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Controlled Electrochemical Pretreatment of Glassy Carbon Electrodes. Its Performance on the Electro-oxidation of Aromatic Amines.

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Eletrodos de carbono vítreo (ECV) são caracterizados pela dificuldade experimental de se estabelecer uma relação entre a sua estrutura superficial e os parâmetros termodinâmicos de adsorção ou de cinética de transferência de elétrons (TE). Geralmente, os métodos de polimento afetam a cinética de TE, e os pré-tratamentos eletroquímicos em meio aquoso ácido levam a um aumento na cinética de TE e na capacidade de adsorção de alguns substratos. Neste trabalho, usamos um método de polimento com um pré-tratamento eletroquímico controlado em meio ácido para estudar os efeitos na adsorção e cinética de oxidação de N,N,N',N'-tetrametil-1,1'naftidina (TMN), usada como uma molécula teste. Não foi observado nenhum efeito cinético por voltametria de varredura linear, a não ser quando o ECV fosse polido sem ter sido submetido a nenhum outro tratamento. Um parâmetro eletroquímico, Q_O, relacionado à carga pseudocapacitiva das funcionalidades redox superficiais sobre o ECV, permitiram-nos predizer a quantidade de TMN que pode ser adsorvida pelo eletrodo.

Glassy carbon electrodes (GCE) are characterized by the experimental difficulty in establishing a relationship between their surface structure and the thermodynamic adsorption parameters or electron transfer (ET) kinetics. In general, the polishing procedures affect ET kinetics, and the electrochemical pretreatments in aqueous acid media lead to an increase in the ET kinetics and in the adsorption capacity of some substrates. In this work, we used a polishing procedure with a controlled electrochemical pretreatment in acidic media to study the effects on the adsorption and kinetics of oxidation of N,N,N',N'-tetramethyl -1,1'- naphthidine (TMN), used as a probe molecule. No kinetics effects were observed by linear sweep voltammetry, except when the GCE were polished without being submitted to any other treatment. An electrochemical parameter Q_O, related to the pseudocapacitance charge of the surface redox functionalities on GCE, enabled us to predict the amount of TMN that can be adsorbed by the electrode.

Keywords: *glassy carbon, amines oxidation*

Introduction

Glassy carbon electrodes (GCE) have been extensively applied in different areas of electrochemistry such as electroanalysis, electrosynthesis and electrochemical energy conversion, for two important reasons: their low cost and their wide potential window in aqueous and non-aqueous systems[1-5].

The variety of GCE surface treatments such as chemical, electrochemical, polishing and irradiation by laser[1], produce changes in the electrochemical performance of GCE, mostly due to the elimination of surface impurities, and structural and surface oxygen/carbon relation (O/C) changes. As a consequence, the background currents and the heterogeneous electron transfer standard rate constant (k^o) for redox reactions in solution can be affected[1].

However, there is no standard method of treatment that permits obtaining a surface with reproducible properties after exposure to air or to an electrolyte solution.

There are many procedures for obtaining electrodes with similarly defined characteristics. The methods can be divided into two main groups: physical and electrochemical. Generally, the physical methods are used first, followed by the electrochemical ones. The physical methods (polishing, ultrasonic cleaning) can change the distribution of edge and basal planes of microcrystallite structure, and can remove surface impurities, thus changing the surface activity. On the other hand, the electrochemical methods in acidic media usually remove the polishing impurities and change the distribution of redox species on the surface, with an increment in the background current and the ionic exchange with the solution.

After the application of a treatment the new electrode is controlled by measuring characteristic electrochemical parameters, such as the charge storage between two selected potential values, the k° of defined redox systems, or the adsorption capacity of selected substrates, mainly by measuring the energy of adsorption.

In a previous work[6] we reported a controlled electrochemical pretreatment (CEP) which involved cycling the electrode between - 0.5 and 1.8 V using 1 M sulfuric acid as the electrolyte solution. This treatment enabled us to obtain reproducible surfaces, with greater selectivity for the formation of the functionalities and behavior as a film modified glassy carbon electrode (MGCE)[6]. We used the same treatment[7] in the study of the electro-oxidation of N,N-dimethyl-1-naphthylamine (DMN). In an MGCE, DMN undergoes an electrochemical-chemical-electrochemical (ECE) reaction to give its oxidized dimer N,N,N',N'-tetramethy-l,1-naphthidine (TMN). The nature of the adsorption process and the characteristics of the electrode in the adsorbed state were studied in detail. The amount of adsorbed DMN was correlated with the degree of the modification of the electrode through an electrochemical parameter[7]. The adsorption of TMN follows Frumkin's isotherm ($\Delta G°_{298}$ = - 24.7 KJ/mol) with a repulsive interaction parameter (a = - 1.02).

In the present work TMN is used as a probe molecule and the degree of modification of the MGCE is correlated with the observed heterogeneous electron transfer standard rate constant ($k°_{obs}$). The charge transfer kinetics for TMN in acetonitrile (ACN) solution has been previously established in our laboratory[8,9].

Experimental

The working electrodes were constructed from rods of glassy carbon (GC) from Atomergic Chemetals Corp., press-fitted into Teflon housing, leaving an exposed area with a diameter of 3 mm. The polishing of the electrodes was made over silicon carbide (600 mesh). The electrodes were then cleaned with dry glass paper and placed in an ultrasonic bath of triple distilled water for ten min.

The counter electrode was a Pt foil with a relatively large area (*ca.* 8 cm^2). All potentials are referred to the aqueous saturated calomel electrode (SCE). The cell (EG&G Princeton Applied Research (PAR) Cell Polarograph Top Assembly) allows a disposition of the electrodes with a uniform electrical field. The ohmic drop was compensated for by the positive feedback technique. All measurements were made under N_2 atmosphere.

$NaClO_4$ (Koch-Light A.R.) was purified by previously described methods[10]. $HClO_4$ (Carlo Erba RP) was used as received. Water was distilled over $KMnO_4$ and then doubly distilled. The solvent-supporting electrolyte (SSE) system for linear sweep voltammetry (LSV), cyclic voltammetry (CV) and volt-coulometric (VC) studies was a 0.1 M $NaClO_4$ / 0.1 M $HClO_4$ aqueous solution.

For CEP of the GCE, an aqueous solution of 1 M H_2SO_4 (Merck) was used where the electrodes were repeatedly cycled between - 0.5 and 1.8 V, then washed with the SSE system and cycled in this media between - 0.5 and 1.0 V until a stable voltammetric profile was obtained.

TMN was synthesized from 1,1' naphthidine and purified as described elsewhere[8]. The saturated solution of TMN was 4.5 x 10^{-5} M in the SSE system. The absorption of TMN was made in an open circuit in this solution. The working temperature was maintained at 25 ± 0.1 °C with a LAUDA K4R thermostat-cryostat.

The measurements were performed with an EG&G PAR 273 potentiostat/galvanostat, and the current and potential values were transferred to a high speed digital double channel oscilloscope Keithley K194 A. The volt-coulograms and volt-amperograms were recorded by a Hewlett-Packard Model 7015 B X-Y plotting system.

The UV-visible spectra of TMN (λ = 288 nm; log (ε/l mol cm^{-1}) = 4.18 were taken on a diode array HP 8452 spectrophotometer.

Results and Discussion

Preparation of MGCE

In order to obtain MGCE with different degrees of modification, the previously described procedure was used[6,7]. Since the solubility of TMN in aqueous acid solution is low (5 x 10^{-5} M)[7] it is experimentally impossible to use a higher degree of modification than that obtained by fifteen cycles. If a higher degree of modification is used, the electrodes become so active that the value of surface coverage, $\Theta = 1$, cannot be reached[7]. The electrodes were characterized by CV and VC in the SSE system, correlating the anodic charge (Q_a) in the studied potential interval (- 0.5 to 1.0 V) with the sweep potential rate (s). As previously described[6,7], Q_a varies linearly with s between 0.04 and 0.3 Vs^{-1}. Thus, Q_a can be considered a composite represented by:

$$Q_a = Q_o + K(E\lambda)\, c\, s^{-1/2} = Q_o + a\, s^{-1/2} \qquad (1)$$

Q_o is the charge obtained by extrapolating at $s = \infty$. On the other hand, $Q_o = (Q_{DL} + Q_{SC})$, where Q_{DL} is the double layer charge and Q_{SC} is the pseudo-capacitance charge of an adsorbed monolayer of surface functionalities. K ($E\lambda$) is a function of the switching potential $E\lambda$, and c is proportional to the concentration of active sites in the film[7].

Typical results are shown in Fig. 1a. The linear dependence resembles that of a diffusion control electrode reaction in solution[11]. The apparent diffusion behavior of MGCE

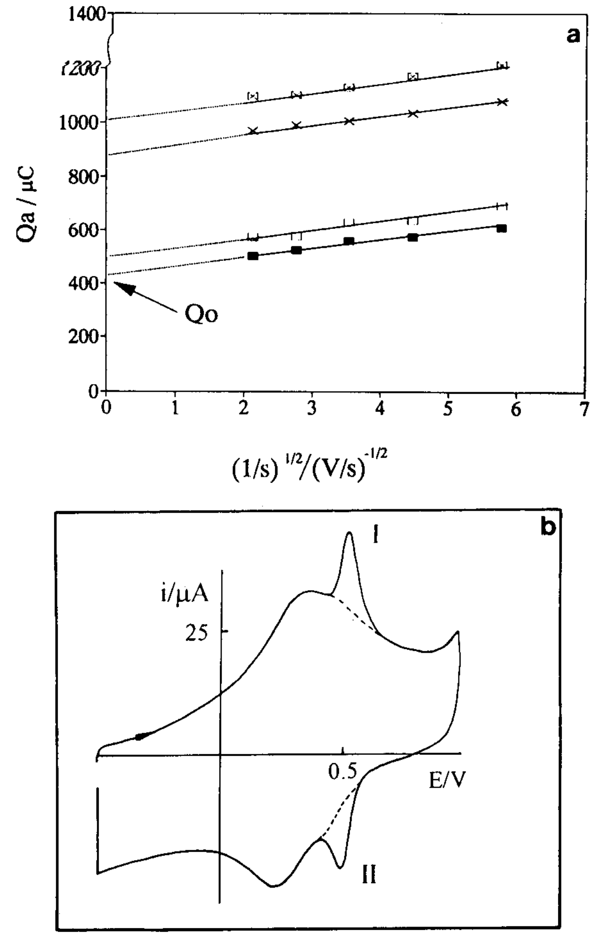

Figure 1. a) VC response of MGCE according to Eq. 1, as a function of the number of cycles in H_2SO_4 media. (■) 4; (□) 7, (X) 10, (☒) 15 cycles. b) CV of adsorbed TMN on MGCE. s = 0.05 Vs^{-1}.

can be attributed to electron hopping[6], with associated proton and counter ion diffusion during the redox processes at the fixed surface functionalities[7].

If the procedure is repeated for GCE of different batches or even polishing the same electrode, similar results are obtained. However, the slopes (a) and the intercept (Q_o) in Eq. 1, as well as the number of cycles to obtain a given degree of modification may be different, depending on the previous history of the electrode.

These studies suggest a relationship of Q_o and (a) with the surface structure, the precursor material and the previous physical treatment.

This may explain the experimental difficulty in obtaining an identical response for MGCE prepared with GC obtained from different sources. However, the determination of Q_o after CEP provides a parameter that allows the comparison of different electrodes.

Adsorption of TMN on MGCE

Several MGCEs with different degrees of modification were used. Prior to each experiment the modified electrodes were characterized as described[7]. Figure 1b shows a typical CV profile after adsorption of TMN. The anodic and cathodic peaks are interpreted by Eq. 2:

$$\mathrm{TMN(ads)} \rightleftharpoons \mathrm{TMN^{2+}(ads)} + 2\,e \qquad (2)$$

The amount of adsorbed TMN was measured through the charge of the oxidation peak of TMN (Q_{OxTMN}). A linear relationship was found between Q_{OxTMN} and Q_o (Fig. 2).

The intercept of the plot has a value of about 70 µC, which could be interpreted as the minimum charge needed to detect the adsorption of TMN. Similar results were obtained for DMN on MGCE[7]. These results reinforce the conclusion that Q_o is an important parameter for characterizing the degree of modification of MGCE, and is useful for predicting the amount of TMN that can be adsorbed by the electrode surface. Consistently, Q_o simultaneously takes into account the electrochemical area and the surface activity.

Oxidation kinetics of adsorbed TMN on MGCE

The effect of degree of modification of MGCE on the kinetic oxidation parameters of adsorbed TMN (Eq. 2) was studied by the LSV method. The theoretical model for an adsorbed monolayer or submonolayer of the type in Eq. 2 was previously described by Laviron[12,13]. A more complete theoretical analysis was given by Conway *et al.*[14,15]. These authors define a new kinetic parameter s, analogous to the exchange current density and related to the standard rate constant k^o. It is shown that s_o is a useful parameter for characterizing the kinetics of electrode surface processes since, unlike i_o, it does not depend on the real area of the electrode.

Hence, the electrochemical characterization of the kinetic parameter can be made without the determination of the real area of the electrode. This is a very convenient experimental situation for working with MGCE in an adsorbed process.

The experimental determination of s_o is performed by measuring the peak potential shifts from the reversible

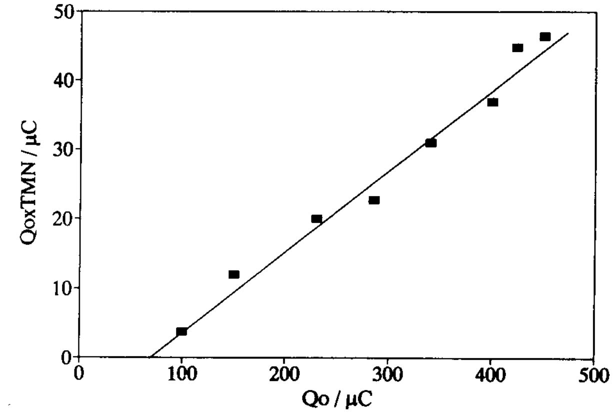

Figure 2. Linear correlation between the amount of adsorbed TMN ($Q_{ox,TMN}$) and the degree of modification of MGCE (Q_o).

value (Ep,r) at sufficiently large values of sweep rate. Under these conditions the process is made irreversible (negligible back reaction), and thus, new values of peak potential (Ep,irr) are obtained. The potential shifts ΔE = Ep,irr - Ep,r, which are analogous to an overvoltage, give a Tafel type relation[15], as shown in Eq. 3:

$$\Delta E = - b \ln s_o + b \ln s \qquad (3)$$

where s is the sweep rate in Vs^{-1}; $b = RT/(1-\alpha)\, nF$; $(1-\alpha)$ is the transfer coefficient for the anodic process; n = 2 (Eq. 2); and R,T, and F have the usual meanings. The s_o value is related to b by $s_o = b\, k^o_{obs}$. In this model no double layer effects are considered.

In order to obtain the kinetic parameter, several MGCEs were prepared and characterized as described. The adsorption of TMN is carried out immediately and detected by CV. Figure 3a shows a typical result at a slow sweep rate. Two well-defined peaks are detected: anodic (I) and cathodic (II), in agreement with our previous results[7].

When the sweep rate increases the voltammogram changes as shown in Fig. 3b, peak (I) is still well defined. However, the potential peak shifts to more positive values in agreement with previous theoretical analyses (Eq. 3). At the same time, peak (II) shifts to more negative values, overlapping with the peak corresponding to immobilized functional groups on the MGCE surface[6,7]. The deconvolution of two cathodic peaks can be performed, and related work is in progress. In this paper only data by LSV of the anodic peak are reported. Figure 4 depicts the experimental results from applying Eq. 3 to one type of MGCE. Three zones can be distinguished: Zone I corresponds to the reversible process, Zone III is the irreversible one, and Zone II shows the quasi-reversible behavior. The intersection of the two extrapolations of the linear Zones I and III gives the value of ln s_o, and from the slope of Zone III the b value can be obtained according to Eq. 3.

The values obtained for different MGCE are shown in Table 1, which also includes data for unmodified GCE for comparison. The values of Q_o give a measure of the number of exposed surface sites responsible for MGCE activity. This parameter increases by four times, and the amount of adsorbed TMN changes in the same proportion, according to Fig. 2. The given values of ln s_o have not been corrected for the effect of lateral interactions described in the original model[15] by an interaction parameter (g), which is important only when $|g| > 2$. For adsorbed TMN the value obtained from Frumkin's isotherm[7] is lower than 2, indicating that the corrections are within experimental error.

The k^o_{obs} values are practically constant for different values of Q_o, within experimental error. This seems to indicate that the electrochemical modification gives electrodes of reproducible kinetic performance.

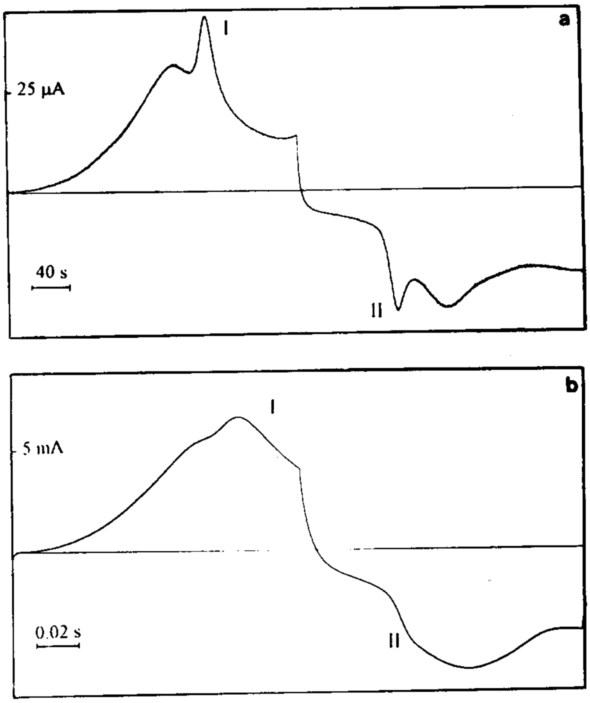

Figure 3. LSV curves for adsorbed TMN on MGCE at: (a) 0.05 and (b) 11 V/s.

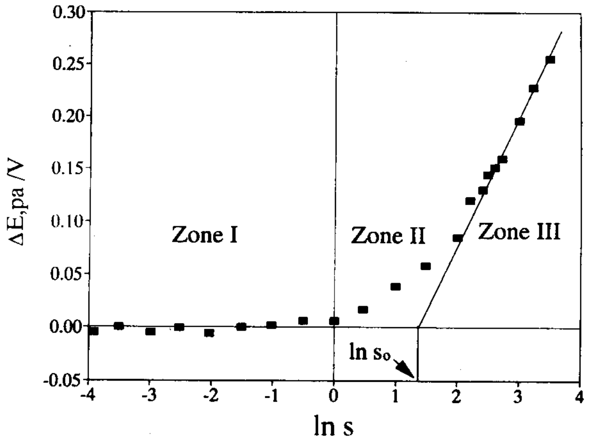

Figure 4. Dependence of anodic peak potential on ln s for adsorbed TMN.

On the other hand, the k^o_{obs} values of the polished GCE, without any further treatment (unmodified), appear to be higher than in MGCE (Table 1). Thus, it seems that the formation of redox functionalities and a larger adsorption capacity are not prerequisites for obtaining high electron transfer kinetics[1]. In fact, GCE fractured *in situ* or with its oxide film removed by exposure to a base or by a pulsed laser[16-19] have fast electron transfer kinetics. Thus, the observed effects in the polished electrodes should be related to the conductivity of the microcrystallite structure free of oxides.

Table 1. Kinetic parameters of electro-oxidation of adsorbed TMN on GCE.

MGCE				
$Q_o/\mu C$	$\ln s_o$	b	$(1-\alpha)$	$k^o (s^{-1})$
255.0	1.65	0.108	0.109	47.9
486.3	1.60	0.119	0.099	41.5
537.0	1.39	0.106	0.111	37.6
657.6	1.39	0.107	0.110	37.6
672.1	1.64	0.113	0.104	45.6
732.3	1.50	0.088	0.134	50.4
747.0	1.34	0.079	0.149	47.9
933.1	1.22	0.091	0.129	37.3
1050.0	1.33	0.091	0.129	41.3
Unmodified GCE				
—	1.91	0.106	0.111	63.7
—	1.96	0.082	0.143	86.5
—	2.36	0.100	0.117	105.9

Assuming an EE type mechanism for the electro-oxidation of adsorbed TMN, in which either the first or the second electron transfer is the rate-determining step, the $(1-\alpha)$ coefficient obtained is abnormally low. This may be indicative of a more complicated mechanism than the one proposed. Similar low values of transfer coefficients were reported for immobilized species on different electrode surfaces[20,21].

Conclusions

The CEP increases the adsorption capacity of GCE. With the use of working curves, as shown in Fig. 2 it is possible to predict the amount of adsorbed TMN with the degree of activity measured by Q_o.

The kinetics of electro-oxidation of TMN on MGCE is reproducible regardless of the degree of electrochemical modification (Q_o). On the other hand, the electron transfer kinetics of adsorbed TMN on unmodified GCE seems to be larger than that of MGCE. This can be explained by considering that the electrogenerated oxidized film can inhibit the electron transfer, probably because the film is less conducting than the amorphous structure of glassy carbon.

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References

1. R.L. McCreery, *Electroanalytical Chemistry* (A.J. Bard, ed., Marcel Dekker, New York, 1991), vol. 17, p. 221.
2. K. Sternitzke, R.L. McCreery, C.S. Bruntlett and P.T. Kissinger, *Anal. Chem.* **61,** 1989 (1989).
3. A. Hagen, J. Mattusch and G. Werner, *Fresenius J. Anal. Chem.* **339,** 26 (1991).
4. G.H. Heider, S.V. Sasso, K. Huang, A.M. Yacynych and H.J. Wieck, *Anal. Chem.* **62,** 1106 (1990).
5. G. Picq, R.M. Reeves, P. Ribourg and P. Vennereau, *Fuel* **63,** 1107 (1984).
6. C. Barbero, J.J. Silber and L. Sereno, *J. Electroanal. Chem.* **248,** 321 (1988).
7. L. Otero, N. Vettorazzi, C. Barbero, M.C. Miras, J.J. Silber and L. Sereno, *J. Electroanal. Chem.* **350,** 251 (1993).
8. M.C. Miras, J.J. Silber and L. Sereno, *J. Electroanal. Chem.* **201,** 367 (1986).
9. M.A. Zon and H. Fernandez, *J. Electroanal. Chem.* **295,** 41 (1990).
10. N. Vettorazzi, J.J. Silber and L. Sereno, *J. Electroanal. Chem.* **125,** 459 (1981).
11. a) R.A. Osteryoung, G. Lauer and F.C. Anson, *Anal. Chem.* **34,** 1833 (1962); b) J.H. Christie, G. Lauer and R.A. Osteryoung, *J. Electroanal. Chem.* **111,** 1420 (1964).
12. E. Laviron, *J. Electroanal. Chem.* **52,** 355 (1974).
13. E. Laviron, *J. Electroanal. Chem.* **101,** 19 (1979).
14. B.E. Conway, H. Angerstein-Kozlowska and F.C. Ho, *J. Vac. Sci. Technol.* **14,** 351 (1977).
15. H. Angerstein-Kozlowska and B.E. Conway, *J. Electroanal. Chem.* **95,** 1 (1979).
16. R. Rice, C. Allred and R. McCreery, *J. Electroanal. Chem.* **263,** 163 (1989).
17. R. Rice, N. Pontikos and R.L. McCreery, *J. Am. Chem. Soc.* **112,** 4617 (1990).
18. R. Bowling, R.T. Packard, R.L. McCreery, *Langmuir* **5,** 683 (1989).
19. P.M. Kovach, M.R. Deakin, R.M. Wightman, *J. Phys. Chem.* **90,** 4612 (1986).
20. R.F. Lane and A.T. Hubbart, *J. Phys. Chem.* **77,** 1401 (1973).
21. M. Sharp, M. Petersson and K. Edstrom, *J. Electroanal. Chem.* **109,** 271 (1980).