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Impedantiometric Behavior of Solid Biopolymer Electrolyte Elaborated from Cassava Starch Synthesized in Different pH

Alvaro Arrieta[1*], Isora Barrera[2], Jorge Mendoza[3]

[1]*Department of Biology and Chemistry, University of Sucre, Road 28 No. 5-267 Red Door neighborhood, Sincelejo, Colombia, Postal Code 700008*
[2]*Mercedes Abrego Educational Institution, Diag. 6-119, Tv. 1 #6-1, Monteria, Colombia, Postal Code 230004*
[3]*Department of Mechanical Engineering, University of Córdoba, Monteria, Colombia, Postal Code 230002*

Abstract. This paper approaches the study of pH's effect on elaborate films of solid biopolymer electrolyte from cassava starch and its impedantiometric response. The films of solid biopolymer electrolyte were elaborated by thermochemical synthesis while varying the pH (2, 4, 5, 7, 9, 10, and 12). Starch was extracted from cassava tubers by a traditional method (disintegrated, washed, decanted, filtered, and dried). Solid biopolymer electrolyte films were processed by thermochemical synthesis by adding plasticizers (glycerol, glutaraldehyde, and polyethylene glycol) and lithium salt (lithium perchlorate). The impedance behavior was studied using the electrochemical impedance spectroscopy technique. The Nyquist and Bode's diagrams registered presented a similar trend in all the films; therefore, they were described by the same equivalent circuit model. However, the equivalent circuit components presented different values in each case. The conductivity and capacitance showed a quadratic polynomial tendency in relation to the pH, obtaining the highest conductivity in the films elaborated at acidic pH and the highest capacitance in the films elaborated at basic pH. The degree of basicity or acids allowed conductivity to be modulated or capacitance of the solid biopolymer electrolyte as required. It could be concluded that the production pH has a marked effect on impedantiometric behavior of films of solid biopolymer electrolyte from cassava starch, which may be useful to modulate the electrochemical properties of this type of material in future Applications.

Keywords: Cassava; Electrochemical impedance; pH; Solid biopolymer electrolyte; Starch

1. Introduction

Within the wide range of materials available, polymers are undoubtedly the most used in the development of an ample variety of utensils and devices for everyday use. Polymers are very popular due to their excellent mechanical properties, high resistance to attack by organic and inorganic solvents, and corrosion resistance, among others. The global use of polymers is so great that they have now become an environmental problem worldwide, as they constitute one of the main sources of pollution (Zhong et al., 2019; Dwivedi et al., 2019; Emi-Cassola et al., 2019).

Polymers are considered highly polluting materials (Dwivedi et al., 2019; Emi-Cassola et al., 2019; Shonnard et al., 2019). This contingency has carried numerous research centers worldwide to seek alternatives to replace synthetic polymers (petrochemical orig-

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*Corresponding author's email: alvaro.arrieta@unisucre.edu.co, Tel.: +57-300 8403075
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in) worldwide to seek alternatives to replace synthetic polymers (petrochemical origin) with polymers elaborated from biological sources (biopolymers). Biopolymers can have similar properties to synthetic polymers, so they can be used in a wide range of applications and are also friendly to the environment, due to their good biodegradability, low production cost and originating from renewable sources (Mohamed et al., 2018).

Due to their high technological and industrial potential, the most used and studied biopolymers are cellulose, alginate, starch, chitosan, among others (Rochardjo et al., 2021; Imani et al., 2022; Jyothi et al., 2019). However, the low electrical conductivity of conventional polymers and biopolymers has limited their applications in various new electronic devices. In recent decades, the development of polymers capable of conducting electric current (i.e., conducting polymers) has opened the possibility of applying such materials in applications as diverse as smart windows, solar cells, sensors, artificial muscles, capacitors, electrochemical accumulators, electroluminescent diodes (LEDs), touch panels, among others (Cichosz et al., 2018; Itik et al., 2015; AL-Barani et al., 2019).

Conducting polymers are divided into two groups; the intrinsic conducting polymers (ICP), which can conduct electric current across the chains with conjugated bonds and charges generated by oxidation or reduction (Awuzie, 2017; Chen et al., 2021). On the other hand, the ionic conducting polymers, which have fixed charges in their chains and mobile ions that produce the electroneutrality in the matrix, in this type of materials the movement of mobile ions gives the conduction, so they are known as polymeric solid electrolytes (Aziz et al., 2018; Angell, 2019). Intrinsic and ionic conducting polymers are mostly synthetic and therefore cause environmental problems typical of polymers from a petrochemical origin.

Few works report the synthesis of biopolymers capable of conducting electric current (Arrieta et al., 2011; Mobarak et al., 2015). Recently, it has been reported the use of cassava starch to generate a conducting biopolymer with the use of plasticizers and lithium salt (Arrieta et al., 2011). This biopolymer has been studied as a solid electrolyte for application in an artificial muscle and as an electrochemical accumulator (Núñez et al., 2016; Arrieta et al., 2019a). However, not many studies have been conducted about the effect of synthesized pH on the electrochemical properties of this biopolymeric solid electrolyte. The effect of the synthesized pH on voltametric response and mechanical properties of this type of biopolymer material was reported recently, showing that factors such as redox potentials (oxidation/reduction), crystallinity, voltametric stability, modulus of elasticity and electrical conductivity can be affected. (Arrieta et al., 2019b; Arrieta et al., 2018). In this work, the study of a synthesized pH effect (pH values; 2, 4, 5, 7, 9, 10, and 12) on a conducting biopolymer elaborated from cassava starch about its impedance behavior is presented.

2. Methods

2.1. Materials

The reagents used were of analytical quality. Solutions were made using milli-Q water. The starch was synthesized from fresh cassava tubers of the *Manihot esculenta* Crantz variety. The purity of the synthesized starch was tested by FTIR-ATR spectroscopy and the Association of Official Analytical Chemists (AOAC) standardized method. These analyses confirmed the extracted starch's quality, achieving purity of 99%.

2.2. Cassava starch extraction and solid biopolymer electrolyte films preparation

The extraction of starch was carried out by the conventional method that consists of washing the material (100 gr of cassava tubers), peeling, and then disintegrating it by liquefying it with 200 mL of water. Subsequently, a screening with muslin cloth was carried out, and three washes with water (100 mL) were carried out to the filtrate. The filtrate was decanted for 24 h, and the supernatant was dismissed. The solid precipitate was dried at 50 °C in an oven for 24 h. The solid dried material was screened in a sieve of 60 µm, and a bright white fine powder was obtained. Figure 1 shows the flow diagram of the cassava starch extraction process.

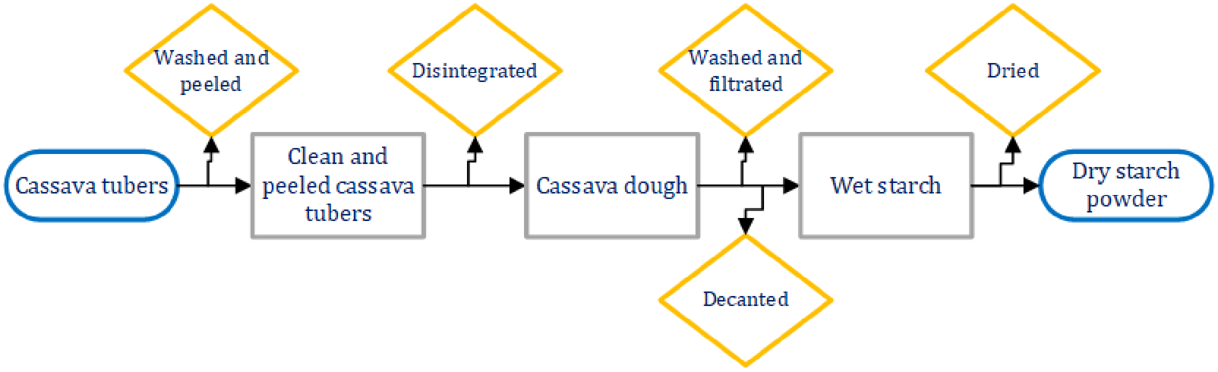

Figure 1 Flow diagram of the cassava starch extraction process

Extracted starch was used to carry out the thermochemical synthesis of the solid biopolymer electrolyte films. In each film, 3 g of cassava starch were used and dispersed in water (100 mL). The pH of the mixture was regulated through the addition of sodium hydroxide (0.1 M) or hydrochloric acid (0.1 M), depending on what was needed to obtain the pH values studied (2, 4, 5, 7, 9, 10, and 12).

The pH values were monitored using a pHmeter (YSI Multilab Ref. 410-3W). Cassava starch and water mixtures were heated for 15 min with constant stirring of 1000 rpm. After gelatinization, the solutions were to remain at room temperature. Then, plasticizers were added: 2 g of glutaraldehyde, 1 g of polyethylene glycol, and 2 g of glycerol, additionally added lithium perchlorate (1.5 g). Next, the solutions were warmed for 15 min at 70 °C in the constant stirring of 1200 rpm. Then they were deposited on Teflon dishes and carried to an oven at 70 °C for 48 H. The thermochemical synthesis process of the cassava starch solid biopolymer electrolyte films is presented in figure 2.

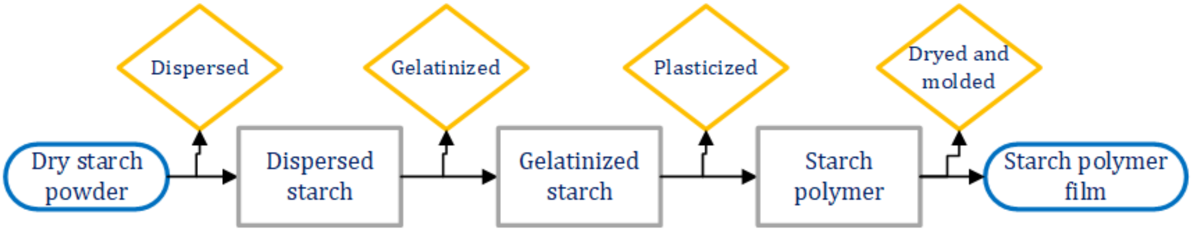

Figure 2 Flow diagram of the thermochemical synthesis process of the solid biopolymer electrolyte films

2.3. Characterization of starch solid biopolymer electrolyte films

The characterization was carried out on samples of 1 cm^2, so the films were removed from the Petri dish and cut with a mold (1 cm x 1 cm). The samples were sandwiched in a dry cell formed by two stainless steel sheets connected to a galvanostat/potentiostat 2263 PARSTAT from PAR, which was handled by the P-Suite software. Electrochemistry impedance spectroscopy records applied a 10 mV r.m.s amplitude (AC) in a 100 mHz to 100 kHz frequency range. Potentials were registered using potential 0.1 V of OCP (open circuit potential) as reference. The spectra obtained in the impedance spectroscopy measurements and their respective equivalent circuits were analyzed with the ZSimWin software V 3.60.

3. Results and Discussion

All films were elaborated under similar conditions while only varying the pH value in the synthesis solution. In general, the films had a thickness of 450 + 5 µm and presented good consistency and mechanical stability during handling. However, the films generated at pH 2 were brittle and had a rupture due to manipulation. Electrochemical impedance spectroscopy studies were carried out on samples of 1 cm^2 films. The measurements were achieved in a solid phase with a dry cell (Arrieta et al., 2019b); without immersing the samples in the electrolytic solution. Sandwiching the films between two stainless steel sheet electrodes. The dry cell scheme is shown in Figure 3. This aimed at evaluating the impedance behavior of solid biopolymer electrolyte without interference from external ions from the electrolyte solution and without interference from the interface with the liquid phase, as is usual in impedance spectroscopy experiments where configured cells are used by using a liquid electrolyte to submerge the sample.

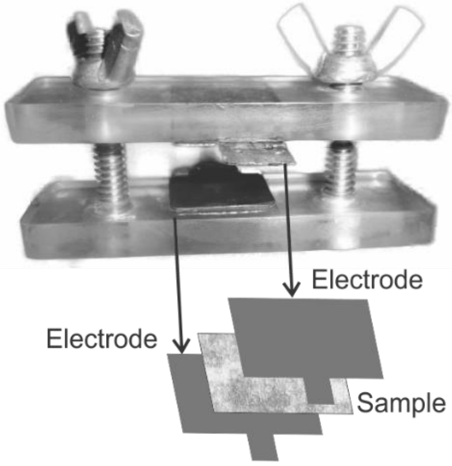

Figure 3 Dry electrochemical cell scheme

Figure 4 shows the Nyquist graphs recorded of solid biopolymer electrolyte films synthesized with different pH values. The graph presents a complex plane of cartesian coordinates (imaginary Z vs. real Z). It can be seen in the Nyquist graphs that, for all samples, the curve consists of a semicircle at the highest frequency (visible by enlargement of the high-frequency zone in Figure 4) and a straight line at the lower frequencies. The semicircle diameter is related to the value of the general resistance.

This type of electrochemical impedance spectroscopy data can be described as an equivalent circuit model; whose impedance coincides with the measured data. The representation of the equivalent circuit models is very often employed to impedance analysis, because it allows a simple and quick interpretation of the complete system image. Therefore, the components of a model circuit are assigned to the physical processes of the film in the cell. The chosen model offers the best possible match between the impedance of the model and the recorded impedance.

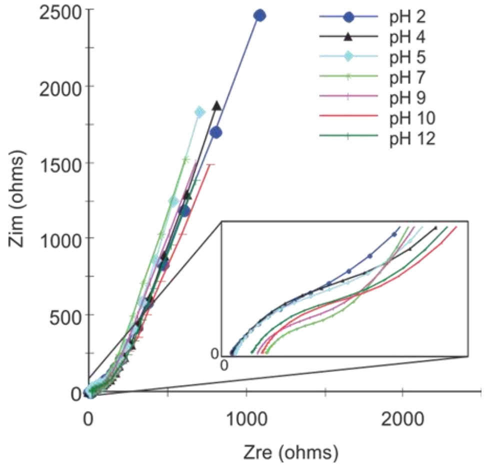

Figure 4 Nyquist graphics recorded with cassava starch solid biopolymer electrolyte films elaborated at different pH

In Figure 5, the equivalent circuit model that corresponds to the impedantiometric behavior recorded in the films is presented. It can be seen that the general resistance in solid biopolymer electrolyte films is composed by the resistance of starch biopolymeric matrix (Rp) and resistance to charge transfer (Rct). Resistance Rp and resistance Rct, can be determined by drawing a semicircle that intercepts the real axis on the Nyquist graph. When expanding the high-frequence zone (zone enlarged in Figure 4), it is observed that impedance curves do not start at the zero point of origin due to the presence of the resistance in the biopolymeric matrix to the current flow (Rp).

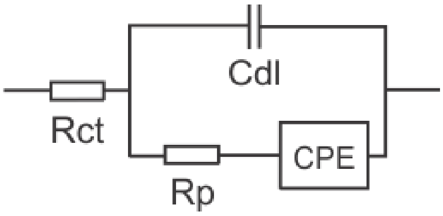

Figure 5 Equivalent circuit model; Rct (resistance to charge transfer); Cdl (electrical double layer); Rp (resistance of starch matrix); CPE (constant phase element)

Due to to the biopolymer film/electrode interface properties, the capacitive impedance increases in the low-frequence regions. The semicircle is formed of a capacitor (Cdl) and a parallel resistance, as shown in the equivalent circuit model. The capacitor Cdl is due to the generation of the electrical double layer in the interface solid biopolymer electrolyte/stainless steel electrode by the accumulation of ions in this area. As mentioned earlier, the resistance is due to the charge transfer resistance (Rct) by the ion transport in the solid biopolymer electrolyte, that is one general behavior of electrolyte/electrode interfaces. The resistance to ion diffusion is the minimum value of energy necessary to form the double electrical layer at the electrolyte/electrode boundary. After the semicircle, the graphs become a line indicating the capacitive nature of the interface and the absence of electronic conductivity. This linear elevation pattern indicates the capacitive behavior of the films represented by the capacitor constant phase element (CPE) in the equivalent circuit and is related to the solid-state diffusion of lithium ions in the films. In this element, the resistance corresponds to the diffusion of the tension in the irregularities, imperfections and porosity present in the films. Table 1 summarizes the values of the components of the equivalent circuit obtained for each biopolymeric film.

Table 1 Values of the equivalent circuit components in each of the solid biopolymer electrolyte films elaborated at different pH

pH	Rct (ohms)	Cdl (F)	Rp (ohms)	CPE (S-sec^{n})
2	5.93	3.73x10^{-6}	21.63	5.52x10^{-4}
4	6.84	4.90 x10^{-6}	19.19	7.24 x10^{-4}
5	7.98	5.63 x10^{-6}	17.50	7.54 x10^{-4}
7	28.36	6.05 x10^{-6}	20.93	9.03 x10^{-4}
9	27.4	6.01 x10^{-6}	27.10	8.85 x10^{-4}
10	25.8	5.50 x10^{-6}	49.98	8.72 x10^{-4}
12	19.54	5.13 x10^{-6}	102.22	9.37 x10^{-4}

Figure 6 presents the behavior of the real impedance against the frequency (Bode graphs) of the solid biopolymer electrolyte films elaborated at different pH. It can be that when is applied a low-frequency voltage to solid biopolymer electrolyte films, the current crosses through the biopolymeric films in the continuous and charged zones; when it increases the voltage frequency, some of the current will cross through the less compact and rough areas. Consequently, the general module impedance decreases. Therefore, the low-frequency impedance of the solid biopolymer electrolyte films is greater than the high-frequency impedance. On the other hand, it can be observed that, for the high-frequency range, solid biopolymer electrolyte films elaborated at higher pH (more basic) have higher impedance modulus values than those elaborated with acidic pH. In the low frequencies the tendency is reversed; however, the differences, in this case, are less pronounced.

The pH used in the synthesis process can produce different changes in the structure of the biopolymer chains in the solid electrolyte, either due to the breaking of the chains (hydrolysis) or differences in the number of charges generated by the alkilinization reaction of the hydroxyl groups (OH), which are converted to alkoxide groups (RO-) of glucose units in amylose and amylopeptin of starch (Arrieta et al., 2011). The alkalinization reaction scheme is presented in Figure 7. Due to this, it is possible that the crystallinity and the degrees of alkilinization of the biopolymeric films can be influenced by the pH of synthesis and this is reflected in its impedantiometric behavior.

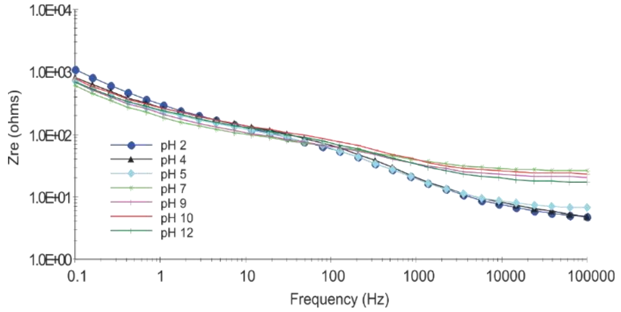

Figure 6 Bode graph of biopolymeric solid electrolyte films elaborated at different pH

In order to evaluate the pH effect on the conductivity of the biopolymeric solid electrolyte films, conductivity calculations were carried out on each of them. The ionic conductivity of the films (σ), can be calculated from the values of resistance of the films (Rp), by applying the following equation: $\sigma = t / Rp\ A$. wherein t is the thickness of the biopolymeric films, Rp the resistance and A the cross-sectional area (Khanmirzaei & Ramesh, 2013).

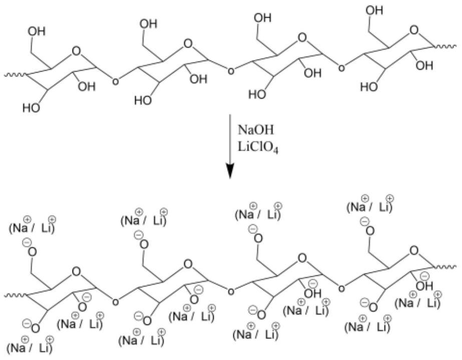

Figure 7 Scheme of the alkalinization reaction in the biopolymeric chains of cassava starch

The ionic conductivity depends on the general ionic mobility and the number of charge carriers; therefore, there is expected to be a relationship between the biopolymeric films conductivity and the elaboration pH. Additionally, the relationship of the capacitance of the films with the pH of synthesis was studied, for this, the Cdl values were plotted versus pH. Capacitance is one of the most significant properties of ionic conductive biopolymers because it is indicative of charge storage capacity and is, therefore, a parameter of interest for applications such as batteries, accumulators, and capacitors, among others. In Figure 8, the conductivity and capacitance values of the films versus the processing pH are presented.

A maximum conductivity of 2.57×10^{-3} S cm^{-1} was obtained in the biopolymeric films elaborated at pH 5 and a minimum of 4.40×10^{-4} S cm^{-1} in the films elaborated at pH 12. In general terms, the films elaborated at low pH (acidic) showed higher conductivity values than the registered in biopolymeric films synthesized at high pH (basic), with a polynomial trend of degree 2 (quadratic polynomial relationship), which corresponds to the equation: $\sigma = -0.3674pH^2 + 3.253pH + 16.563$, with a correlation index (R2) of 0.948. This trend may be due to the fact that acidic pH has been shown to decrease the crystallinity of the films (Zhang et al., 2010), so that, at low pH, fewer crystalline films are generated, allowing greater mobility of ions in the biopolymer matrix.

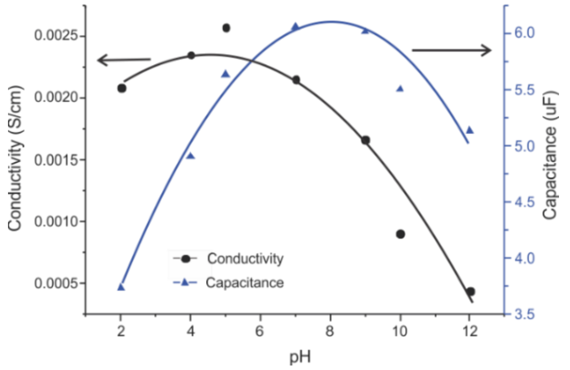

Figure 8 Conductivity and capacitance of solid biopolymer electrolyte elaborated from cassava starch synthesized in different pH values

The ions are more mobile in the amorphous phase due to their motion being aided by biopolymer segmental motion (Li et al., 2008). Moreover, the capacitance trend showed that the films elaborated at low pH presented lower values of capacitance compared to the capacitances registered in the films elaborated at high pH. The trend was also of the degree 2 polynomial type, corresponding to the equation: $\sigma = -1{,}156pH^2 + 25{,}716pH + 15.25$, with a correlation index (R2) of 0.935. The decrease in crystallinity at low pH can cause this behavior because the films with less crystallinity (i.e. amorphous) are less organized and therefore the double layer regions are reduced, thus, decreasing the possibility of forming capacitive zones.

4. Conclusions

Films of solid biopolymer electrolytes can be elaborated using cassava starch. The films were stable against handling; however, the films synthesized at pH 2 values were brittle and broke during handling. Therefore, the films presented stability when they were elaborated at a pH higher than 4. The impedaciometric behavior of the films showed a similar trend in all cases, is defined by a similar equivalent circuit model. However, the values of the equivalent circuit components were different in each case. The pH used during the synthesis process affects the electrochemical properties of cassava starch solid biopolymer electrolyte films. The conductivity in the films presented a polynomial relationship (degree 2). The films elaborated at low pH registered a higher conductivity. On the other hand, the capacitance of the films showed a behavior opposite to the conductivity, being higher in the films synthesized at a more basic pH. This behavior could be due to the variation in the crystallinity of the biopolymeric films, which is influenced by the synthesized pH. The conduction mechanisms in solid biopolymer electrolyte films are not affected by pH; however, their capacitive and electrical conduction capacity are altered. In this way, it was determined that the variation in the synthesized pH allows to modulate the properties of conductivity or capacitance according to the application to which the solid biopolymer electrolyte is intended. In future works, the application of this material in smart fertilizer release systems will be studied.

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