ELECTROCHEMICAL STUDY OF DOPAMINE ADSORBED ON GOLD

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ABSTRACT

The redox reaction of dopamine adsorbed layer on gold is studied. The adsorption takes place at open circuit condition. The adsorbed substance presents a reversible oxidation of the OH groups on the ring, and an irreversible oxidation at higher potentials. The dopamine metal bond is weak and the substance may be removed by a physical procedure. Moreover, multilayers are formed over the first layer. An estimation of the dopamine co-area over gold is reported.
Key Words: dopamine, gold, open circuit, adsorption, oxidation

INTRODUCTION

The electroanalytical techniques to determine in vivo neurotransmitter concentration has been introduced in the medical research during the last two decades (1-15).

The aim of the present work is to obtain knowledge of the electrochemical behaviour of dopamine, since the development of an electroanalytical technique will need this knowledge. We have studied dopamine adsorbed in the open circuit condition. This technique has some advantages (16-18): 1) It let us to study only the adsorbed layer. Therefore, we do not have complications due to diffusion. 2) We do not have complications due to re-adsorption. 3) We have experience in the use of this technique (16-18).

On the other hand, if the substance is weakly adsorbed, it may be desorbed during the washing procedure. Moreover, it may be oxidized during the contact with the atmosphere. In the present study, we evaluate the possible error due to these effects as is shown in the description of the experimental procedure.

We choose gold as electrode material because it has a high oxidation potential and the absence of adsorbed hydrogen let us to study adsorbed substances in a wide potential range without complications.
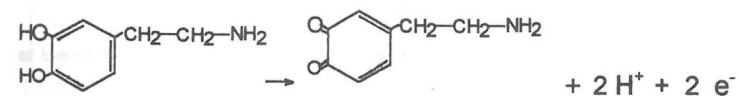
On noble metal electrodes, cathecolamines present two types of oxidation (19): One at low potentials (0,6-0,8V) and the other at high potentials (1,4-1,7V). The first one, is a reversible reaction on the cathecol ring and it does not influence the C-C bonds. The second oxidation occurs simultaneously with the metal oxide formation. In this reaction the substance oxidates irreversibly and the C-C bonds break.

In the present work we study the first reaction of the adsorbed dopamine.

RESULTS AND DISCUSSION

A typical current-potential response of adsorbed dopamine is showed in Fig.1a.

An anodic current peak at 0,85 V, and a cathodic one at 0,78 V were observed. The behaviour of both peaks corresponds to complementary peaks due to the reversible oxidation of the cathecol ring :

$$HO\text{-}C_6H_3\text{-}CH_2\text{-}CH_2\text{-}NH_2 \longrightarrow O\text{=}C_6H_3\text{-}CH_2\text{-}CH_2\text{-}NH_2 + 2H^+ + 2e^-$$

As a complementary cathodic current peak appears, we conclude that the oxidation product remains on the surface. In addition, both peaks appear in successive cycles. Only slight current

lowering is observed as the number of cycles increases. Thereby, the adsorbed dopamine is slowly desorbed while it reacts.
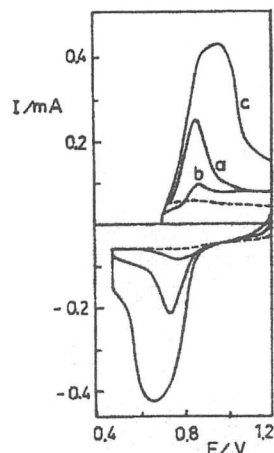

Fig.1: Voltammograms obtained with dopamine covered electrode at: $v = 200mV.s^{-1}$, t=15min and T=25°C
(a) $c = 5x10^{-3}$ M
(b) $c = 5x10^{-3}$ M with introducing the 30 min desoption step.
(c) $c = 2.5x10^{-2}$ M
The dashed line is the voltammogram obtained with the electrode free of adsorbed dopamine.

ble diminution of the dopamine peaks (Fig 1b compared with Fig 1a). Therefore, the dopamine is desorbed during the electrode stay in the desorption cell and hence the dopamine-gold bond is weak. At the same adsorption time, the amount of adsorbed substance increases with dopamine concentration (Fig 1c). Simultaneously, the peaks unfold themselves in two contributions. The new current contribution appears at more anodic potential, in the anodic current peak, and at more cathodic potentials, in the cathodic peak. It is not so well defined for the cathodic current peak as it is for the anodic one. Its behaviour corresponds to less reversible reaction than that which originated the single couple of peaks firstly described.

The plot of the reaction charges against the concentration (Fig.2a) gives a slightly defined plateau between 60-70 µC/cm² for all the sweep rates used in the different experiments. Moreover the value is the same of the plateau found in the charge-time plot(Fig2b) (23).
The figures 2a seem an adsorption isoterms for multilayers adsorbed on a monolayer. The plateau would give the charge corresponding to a monolayer.(*)

If we asume 70 µC as the charge of a complete monolayer, we may estimate the area occupied by adsorbed dopamine. The estimated value is 22,7 A². This value is of the order of that reported in the literature for adsorbed bencene (between 16 and 34 A²) (22). It is probable that the contact between the dopamine and the surface is done only by the cathecol ring. If only the ring is adsorbed (19) as in the case of hidroquinone, the experimental response is very similar. The peak currents behave well enough linearly with the potential sweep rate v.(Fig.3a and 3b).

Peak potentials do not change with increasing potential sweep rate (v) (Table 1). Together with the anodic current peak at 0,85V, a shoulder appears at ca. 0,9 V. Its potential shifts slightly toward more positive potentials with increasing v.

(*) It must be clarified that the plot is not exactly an adsorption isoterm, becausa the coverages measured as reaction charges of adsorbed substance are not exactly equilibrium values.
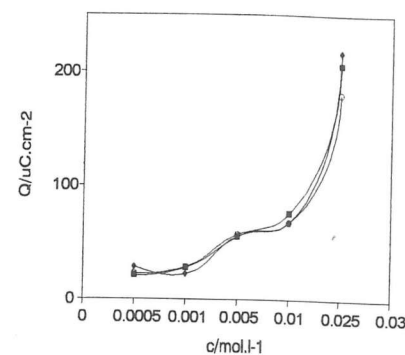
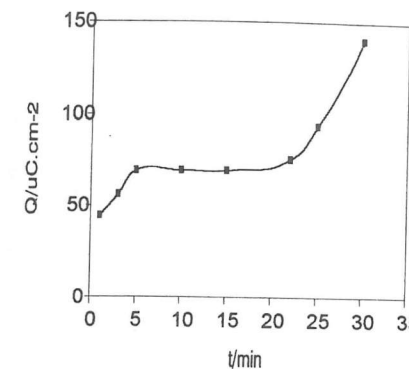**Fig. 2a.:** Plot of the cathodic charge vs concentration: (■)130 mV.s⁻¹, (◆)200 mV.s⁻¹, (●)250 mV.s⁻¹

Fig. 2b.: Plot of the anodic charge vs adsorption time. $v = 200$ mV.s⁻¹ , T = 25°C , $c = 1x10^{-2}$M

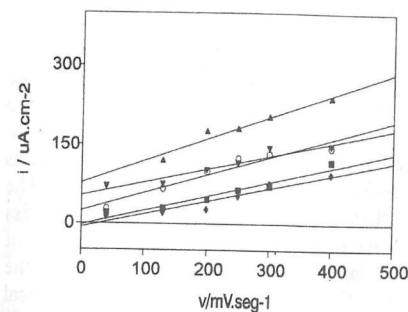**Fig.3a.:** Plot of the anodic peak current densities against the potential sweep rate for different dopamine concentrations. t=15 min.
(■) 5x10⁻⁴ M, (◆) 1x10⁻³ M, (●) 5x10⁻³ M, (∇) 1x10⁻² M, (Δ) 2.5x10⁻² M

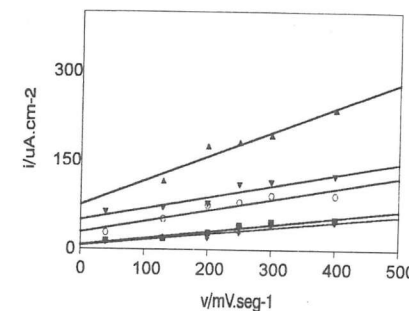**Fig.3b.:** Plot of the cathodic peak current densities against the potential sweep rate v for different dopamine concentrations. t=15min. Symbols have the same meaning as in the fig. 3a.

v (mV.s⁻¹)	5x10⁻⁴ M		1x10⁻³ M		5x10⁻³ M		1x10⁻² M		2,5x10⁻² M	
	Anod.- Catod.		Anod.-Catod.		Anod.-Catod.		Anod.-Catod.		Anod.-Catod.	
40 mV/s	0.83	0.76	0.83	0.76	0.83	0.76	0.86	0.72	0.84	0.68
130 mV/s	0.85	0.80	0.85	0.79	0.86	0.75	0.85	0.73	0.84	0.68
200 mV/s	0.84	0.78	0.84	0.78	0.84	0.75	0.86	0.73	0.84	0.65
250 mV/s	0.84	0.77	0.84	0.79	0.83	0.74	0.85	0.70	0.84	0.65
300 mV/s	0.84	0.77	0.84	0.78	0.84	0.74	0.86	0.70	0.84	0.63
400 mV/s	0.84	0.76	0.84	0.78	0.85	0.73	0.87	0.70	0.84	0.60

TABLE 1: Anodic and cathodic current peak potentials, in Volts, for different potential sweep rates and different dopamine concentrations. t = 15 min.

The integrated charges are approximately constant with v (Table 2).

v (mV.s^{-1})	5x10^{-4} M		1x10^{-3} M		5x10^{-3} M		1x10^{-2} M		2.5x10^{-2} M	
	Anod	Catod.	Anod.- Catod.		Anod.- Catod.		Anod. -Catod.		Anod. - Catod.	
40 mV/s	26.6	25.3	28.32	24.0	58.46	56.7	74.20	74.3	214.33	200.0
130 mV/s	20.8	24.7	27.86	24.4	55.29	55.3	75.76	75.8	206.30	197.0
200 mV/s	28.5	21.5	22.40	18.7	59.61	58.8	67.84	73.4	217.80	202.0
250 mV/s	22.5	26.7	28.50	20.5	57.21	50.5	67.48	81.1	180.90	181.4
300 mV/s	27.5	19.3	36.11	16.5	50.25	47.7	56.78	65.0	187.40	158.3
400 mV/s	27.3	29.2	31.43	28.0	45.27	48.1	60.00	59.0	212.62	153.0

TABLE 2: Integrated anodic and cathodic charges of adsorbed dopamine for different potential sweep rates and different dopamine concentrations. t = 15 min. The values are given in $\mu C.cm^{-2}$.

Moreover, the anodic charges are approximately the same as the cathodic charges, except for the last two values in the last columns. In these points, the cathodic charges are lower than the anodic charges. The integrated peak charges increase abnormally for the more concentrated solution (Table 2). At the same time, new current peaks begin to hint.

If more charge is needed for the reaction, it may be explained in two ways: The same substance needs more charge to react, or there is more dopamine adsorbed on the surface. To discuss the first way, we have to suppose that dopamine molecule gets another reaction centre, which can behave reversibly. The two OH groups must be in the ortho or para positions in the ring to behave reversibly . They cannot be in the two positions in the same molecule to behave reversibly. If there would be a part of adsorbed molecules with other configuration, the charge would not increase. In that case, only the distribution of charge below the two current peaks would change. Then, we have to think that more dopamine is adsorbed over the first layer. The new dopamine adsorbed is energetically different than that in the first layer. Then, it reacts less reversibly. The presence of the first layer does not hinder the reaction on the second layer but creates an obstacle. Then, the dopamine in the second layer, behaves less reversibly than the dopamine in the first one. Both layers may be removed from the surface by the physical desorption procedure.

In the condition of an adsorbed monolayer reaction, the potentiodynamic behaviour is similar to the case of a reversible monolayer formation (21): 1) The peak currents are linear with the potential sweep rate. 2) The peak potentials do not shift with the potential sweep rate. 3)The reaction charges do not change with v. 4) The anodic charges are the same as the cathodic charges.

When the dopamine concentration increases (Fig 5), the current peaks disappear and two complementary flat waves are observed. In the experience of the figure, the scan has been done between 0.1 and 1.7 V. In the voltammogram the current peaks due to the electroformation and the electroreduction of the metal appear (1.4 and 1.15 V respectively).

This fact may be explained supposing multilayer formation. The dopamine in one layer reacts less reversible than the dopamine in the layer bellow it. In this way, the reaction potentials of juxtaposed layers become more and more separated. The potentials of different layers are very near and so no current peaks are observed. Finally, the current-potential response becomes like that of an ohmic resistance. As the film becomes thick, it hinders the electron transfer and becomes an electric insulator. In this sense, the behaviour of dopamine is similar to that of the epinephrine (19).

If we compare these results to that of the SO$_2$ adsorbed on platinum (16-18) we observe a similarity in the sense that multilayer formation may be electrochemically proved.
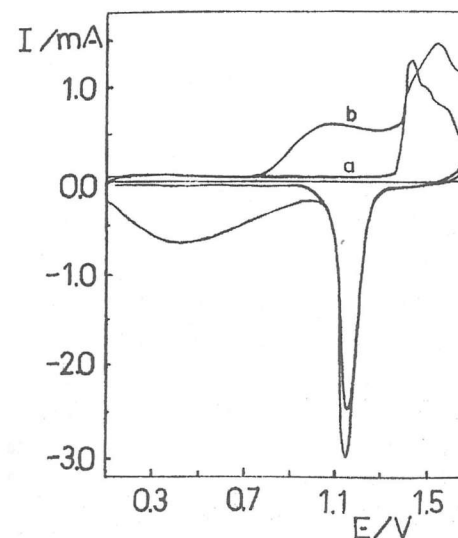
Fig.5: Voltammograms obtained with dopamine adsorbed from 1x10^{-1}M solution (b); t=15min; v=130mV.s^{-1}; 25°C Fig.(a) is the blank.

EXPERIMENTAL

We have worked with two cells: the electrochemical one and the adsorption one. The first contained 0,5 M sulphuric acid saturated with nitrogen. The second cell contained dopamine solution of concentration c in 0,5 M sulphuric acid saturated with nitrogen. The working electrode was a 3 cm long and 1 mm diameter gold wire. A gold sheet of 4 cm^2 was used as an auxiliary electrode.

A two compartment Pyrex glass cell was the electrochemical cell. The potentials were measured against an Hydrogen reference electrode in the same solution as that of the cell. The reference electrode was installed in a separate compartment connected with the central compartment through the Luggin capillary.

A third cell was used. We called it "the desorption cell" because we used it to perform the physical desorption experiment described below. It contained three-distilled water stirred with nitrogen bubbling. All cells were thermostatized at 25° C.

The electrode was pre-treated with potentiodynamic cyclic sweeps between 0,1 and 1,7 V. One cycle was registered to control surface and solution purity. If the spectrum of pure gold was obtained, the electrode was taken out of the cell and put into the adsorption cell during the adsorption time, t. Then, it was washed with 0,5 M sulphuric acid, and returned to the electrochemical cell. A linear potential sweep was applied between 0,75 and 1,2 V. Then, another potential sweep was carried out in the reverse direction between 1,2 and 0,45 V. The potential – time program is showed in Fig 6.

The selected starting potential (0.75 V) was more anodic than the cathodic limit of the sweep, to avoid the dopamine reduction during the short time between closing of the circuit and the start of the sweep. The current-potential response was registered.

In some cases, after the adsorption step, a desorption step was included. It consisted of an electrode stay in the desorption cell during 30 min. This step permits to determine if the adsorbed substance is weakly or strongly adsorbed.
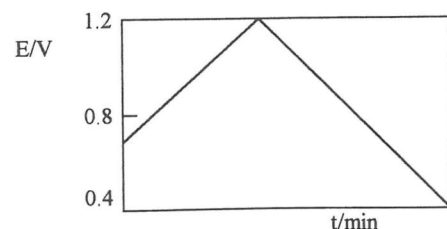
Fig.6: Potential-time program applied to the electrode to study the adsorbed dopamine layer.

The electrode real areas were obtained by measuring the gold oxide monolayer charge, as it has been previously described (20). All charges showed in this work were measured by graphical integration.

As the electrode with the adsorbed dopamine layer was in contact with the atmosphere for a few seconds before putting it in the electrochemical cell, we had to verify that there was no chemical oxidation during this time. Then, we studied the influence of the time during the contact of the electrode with the air on the current-potential response obtained. We did not observe any change for times as long as five minutes. Moreover, we studied the influence of the washing time on the current-potential response obtained. We did not observe any change for times as long as 30 s. (The electrode washing normaly last 5 s.)

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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC INVESTIGATION OF Ir-BASED CERAMIC COATINGS CONTAINING CeO2 UNDER CONDITIONS OF ACCELERATED ANODIC CORROSION

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Abstract

Ti-supported electrodes of nominal composition $Ti/Ir_{0.3}Ti_{(0.7-x)}Ce_xO_2$ ($0 \leq x \leq 0.7$) were prepared by thermal decomposition of the chloride precursor mixtures (450 °C). A systematic study of the corrosion behaviour of these anodes was performed under conditions of accelerated corrosion ($j=800$ mA cm^{-2}) in acidic medium. Impedance measurements, carried out at regular time intervals, showed to be a very useful technique to accompany the changes occurring at the Ti^0/oxide layer and oxide layer/supporting electrolyte interfaces, during corrosion of the electrodes. The simulation of the impedance spectra through an appropriate equivalent circuit allowed to quantify the parameters.

Key Words: electrocatalysis; oxygen evolution; corrosion; iridium oxide; impedance.

Introduction

The effect of CeO_2 introduction on the service life of the IrO_2/TiO_2 system has been presented elsewhere [1]. It was observed that the gradual substitution of TiO_2 by CeO_2 produces anodes which present a lower service life for the oxygen evolution than the initial system. This rather instability is possibly related to the preferential dissolution of Ce in association with the crystalline structure of these coatings (amorphous phase or low degree of crystallinity). Normally, the service life of an electrode is determined under conditions of accelerated corrosion, imposing a high constant current to the system and measuring the potential vs time response [2]. We have demonstrated [3] that the electrochemical impedance spectroscopy, EIS, can be a useful technique to avaliate the corrosion behaviour of a DSA®. The aim of this study is to utilize the EIS to monitor the variations occurring in the coating layer during the service life of the $IrO_2/TiO_2/CeO_2$ system.

Experimental

Electrode preparation. Ti-supported electrodes of nominal composition $Ti/Ir_{0.3}Ti_{(0.7-x)}Ce_xO_2$ ($0 \leq x \leq 0.7$, changed in 10 mol% steps) were prepared by thermal decomposition (T:450 °C; t_{calc}:1 h; O_2 flux: 5 L min^{-1}) of mixtures of *ca.* 0.14 mol dm^{-3} solutions of $IrCl_3.xHCl.xH_2O$ (Aldrich), $TiCl_4$ (Ventron) and $CeCl_3.7H_2O$ (Pierce) dissolved in 1:1 (*v/v*) HCl (Merck). A detailed description of the experimental procedure used is found in a previous paper published by us [4].

Solution. 1.0 mol dm^{-3} $HClO_4$ (Merck) aqueous solution was used as supporting electrolyte. Experiments were conducted at 32±2 °C.

Technique and instrumentation. Impedance spectra were obtained at regular time intervals during the corrosion experiment, until the end of the service life of the anodes, at constant *dc* potentials (0.9, 1.48 and 1.50 V/rhe). The service life, SL, of the electrodes was taken as the time necessary for complete deactivation of the electrode material (E=6 V/rhe). Impedance measurements were carried out using a PAR model 5210 lock-in amplifier coupled to a PAR model 273A potentiostat, monitored by an IBM, model 55/SX, personal computer.

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