Development of an Alternative Route for Production of Glassy Polymeric Carbon Electrodes in Laboratorial Scale

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Summary: A complete alternative and cheaper route for production of glassy polymeric carbon electrodes in laboratorial scale is described. Two kinds of polyphenolic resins were synthesized by mixing the precursors phenol and formaldehyde with 1) ammonium or 2) sodium hydroxide as catalyst. A shorter treatment time of 3.5 days (from 25 to 1000 °C) was employed for preparation of the electrodic material compared with the 5–7 day period proposed in the literature. The obtained materials were inserted into conventional hollow plastic bodies and electrically contacted with copper wire. After proper polishing, the electrodic materials were tested as working electrodes by cyclic voltammetry technique. The data demonstrated that the use of sodium hydroxide causes peculiar problems such as alkaline residues in the electrodic materials and subsequent fading of final product. On the other hand, the materials obtained by the ammonium hydroxide route presented good results in terms of mechanical resistance, glassy appearance, conductivity and voltammetric response, allowing for application of such materials in electrochemistry.

Keywords: bakelite; glassy carbon electrode; homemade electrode; polyphenolic polymer; voltammetry

Introduction

Bakelite is a synthetic resin (polyphenol) commonly obtained by reaction between hydroxybenzene and formaldheyde. A large variety of materials, such as the glassy polymeric carbon, can be made from this resin. Bakelite production requires specific heating treatment of the resin (temperatures of 1000 °C under controlled atmosphere, for example), and the properties of the resulting glassy carbon differ from those of other carbon materials (graphite, for example) in many parameters such as mechanical resistance, porosity, conductivity and chemical stability.[1]

Bakelite is commercially available in two forms namely resol and novolac. The former is liquid and is applied in different materials, while the latter is solid, has a dark color and its final polymerization occurs during the modeling stage, which is facilitated by the melting point (55 to 85 °C). Previous studies using bakelite as the precursor material for glassy carbon have indicated that a considerable time interval is demanded for the synthesis, which can reach up to 64 hours and does not include the gelling time.[2–7]

The production of glassy carbon from phenolic resins had already been developed and explained. Briefly, a carbonization processes takes place at 300 °C, and oxygen and nitrogen are eliminated. Hydrogen is lost over the range 500–1200 °C and as a result, glassy carbon is ready.[2] When resol is employed, heating to 137 °C leads to polymerization and formation of a gel; at

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167 °C, this gel forms a hard crosslinked resin that undergoes a color change to brown between 167 and 267 °C. From 267 °C to 602 °C, a precarbonization step is produced and a dark opaque glass is consequently formed, with some hydrogen content. In the range of 602 °C–1227 °C, there are no changes in the appearance, but hardness and density are modified due to structure shrinkage. Additionally, an electrical conductor material is formed as hydrogen is removed, all this process being known as carbonization.[8]

One of the most important applications of glassy carbon materials is related to their excellent electrical properties, which allow for their use as electrodic materials, such as commercial or homemade electrodes. Therefore, electrochemical transducers with different shapes and sizes are available, once the polymeric precursor can be easily molded. Also, these transducers display properties that include low residual current over a range of about ±1V in aqueous media and organic solvents. The use of glassy carbon in electrochemistry has increased over the last years, because of its chemical inertness and good electrical properties.[2] This substrate can be employed directly as a transducer for chemical species[9,11] or it can be superficially modified by specific chemical films.[12–14] The latter process provides substances with chemical specificity that can be employed in different areas, such as pharmacology, industry, among others.

In terms of electrochemical studies, because its heterogeneous electron transfer has been extensively studied, hexacyanoferrate II/III is often chosen as the redox system to test the applicability of the glassy carbon. In addition, the system is believed to be a simple outer sphere reaction and is very sensitive to the glassy carbon surface. [1,15]

Despite the excellent properties of glassy polymeric carbon as electrodic material, commercially available electrodes are still very expensive. Considering the polymeric nature of glassy carbon precursors and the relative easiness of molding and obtaining the final electrodic product, the aim of this study is to propose an alternative methodology for the preparation of glassy carbon in a laboratory scale, departing from the synthesis of the polymeric precursor and proceeding until the mounting of the electrode in a shorter time interval than the ones reported in the literature. Additionally, we aim to evaluate the results of the final product in terms of electrochemical application by cyclic voltammetric measurements.

Experimental Part

Apparatus and Chemicals

For the bakelite preparation, a heat plate with magnetic stirrer EDG model FVII stove was used. Cyclic and linear sweep voltammetric measurements were carried out on a μAutoLabIII potentiostat, under the control of a microcomputer. A 5.0 mL conventional electrochemical cell with a synthesized glassy carbon disc as working electrode, an Ag/AgCl (saturated aqueous KCl) reference electrode, and a platinum spiral auxiliary electrode were employed. TGA/DTA measurements were carried out in a thermogravimetric analyser from TA Instruments, model SDT 2960, using a nitrogen atmosphere.

All chemical reagents were analytical grade: Ammonium hydroxide, sodium hydroxide, formaldehyde, potassium chloride, and phenol were purchased from Merck, potassium hexacyanoferrate was acquired from Carlo Erba.

Bakelite and Glassy Carbon preparation

Bakelite preparation was carried out on a heat plate under stirring at 80 °C, by mixing 15.06 g phenol, 49.2 mL fomaldheyde and 9.0 mL 38% ammonium hydroxide as catalyst until an opaque mixture was obtained. After cooling, the aqueous coat was removed, and the viscous material at the bottom of the recipient was heated at 60 °C for 30 minutes. After a fast exchange from an opaque to a yellow transparent and more viscous solution, the resin was promptly transferred to tubular molds (5cm length and 3 mm internal diameter), and a solid resin was obtained under 75 °C in a stove for 24 hours. After the solidification process, the glass tubular molds were removed, and cylindrical tubes of yellow bakelite were obtained.

A similar process was employed for preparation of Bakelite using sodium hydroxide as catalyst. After addition of 12.5 g phenol, 34.0 mL formaldehyde, and 2.4 mL 50% sodium hydroxide solution, the mixture was treated in the same conditions described before, until the production of a red viscous and transparent solution, which was promptly transferred to the mold. The resin was also kept in a stove under 75 °C for 24 hours. After the solidification process, the glass tubular molds were also removed, and cylindrical tubes of red bakelite were obtained.

In order to prepare the glassy polymeric carbon from both resins obtained in the presence of ammonium and sodium hydroxides, the stove was programmed to run through the following heating ramp in a nitrogen inert atmosphere, under a gas flow rate of 2.0 L/min. The heating rate was equal to 1.0 °C/min.

25 °C to 200 °C
200 °C for 3 hours
200 °C to 600 °C
600 °C for 24 hours
600 °C to 1000 °C
1000 °C for about two hours

After the thermal treatment, the carbonized materials were washed with deionized water, dried, and inserted into a plastic bracket (micropipette tip) using a commercial epoxy-based adhesive glue. For the electric connection, a copper wire was employed in one of the tube extremities. After drying of the glue, the other carbon tube extremity was polished with alumina, in order to obtain a glassy surface.

Cyclic Voltammetry

A potassium chloride 1.0 mol L^{-1} aqueous solution was prepared and used as supporting-electrolyte for preparation of the $K_3[Fe(CN)_6]$ 5.10^{-2} mol L^{-1} solution. In order to remove electroactive oxygen, all solutions were left under previous nitrogen gas flow for 15 minutes. The potentiostat was scheduled to work in the 0.8 to −0.2 V (vs. Ag/AgCl) interval, in which voltammograms were obtained at the scan rates 5, 10, 20, 50, 100, and 150 mV s^{-1} . The base line extrapolation in these graphics allowed for calculation of the anodic and cathodic currents. In addition, a relation between each current and the square root of the scan rate was plotted from these data.

The study of the dependence of peak current on analyte concentration was performed by the standard addition method. Into 4.0 mL of the supporting electrolyte, successive additions of 0.1; 0.2; 0.2; 0.2; 0.3; and 0.5 mL of $K_3[Fe(CN)_6]$ 5×10^{-2} mol L^{-1} solution were accomplished, being the respective voltammograms recorded at a scan rate of 100 mV s^{-1}.

TGA/DTA Analysis

Aliquots of 20 mg of baquelites obtained from sodium and ammonium routes were analysed by TGA/DTA techniques from room temperature to 1000 °C, under a heating rate of 10 °C min^{-1}.

Results and Discussion

Bakelite and Glassy Carbon

Resins, like other kinds of polymers, present some typical characteristics of polymeric materials, such as high viscosity, as observed in the experiment, and the high melting points related to elevated temperature values. A schematic simplified route of the resin and subsequent polymeric glassy carbon preparation is presented in Figure 1.

After bakelite preparation, some comparisons were made between the two alkaline routes employed for the glassy carbon synthesis. When ammonium hydroxide was used, a light yellow colored polymer was obtained. When the catalyst was sodium hydroxide, a dark red color was

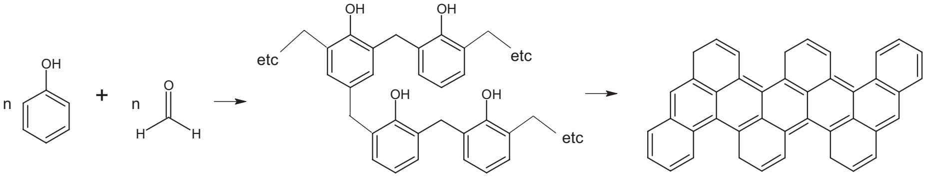

Figure 1.
Schematic route for glassy polymeric carbon production from hydroxybenzene and formaldehyde.

verified. A better comparison between both yellow and red bakelites can be made by observing Figure 2.

Although both ammoniacal and sodic bakelites presented good mechanical resistance, with several applications in the polymer industry, it is necessary to compare the applicability of these precursors in relation to the carbonization process employed for production of the glassy polymeric carbon. After the carbonization process, the carbon materials obtained by the sodium hydroxide route presented several problems, including low mechanical resistance, high porosity and large amounts of alkaline residues, derived from catalyst. These residues could be easily detected in the washing water, when pH values up to 11 were observed. In contrast, the carbon materials obtained by the ammonium route did not present alkaline residues in water, as seen from the neutral pH of the washing water. Additionally, these materials exhibited high mechanical resistance, glassy appearance after polishing, and low porosity.

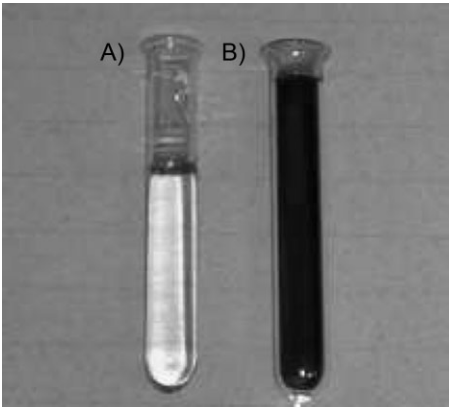

Figure 2.
Bakelite samples prepared using different alkaline catalysts. (A) Ammonium hydroxide. (B) Sodium hydroxide.

TGA/DTA analyses of the synthesized resins have shown weight loss of 41 and 56% for ammoniacal and sodic bakelites, respectively (Figure 3). These results are consistent with those presented in the literature, which suggest carbon yields for phenol formaldehyde resins carbonization between 45 and 60%.[7] The weight loss during carbonization takes place predominantly in the temperature range from 400 to 700 °C and occurs in three zones, which is in good agreement with observed in literature.[2,7] Weight loss for both sodic and ammoniacal Bakelite occurs at the same temperature range, suggesting that the alkaline catalyst does not change the chemical reactions involved in the carbonization stages. However, sodium hydroxide promotes a faster weight loss, indicating a faster carbonization process. This observation is consistent with the poor mechanical resistance and high porosity presented by the carbon prepared from sodic Bakelite. The faster carbonization process promotes fast volatile products elimination, which can produce many cracks and pores leading to a very fragile final material. On the other hand, the slower carbonization using ammonium hydroxide as catalyst leads to a more compact and rigid material, since volatile products are eliminated slowly.

Figure 4 illustrates some pieces of carbon materials obtained by the ammonium route.

Considering the peculiar differences of both sodic and ammoniacal carbon materi-

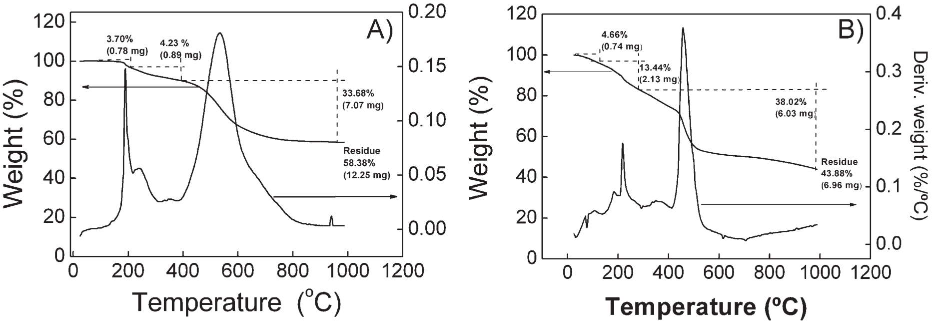

Figure 3.
TGA/DTA analyses of phenolic resin. (A) Ammonium route. (B) Sodic route.

als, specially in terms of porosity and mechanical resistance, only the ammoniacal glassy carbon was employed in the further electrochemical measurements. After being sectioned, immobilized in a plastic bracket, and finally polished until a glassy appearance, the dispositive resulted in a typical homemade electrode for voltammetric applications, as illustrated in Figure 5.

Considering the boiling point of 1388 °C reported for sodium hydroxide in the literature, it is possible to explain the presence of alkaline residues in the carbon material, once the upper heating limit was 1000 °C. Additionally, the presence of sodium species in the carbon material can contribute to the low mechanic resistance observed for the final product. Ammonia species, in turn, have a boiling point of 24.7 °C and are completely eliminated from the polymeric matrix in the initial heating stages (temperatures lower than 100 °C). In this sense, this catalyst does not interfere in the final glassy carbon composition, representing a better choice compared with sodium hydroxide.

Cyclic Voltammetry

After polishing with alumina powder, the homemade electrodes were rinsed with water, cleaned in an ultrasonic aqueous bath for 5 minutes, and rinsed again with water before use. The voltammetric behavior of the manufactured devices was checked by analyzing the dependence of the cathodic and anodic peak currents for the known system $[Fe(CN)_6]^{3-}$ /$[Fe(CN)_6]^{4-}$[1,2] on scan rate and concentration.

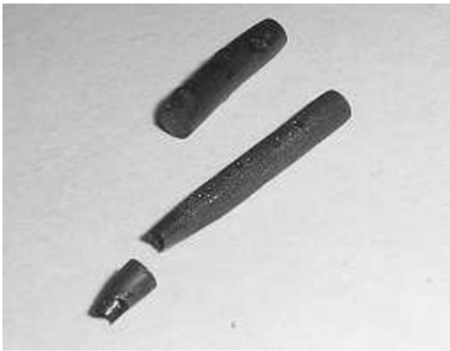

Figure 4.
Unpolished glassy carbon samples obtained from ammoniacal bakelite after the carbonization process.

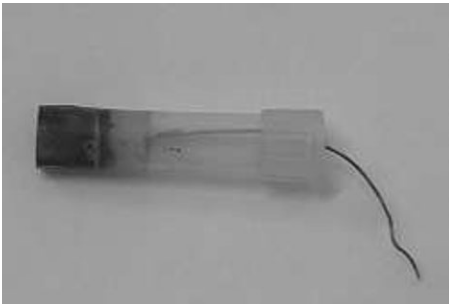

Figure 5.
Final homemade glassy polymeric carbon device obtained for voltammetric applications.

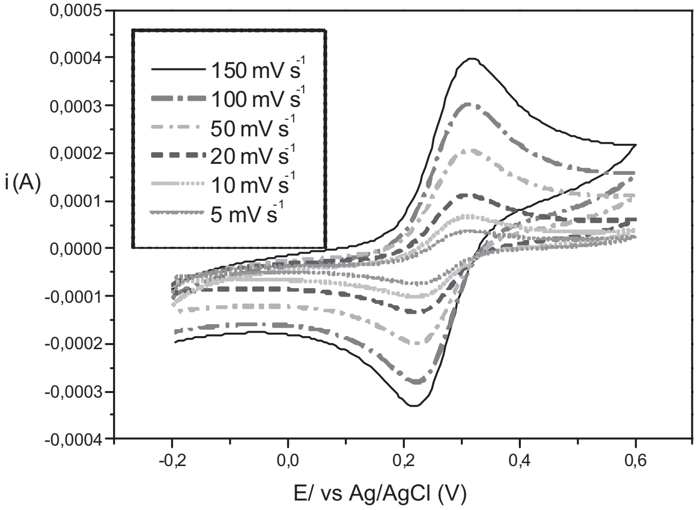

Figure 6.
Successive cyclic voltamograms obtained for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system, recorded at different scan rates. Potassium chloride 1.0 mol L^{-1} aqueous solution containing $K_3[Fe(CN)_6]$ 1.0 10^{-2} mol L^{-1}.

The voltammograms obtained in a situation of constant concentration and different scan rates are depicted in Figure 6.

Analysis of these voltammograms indicates that both peak currents increase linearly in relation to the square root of the scan rate, and that the relation i_{ap}/i_{cp} is close to unity. These results obey the Randles-Sevcik equation[15] and are in accordance with the results expected for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ reversible electron transfer redox system with a diffusion-controlled mass transport. Furthermore, the peak potential values did not depend on the applied scan rates, which is another important characteristic of

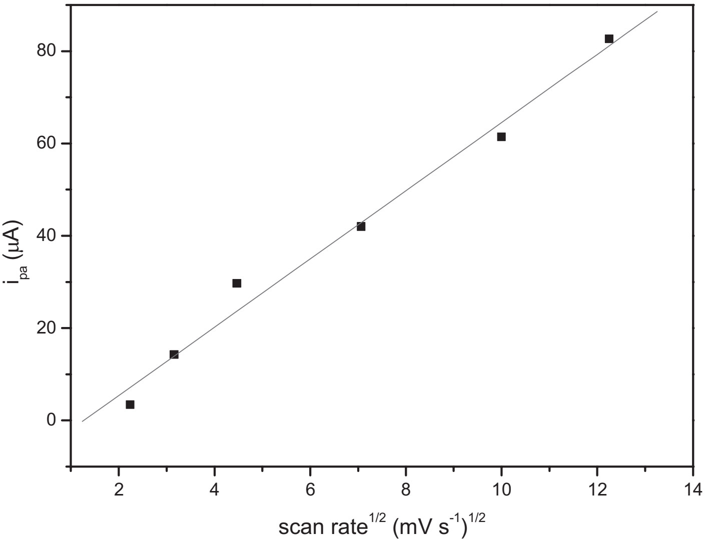

Figure 7.
Investigation of the effect of the scan rate on the magnitude of the anodic peak current.

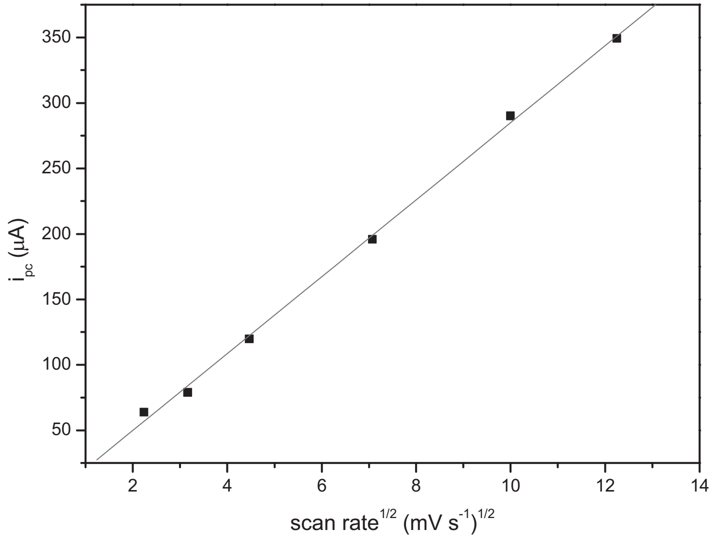

Figure 8.
Investigation of the effect of scan rate on the magnitude of the cathodic peak current.

reversible systems. In addition, the observed differences between cathodic and anodic peak potentials were close to 60 mV, confirming the reversibility of this one-electron transfer system.

The linearity of the peak currents in relation to the square root of the scan rate is presented in Figures 7 and 8. Linear correlation coefficients of 0.9991 and 0.9994 were obtained for equations $|i_{cp}| = 8.91\ 10^{-5} + 2.94\ 10^{-5}\ v^{1/2}$ and $|i_{ap}| = 1.11\ 10^{-6} + 2.64\ 10^{-7}\ v^{1/2}$, being $|i_{ap}|$and $|i_{cp}|$ the modules of anodic and cathodic peak currents, respectively.

Figure 9 presents the dependence of peak currents on analyte concentration, by

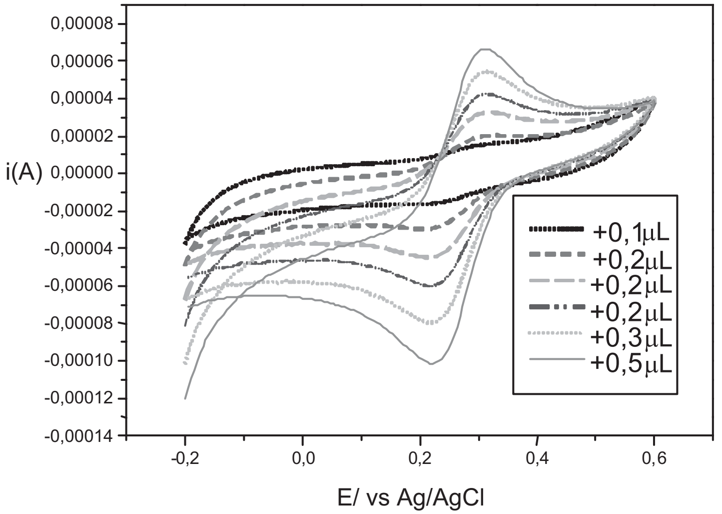

Figure 9.
Cyclic voltamograms obtained for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system, recorded at different $K_3[Fe(CN)_6]$ concentrations. Potassium chloride 1.0 mol L^{-1} aqueous solution as supporting-electrolyte. $v = 100 mV\ s^{-1}$.

means of voltammograms obtained at different concentrations. The linearity of the peak currents in relation to the $[Fe(CN)_6]^{3-}$ concentration is shown in Figures 10 and 11. Linear correlation coefficients of 1.0000 and 0.9997 were obtained for equations $|i_{cp}| = 2.52\ 10^{-6} + 0.01[\text{analyte}]$ and $|i_{ap}|$ and $= 4.26\ 10^{-6} + 0.01[\text{analyte}]$ respectively. This experiment is a classical study in electrochemistry, and consists of a simple and well-known methodology. The results check the

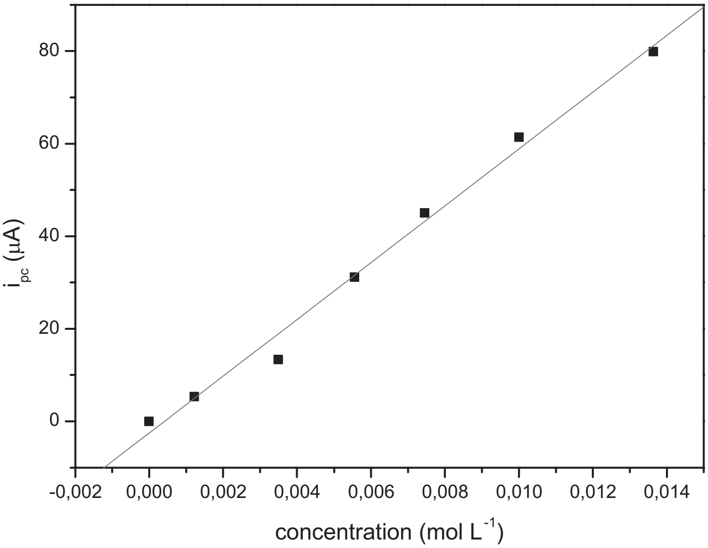

Figure 10.
Investigation of the analytical curve for $[Fe(CN)_6]^{3-}$ species using the cathodic peak current.

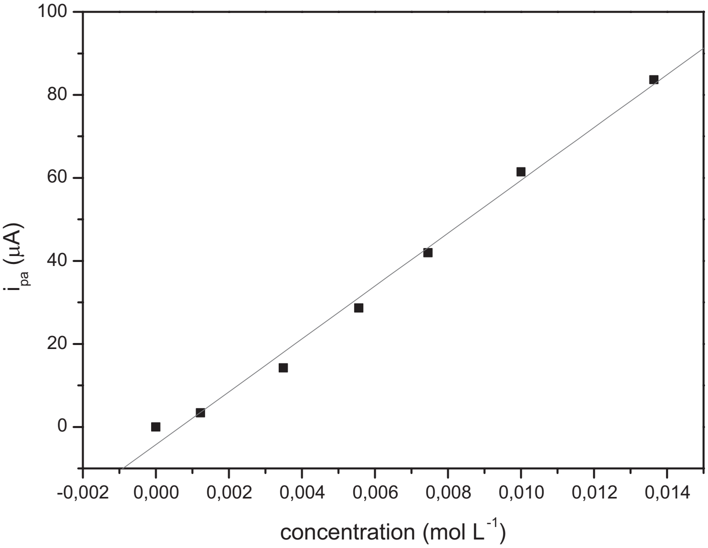

Figure 11.
Investigation of the analytical curve for $[Fe(CN)_6]^{3-}$ species using the cathodic peak current.

reversibility of the Fe^{3+}/Fe^{2+} redox process occurring in the electrochemical system:

$$Fe^{III}(CN)_6^{3-} + e \rightarrow Fe^{II}(CN)_6^{4-} \qquad (1)$$

$$Fe^{II}(CN)_6^{4-} - \rightarrow Fe^{III}(CN)_6^{3-} + e \qquad (2)$$

Equation (1) represents the electrode processes for cathodic current, which increases until the $Fe^{III}(CN)_6^{3-}$ concentration at the electrode surface approaches zero. At this point, the cathodic current reaches its maximal value. Then, it decreases because the conversion of $Fe^{III}(CN)_6^{3-}$ into $Fe^{II}(CN)_6^{3-}$ is now strongly limited by the mass transport of electroactive specie to the electrode/solution interface. Equation (2) corresponds to the anodic current, which increases until the surface concentration of $Fe^{II}(CN)_6^{4-}$ approaches zero. It decays thereafter, as the solution surrounding the electrode is depleted of $Fe^{II}(CN)_6^{3-}$.

Conclusion

The proposed methodology for production of glassy polymeric carbon electrodes in laboratorial scale from their precursor resins (bakelite) calls for shorter period treatment (3.5 days), being faster and more economical than the routes presented in the literature (5–7 days). It was also possible to check the experimental advantages in using ammonium hydroxide as catalyst, once no alkaline residue was observed in the final product. Additionally, the electrochemical results obtained in this work demonstrated that the homemade devices can be applied in voltammetric modalities, once it was possible to check the reversibility of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox system. In conclusion, we have prepared a glassy polymeric carbon in a faster and more economical way, while maintaining the electrodic properties of the final material, which is a great advance in the field of carbonaceous electrodes synthesis.

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