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Effect on electrochemistry of hexacyanoferrate at carbon fibers after pretreatment with titanium chloride

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Abstract

A simple and fast method for carbon fiber activation is proposed to improve the electrochemical activity of electrodes made of carbon fibers. A layer of titanium (IV) oxide was coated on the carbon fiber surface, using titanium tetrachloride dissolved in carbon tetrachloride. The fibers were treated for 1 h at room temperature followed by hydrolyzation of the remaining chloride and finally dried. The electrochemical activity was evaluated by means of cyclic voltammetry. The titanium oxide layer dispersed onto the fiber surface was very stable and a large improvement in the electrochemical response was observed. The electrochemical response obtained for hexacyanoferrate was similar to that observed for reversible systems. The reproducibility of the proposed method was very good and no significant change in the electrochemical response was observed between equally prepared carbon fibers. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hexacyanoferrate; Microelectrode; Ultramicroelectrode

1. Introduction

In recent years carbon fibers have been widely explored in electrochemical studies [1–3], mainly for microelectrode and ultramicroelectrode construction [3,4]. Microsensors present great advantages due to their efficient radial mass transport properties leading to high sensitivity, short response time allowing for fast scanning, low ohmic drop and measurements in solutions with high resistivity [2]. Another important advantage displayed by carbon fibers as micro and ultramicroelectrodes is their high surface area containing oxygen groups, which allow modification possibilities [1,5,6]. This fact can be used to improve further the selectivity and sensitivity of such microsensors [7,8].

Although carbon fibers have several advantages compared to macrosized ones, their pre-treatment is often necessary to enhance the reproducibility and electrochemical response [9]. There are several methods of pre-treatment described in the literature [3,10–14], the most used being various electrochemical procedures [3,11,13,15]. Many of them require complex steps, a long preparation time and generally are not very reproducible [16]. Depending on the fabrication process of the carbon fibers, problems with reproducibility are critical [17]. In the present work a new method for the treatment of carbon fiber electrodes is proposed, resulting in highly reproducible carbon fiber electrodes with enhanced electrochemical responses. The proposed fast immobilization of titanium (IV) oxide onto the carbon fibers is presented in detail and its effect on the electrochemical signal is also discussed.

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2. Experimental

2.1. Reagents and materials

PAN type T-sized 800 carbon fibers with 8 μm diameter were acquired from Toray Industries INC. Tokyo Japan. Titanium tetrachloride (99,9% Aldrich, Milwaukee, WI), CCl_4 and $K_4Fe(CN)_6$ (Merck–Darmstadt Germany), KNO_3 (Nuclear-São Paulo Brazil) and KCl (Vetec, São Paulo Brazil), the latter three all of analytical grade, were used.

2.2. Electrochemical measurements

A classical electrochemical system with three electrodes (a saturated calomel as the reference, a platinum wire as the counter and about 10 carbon fibers (5 mm length) as the working electrodes, respectively), was used throughout this work. A potentiostat model MQPG01 from Microquímica (Florianópolis, Brazil) connected to a PC microcomputer was used for potential control and data acquisition. The solutions were deoxygenated with nitrogen before use.

2.3. Scanning electron micrographs

Scanning electron micrographs (SEM) of untreated and treated carbon fibers were obained using a scanning electron microscope ISI Model 100 A (Santa Clara, CA).

2.4. Carbon fiber treatment

First a bundle of carbon fibers was immersed in distilled water for 10 min and these wet fibers were dipped into a titanium tetrachloride solution (diluted in carbon tetrachloride 99.9% purity) for 60 min in concentrations of 1:20, 1:10, 1:5, 1:2, 1:1 and 1:0 (v:v). In a following step the carbon fibers were dried in a thermostated oven at 70°C for 1 h, and the remaining chloride was carefully hydrolyzed with a large amount of bidistilled water [18]. Finally, the carbon fibers were dried again in the thermostated oven at 70°C for 1 h.

3. Results and discussion

Fig. 1 shows cyclic voltammograms obtained in 0.1 M KCl solution for untreated carbon fibers (A), treated for 30 min (B), and treated for 60 min (C) with concentrated titanium tetrachloride. The cyclic voltammogram obtained with untreated fiber presents a lower capacitive current, indicating that the surface area is smaller, however, when the carbon fiber is treated the capacitive current increases, suggesting an increase in the surface area or that the double layer is affected by the presence

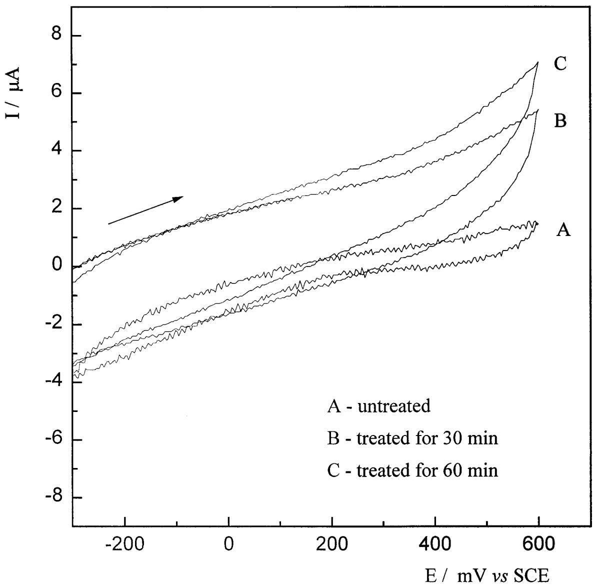

Fig. 1. Cyclic voltammograms obtained with untreated (A) and treated (30 min (B), 60 min (C) with undiluted $TiCl_4$) carbon fiber electrodes at a scan rate of 100 mV s^{-1}, in 0.1 M KCl solution. The scanning was started at −400 mV versus SCE.

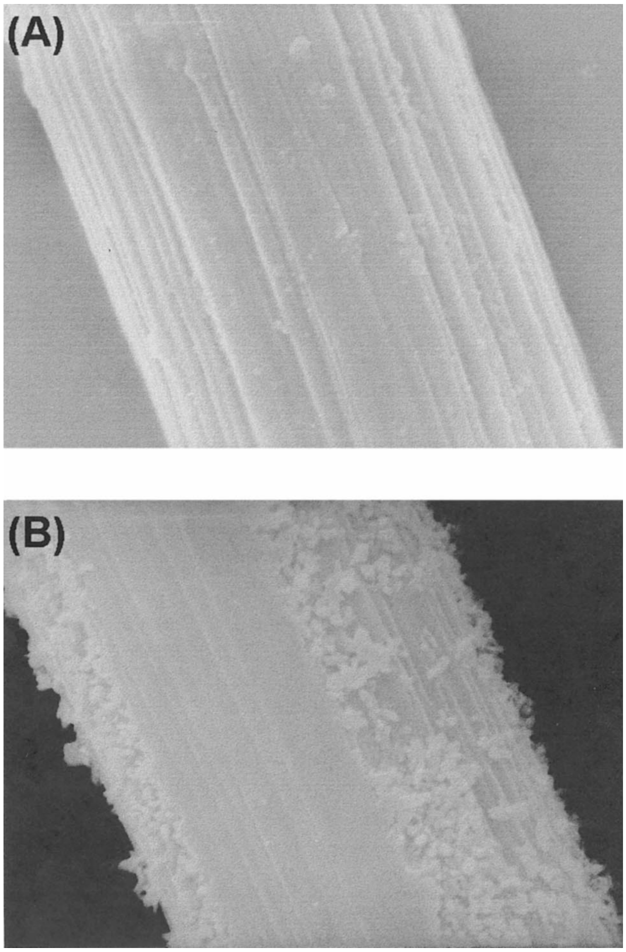

Fig. 2. SEMs of untreated (A) and treated for 60 min (B) (with undiluted $TiCl_4$) T-800 sized fibers. Magnification × 15000.

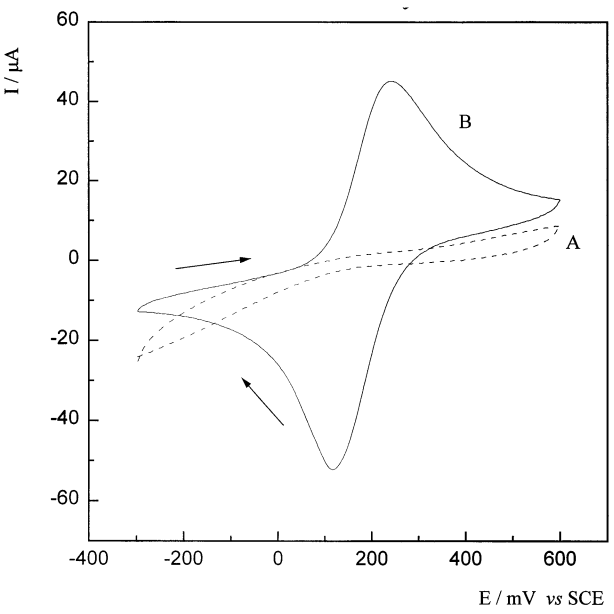

Fig. 3. Cyclic voltammograms obtained with untreated (A) and treated for 60 min with undiluted $TiCl_4$ (B) carbon fiber electrodes at a scan rate of 100 mV s^{-1}, in 0.1 M KCl solution and in the presence of 1.0×10^{-3} M hexacyanoferrate (III).

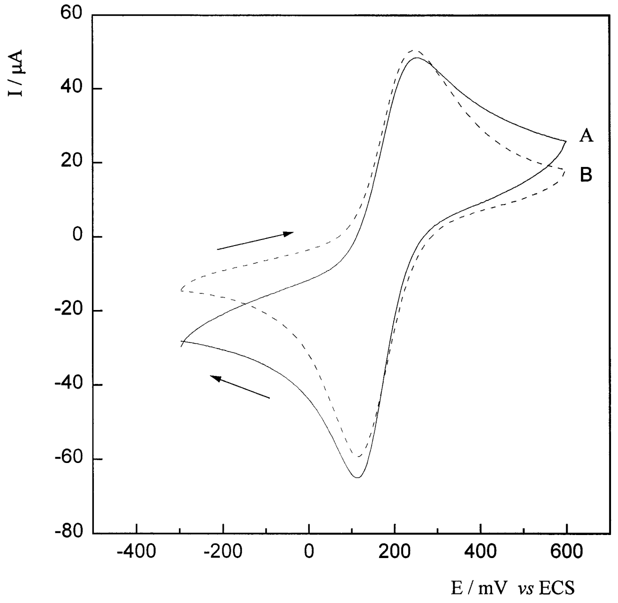

Fig. 4. Cyclic voltammograms obtained with treated (30 min (A) and 60 min (B) with undiluted $TiCl_4$) carbon fiber electrodes at a scan rate of 100 mV s^{-1}, in 0.1 M KCl solution and in the presence of 1.0×10^{-3} M hexacyanoferrate (III).

of the titanium oxide. The carbon fibers after the titanium tetrachloride treatment looked very similar; no visual changes could be observed. However, from scanning electron micrography (Fig. 2) obtained for naked (2A) and treated with concentrated titanium chloride for 60 min (2B) carbon fibers it is possible to observe an increase in the surface area. The naked carbon fiber is smooth while the treated carbon fiber has some flakes, which should be titanium dioxide aggregates dispersed onto the fiber, thus increasing its surface. The diameter of the fiber increased slightly between 5 and 10% indicating that a significant amount of titanium dioxide is deposited onto the carbon fiber as a dispersed layer.

A great electrochemical difference between treated and untreated carbon fibers can be verified by the cyclic voltammograms shown in Fig. 3, reflecting the behavior of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system, obtained with

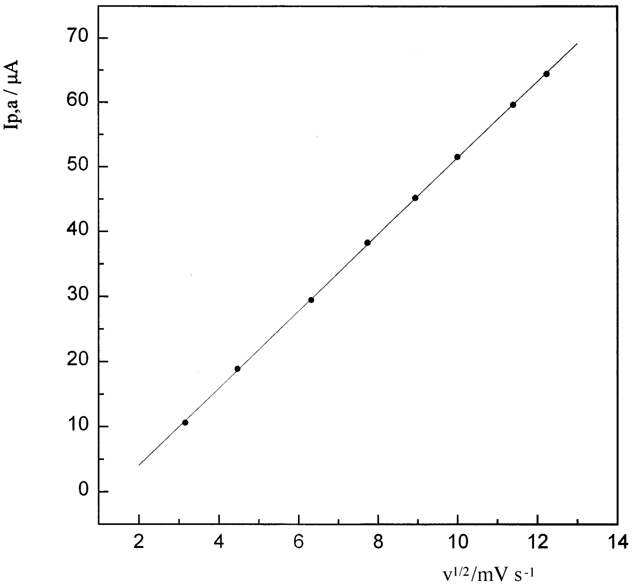

Fig. 5. Dependence of the peak current on the square root of the scan rate, obtained in 0.1 M KCl solution and in the presence of 1.0×10^{-3} M hexacyanoferrate (III) for a carbon fiber treated for 60 min with undiluted $TiCl_4$.

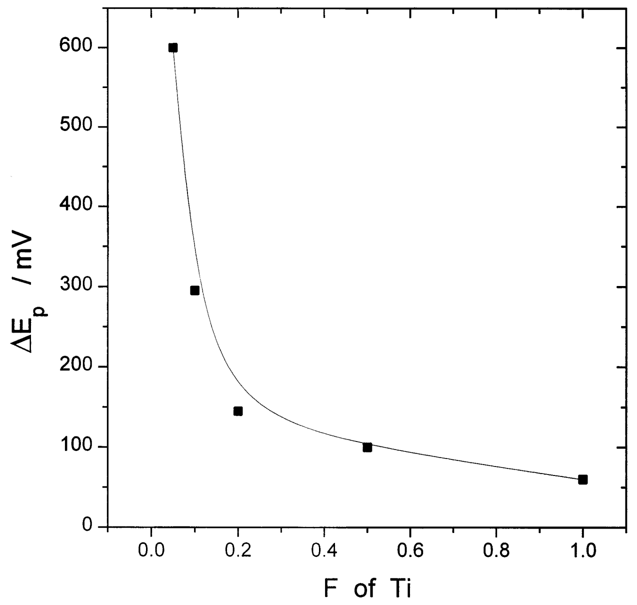

Fig. 6. Dependence of the peak separation on the molar fraction (*F*) of titanium chloride used for the pretreatment of carbon fibers for 60 min. Scan rate of 50 mV s^{-1}, pH = 6 and 1.0×10^{-3} M hexacyanoferrate (III) solution.

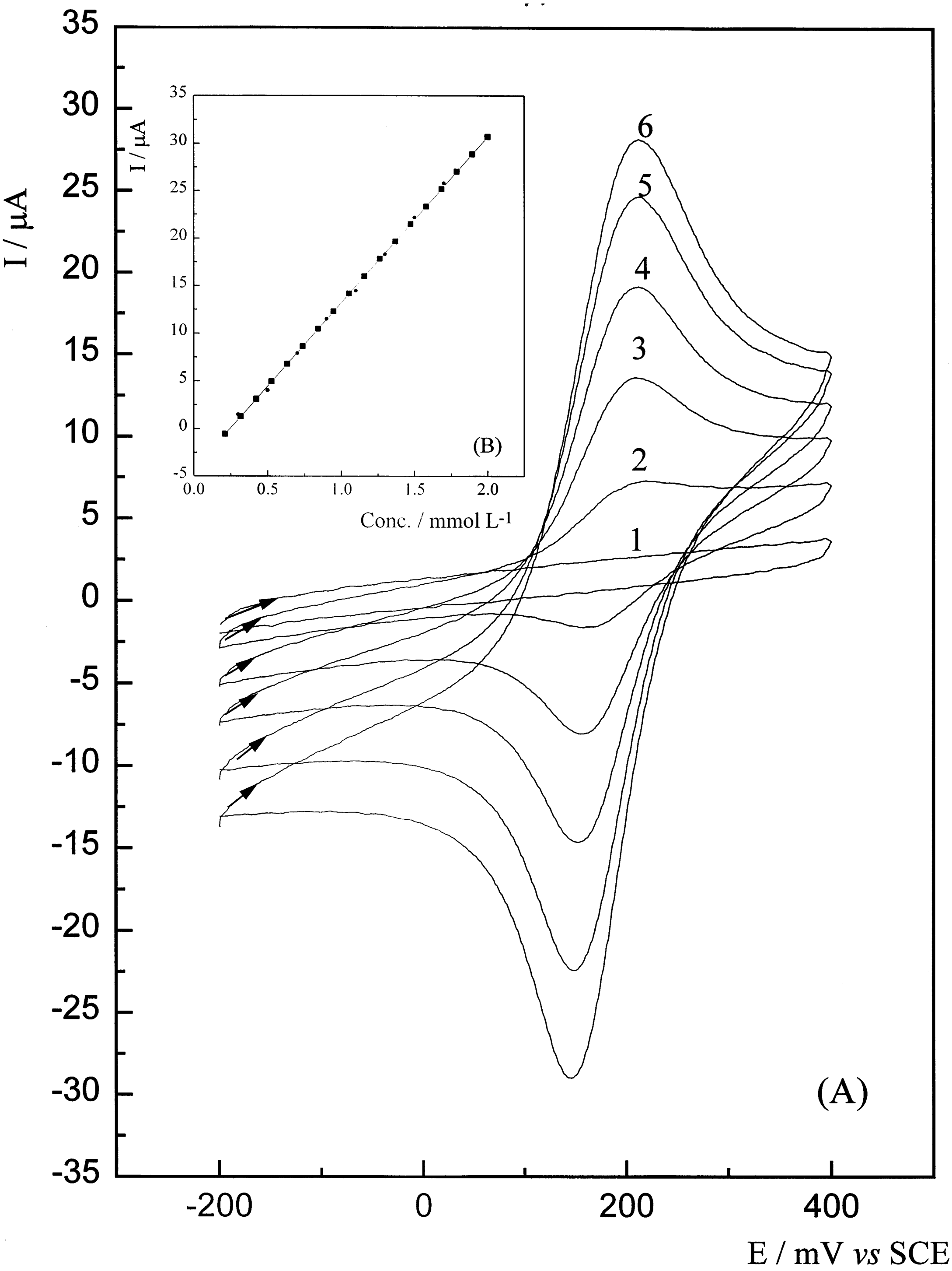

Fig. 7. Cyclic voltammograms obtained carbon fibers treated with undiluted $TiCl_4$ for 60 min in different concentrations of hexacyanoferrate (III) at a scan rate of 20 mV s^{-1} at pH = 6. (1) Blank, (2) 0.2, (3) 0.5, (4) 0.7, (5) 1.0 and (6) 1.3 M hexacyanoferrate (III)

a solution of 1.0×10^{-3} M $[Fe(CN)_6]^{3-}$ in 0.1 M KCl. For the untreated carbon fibers, a very low current was observed, indicating a poor electroactivity. In contrast, when fibers treated with titanium chloride solutions in concentration higher than 1:5 (v:v), were used, an enhanced current was observed for the electrochemistry of $[Fe(CN)_6]^{3-}$ evaluated as the mean of the anodic and cathodic peak potentials (formal potential $E^{0'} = 182$ mV vs SCE). This formal potential value is very similar compared to those observed when a platinum or glassy carbon electrode was used [18]. The ratio of current peaks (cathodic and anodic) was about 1.0 and the

Table 1
Formal potential (E^0) obtained for hexacyanoferrate in solutions with different pHs using a pretreated carbon fiber as the working electrode, $[Fe(CN)_6]^{3-} = 1.0 \times 10^{-3}$ M at a scan rate of 20 mV s^{-1}

pH	$E^{0'}$ mV versus SCE
2.2	229
3.0	194
4.3	188
5.1	181
6.0	182
7.2	190
8.2	204

separation of the peak potentials was 62 mV for a sweep rate of 100 mV s^{-1}. This behavior indicates that the redox process on the treated carbon fibers is similar to that observed for reversible systems [18]; the same behavior was observed with KNO_3. Although a higher capacitive current is observed for the fibers treated for 60 min (Fig. 1(C)) than for 30 min (1B), in the presence of the electroactive species, an improved response is observed, as shown in Fig. 4. This behavior suggests that the titanium oxide layer formed onto the carbon fiber surface for 60 min improves the electrochemical characteristics compared with those obtained when the fiber was treated for 30 min. The linear dependence of the current as a function of the square root of the scan rate, shown in Fig. 5 and the invariance of both cathodic and anodic peak potentials with scan rates between 5 and 150 mV s^{-1}, suggests that the process is controlled by diffusion in a similar way as that observed for reversible systems [19] (note that the working electrode consisted of a bundle of ten carbon fibers clustered together). The use of more dilute titanium chloride solutions to avoid a drastic treatment of the carbon fibers was investigated and the effect is shown in Fig. 6. The peak separation for cyclic voltammograms obtained for ferrocyanide at 50 mV s^{-1} increases exponentially for more dilute solution than 1:5 (v:v) titanium chloride to carbon tetrachloride. This behavior suggests that the electroactivity of the carbon fiber is improved by using treatments with more concentrated titanium solutions.

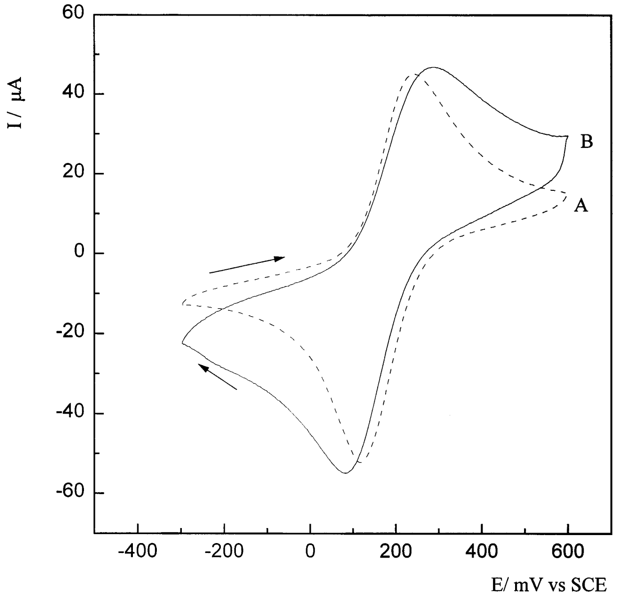

Fig. 8. Cyclic voltammograms obtained with treated carbon fibers after different immersion times: initially (A) and after 25 h (B), at a scan rate of 100 mV s^{-1}, in 0.1 M KCl solution and in the presence of 1.0×10^{-3} M hexacyanoferrate (III).

Fig. 7 shows cyclic voltammograms obtained with treated carbon fibers, with undiluted $TiCl_4$ during 60 min, in the presence of different concentrations of hexacyanoferrate. The linear relation obtained between the peak current and the concentration shows a good activity for electrochemical response. The peak potentials kept constant even in more concentrated hexacyanoferrate solution, indicating that there is no strong interaction or adsorption of electroactive species on the fiber surface.

The electrode showed interesting behavior concerning the pH of the solution, as is shown in Table 1. The formal potential was dependent on the solution pH, presenting the lowest value at a pH of about 5 while increasing for both lower and higher pH values. It is very interesting to compare this to the surface charge of hydrated titanium oxide, which presents an isoelectric point at a pH of about 5.6 [20]. The increase in the formal potential at a higher pH can be explained by the surface charge of the titanium oxide, which becomes negative and the interaction of the negatively charged species with the electrode surface is prejudiced. At a lower pH than 5, the formal potential is increased due to the protonation of the electroactive species in the reduced form, as normally observed for hexacyanoferrate in solution [21,22].

The characteristics of the film formed onto the carbon fiber surface modified with titanium chloride, such as resistivity and electrochemical activity, were stable for a long time, at least for three months, even in acid or neutral media, but in alkaline solution, i.e. in pH > 9, they showed rapid changes, probably due to the solubilization of the titanium oxide layer [23].

The stability of the modified electrode was tested many times (at least 500 times) over three months and no significant change was observed when stored at room temperature in a dry state. A small change in the peak shape was observed when the electrode was stored in an aqueous solution for two days, as shown in Fig. 8. However, when the electrode was dried again, it returned to its original response, showing a great stability of the titanium oxide film dispersed onto the carbon fiber surface.

4. Conclusions

The results obtained in this work show a new pretreatment procedure to make carbon fibers become more electroactive with good reproducibility. The great efficiency and sensitivity reached with this procedure show excellent potential for the preparation of carbon fiber electrodes in a reproducible form. Aspects such as stability, facility and simplicity of this procedure, besides the possibility of immobilizing new compounds onto the pretreated electrode surface make the procedure described very attractive for routine use. The sensitivity for other analytes of interest after the pretreatment is the subject of current investigations as well as the use of these $TiCl_4$ treated carbon fibers for the development of new sensors and biosensors.

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