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Use of the optical lithography in the development of disposable carbon based electrodes

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ABSTRACT. In this study, carbon-based electrodes for disposable use were constructed using the technique of optical lithography. The process consisted in the irradiation of UV light on a layer of photosensitive resin (SU-8 50) deposited on a substrate of PVC. The pattern obtained electrode was filled with carbon paste. The electrodes were characterized by cyclic voltammetric using the reversible system $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in KCl 0.1 mol L^{-1} and electrochemical impedance spectroscopy (EIS). The electrodes showed an $E°' = ½ (E_{pa} + E_{pc}) \approx 229 (\pm 2)$ mV *vs* SCE (n = 4), with $\Delta Ep \approx 235 (\pm 14)$ mV (n = 4). Other studies showed a linear behavior of the peak current (I_p) both anode and cathode with $v^{1/2}$, probably due to diffuse contribution and/or electron transfer kinetics of the reaction. These parameters are in accordance to with those obtained for screen-printed electrode described in the literature. The good results obtained show the suitability of the electrodes for analytical applications such as development of sensors.

Keywords: optical lithography, carbon-paste electrode, cyclic voltammetric.

Uso da litografia óptica no desenvolvimento de eletrodos descartáveis à base de carbono

RESUMO. No presente trabalho, foram construídos eletrodos a base de carbono para uso descartável utilizando a técnica de litografia óptica. O processo consistiu na irradiação de luz UV sobre uma camada de resina fotossensível (SU-8 50) depositada em um substrato de PVC. O molde de eletrodo obtido foi preenchido com pasta de carbono. Os eletrodos foram caracterizados por voltametria cíclica utilizando o sistema reversível $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ em KCl 0,1 mol L^{-1} e espectroscopia de impedância eletroquímica (EIE). Os eletrodos apresentaram um $E°' = ½ (E_{pa} + E_{pc}) \approx 229 (\pm 2)$ mV *vs* ECS (n = 4), com $\Delta Ep \approx 235$ ($\pm$ 14) mV (n = 4). Outros estudos mostraram um comportamento linear da corrente de pico (I_p) tanto anódica quanto catódica com $v^{½}$, possivelmente devido à contribuição difusa e/ou da transferência eletrônica na cinética da reação. Estes parâmetros estão em conformidade com os obtidos para eletrodos tipo screen-printed comerciais, descritos na literatura. Os bons resultados obtidos mostram a adequação dos eletrodos construídos para aplicações analíticas como no desenvolvimento de sensores.

Palavras-chave: litografia óptica, eletrodo de carbono, voltametria cíclica.

Introduction

The use of carbon based electrodes to electroanalytical applications has become very important due to the ability for employing such electrodes in the oxidation or reduction of organic and inorganic species (SVANCARA; ZIMA, 2011). The wide application of carbon based electrodes is mainly related owing to their reliability, low cost, low residual currents and low electrical resistance (QUERESHI et al., 2009). Carbon can be found in nature in several forms that can be specifically applied in electrochemistry, such as carbon fibers, glassy carbon, carbon paste and other composites. Among all these carbon platforms to the construction of electrodes, carbon paste is the most employed since it presents important operational characteristics. Carbon paste electrodes exhibit low faradaic current, wide potential range for operation, low reactivity, easily renewable surface and suitability to the construction of relatively small electrodes. Apart from these, the application of carbon paste electrodes is widely versatile, thus enabling their application in electroanalytical. Unlike most of solid and compact electrodes, carbon paste can be chemically modified not only on the surface, but also in its internal structure. Thereby, allowing the co-immobilization of biological species such as enzymes, antibodies, co-factors, mediators and stabilizing agents forming an electrode configuration without the use of further reactants during the measurements (SVACARA et al., 2009). Carbon pastes are usually prepared by mixing graphite and mineral oil. The oil acts as an agglutinant agent that holds the graphite powder on the electrode and fills cavities formed between the graphite particles, thus isolating the graphite from the direct contact with aqueous solutions (SVANCARA et al., 2011). The main disadvantage of the mineral oil is the structural instability of the semi-solid matrix.

The numerous strategies to chemically modify carbon paste electrodes opens up several possibilities to apply them in the fabrication of electrochemical sensors. However, the regeneration of the surface of the electrodes is the greatest challenge to the development commercial electrodes. In most of cases, neither physical nor chemical treatments are efficient enough to regenerate the surface of the electrodes. An alternative to this problem is the use of disposable electrodes, thereby avoiding the need of regeneration of the electrodes surface (VILLABA; DAVIS, 2008).

The screen-printing method is a well established technology to large scale production of devices such as capacitors and resistors, and it has been also applied in the fabrication of disposable electrodes (DOMINGUEZ-RENEDO et al., 2007). In addition it is important to take into account that the screen-printing method can be also combined with microfabrication techniques as optical lithography. Specifically, the optical lithography is a technique used to produce patterns in micro/nanoscale into the integrated circuits. The process of lithography basically consists in transferring well defined geometric patterns written in a mask to a substrate utilizing UV-visible (UV-vis) light (HARRY; JAN, 2009; NOBUJI, 2009). That is, during the lithography the substrate is covered by spin-coating with a specific photosensitive resin, which is also known as photoresist. The thickness of the photoresist is controlled by the speed of the spinner. After the spinning process, the substrate is submitted to a pre-bake (usually in hot-plate) process to evaporate the solvents that compose the photoresist and increase its hardness. The final step of the lithographic process is then performed in a mask-aligner, in which the substrate coated with the photoresist is aligned against a lithographic mask containing the patterns to be transferred to the substrate. The masks are made of quartz and can be placed in direct contact or semi-contact with the substrate. After the mask has been aligned in relation to the substrate, the UV light in a specific wavelength is turned on and the mask act as a filter, allowing the light to pass in some regions and blocking it in others. As a result, the photoresist covering the substrate is exposed to UV light in some parts, but not in others because the patterns of the mask block the light (HARRY; JAN, 2009; NOBUJI, 2009). Two types of photoresists can be used in the lithographic process, i.e., positive or negative resins. Thus, depending on the photoresist, the areas exposed to the UV light can become harder as is the case of negative photoresists or soluble in certain solvents (positive photoresists). This process allows the patterns of the mask to be transferred to the substrate (WILLIAMS; WANG, 2004).

Herein, we describe studies using optical lithography to produce disposable electrodes in PVC substrates. The process is based on the exposure of a PVC substrate coated with a photoresist and in direct contact with a mask to the UV light in a certain wavelength. During the exposure process, photochemical reactions occurred in the photoresist and a template to fabricate disposable electrodes was produced. The electrodes were characterized employing the cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques.

Material and methods

Procedure to fabricate the pattern of the disposable electrodes

a) Designing the electrodes in the optical mask

The electrodes were designed using the software CorelDraw® versão 8 (Microsoft), following an electrode configuration usually employed in the screen printed technique. The designed electrode was then printed in a PVC platform. For the fabrication of the electrodes, a PVC substrate was also employed.

b) Coating the substrate with photoresist and cure

For the lithographic process, the negative photoresist SU-8 50 (Microchem Corp., Massachusetts, USA) was used. Initially, 2 mL of SU-8 50 were applied on top of the PVC substrate, which was then spun (Headway Research Inc.) at a certain speed and time. The thickness of the SU-8 50 layer obtained using the following program: 500 rpm/10 seconds; 1000 rpm/30 seconds, was 200 μm. Sequentially, in order to remove the solvents in the photoresist, the PVC substrate was submitted to the pre-bake process. This step was carried out in a hot-plate employing the following temperature and times: 60°C/2 minutes; 95°C/20 minutes. Afterwards, the substrate was left resting per 1 hour in the dark.

c) Exposure to UV light and development of the photoresist

The next step consisted in set the substrate and the optical mask into a mask aligner KSM model MJB 3 with a mercury lamp (900 W) and expose both to the UV light (λ = 405 nm) per 70 seconds. The exposure of the photoresist to the UV light changed its chemical structure and the exposed parts became harder, while the non-exposed areas were vulnerable to the removing action of the developer.

Before the development step, the PVC substrate was led to a second process of bake, also called post-bake. In this step, the substrate was left on a hot-plate following the temperatures and times described in sequence: 60°C/1 minute; 95°C/15 minutes; 65°C/3 minutes. Then, the development was carried out by immersing the substrate into a solution of 1-metoxyl-2-propyl acetate (Microchem Corp., Massachusetts, USA) for 5 minutes. In sequence, the excess of developer was removed by washing the surface of the substrate with iso-propyl alcohol and the substrate was dried with N_2. After this step, well defined trenches were formed in the PVC substrate. These trenches were then filled with carbon paste and the electrodes were produced.

d) Electrochemical characterization

The electrochemical characterization of the produced electrodes were performed employing a potentiostat PGSTAT 30 Autolab (Eco Chimie B.V., Utrecht, Netherlands) connected to a PC with the softwares GPES and FRA to control the potential, data acquisition and treatment. The experiments were conducted using a conventional electrochemical cell with three electrodes, where a saturated calomel electrode (SCE) was employed as reference electrode and a platinum wire was used as counter-electrode. The produced paste carbon electrode was employed as a working electrode presenting a geometrical area of 0.16 cm^2. The solution used to characterize the electrodes was composed of 0.1 mol L^{-1} potassium ferricyanide ($K_3Fe(CN)_6$) and potassium ferrocyanide ($K_4Fe(CN)_6$) in 1 mol L^{-1} KCl. The resistance of the solution was obtained from EIS experiments in a frequency range of 0,01 Hz – 100 kHz.

All the employed reactants were of analytical degree (Merck or Sigma-Aldrich) and were used without previous purification. The solutions were prepared in Milli-Q water 18.2 MΩ.cm (Millipore Corporation USA).

Results and discussion

Figure 1 depicts a scheme of the electrode fabrication by optical lithography. This technique is based on the use of photosensitive resins that can form films as thick as a few millimeters by employing multiple steps of deposition. Because of its chemical stability, the SU-8 photoresist has been widely employed in the microfabrication processes. The SU-8 photoresist is an epoxyl resin of high viscosity based on diglycidyl ether of bisphenol A that when exposed to the UV light becomes soluble in the developer due to the break of polymeric chains. Thus enabling the removal of these areas during the step of development.

During the experiments, it was observed that in trenches with thickness higher than 200 μm it was difficult to remove the excess of SU-8 in the step of development. Based on this, some general parameters of the lithography such as volume of photoresist to be deposited in the substrate, time of exposure to UV light, time of development and time and temperature of bake were previously adjusted to obtain trenches with walls no higher than 200 μm. Measurements using a micrometer demonstrated that a single step of deposition of SU-8 and spin-coating yielded a layer with thickness of about 150 μm.

The carbon paste used to fill the trenches consisted only of graphite powder and some drops of mineral oil in a proportion of 10 mg/drop of oil. Several configurations for the electrode were previously tested. Figure 1b shows an illustration of the final configuration of the electrode with its dimensions optimized for further electrochemical characterization.

The produced electrode was characterized by cyclic voltammetry using a solution containing 0.1 mol L^{-1} of the redox pair $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in 1.0 mol L^{-1} KCl in a potential range from -0.2 a 0.8 V *vs* SCE. The choice of this solution with $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ was based in the well known electrochemical characteristics of this redox pair. The oxidation/reduction of these species is strongly influenced by the surface of the electrode, which opens up the opportunity to gain information about the solid/liquid interface. Moreover, this redox pair exhibits a reversible kinetics, thus allowing comparison of these results with other obtained in the same conditions in a glassy carbon electrode that is well established in the literature. The following reactions take place on the electrode when a potential of around 358 mV (standard potential) is applied:

$$Fe(CN)_6^{3-} + e^- \longrightarrow Fe(CN)_6^{4-} \quad \text{(reduction)}$$

$$Fe(CN)_6^{4-} \longrightarrow Fe(CN)_6^{3-} + e^- \quad \text{(oxidation).}$$

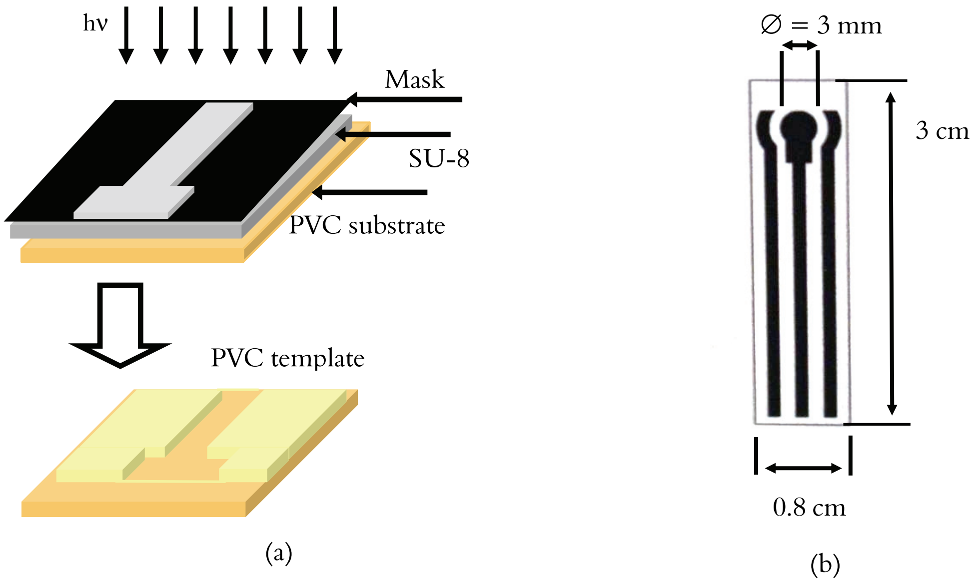

Figure 1. (a) Schematic illustration for the fabrication of the template to produce electrodes by optical lithography. (b) Final configuration of the obtained electrode with the dimensions optimized.

According to Nicholson and Stain's (1964) theory, the parameters such as cathodic (I_{pc}) and anodic (I_{pa}) peak current and cathodic (E_{pc}) and anodic (E_{pa}) peak potential are used to characterize the kinetics of a redox pair. Figure 2 shows the cyclic voltammogram of a disposable paste carbon electrode obtained at 20 mV s^{-1} in 1 mol L^{-1} KCl. As it can be seen, the redox process of the pair $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ is not completely ideal at low voltage scan. The voltammogram reveals a well defined pair of current peaks at +0.42 V (anodic peak) and +0.13 V (cathodic peak). Taking into account that $\Delta Ep \approx 235$ (± 14) mV (n = 4), which is above a monoelectronic system, the curves indicate a quasi-reversible electronic transfer (BARD; FAULKNER, 1981). The values of ΔEp found for commercially available printed electrodes characterized in the same conditions were 416 a 470 mV (MORRIN et al., 2003). This behavior can be attributed to several factors such as the electrical resistance of the electrode and the diffusion processes of the redox pair on the electrodes surface, once the charge transfer resistance measured by EIS demonstrated a value of 201.2 (± 94,9) Ω for n = 4.

Figure 3 shows the cyclic voltammograms of the carbon paste electrode in different voltage scans for the system $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$. The peak potential extracted from the curves shows that ΔE_p increases with the increase of the voltage scan (data not shown) indicating a quasi-reversible process on the electrode surface. The apparent redox potential was taken from the voltammograms measured at relatively low voltage scan and the valued obtained was $E°' = \frac{1}{2}(E_{pa} + E_{pc}) \approx 229$ (± 2) mV / ECS (n = 4). This value is in agreement with values reported in the literature (KISSINGER; HEINEMAN, 1983).

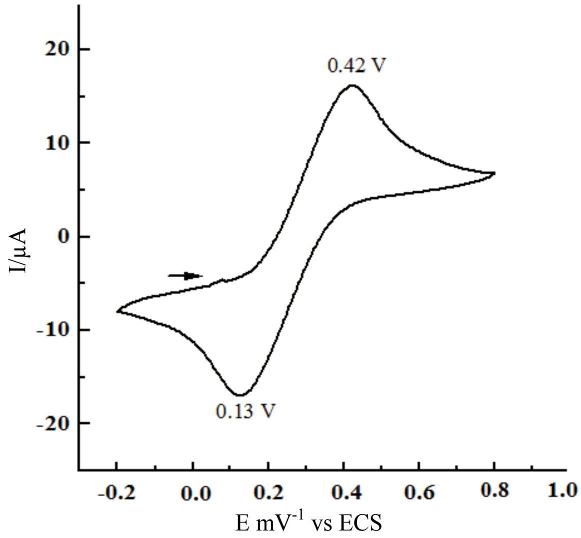

Figure 2. Cyclic voltammogram of the paste carbon electrode fabricated by optical lithography. The solution used for the measurements was composed of 0.1 mol L^{-1} of the redox pair $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in 1 mol L^{-1} KCl, v = 20 mV s^{-1}.

Figure 4 shows the dependence of the anodic and cathodic current peaks as a role of the square root of the voltage scan. As observed, the I_p for anodic and cathodic currents presents a linear behavior as a function of $v^{1/2}$. The linear dependence is mainly based due to the diffuse contribution of the redox pair and/or due to their electronic transfer on the electrode (BARD; FAULKNER, 1981).

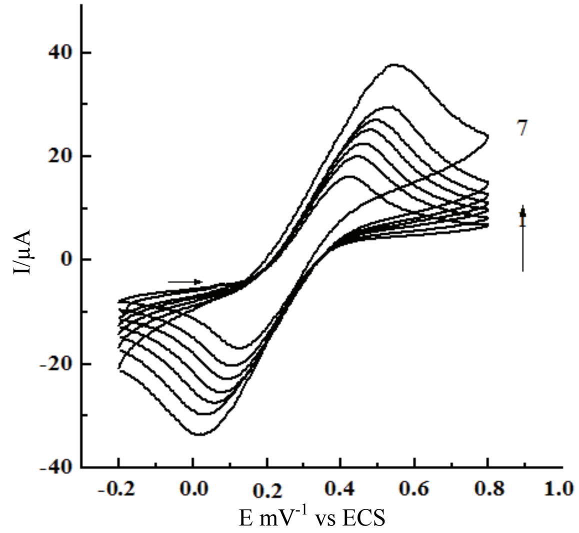

Figure 3. Cyclic voltammograms of the carbon paste electrode in 0.1 mol L^{-1} of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and 1 mol L^{-1} KCl at different voltage scans. The numbers 1-7 correspond to 20, 30, 40, 50, 60, 75 e 100 mV s^{-1}, respectively.

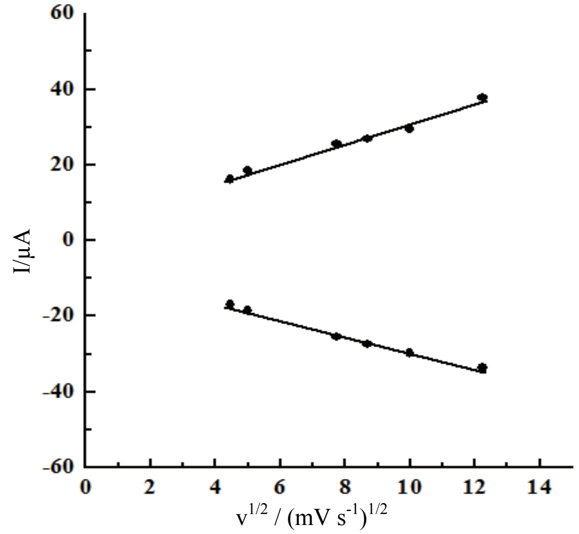

Figure 4. Dependence of the anodic and cathodic current peaks versus $v^{1/2}$ for the redox pair of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in 1 mol L^{-1} KCl for the carbon paste electrode.

The value found for the heterogeneous rate constant of electrons transfer (k_0) of the redox pair $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in the paste carbon electrode fabricated by the lithographic method was also in agreement with that for the glassy carbon electrode. The values of k_0 found from the Tafel curves ($\ln|j| \times \eta$) for the paste carbon electrode and for the glassy carbon electrodes were 2.23×10^{-2} cm s^{-1} and 5.9×10^{-2} cm s^{-1}, respectively. Data from the literature for carbon printed electrodes present k_0 with magnitudes from 1.7×10^{-5} to 4.87×10^{-5} cm s^{-1} (MORRIN et al., 2003). Our results are in satisfactory agreement with the data from the literature and suggest that the produced carbon paste electrodes can be applied in the development of electrochemical sensors.

Taking into that these electrodes are disposable and can be produced in large scale by the lithographic method, the approach described here represents an advance to the field, since usual problems as contamination with the electrochemical sensors can be avoided. In addition, by changing the configuration of the masks, electrodes with different geometries can be produced. Moreover, the good analytical performance of the paste carbon electrodes suggest that these electrodes could be also miniaturized and integrated into small and portable devices that are inexpensive and suitable for field applications.

Conclusion

In this work we presented a methodology based on optical lithography to produce from simple tools, disposable carbon paste electrodes. The electrochemical characterization of the electrodes using the redox pair $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ demonstrated that the electrochemical parameters extracted from cyclic voltammograms for these electrodes were superior than those obtained with commercially available printed electrodes.

The electrodes produced by lithography demonstrated some key features as low cost of production and versatility for handling. Furthermore, the lithographic technique allows other kind of configurations of electrodes that can be applied in different fields to be produced in large scale.

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