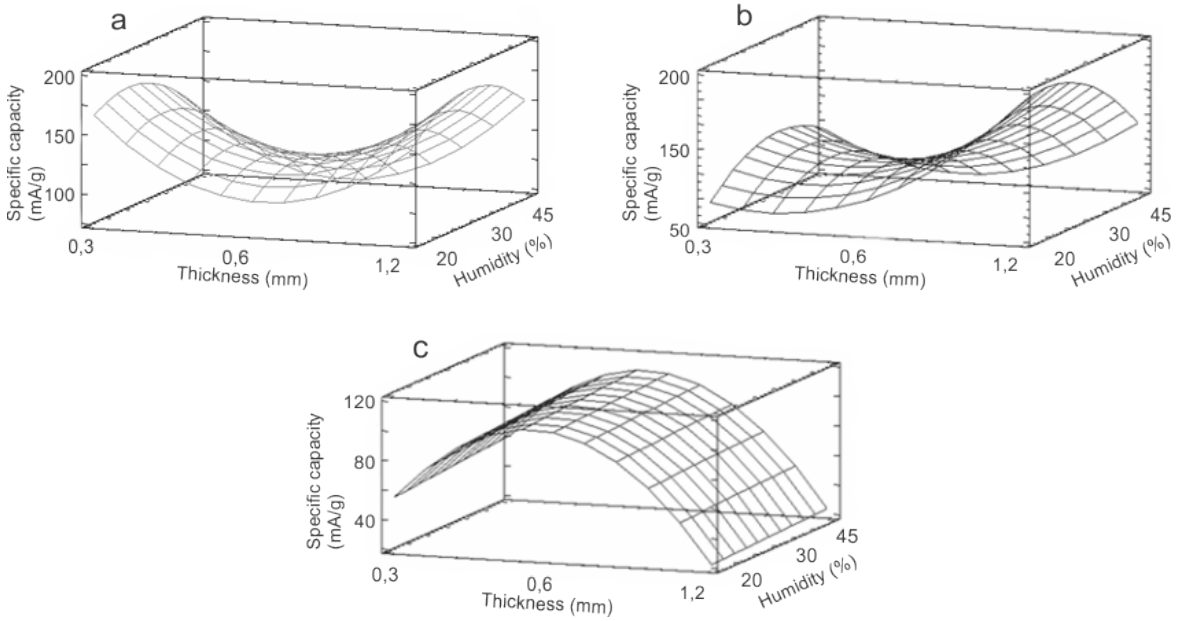

Fig. 4. Surface response graphs of the specific capacity of the charge accumulators made with cassava starch SBPSs films with different composition: a) composition 1, b) composition 2 and c) composition 3.

To determine specific capacitance and specific energy density, the accumulators were assembled with the different SBPE films under study and the galvanostatic measurements were carried out. The charging and discharging cycles were carried out in a potential range of -1.0 V to 0.5 V and a sweep speed of 50 mV / s. The specific capacities (Cs) were calculated by the equation $Cs = It/m$; where I is the charge and discharge current, t the time of full charge or discharge and m the mass of the accumulator. The specific energy (Es) was calculated by $Es = VIt/m$; where V is the cell voltage, I is the charge and discharge current, t the time of full charge or discharge and m the mass of the accumulator (Thackeray *et al*., 2012).

The specific capacity and specific energy density values were used to feed the response surface experiment design used to evaluate the composition, humidity and thickness incidence of cassava starch SBPE films on their performance in the electrochemical charge accumulator from polypyrrole.

In Figure 4, the response surface graphs obtained for the specific capacity of the accumulators are presented. As can be seen, the three factors under study (composition, humidity and thickness of the films) affect the performance of the specific capacity of the accumulators. In compositions 1 and 2, a similar behavior is observed, which contrasts with the behavior of composition 3.

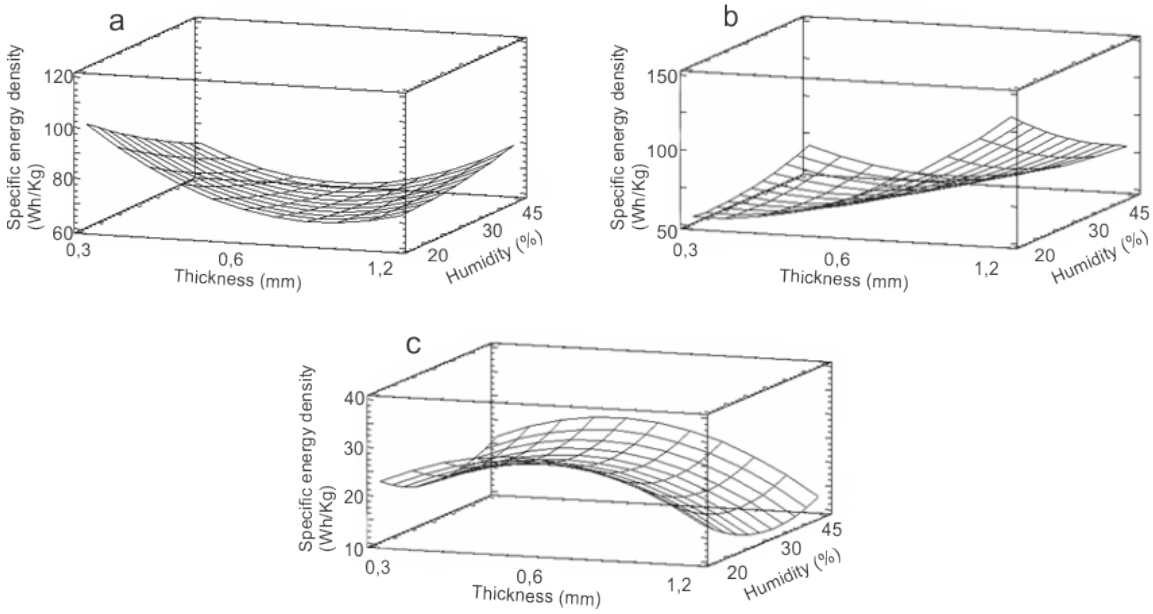

Fig. 5. Response surface graphs of the specific energy density of the charge accumulators made with cassava starch SBPS films with different composition: a) composition 1, b) composition 2 and c) composition 3.

This fact may be due to the absence of lithium perchlorate in composition 3 and which is the origin of the highest content of conductive ions in the films of SBPEs from cassava starch.

Additionally, it is observed that the behavior of the accumulators made with SBPE films with lithium salt, increase the specific capacity to greater thickness and with an average humidity of 45% approximately. While accumulators made with starch SBPE films without lithium ions, they generally have lower values of specific capacity. The highest values were achieved with average thickness of 0.6 mm, while the humidity of the films does not seem to significantly affect its performance. This behavior is perhaps due to the fact that the humidity affects the mobility of the ionic charges, therefore in the absence of ions in the SBPE films, this factor is not determinant.

Figure 5 shows the response surfaces obtained in the study of the relations of the preparation parameters of the SBPE films on the specific energy density of the accumulators prepared with these. In the figure 5, it can be seen a less marked influence than in the specific capacity. However, the behavior of compositions 1 and 2 (films with lithium perchlorate), remains similar in its tendency and markedly different from the behavior of composition 3. This coincides in both electrical parameters studied. In the responses of the accumulators made with films of composition 1, the parameters of thickness and humidity are slightly influential in the specific energy density of the accumulators.

In the case of accumulators made with composition 2 films, the influence of humidity and thickness are slightly more marked than with composition 1, presenting higher values of specific energy density with higher humidity and higher thicknesses. In the case of the composition 3, a marked influence of the thickness is observed, showing higher values of specific energy density in the average values. On the other hand, the humidity does not show a marked influence, but rather subtly influences the extreme values of humidity studied (20 and 45%).

Conclusions

Films of solid biopolymeric starch electrolyte allowed to produce stable electrochemical charge accumulators without detachment of the layers, due to the adhesive properties of the cassava starch used.

The elaboration parameters of the solid biopolymer electrolytes of cassava starch under study (humidity, thickness and composition) did not influence the conduction mechanism. However, they did have a marked influence on their resistance and capacitance values.

The composition of the biopolymer solid

electrolytes of cassava starch markedly affected the specific energy density and specific capacity of the accumulators. Of the compounds used, lithium perchlorate was the substance with the highest incidence in the performance of cassava starch electrolyte.

Humidity was the least influential factor and did not generate variations of less than an order of magnitude in the response parameters studied (specific energy density and specific capacity). On the other hand, the thickness of the films can affect the performance of the solid electrolyte of cassava, however its influence was discrete and does not seem to have a well-defined tendency.

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