

"PARA-Ni-TETRAAMINOPHENYLPORPHYRIN/Co-COBALTITE/SnO₂:F MODIFIED ELECTRODES: ELECTROCATALYTIC BEHAVIOR TOWARD THE OXIDATION OF HIDRAZINE"

PAZ BRAVO¹, FABIOLA ISAACS¹, GALO RAMÍREZ¹, FRANCISCO ARMIJO¹, MAURICIO ISAACS², MARÍA JESÚS AGUIRRE¹, CLAUDIA ZAMORA¹, EJNAR TROLLUND^{1}.*

¹Departamento de Química de Los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, USACH, casilla 40, correo 33, Santiago, Chile. E-mail: etrollun@lauca.usach.cl. Fax: 56-2-6812108.

²Departamento de Química, Facultad de Ciencias, Universidad de Chile, Las Palmeras 3425, Santiago, Chile.

ABSTRACT

The aim of this work was the study of three different modified electrodes where the substrate and the porphyrin used to modify the electrodic surface was the same. The surface electrode was a glass covered by a layer of SnO₂ doped with fluor. On this layer was formed a cubic spinel of Co-cobaltite. On this modified electrode was deposited or polymerized para-tetraaminophenylporphyrin of Ni (II). In each case, the treatment of the deposition of the porphyrin was different and the electrocatalytic behavior of the modified electrodes toward the oxidation of hydrazine drastically changes. In the case of a simple physically adsorbed layer of porphyrin, practically no electrocatalytic activity was found. In the case of a porphyrin deposited by reflux and cycled in basic solution, there is an important electrocatalytic activity giving N₂ as product. This electrode was proved as an amperometric sensor of hydrazine and a very good linear relationship between current and concentration was determinate. Also, the polymeric electrode showed an important catalytic behavior toward the oxidation of hydrazine.

Key words: Electrooxidation of hydrazine, amperometric sensor of hydrazine, modified electrodes, Ni(II)-p-tetraaminophenylporphyrin, Co-cobaltite electrodes.

INTRODUCTION

Azamacrocycles containing transition metals have been widely studied due to its catalytic properties (1-18). They can be used in the modification of electrodic surfaces in order to obtain electrocatalysts for many reactions like the oxidation of hydrazine (1, 18), reduction of oxygen (3, 4), reduction of CO₂ (6, 8, 9, 13), oxidation of thiols (2, 5), reduction of nitrites (11) and nitrates (12) among others. On the other hand, the nature of the substrate could strongly change the catalytic behavior of the modified electrodes (19-21). In spite of using the same complex and the same electrodic surface, the electrocatalytic properties can be modified if the method used to adsorb the molecules changes. In the case of electrodes modified with physically adsorbed layers of azamacrocycles, there are not reports on the differences in its behavior when

the modification is made under different conditions. However, for polymeric films, it is well known that changes in the polymerization conditions strongly affect its properties (19, 22-24).

On the other hand, hydrazine is a very reacting molecule that can be oxidized to many products. An oxidation of 4 electrons give N_2 ($E^\circ = 1.16V$ vs ECS in aqueous solution). Hydrazine has two non-bonding orbitals and it has a sp^3 hybridization. These characteristics permit its coordination with Lewis acids or metallic cations (25). Hydrazine is widely used as corrosion inhibitor, desiccant agent and as a fuel in fuel-cells (26). However, it is very toxic and hence, its detection and conversion to N_2 is very important from an industrial or environmental point of view. In this work we prepared 3 electrodes modified with the same porphyrin in order to compare its activity toward the oxidation of hydrazine. We found two types of modified electrodes that are very actives and stables. One of them was proved as an amperometric sensor of hydrazine.

EXPERIMENTAL

Electrodes:

The working electrode was prepared by deposition of $SnO_2:F$ and Co_3O_4 on glass sheets (2 cm^2 of geometrical area) previously polished, scoured and neutralized in acid medium. On the glass sheet maintained at 420°C a methanolic solution containing ($SnCl_4$) 53.074 g/L, 0.05 M ammonium monofluoride and 18 mL of water were sprayed. The flow rate was constant (6 mL/min) and the gas pressure was 2 bars. After this treatment, using a similar method, a solution containing 0.149M of $Co(NO_3)_2$ was sprayed on the $SnO_2:F$ glass sheet, but the temperature was fixed at 250°C , the flow rate of the solution was the same and the gas pressure; 2.5 bars. Finally, the electrode was exposed to O_2 atmosphere during 24 hours at 250°C . Reproducibility and characterization of the working electrode was measured by X-ray diffractometry using Cu K α radiation ($\lambda = 1.5406\text{\AA}$), with diffraction angles were $2\theta = 5^\circ - 90^\circ$ at a scan rate of $0.02^\circ/\text{step}$ (see Figure 1 and Table 1).

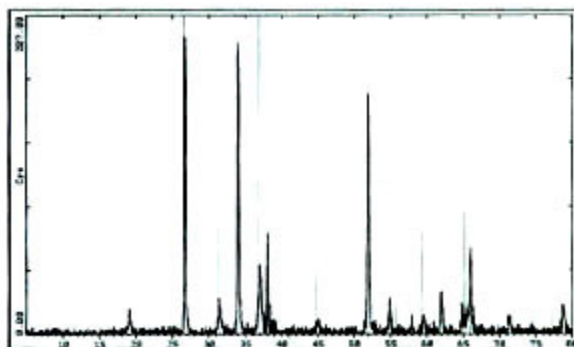


Figure 1. X-ray diffractometry of a $SnO_2:F/Co_3O_4$ electrode. This diffractometry indicates that the structure is pure and highly crystalline. Results are consistent with a cubic spinel of $F3dm$ spatial group.

Table 1: X-ray diffraction of Co₃O₄ on SnO₂:F

2θ	d_{hkl}	% Peak Intensity	Spatial plane (hkl)
19.129	4.6359	8.88	1 1 1
31.374	2.8489	13.08	2 2 0
36.972	2.4294	26.28	3 1 1
45.031	2.0115	6.89	4 0 0
59.513	1.5520	9.57	5 1 1

As reference, an Ag/Ag/Cl electrode was used and as counter electrode, a Pt wire of high area was used.

Modification of the working electrode with Ni(II) p-tetraaminophenylporphyrin (NiTAPP): Type 1-electrode: The electrode was submerged in a solution (dimethylformamide, DMF) containing 1mM NiTAPP at 20°C during 30 minutes. Then, it was exposed to air in order to evaporate the solvent and was thoroughly washed with bi-distilled water.

Type 2-electrode: The electrode was refluxed in a solution in a similar way to the method for type 1 electrode, but in this case, at 150°C during six hours. After this treatment, the solvent is evaporated and the electrode is washed in the same way that the type 1 electrode. Before its use it was cycled in a solution 1M KOH.

Type 3-electrode was obtained by electropolymerization submerging the modified electrode in a solution of DMF containing 1 mM NiTAPP and as supporting electrolyte, 0.1M tetrabutylammonium perchlorate. The potential was sweeping between -0.1 to 1.2V at 0.1Vs⁻¹ during 25 cycles. After the electropolymerization the electrode was rinsed with methanol and bi-distilled water.

Electrochemical measurements: Cyclic voltammetry and polarization curves were carried out in a quartz one-compartment cell, under nitrogen atmosphere (see Figure 2).

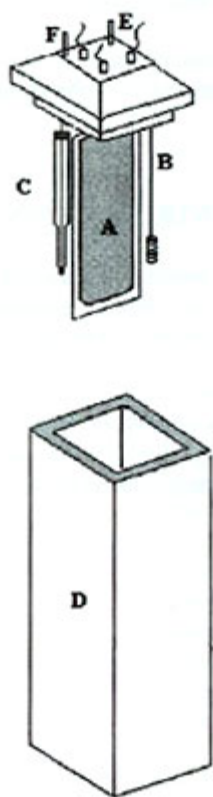


Figure 2. One compartment quartz electrochemical cell. A= working electrode. B= counter electrode. C= reference electrode. D= quartz cell. E= N₂ gas entrance. F= N₂ gas exit.

Reactants: hydrazine sulphate (p.a., Riedel de Haën), methanol (p.a., Caledon), tin (IV) chloride, (anhydrous, 99%, Aldrich), Ni (II)-p-tetraaminophenylporphyrin (Mid-Century), dimethylformamide (p.a., Merck), potassium hydroxide (p.a., Merck), ammonium monofluoride (p.a., Riedel-de Haën), tetrabutylammonium perchlorate (99%, Alfa Aesar), Nitrogen (99.99% Indura).

Equipment: X-ray diffractometry was performed in a Siemens-D5000 powder diffractometer equipped with a graphite monochromator.

Cyclic voltammetry and polarization curves were performed using a Wenking POS 73 potentiostat.

RESULTS AND DISCUSSION.

Figure 3 shows the complex used in this study. This complex has a core with D_{4h} symmetry and phenyl groups that are practically perpendicular to the core (27). In spite of the position of the phenyl groups, the complex easily adsorbs on an electrodic surface forming a stable film.

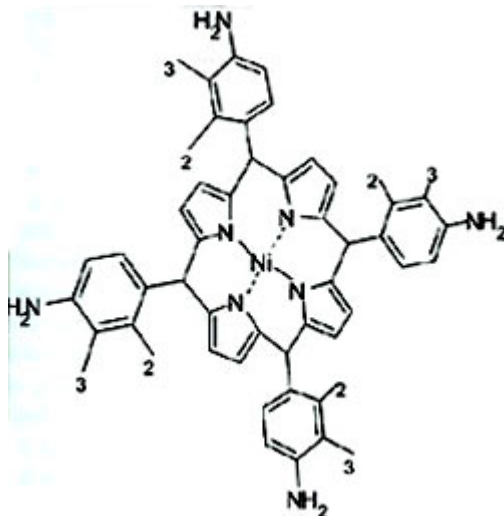


Figure 3. Structure of para-tetraaminophenylporphyrin. M = Ni.

However, the stability is strong dependently on the conditions used in the modification of the electrode surface (19, 22-24). Also, in the majority of the cases, the interaction between the complex and the electrode changes with the nature of the electrodic surface (19-21). Then, the modified electrode will have a behavior that depends on the method of preparation, the nature of the surface and the complex. In our work we prove three ways to modify the surface of the electrode. The electrodic surfaces were prepared in the same way and modify with the same porphyrin but using three different methods. Electrodes, type 1, type 2 and type 3 (see experimental section) have very different behaviors on promoting the oxidation of hydrazine as will be demonstrated in the following results.

Figure 4 shows the catalytic response of the modified electrode (type 1) compared to the blank (bare electrode) for the oxidation of hydrazine. The polarization curve of the modified electrode shows low currents and the same potential than the blank (unmodified electrode) toward the oxidation of hydrazine. In fact, both electrodes show similar response.

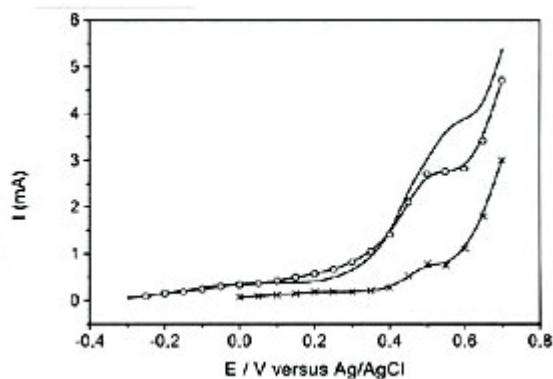


Figure 4. Polarization curves of blank (continuous line) and type 1 electrode (line + white circles) in the presence of 5mM

hydrazine. The bare electrode (blank) in the absence of hydrazine is shown by the line + crosses. Electrolyte: 1M KOH saturated with N_2 . Scan rate = $5mVs^{-1}$. Area of the electrode: $2cm^2$.

Indeed, the modification of the electrode lightly diminishes the catalytic activity of the electroodic surface toward the studied reaction. In the case of the type 2-electrode, the stabilization voltammetric response of the modified electrode in aqueous KOH solution indicates a changing surface, as shown in Figure 5. The growing signals of the adsorbed complex probably indicate the formation of Ni hydroxides between the layers of the porphyrin (28).

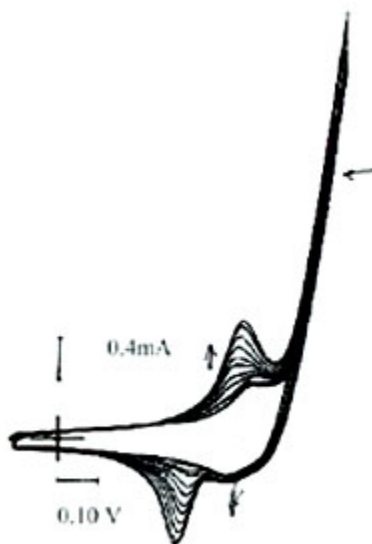


Figure 5. Cyclic voltammogram of type 2 electrode in 1M KOH (purged with N_2) during 500 cycles. (In the Figure only appears the last cycles). Potential range: -0.110 to 0.7V vs. Ag/AgCl. Scan rate: $100 mVs^{-1}$.

On the other hand, the behavior of this type 2-modified electrode drastically changes compared to the blank or the type-1 electrode. Now, the refluxed electrode is strongly catalytic toward the oxidation of hydrazine, as shown in Figure 6. The enhanced catalytic activity toward the oxidation of hydrazine probably is due to a change of the metal because hydroxo bridges between them must change its electronic density (28).

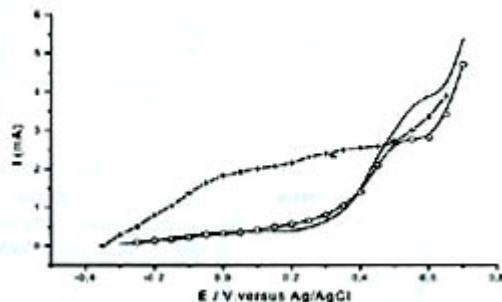


Figure 6. Polarization curves of blank (continuous line), type 1 electrode (line + white circles) and type 2 electrode (line + crosses) in the presence of 5mM hydrazine. Electrolyte: 1M KOH saturated with N_2 . Scan rate = $5mVs^{-1}$. Area of the electrode: $2cm^2$.

On the other hand, both electrodes are stable during the measurements in the presence of hydrazine, indicating that the similar response between the blank and the modified electrode (type 1) shown in Figure 4 is not due to a degradation process or a loss of the complex by diffusion to the solution. Then, electrodes, type 1 and type 2 are modified with the same porphyrin but in the second case the chemical nature of the metal is modified by the hydroxo substituents coordinates to the metal formed during the cyclic voltammetry in the basic medium. Also, type-3 electrode was proved toward the oxidation of hydrazine. Its catalytic behavior is better than the type-2 electrode at lower potentials, as can be seen in Figure 7. In this case, the nature of the active site (the metal center of the porphyrin is not changes by the formation of hydroxo groups. It occurs by polymerization of the complex. It is not common that an electrode modified with a mono or multilayer of monomers do not show electrocatalytic activity compared with a polymeric film of the same complexes as shown in Figure 7 (8). However, it is known that in the majority of the cases, the polymerization enhances the catalytic behavior of the modified electrodes (1, 3-5). In fact, the polymerized complexes change the electronic density on the ligand and on the metal due to a higher charge delocalization on the macromolecule (18). It is known that the interactions between the complexes play an important role in the conductivity, electronic density of the metal, and hence, in its electrocatalytic behavior. For example, in the case of a supramolecular electrode, the p-package of the porphyrins is the only way to catalyze the CO_2 reduction (13). The electrode modified with physically adsorbed layers of the same porphyrin does not present any activity to the reduction process. The same behavior for the oxidation of hydrazine is observed here. However, the change in the electrocatalytic activity between the monolayer and the polymer is due to the formation of covalent bonds that increase the conjugation of the film. Type 3 electrode is easily obtained and presents high stability and reproducibility. Its behavior is similar to that obtained with electropolymerized Co-phthalocyanines (1) although in this case, the monolayer was also active to the oxidation of hydrazine. However, at our knowledge, type 2 electrode (i.e., an electrode modified with layers of azamacrocyclic complexes were hydroxo groups act as bridges or substituents of the metal centers in a random way) was not used for the oxidation of hydrazine before.

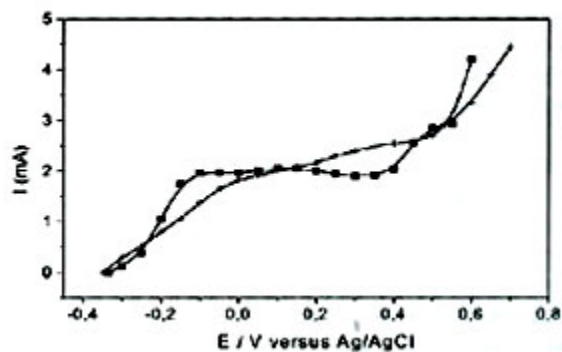


Figure 7. Polarization curves of type 2 electrode (line + crosses) and type 3 electrode (line + black squares) in the presence of 5mM hydrazine. Electrolyte: 1M KOH saturated with N₂. Scan rate = 5mVs⁻¹. Area of the electrode: 2cm².

For that reason we investigate the oxidation of hydrazine promoted by type 2 electrode. For that reason, we made a disk-electrode to rotate it at different rotation rates (see Figure 8A and B). In order to determinate the number of transferred electrons, the Koutecky-Levich equation was used (29):

$$1 / I_{exp} = 1 / I_k + 1 / (0,620 n F A C_0 D_0^{2/3} n^{-1/6} W^{1/2})$$

where I_{exp} is the measured current and I_k is the kinetic current.

Where F is the Faraday constant, A , the electrode area, (we used the geometrical exposed area = 0,2827 cm²) D_0 is the diffusion coefficient of the hydrazine, w is the rotation rate of the electrode, n is the kinematical viscosity of the solution and C_0 is the concentration of hydrazine in the bulk of the solution.

The used values were: $D_0 = 1,4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ $n = 9,97 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ $C_0 = 6 \times 10^{-6} \text{ mol cm}^{-3}$. The real area of the electrode is unknown and it was not possible to measure its roughness, in order to obtain this data. For that reason we used the exposed area. If a plot of $1 / I$ (mA) versus $1 / W^{1/2}$ (rad^{1/2} s^{-1/2}) a slope of $1/B$ where $B = 0,620 n F A C_0 D_0^{2/3} n^{-1/6}$, the number of transferred electrons can be calculated.

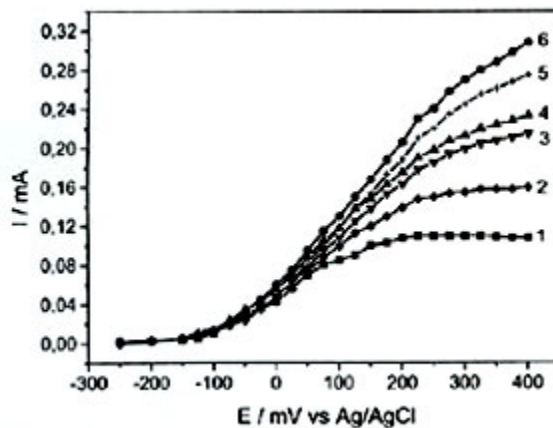


Figure 8A. Polarization curves of type 2 electrode at different rotation rates: 1) 0 rpm, 2) 20 rpm, 3) 50rpm, 4) 100 rpm, 5) 300 rpm, and 6) 500 rpm in the presence of 6×10^{-6} M of hydrazine.

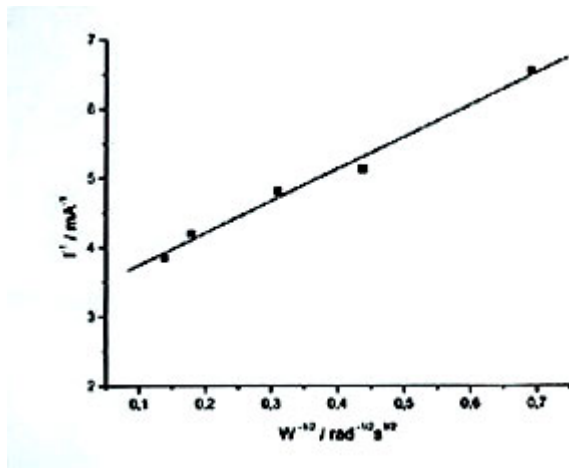


Figure 8B. Plot of $1/I$ versus $1/W^{1/2}$ of data obtained in Figure 8A.

From data obtained with the Koutecky-Levich equation, we determinate that 4.6 electrons were transferred, indicating that N_2 was the product of the oxidation. The difference between 4.6 and 4 could be attributed to the difference between the real and geometrical area of the electrode. Finally, we proved the behavior of type-2 electrode as an amperometric sensor of hydrazine due the linear relationship between the current and the hydrazine concentration, as shown in Figure 9.

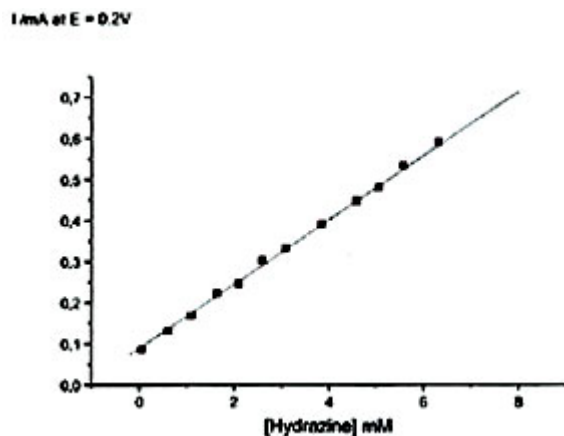


Figure 9. Linear relationship between I (from polarization curves at 0.2V) and hydrazine concentration for type 2 electrode.

This linear relationship corresponds to a calibration curve that was tested for many prepared solutions of known concentrations. At higher concentrations than those that appear in the Figure, the linear correlation disappears and higher currents than the expected are obtained, probably due to the high amount of bubbles formed on the surface of the electrode due to the nitrogen that is the product of the oxidation. For lower concentrations, it is not possible to separate the current from the noise of the equipment.

CONCLUSIONS.

In this work three modified electrodes were proved toward the oxidation of hydrazine. In all the cases, the electrocatalytic behavior strongly depends on the method used for the modification. The electrode submerged in a solution containing the porphyrin does not show activity to the reaction. Instead, the electrodes prepared by reflux or by electropolymerization show high catalytic behavior. The refluxed electrode was also proved as an amperometric sensor of hydrazine and shows a good linearity between the current and the hydrazine concentration in a wide range of concentrations. Also, I is stable and its behavior is highly reproducible.

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