

COMPORTAMENTO ELETROQUÍMICO DE UM MATERIAL COMPOSTO DE BIOPOLÍMERO SÓLIDO ELETRÓLITO DE AMIDO DE MANDIOCA / ÓXIDO DE GRAFENO PREPARADO EM DIFERENTES pH

ELECTROCHEMICAL BEHAVIOR OF A COMPOSITE MATERIAL OF SOLID BIOPOLYMER ELECTROLYTE FROM CASSAVA STARCH / GRAPHENE OXIDE PREPARED AT DIFFERENT pH

COMPORTAMIENTO ELECTROQUÍMICO DE UN MATERIAL COMPUESTO DE ELECTROLITO SÓLIDO DE BIOPOLIMERO DE ALMIDÓN DE YUCA / OXIDO DE GRAFENO ELABORADO A DIFERENTES pH

ARRIETA, Alvaro^{1*}; MENDOZA, Jorge²; PALENCIA Manuel³;

¹ University of Sucre, Faculty of education and Science, Department of Biology and Chemistry. Sincelejo, Colombia.

² University of Córdoba, Faculty of Engineering, Department of Mechanical Engineering. Monteria, Colombia.

³ Department of Chemistry, University of Valle, Cali, Colombia

* Corresponding author

e-mail: alvaro.arrieta@unisucre.edu.co

Received 18 August 2021; received in revised form 29 September 2021; accepted 14 October 2021

RESUMO

Introdução: Os materiais compósitos permitem modular as propriedades dos materiais de origem e expandir o seu potencial tecnológico. Nesse sentido, materiais compósitos feitos de eletrólitos sólidos biopoliméricos e óxido de grafeno podem ser uma alternativa atraente para aplicações em eletrônica orgânica devido às suas propriedades eletroquímicas. **Objetivo:** O presente trabalho tem como objetivo avaliar o comportamento eletroquímico de um material compósito constituído de eletrólito sólido biopolimérico de amido de mandioca e óxido de grafeno em diferentes concentrações para determinar o efeito dessa concentração e do pH utilizado no processo de produção. **Métodos:** O material compósito foi feito a partir da utilização de amido de mandioca plastificado com glicerol, glutaraldeído, polietilenoglicol e com perclorato de lítio como eletrólito. Durante o processo de síntese, óxido de grafeno foi adicionado em diferentes concentrações (0, 0,25, 0,50, 1,00, 1,25, 1,50 e 1,75 %p/p) para avaliar o efeito da concentração deste componente. A síntese foi realizada por método termoquímico com aquecimento constante em estufa a 75 ° C por 48 horas. Os filmes foram preparados usando soluções de síntese em diferentes pH (5,0 e 9,0). O pH foi regulado pela adição de HCl ou NaOH à solução de síntese, conforme apropriado. **Resultados e Discussão:** Os resultados mostraram que os filmes de eletrólito sólido biopolimérico de amido de mandioca sem plastificantes eram rígidos e quebradiços, portanto, quebravam facilmente. Os filmes com plastificantes e os filmes de material compósito foram estáveis ao tracionamento manual, permitindo sua fácil manipulação sem quebrar. Os filmes apresentaram comportamento eletroquímico semelhante em termos de processos de redução de óxido, porém os filmes com óxido de grafeno apresentaram sinais com maiores correntes de pico. Filmes feitos em pH 9,0 mostraram 50% mais intensidade nas correntes de pico. A adição de óxido de grafeno afetou os parâmetros de corrente e potenciais de pico, sendo mais marcante nos filmes preparados em pH 9,0, neste pH os filmes com concentrações de óxido de grafeno menores que 1%p/p apresentaram E_p e I_p variáveis, enquanto que nas concentrações de óxido de grafeno maior que 1.00 %p/p, o comportamento não apresentou variações significativas. **Conclusões:** A adição de óxido de grafeno modula ou modifica o comportamento eletroquímico de filmes eletrolíticos sólidos biopoliméricos de amido de mandioca e o pH de processamento pode variar o efeito da adição de óxido de grafeno.

Palavras-chave: Óxido de grafeno, voltametria cíclica, mandioca, eletrólito de biopolímero sólido, amido.

ABSTRACT

Background: Composite materials make it possible to modulate the properties of the source materials and expand their technological potential. In this sense, composite materials made from solid biopolymeric electrolytes and graphene oxide can be an attractive alternative for applications in organic electronics due to their electrochemical properties. **Aim:** The present work aims to evaluate the electrochemical behavior of a composite material made of solid biopolymeric electrolyte of cassava starch and graphene oxide at different concentrations to determine the effect of this concentration and the pH used in the production process. **Methods:** The composite material was made from the use of cassava starch plasticized with glycerol, glutaraldehyde, polyethylene glycol and with lithium perchlorate as electrolytes. During the synthesis process, graphene oxide was added in different concentrations (0, 0.25, 0.50, 1.00, 1.25, 1.50, and 1.75 %w/w) to evaluate the effect of the concentration of this component. The synthesis was carried out by thermochemical method with constant heating in an oven at 75 ° C for 48 hours. Films were prepared using synthesis solutions at different pH (5.0 and 9.0). The pH was regulated by adding HCl or NaOH to the synthesis solution as appropriate. **Results and Discussion:** The results showed that the cassava starch biopolymeric solid electrolyte films without plasticizers were stiff and brittle, so they broke easily. The films with plasticizers and the films of the composite material were stable to the manual traction, allowing their easy manipulation without breaking. The films presented a similar electrochemical behavior in terms of oxide reduction processes; however, the films with graphene oxide presented signals with higher peak currents. Films made at pH 9.0 showed 50 % more intensity in peak currents. The addition of graphene oxide affected the current parameters and peak potentials, being more marked in the films prepared at pH 9.0; at this pH the films with concentrations of graphene oxide lower than 1.00 %w/w presented variable E_p and I_p , while at concentrations of graphene oxide greater than 1%w/w, the behavior did not show significant variations. **Conclusions:** The addition of graphene oxide modulates or modifies the electrochemical behavior of cassava starch biopolymeric solid electrolyte films, and the processing pH can vary the effect of the graphene oxide addition.

Keywords: *Graphene Oxide, Cyclic Voltammetry, Cassava, Solid biopolymer electrolyte, Starch.*

RESUMEN

Antecedentes: Los materiales compuestos permiten modular las propiedades de los materiales de origen y ampliar sus potencialidades tecnológicas. En este sentido, los materiales compuestos elaborados a partir de electrolitos sólidos biopoliméricos y óxido de grafeno pueden ser una alternativa atractiva para aplicaciones en la electrónica orgánica debido a sus propiedades electroquímicas. **Objetivo:** El presente trabajo tiene como objetivo evaluar el comportamiento electroquímico de un material compuesto elaborado de electrolito sólido biopolimérico de almidón de yuca y óxido de grafeno a diferente concentración para determinar el efecto de la concentración éste y del pH utilizado en el proceso de elaboración. **Métodos:** El material compuesto fue elaborado a partir de la utilización de almidón de yuca plastificado con glicerol, glutaraldehído, polietilenglicol y con perclorato de litio como electrolito. Durante el proceso de síntesis se adicionó óxido de grafeno en diferentes concentraciones (0, 0.25, 0.50, 1.00, 1.25, 1.50 y 1.75 %p/p) para evaluar el efecto de la concentración de este componente. La síntesis fue realizada mediante método termoquímico con calentamiento constante en un horno a 75 °C durante 48 horas. Se prepararon películas utilizando soluciones de síntesis a diferente pH (5.0 y 9.0). El pH fue regulado por adición de HCl o NaOH a la solución de síntesis según el caso. **Resultados y Discusión:** Los resultados mostraron que las películas de electrolito sólido biopolimérico de almidón de yuca sin plastificantes, fueron rígidas y quebradizas por lo que se rompieron con facilidad. Las películas con plastificantes y las películas de material compuesto fueron estables a la tracción manual, permitiendo su fácil manipulación sin romperse. Las películas presentaron un comportamiento electroquímico similar en términos de procesos de oxidación-reducción, sin embargo las películas con óxido de grafeno, presentaron señales con corrientes de pico mayores. Las películas elaboradas a pH 9.0, mostraron un 50 % más de intensidad en las corrientes de pico. La adición de óxido de grafeno afectó los parámetros de corriente y potenciales de pico, siendo más marcado en las películas preparadas a pH 9.0, a este pH las películas con concentraciones de óxido de grafeno menores al 1%p/p presentaron E_p y I_p variables, mientras que a concentraciones de óxido de grafeno mayores de 1.00 %p/p, el comportamiento no presentó variaciones significativas. **Conclusiones:** La adición de óxido de grafeno modula o modifica el comportamiento electroquímico en películas de electrolito sólido biopolimérico de almidón de yuca y el pH de elaboración puede hacer variar el efecto de la adición de óxido de grafeno.

Palabras clave: *Óxido de grafeno, Voltamperometría cíclica, Yuca, electrolito sólido de biopolímero, almidón*

1. INTRODUCTION:

Since its introduction into the industry, polymers are undoubtedly one of the materials that have generated the greatest impact on the socio-economic and technological development of humanity. However, a large number of tons of polymers of petrochemical origin generated have negatively impacted the environment due to their long periods of degradation, the polluting footprint of their production processes, and the remnants of micro-contamination produced during their decomposition in the ecosystems (Mason *et al.*, 2018; Castelvetro *et al.*, 2020; Toussaint *et al.*, 2019). This has generated great interest in developing polymeric that are friendly to the environment and have a low impact on their polluting footprint. In this sense, biopolymers are an attractive alternative because they combine qualities such as their lower impact on the environment, lower energy consumption in production processes, origin from renewable sources, and easy degradability (Goudarztalejerdi, *et al.*, 2015; Palit and Hussain, 2018; Verghese *et al.*, 2020; Nasrollahzadeh *et al.*, 2020)

Biopolymers can be synthesized from natural products such as cellulose, starches, lignin, keratin, alginate, etc. These biomaterials have been used in edible packaging, bags, medical supplies, and reinforcements (Nasrollahzadeh *et al.*, 2020; Hu *et al.*, 2014; Altomare, *et al.*, 2018; 5. Janjarasskul and Krochta, 2010). Starches, due to their natural abundance, constitute one of the main sources of interest in developing biopolymers and biomaterials.

Starch is a natural product found in plants and serves a reserve function. It is stored mainly in seeds and tubers, so it is very abundant in nature. The structure of starch is made up of granules composed of two types of polymers; amylose and amylopectin. Amylose is a linear polymer of glucose linked by α 1,4 bonds, while amylopectin has α 1,4 bonds and branches in sectors with α 1,6 bonds. The amylose/amylopectin ratio varies according to the plant species and, therefore, the structure of the starch (Hoover *et al.*, 2010; Malumba, *et al.*, 2017). The molecular structure of starch allows hydrogen bonding interactions due to the hydroxyl groups of the glucose molecules, which will enable it to interact with other chains to form packings. Many works on applying starch in the development of biopolymers have been carried out (Liew and Ramesh, 2015; Mohan and Kanny, 2015;

Tabasum *et al.*, 2018). However, most of them focus on the use of cornstarch. More recently,, cassava starch has been used to develop biopolymers.

Starch biopolymers have been combined with other materials to modulate or vary some of their physicochemical properties. The elaboration of composite materials from the combination of starch biopolymers and other materials such as poly (vinyl alcohol), halloysite, polycaprolactone, montmorillonite has been reported among others (Abdullah and Dong, 2019; Ali *et al.*, 2014; Ghanbarzadeh *et al.*, 2013).

Recently, the electronics industry has sought alternatives to develop what is known as organic electronics, which consists of developing electronic devices from organic materials. Conductive polymers are promising materials in developing devices such as muscles, artificial, electronic tongues, solar panels, smart windows, among others (Dubey *et al.*, 2019; Nuñez *et al.*, 2016; Arrieta *et al.*, 2019). Conductive polymers are mainly divided into intrinsically conductive polymers (ICPs) and solid polymeric electrolytes (SPEs). ICPs conduct electric current by displacing charges transmitted through their molecular structure, SPEs conduct electric current by moving ions through the polymer matrix. Cassava starch has been used to develop a solid biopolymeric electrolyte (SBPE), which has been used for applications such as artificial muscles, accumulators, and solar cells (Arrieta *et al.*, 2011; Nuñez *et al.*, 2016; Acosta *et al.*, 2015). In addition, it has been combined with other materials to modulate or improve some of its properties. The solid biopolymeric electrolyte of cassava starch has been combined with polypyrrole, poly (3,4-ethylenedioxythiophene), polystyrene sulfonate, polyaniline, multiwall carbon nanotube, among others (Arrieta *et al.*, 2016; Domene-López *et al.*, 2019; Arrieta *et al.*, 2018).

In its oxidized form, Graphene has also been used in combination with starch to improve its characteristics and properties. Graphene oxide (GO) is a graphene sheet (2D) fused to different oxygenated functional groups on its edges and surfaces, mainly hydroxyls (R-OH), epoxides (R-O-R), carbonyls (R-CO-R) and carboxyls (R-COOH). These functional groups allow the GO to form hydrogen bonds with other molecules to obtain composite materials. Due to its thermal, conductive and mechanical properties, the OG is an attractive material for elaborating composite materials and achieving properties of interest for

technological applications (Zhao *et al.*, 2015; Ahmad *et al.*, 2018; Khan *et al.*, 2016).

Although the elaboration of starch biopolymer composites with GO has been reported, the combination of a solid biopolymer electrolyte from cassava starch (SBPE-CS) with GO has not been reported. Therefore, this work studies the electrochemical behavior of composite material films of solid biopolymer electrolyte from cassava starch with GO (SBPE-CS/GO) at different concentrations and processing pH (5.0 and 9.0) is presented.

2. MATERIALS AND METHODS:

The study was carried out on films of solid biopolymeric electrolytes composite material made from cassava starch plasticized with different concentrations of graphene oxide elaborated at pH 5.0 and 9.0.

2.1. Materials and Reagents

For the synthesis of the composite material, the following reagents were used: glutaraldehyde ($\text{OHC}(\text{CH}_2)_3\text{CHO}$), polyethylene glycol ($\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$), glycerol ($\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$), lithium perchlorate (LiClO_4); these reagents were purchased from Sigma aldrich. Cassava starch ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$) was extracted in the laboratory and graphene oxide ($\text{C}_x\text{O}_y\text{H}_z$) was purchased from Merck. All solutions and reactions were performed using Milli-Q quality ultrapure water, purified with a Millipore Direct Water Purification System purification equipment.

2.2. Cassava starch extraction

The cassava starch extraction was carried out from 100 g of the tuber of the *Manihot esculenta* Crantz variety. The tubers were completely peeled and disintegrated by liquefaction in an industrial blender at 24 000 r.p.m., using 500 mL of ultrapure water. The liquefied material (pulp) was sieved with a 200 μm canvas. The filtrate was dried in an oven at 50 °C for 24 hours. The starch obtained was washed three times with ultrapure water and dried again at 50 °C for 24 hours. Finally, the dried and extracted starch was sieved through a 50 μm sieve, obtaining a powder-fine bright white.

2.3. Purity determination

The purity of the extracted starch was tested by infrared FTIR spectroscopy with ATR.

The spectra were recorded on a PerkinElmer (Spectrum Two) controlled with Spectrum 10 Software. The spectra were recorded at a resolution of 4 cm^{-1} , in a wave number range of 650 to 4000 cm^{-1} with a record of 100 scans. Additionally, the official method of enzymatic hydrolysis of the AOAV (Association of Official Analytical Chemists) was used. With both methods, a purity of the extracted starch greater than 99 % was recorded.

2.4. Preparation of SBPE-CS/GO composite material

The composite material was prepared in film format. 3 g of cassava starch were dispersed in 100 mL of pH-adjusted water, applying constant stirring at 1 500 r.p.m. for 15 min. The pH of the synthesis water was adjusted by adding HCl 0.1 mol L^{-1} or NaOH mol L^{-1} , depending on the case, to prepare synthesis solutions of pH 5.0 and 9.0. The pH was controlled using a YSI pHmeter (ref. Multilab 4010-3W). The dispersed starch mixture was heated for 15 min at 75 °C, with constant stirring at 1 500 r.p.m. to promote complete dissolution of the starch.

The starch solution was cooled to room temperature to add plasticizers and electrolytes (lithium salt). In all cases, the same order of addition was followed; 1 g of glycerol, 1 g of polyethylene glycol, 2 g of glutaraldehyde, and 1.5 g of lithium perchlorate were added. The solutions were heated again to 75 °C with constant stirring (1,500 rpm) for 15 min. Once all the plasticizers were completely solubilized, without stopping heating and stirring, GO was added according to the required amount and heating and stirring were continued for another 15 min. The concentrations of GO used were 0.25, 0.50, 0.75, 1.00, 1.25, 1.50 and 1.75 %w/w. Additionally, control films were prepared with plasticized starch without GO (GO 0 %w/w) and starch films without plasticizers.

The starch solutions were placed in Teflon Petri dishes and heated in an oven at 70 °C for 48 hours. The films were manually detached from the Petri dishes. All the specimens were prepared in triplicate.

2.5. Electrochemical measurements

The evaluation of the electrochemical behavior of the films was carried out by DC cyclic voltammetry. The measurements were made using a Gamry potentiostat/galvanostat (ref. 1010), controlled with the Gamry V 7.8 software. Sweep speed were used at 100 mV s^{-1} , the potential range of -2.0 V to 2.0 V, with a record of

5 scans per measurement. For the assembly of the samples, a dry cell was used, which consisted of two 1 x 1 cm steel sheets adhered to acrylic sheets. The sample was sandwiched between the two plates to which the electrode terminals were connected. The records were made using the open circuit potential as reference potential (0.10 V).

3. RESULTS AND DISCUSSION:

All the SBPE-CS/GO films made with plasticizers showed good consistency and mechanical stability, which allowed them to be easily detached from the petri dishes. However, the films used as control, made with starch without any plasticizer, presented a brittle consistency, which caused them to break when detached from the petri dishes. Figure 1 shows the films images of cassava starch biopolymer without plasticizer (Figure 1a), cassava starch biopolymer plasticized (SBPE-CS) (Figure 1b), and cassava starch biopolymer plasticized with GO 0.75 %w/w (SBPE-CS/GO) (Figure 1c). This behavior may be due to the fact that the plasticizers allow greater flexibility of the films by interacting through hydrogen bonds with the glucose chains of the starch and generating intermolecular spaces that decrease the crystallinity and the stiffness in the biopolymer (Zhu, *et al.*, 2013; Mikus *et al.*, 2014).

The addition of GO can generate the same effect as plasticizers because the molecules can interact through electrostatic forces and hydrogen bonds with the glucose chains present in starch. In Figure 2, a diagram of the possible interactions of GO with the cassava starch biopolymer is presented. GO has functional groups with oxygenates (alcohol, ethers, aldehydes, ketones, carboxylic acids, and esters). These groups, since they are generally located, projecting on the surface and edges of the 2D structure of the GO molecule, could allow interactions with the hydroxyl groups of the glucose molecules of starch, generating hydrogen bonds between both structures, this type of interaction was reported by Peregrino *et al.* (2014).

Once the films were prepared, the electrochemical characterization was carried out by cyclic voltammetry. Figure 3 shows the electrochemical response of the films made at pH 5.0. It can be observed that in all cases, the voltammetric curves show an oxidation process in the anodic sweep and a reduction process in the cathode sweep. Furthermore, in both cases the peaks are wide, suggesting a possible overlap of

electron exchange processes in the area of oxidation and reduction potentials.

The voltammetric signal of the films without GO was similar to those that contain GO in different concentrations; only a slight difference could be seen in the intensity and potentials of the oxide/reduction processes. This result may be because at acid pH, the opening of the starch chains and the unfolding and loss of crystallinity is low, so the presence of GO does not significantly affect the electrochemical behavior of the composite material.

The electrochemical behavior of the films made at pH 9.0 is presented in Figure 4. It can be observed that the current intensity of the anodic (I_{pa}) and cathode peaks (I_{pc}) of the biopolymer films with GO made at pH 9.0, did not present significant variations among themselves, being located at values close to 0.151 mA for the I_{pa} and -0.160 for the I_{pc} . However, the peak intensities were higher than those registered with the biopolymer films without GO, 0.016 mA and -0.020 for the I_{pa} and I_{pc} , respectively. Therefore, the addition of GO generated an increase in the peak current of the oxidation and reduction processes by an order of magnitude. This may be due to the fact that the basic pH favors the opening of the glucose chains of the biopolymer and allows the GO to penetrate the starch structure as well as the plasticizers and interact through hydrogen bonds, which can have repercussions in a decrease of the crystallinity of the biopolymer generating greater mobility of ionic charges and therefore in the conductivity of the biopolymer, reflected in higher peak current intensities.

On the other hand, the potentials of the oxide/reduction processes showed that the films with low concentrations of GO (0, 0.25, 0.50, 0.75 and 1.0 %w/w), presented more positive potentials in the anodic scans (E_{pa}) and more negative in the cathode scans (E_{pc}). Additionally, the oxidation potentials (E_{pa}) were markedly more positive than those recorded in the SBPE-CS/GO films made at pH 5.0 and the reduction potentials (E_{pc}) more negative.

Figure 5 shows the graph of the I_{pc} , I_{pa} , E_{pc} and E_{pa} values versus the GO concentration in the biopolymer films made at pH 5.0. An almost linear behavior can be seen in each of the peak parameters (potentials and currents). The peak cathode current (I_{pc}) values are in all cases approximately 0.10 mA and in the anode peak (I_{pa}) they present currents close to -0.10 mA. The anodic (E_{pa}) and cathodic peak potentials (E_{pc}) are located at the values of 0.25 V and -0.27 V,

respectively, showing a small difference in the potential of the cathodic peak of the film made without OG, which registered an Epc of -0.33 V.

Figure 6 presents the graph of the Ipc, Ipa, Epc and Epa values of the composite biopolymer films made at pH 9.0. The figure clearly shows that the currents and peak potentials of the films without GO were markedly different. The current values of the films without GO were lower (0.016 mA) than those with GO, which registered currents practically equal to each other, with values of around 0.150 mA.

The oxidation peak potentials showed a tendency to decrease as the concentration of GO in the films increased, registering values of 0.48 V for OG concentration of 0 %w/w, 0.34 V for OG 0.25 %w/w, 0.30 V for OG 0.50 %w/w and 0.25 V for 0.75 %w/w. Stabilizing at 0.16 V at the values of GO concentrations of 1.00 %w/w, 1.25 %w/w, 1.50 %w/w and 1.75 %w/w. In the anodic sweep, the reduction processes showed similar behavior, increasing the potential reduction values in films with less than 1.00 %w/w OG and stabilizing the values in films with more than OG 1.00 %w/w.

Films without GO (OG 0 %w/w) presented a reduction peak at -0.48 V, films with GO concentrations of 0.25 %w/w and 0.50 %w/w, presented peaks at -0.41 V and -0.38 V respectively, -0.36 V for 0.75 %w/w of OG and 0.33 V for 1.00 %w/w of OG, stabilizing at this value for concentrations of 1.25 %w/w, 1.50 %w/w and 1.75 %w/w. This behavior shows that at pH 9.0, GO can modify the electrochemical behavior in SBPE-CS films and that concentrations of GO lower than 1.00 %w/w generate a greater oxidation capacity. In comparison, concentrations higher than GO 1.00 %w/w do not modify the oxidation or reduction capacity of the SBPE-CS/GO films. This behavior may be due to a possible saturation of the oxidation points or zones at this OG concentration value.

Table 1 shows the values of the cathode peak currents (Ipc) and anodic peaks (Ipa), the cathode peak potentials (Epa) and anodic peak (Epc), the ratio of cathode/anode current (Ipc/Ipa) and the half-wave potentials ($E_{p/2}$) of the SBPE-CS/GO films elaborated with several GO concentrations at pH 5.0 and 9.0. It can be seen that all the redox processes recorded were reversible because the proportionality values of cathode/anodic currents were close to 1. Films made at pH 5.0 showed Ipa/Ipc values closer to 1, which shows greater reversibility of its oxide/reduction processes.

The synthesis pH affects the electrochemical behavior of the solid biopolymer electrolyte films with OG, showing less positive values in the films synthesized at pH 5.0 and more positive in the films generated at pH 9.0. Possibly due to the loss of compaction of the molecular chains in the starch produced by low crystallinity of the structure. Additionally, the Ipa/Ipc ratio in the films without OG at both pH values (5.0 and 9.0), present the lowest reversibility (Ipa/Ipc = 0.80), so it could be stated that OG facilitates the reversibility of the oxidation/reduction processes. If the average currents recorded with the films made at both pHs are compared, it can be seen that the films made at pH 9.0 recorded signals with higher currents by 51 % on average.

4. CONCLUSIONS:

It was possible to elaborate a composite material of solid biopolymer electrolyte from cassava starch with various concentrations of graphene oxide (SBPE-CS/GO) at pH 5.0 and 9.0. The composite material films presented good consistency and stability to manual traction and detachment from the petri dishes prepared.

SBPE-CS/GO films exhibited redox electrochemical activity with well-defined oxidation and reduction peaks. The redox processes in the SBPE-CS/GO films made at pH 5.0 did not show significant variations in their behavior, oxidation and reduction potentials, and peak currents. On the other hand, SBPE-CS/GO films prepared at pH 9.0 showed substantial variations in concentrations lower than 1.0 %w/w of GO and a stable behavior without significant variations at concentrations higher than this concentration value.

In general, the composite material films (SBPE-CS/GO) made at a pH of 9.0 showed more intense signals in terms of current intensity, with current values 50 % higher than the films made at a pH of 5.0. In addition, the electrochemical processes showed a higher degree of reversibility (determined by the Ipc/Ipa coefficient) in the films generated at pH 9.0.

5. DECLARATIONS

5.1. Study Limitations

No limitations were known at the time of the study.

5.2. Acknowledgements

The authors acknowledge the University of

Sucre for financial support.

5.3. Funding source

This research was funded by the University of Sucre.

5.4. Competing Interests

The author declares no conflicts of interest.

5.5. Open Access

This article is licensed under a Creative Commons Attribution 4.0 (CC BY 4.0) International License, which permits use, sharing, adaptation, distribution, and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third-party material in this article are included in the article's Creative Commons license unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

6. REFERENCES:

1. Abdullah, Z. W., and Dong, Y. (2019). Biodegradable and Water Resistant Poly(vinyl Alcohol (PVA)/Starch (ST)/Glycerol (GL)/Halloysite Nanotube (HNT) Nanocomposite Films for Sustainable Food Packaging. *Frontiers in Materials*, 6. doi:10.3389/fmats.2019.00058
2. Acosta, M.F., Arrieta, A., Ávila, A., Martínez, A., Palacio, M., Nova, V. (2015). Development of Charge Electrochemical Accumulator of Conductive Polypyrrole/Cassava Starch Biopolymers. *ASME-Energy*. 6A, 1-5. doi:10.1115/IMECE2015-52575
3. Ahmad, H., Fan, M., and Hui, D. (2018). Graphene oxide incorporated functional materials: A review. *Composites Part B: Engineering*, 145, 270–280. doi:10.1016/j.compositesb.2018.02
4. Ali Akbari Ghavimi, S., Ebrahimzadeh, M. H., Solati-Hashjin, M., and Abu Osman, N. A. (2014). Polycaprolactone/starch composite: Fabrication, structure, properties, and applications. *Journal of Biomedical Materials Research Part A*, 103(7), 2482–2498. doi:10.1002/jbm.a.35371
5. Altomare, L., Bonetti, L., Campiglio, C. E., De Nardo, L., Draghi, L., Tana, F., and Farè, S. (2018). Biopolymer-based strategies in the design of smart medical devices and artificial organs. *The International Journal of Artificial Organs*, 41(6), 337–359. doi:10.1177/0391398818765323
6. Arrieta A. A., Arrieta P. L., Mendoza J. M. (2019). Analysis of coffee adulterated with roasted corn and roasted soybean using voltammetric electronic tongue. *Acta Sci. Pol. Technol. Aliment.*, 18 (1), 35-41 <https://doi.org/10.17306/J.AFS.2019.061>
7. Arrieta, A. A., and Palencia, M. S. (2016). Estudio electroquímico de un biopolímero compuesto PPy/almidón de cassava. *Rev. LatinAm. Metal. Mater.*, 36 (1), 26-35 <http://ve.scielo.org/pdf/rlmm/v36n1/art05.pdf>.
8. Arrieta, A., Gañán, P.F., Márquez, S.E., Zuluaga, R. (2011). Electrically conductive bioplastics from cassava starch. *Journal of the Brazilian Chemical Society*, 22(6), 1170-1176. doi:10.1590/S0103-50532011000600024
9. Arrieta, A., Palencia, M., and Pestana, R. (2018). New Composite Biopolymer with Conductive Properties Obtained from Cassava and Poly Starch (3, 4-Ethylenedioxythiophene). *Indian Journal of Science and Technology*, 11(2), 1–10. doi:10.17485/ijst/2018/v11i2/1173
10. Castelvetro, V., Corti, A., Bianchi, S., Giacomelli, G., Manariti, A., and Vinciguerra, V. (2020). Microplastics in fish meal: contamination level analyzed by polymer type, including polyester (PET), polyolefins, and polystyrene. *Environmental Pollution*, 115792. doi:10.1016/j.envpol.2020.115792
11. Domene-López, D., Delgado-Marín, J. J., García-Quesada, J. C., Martín-Gullón, I., and Montalbán, M. G. (2019). Electroconductive starch/multi-walled carbon nanotube films plasticized by 1-ethyl-3-methylimidazolium acetate. *Carbohydrate Polymers*, 115545. doi:10.1016/j.carbpol.2019.115545

12. Dubey, N., Kushwaha, C. S., and Shukla, S. K. (2019). A review on electrically conducting polymer bionanocomposites for biomedical and other applications. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 1–19. doi:10.1080/00914037.2019.1605513
13. Ghanbarzadeh, B., Almasi, H., and Oleyaei, S. A. (2013). A Novel Modified Starch/Carboxymethyl Cellulose/Montmorillonite Bionanocomposite Film: Structural and Physical Properties. *International Journal of Food Engineering*, 10(1). doi:10.1515/ijfe-2012-0197
14. Goudarztalejerdi, A., Tabatabaei, M., Eskandari, M. H., Mowla, D., and Iraj, A. (2015). Evaluation of bioremediation potential and biopolymer production of pseudomonads isolated from petroleum hydrocarbon-contaminated areas. *International Journal of Environmental Science and Technology*, 12(9), 2801–2808. doi:10.1007/s13762-015-0779-0
15. Hoover, R., Hughes, T., Chung, H. J., and Liu, Q. (2010). Composition, molecular structure, properties, and modification of pulse starches: A review. *Food Research International*, 43(2), 399–413. doi:10.1016/j.foodres.2009.09.001
16. Hu, B. (2014). Biopolymer-Based Lightweight Materials for Packaging Applications. *Lightweight Materials from Biopolymers and Biofibers*, 239–255. doi:10.1021/bk-2014-1175.ch013
17. Janjarasskul, T., and Krochta, J. M. (2010). Edible Packaging Materials. *Annual Review of Food Science and Technology*, 1(1), 415–448. doi:10.1146/annurev.food.080708.1
18. Khan, Z. U., Kausar, A., Ullah, H., Badshah, A., and Khan, W. U. (2016). A review of graphene oxide, graphene buckypaper, and polymer/graphene composites: Properties and fabrication techniques. *Journal of Plastic Film and Sheeting*, 32(4), 336–379. doi:10.1177/8756087915614612
19. Liew, C.-W., and Ramesh, S. (2015). Electrical, structural, thermal and electrochemical properties of corn starch-based biopolymer electrolytes. *Carbohydrate Polymers*, 124, 222–228. doi:10.1016/j.carbpol.2015.02.024
20. Malumba, P., Doran, L., Zanmenou, W., Odjo, S., Katanga, J., Blecker, C., and Béra, F. (2017). Morphological, structural and functional properties of starch granules extracted from the tubers and seeds of *Sphenostylis stenocarpa*. *Carbohydrate Polymers*, 178, 286–294. doi:10.1016/j.carbpol.2017.09.013
21. Mason, S. A., Welch, V. G., and Neratko, J. (2018). Synthetic Polymer Contamination in Bottled Water. *Frontiers in Chemistry*, 6, 1-11. doi:10.3389/fchem.2018.00407
22. Mikus, P.-Y., Alix, S., Soulestin, J., Lacrampe, M. F., Krawczak, P., Coqueret, X., and Dole, P. (2014). Deformation mechanisms of plasticized starch materials. *Carbohydrate Polymers*, 114, 450–457. doi:10.1016/j.carbpol.2014.06.087
23. Mohan, T., and Kanny, K. (2015). Thermoforming studies of corn starch-derived biopolymer film filled with nanoclays. *Journal of Plastic Film and Sheeting*, 32(2), 163–188. doi:10.1177/8756087915590846
24. Nasrollahzadeh, M., Sajjadi, M., Irvani, S., and Varma, R. S. (2020). Starch, cellulose, pectin, gum, alginate, chitin and chitosan derived (nano)materials for sustainable water treatment: A review. *Carbohydrate Polymers*, 116986. doi:10.1016/j.carbpol.2020.116986
25. Nuñez, Y.E., Arrieta, A.A., Segura, J.A., Bertel, S.D. (2016). Synthesis of an air-working trilayer artificial muscle using a conductive cassava starch biofilm (*manihot esculenta*, cranz) and polypyrrole (PPy). *Journal of Physics: Conference Series*, 687, 1-7. doi:10.1088/1742-6596/687/1/012042
26. Palit, S., and Hussain, C. M. (2018). Biopolymers, Nanocomposites, and Environmental Protection: A Far-Reaching Review. *Bio-Based Materials for Food Packaging*, 217–236. doi:10.1007/978-981-13-1909-9_10
27. Peregrino, P. P., Sales, M. J. A., da Silva, M. F. P., Soler, M. A. G., da Silva, L. F. L., Moreira, S. G. C., and Paterno, L. G. (2014). Thermal and electrical properties of starch-graphene oxide nanocomposites improved by photochemical treatment. *Carbohydrate Polymers*, 106, 305–311.

- doi:10.1016/j.carbpol.2014.02.008
28. Tabasum, S., Younas, M., Zaeem, M. A., Majeed, I., Majeed, M., Noreen, A., ... Zia, K. M. (2018). A review on blending of corn starch with natural and synthetic polymers, and inorganic nanoparticles with mathematical modeling. *International Journal of Biological Macromolecules*. doi:10.1016/j.ijbiomac.2018.10.09
29. Toussaint, B., Raffael, B., Angers-Loustau, A., Gilliland, D., Kestens, V., Petrillo, M., ... Van den Eede, G. (2019). Review of micro- and nanoplastic contamination in the food chain. *Food Additives and Contaminants: Part A*, 1–35. doi:10.1080/19440049.2019.1583381
30. Varghese, S. A., Siengchin, S., and Parameswaranpillai, J. (2020). Essential oils as antimicrobial agents in biopolymer-based food packaging - A comprehensive review. *Food Bioscience*, 100785. doi:10.1016/j.fbio.2020.100785
31. Zhao, J., Liu, L., and Li, F. (2015). Graphene Oxide: Physics and Applications. *Springer Briefs in Physics*. doi:10.1007/978-3-662-44829-8
- 32.** Zhu, J., Li, X., Huang, C., Chen, L., and Li, L. (2013). Plasticization effect of triacetin on structure and properties of starch ester film. *Carbohydrate Polymers*, 94(2), 874–881. doi:10.1016/j.carbpol.2013.02.020

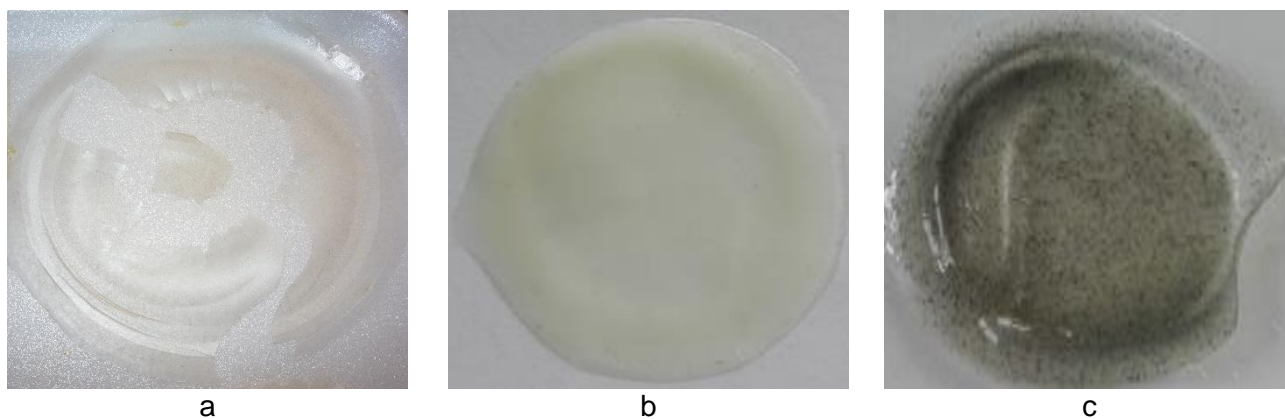


Figure 1. Films Images of a) cassava starch biopolymer without plasticizer b) cassava starch biopolymer plasticized (SBPE-CS) and c) cassava starch biopolymer plasticized with GO 0.75 %w/w (SBPE-CS/GO)

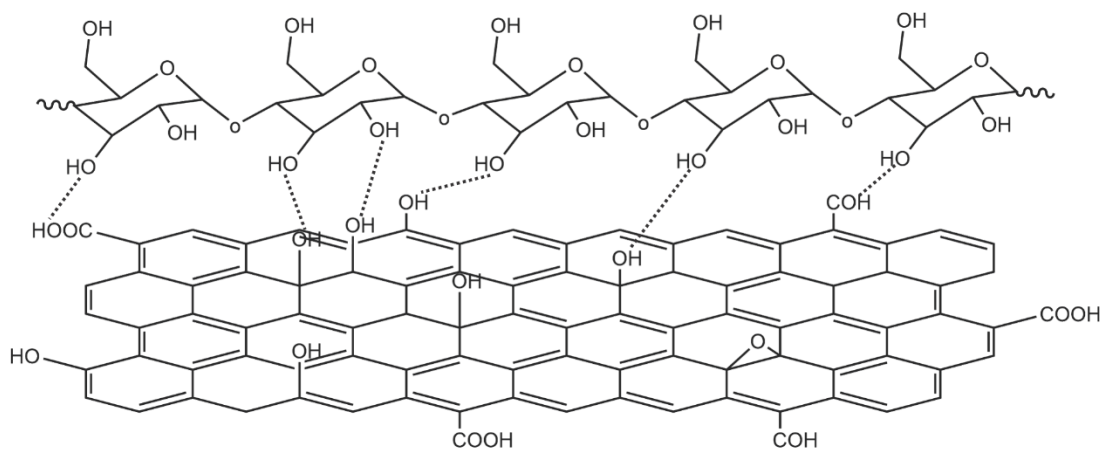


Figure 2. Scheme of hydrogen bonds interactions between starch and graphene oxide molecules

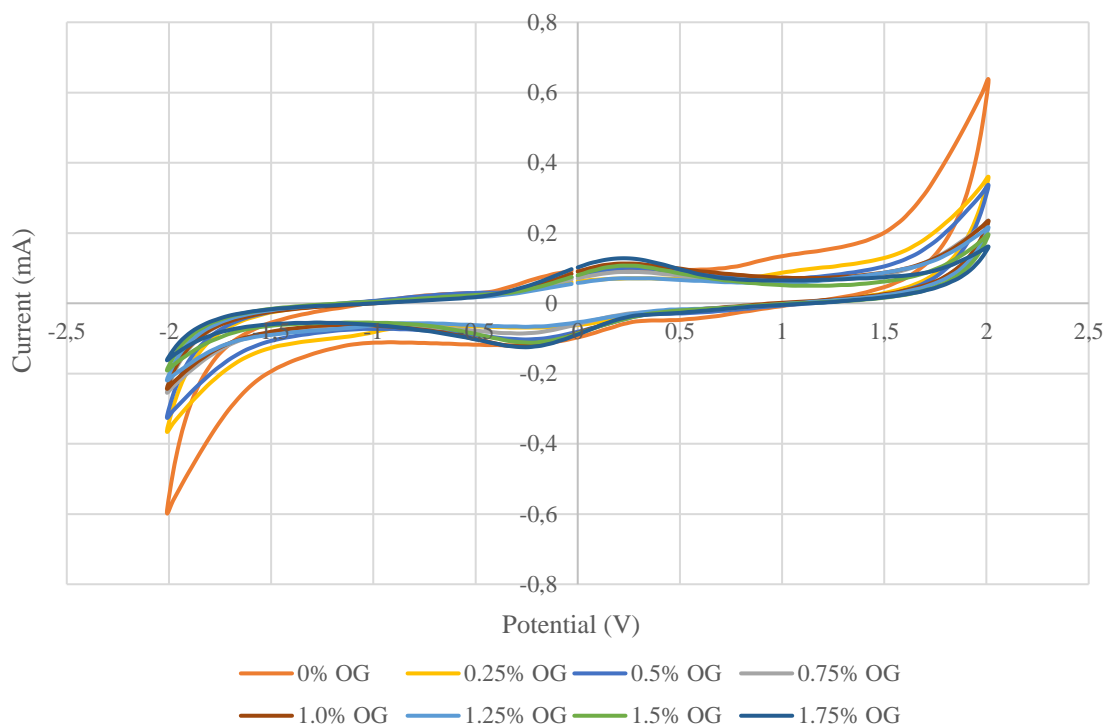


Figure 3. Cyclic voltammetry recorded with SBPE-CS elaborated with various concentrations of GO at pH 5.0

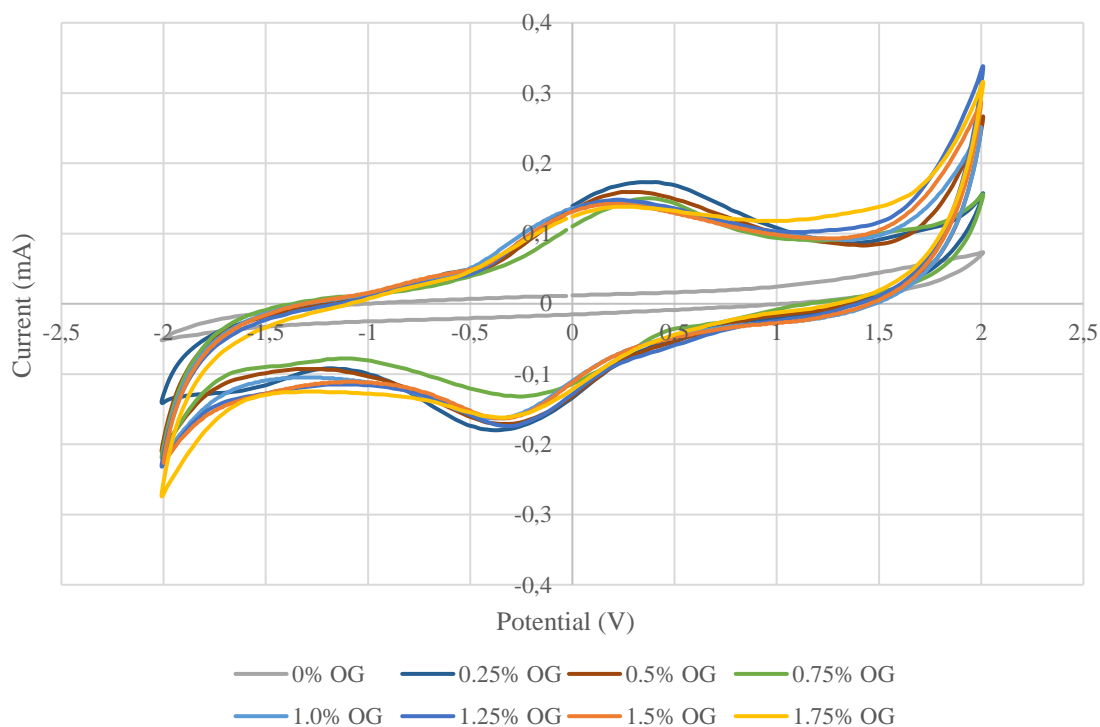


Figure 4. Cyclic voltammetry recorded with SBPE-CS elaborated with various concentrations of GO at pH 9.0

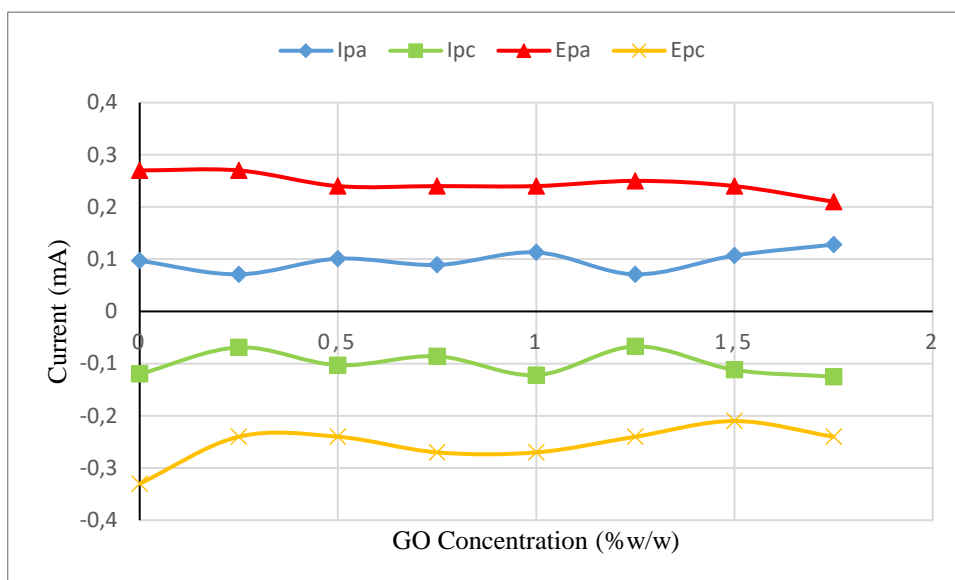


Figure 5. Parameters of anodic and cathode peaks (I_{pa} , I_{pc} , E_{pa} , E_{pc}) versus GO concentration (%w/w) used in the elaboration of SBPE-CS / GO films at pH 5.0

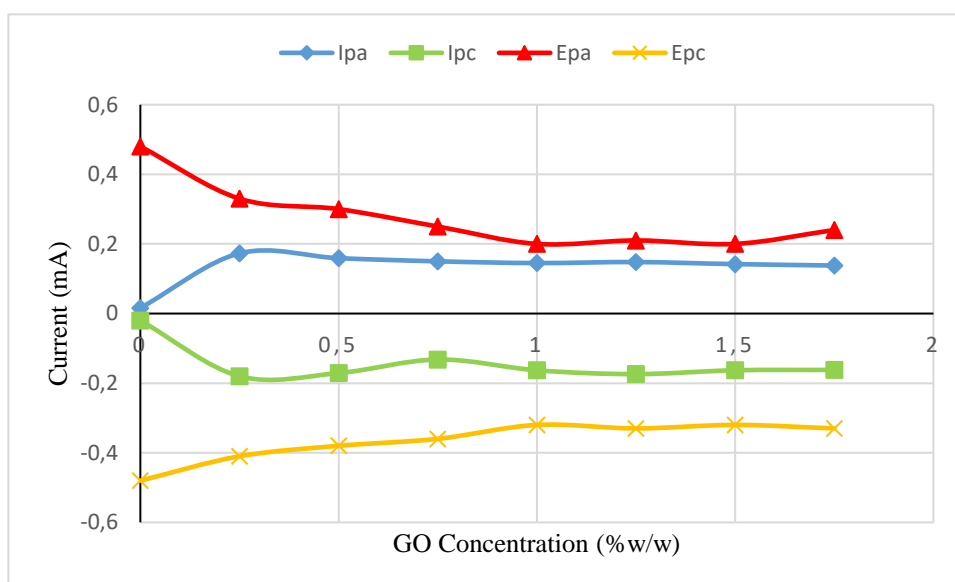


Figure 6. Parameters of anodic and cathode peaks (I_{pa} , I_{pc} , E_{pa} , E_{pc}) versus GO concentration (%w/w) used in the elaboration of SBPE-CS / GO films at pH 9.0

Table 1. Values of cathode peak currents (I_{pc}), anodic peaks currents (I_{pa}), cathode peak potentials (E_{pa}), anodic peak potentials (E_{pc}), ratio of cathode/anode currents (I_{pc}/I_{pa}) and the half-wave potentials ($E_{p/2}$) of the SBPE-CS/GO films elaborated with several GO concentrations at pH 5.0 and 9.0

pH	% w/w OG	I_{pa}	I_{pc}	I_{pa}/I_{pc}	E_{pa}	E_{pc}	$E_{p/2}$
5.0	0.00	0.097	-0.120	0,808	0.27	-0.33	-0.03
	0.25	0.071	-0.069	1,029	0.27	-0.24	0.02
	0.50	0.101	-0.103	0,981	0.24	-0.24	0.00
	0.75	0.089	-0.086	1,035	0.24	-0.27	-0.02
	1.00	0.113	-0.122	0,926	0.24	-0.27	-0.02
	1.25	0.071	-0.067	1,060	0.25	-0.24	0.01
	1.50	0.107	-0.112	0,955	0.24	-0.21	0.02
	1.75	0.128	-0.125	1.024	0.21	-0.24	-0.02
9.0	0.00	0.016	-0.020	0,800	0.48	-0.48	0.00
	0.25	0.173	-0.180	0,961	0.33	-0.41	-0.04
	0.50	0.159	-0.171	0,930	0.30	-0.38	-0.04
	0.75	0.150	-0.132	1,136	0.25	-0.36	-0.06
	1.00	0.145	-0.163	0,890	0.20	-0.32	-0.06
	1.25	0.148	-0.174	0,851	0.21	-0.33	-0.06
	1.5	0.142	-0.163	0,871	0.20	-0.32	-0.06
	1.75	0.138	-0.162	0,852	0.24	-0.33	-0.05