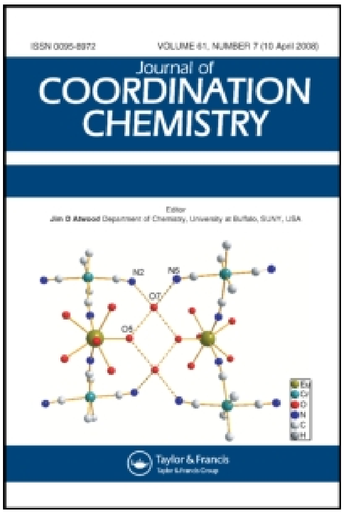

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A potentiometric hydrazine sensor: para-Ni-tetraaminophenylporphyrin/Co-cobaltite/SNO_2:F modified electrode

Paz Bravo[a]; Fabiola Isaacs[a]; Galo Ramírez[a]; Ignacio Azócar[a]; Ejnar Trollund[a]; María J. Aguirre[a]
[a] Facultad de Química y Biología, Departamento de Química de Los Materiales, Universidad de Santiago de Chile, Santiago, Chile

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A potentiometric hydrazine sensor: para-Ni-tetraaminophenylporphyrin/Co-cobaltite/SNO_2:F modified electrode

PAZ BRAVO, FABIOLA ISAACS, GALO RAMÍREZ, IGNACIO AZÓCAR,
EJNAR TROLLUND and MARÍA J. AGUIRRE*

Facultad de Química y Biología, Departamento de Química de Los Materiales,
Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile

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Three glass electrodes covered with Co-cobaltite/SnO_2:F (to obtain conducting glass electrodes) modified with *p*-Ni-tetraaminophenylporphyrin are described. In one electrode the porphyrin was absorbed on the electrode surface at room temperature, in another the porphyrin was electropolymerized on the electrode surface by cyclic voltammetry, and in the third the bare electrode was immersed in DMF containing the porphyrin and refluxed 6 h at 150°C. The three electrodes were tested as electrocatalysts for the oxidation of hydrazine and as potentiometric sensors of this chemical. The electrode modified by refluxing showed good electrocatalytic behavior as well as a linear relationship between its open circuit potential and the concentration of hydrazine in a concentration range from 0.16 to 12 μM, with fast response. These characteristics indicate that the conducting glass electrode of Co-cobaltite/SnO_2:F covered with *p*-Ni-tetraaminophenylporphyrin by the reflux method is a good potentiometric sensor of hydrazine. The active site is probably the ligand that changes its electron density by formation of a supramolecular system.

Keywords: Potentiometric sensor; Hydrazine detector; Modified electrode; *p*-Ni-tetraaminophenylporphyrin; Supramolecular assembly

1. Introduction

Hydrazine compounds are used in many industrial fields, but are highly toxic and their detection and quantization is a problem of considerable analytical interest. There are many papers [1–34] referring to oxidation of hydrazine in order to convert it into innocuous products or concerning its detection by a variety of methods. In the case of the amperometric detection of hydrazine, carbon fiber microelectrodes modified with rhodium under flow-injection conditions have been used [25]. These microelectrodes show good stability and reproducibility, with a detection limit of 2×10^{-5} M. Using a chemiluminescence method the range of linear relationship between oxidation current and chemiluminiscence was 1×10^{-6} to 5×10^{-5} M. After optimization, the method yielded a 2σ detection limit of 5×10^{-7} M. [34]. This method is based on the chemiluminescence emitted during oxidation of hydrazine by *N*-bromosuccinimide

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*Corresponding author. Fax: 56-2-6812108. Email: maguirre@lauca.usach.cl

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in the presence of dichlorofluorescein. Using a Nafion/ruthenium(III) chemically modified electrode [33] it is possible to determine the concentration of hydrazine in flow-injection experiments measuring the oxidation current. Nakagaki *et al.* [35, 36] have reported the electrochemical behavior of copper porphyrin in zeolite cavities and of cobalt porphyrins immobilized on niobium(V) oxide grafted-silica gel surfaces as hydrazine sensors. These few examples show the wide variety of methods for detecting hydrazine. However, in most cases electrochemical methods involve amperometric measurements. Indeed, using the same electrode surface and the same porphyrin proposed in this work, an amperometric hydrazine sensor was obtained [27]. In this work we present a potentiometric method for detecting hydrazine that shows fast response, good reproducibility, stability, and a reasonable linear concentration range.

2. Experimental

2.1. *Electrodes*

Three kinds of electrodes modified with *p*-Ni-tetraaminophenylporphyrin were used in this work. In all cases the modification was on the same electrode surface, a Co-cobaltite/SnO_2:F electrode: The working electrode surface 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. A methanolic solution containing 53.074 $g\,L^{-1}$ of $SnCl_4$, 0.05 M ammonium monofluoride and 18 mL of water was sprayed on a glass sheet kept at 420°C. Flow rate was constant (6 $mL\,min^{-1}$), and gas pressure was 2 bar. After this treatment, using a similar method, a solution containing 0.149 M $Co(NO_3)_2$ was sprayed on the SnO_2:F glass sheet, but the temperature was set at 250°C, the flow rate of the solution was the same, and gas pressure was 2.5 bar. Finally, the electrode was exposed to an O_2 atmosphere during 24 h at 250°C. The Co-cobaltite/SnO_2:F electrode obtained was characterized by X-ray diffraction using Cu-Kα radiation ($\lambda = 1.5406$ Å), with diffraction angles $2\theta = 5{-}90°$ at a scan rate of 0.02°/step. An Ag|AgCl electrode was used as reference, and a Pt wire as counter electrode.

2.1.1. Modification of the working electrode surface

Electrode 1. The electrode surface was immersed during 15 min at 20°C in a solution containing *p*-tetraaminophenylporphyin Ni(II) (NiTAPP) (saturated DMF solution). Then, the electrode was rinsed with methanol and with doubly distilled water.

Electrode 2. The electrode surface was potentiodynamically cycled in a DMF solution containing 0.1 M tetrabutylammonium perchlorate (TBAP) and saturated with the porphyrin. The potential was swept from –0.1 to 1.2 V at 0.1 Vs^{-1} during 25 cycles. After electropolymerization the electrode was rinsed with methanol and with doubly distilled water.

Electrode 3. The electrode was treated in the same solution as that of the first method, but in this case it was refluxed at 150°C for 6 h. After this treatment the solvent was evaporated and the electrode was washed in the same way as before.

In all cases the electrochemical response was stabilized by continuously cycling the potential in basic medium before hydrazine detection.

2.1.2. Electrochemical measurements. X-ray diffractometry was performed in a Siemens-D5000 powder diffractometer equipped with a graphite monochromator. Open circuit potential was measured with the modified electrodes and the reference Ag|AgCl electrode immersed in a 0.1 M KOH solution containing different hydrazine concentrations. The potential of the working electrode was recorded on a Voltalab PGZ100 Potentiostat and simultaneously measured with a UYUS DT890B digital multitester. The measurement time was ten minutes.

2.2. *Reactants*

Hydrazine sulfate (p.a., Riedel de Haën), methanol (p.a., Caledon), tin(IV) chloride, (anhydrous, 99%, Aldrich), Ni(II) hydroxide (p.a., Merck,), Ni(II)-*p*-tetraaminophenylporphyrin (Mid-Century), H_2-tetraaminophenylporphyrin (free-ligand) (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).

3. Results and discussion

In general, transition metal porphyrins adsorbed on different electrode surfaces catalyze redox reactions such as the electroreduction of molecular oxygen [1–5], carbon dioxide [6–11], nitrites [12, 13–17], nitrates [18, 13–17], and the electrooxidation of sulfite [19–23] and hydrazine [24–27]. In our case the electrode surface was chosen because it shows very interesting electrocatalytic behavior toward the electrooxidation of hydrazine when modified with nickel porphyrins [27, 36, 37]. X-ray difractommetry of the electrode surface [27] indicates that the structure is highly crystalline and corresponds to cubic spinels of spatial group F3dm. In our case we tested the electrooxidation of hydrazine with three different modified electrodes.

Electrodes 2 and 3 catalyze the oxidation of hydrazine. Electrode 3 showed a linear relationship between current and hydrazine concentration [27]. The bare electrode is active to that reaction, but its electrocatalytic behavior is better when modified. Its activity increases when the porphyrin is metallized with Ni, but not with Co. We still do not have an explanation for this fact.

The porphyrin used in this work is shown in figure 1. The cyclic voltammogram of the type-3 electrode, covered by the porphyrin (reflux method) in aqueous solution, is depicted in figure 2(a), and the bare conducting glass electrode is shown in figure 2(b). Figure 2(b) shows a redox couple at ca 0.47 V corresponding to the Co(IV)/Co(III) couple [38] that shifts 30 mV to more negative potentials and becomes more irreversible when the porphyrin is adsorbed on the surface. We attribute the redox couple of figure 2(a) to the same process of figure 2(b) because the porphyrin does not undergo redox processes at those potentials [39]. The only possibility of assigning this process is that the Co(IV)/Co(III) redox couple of the cobaltite modifies its potential by

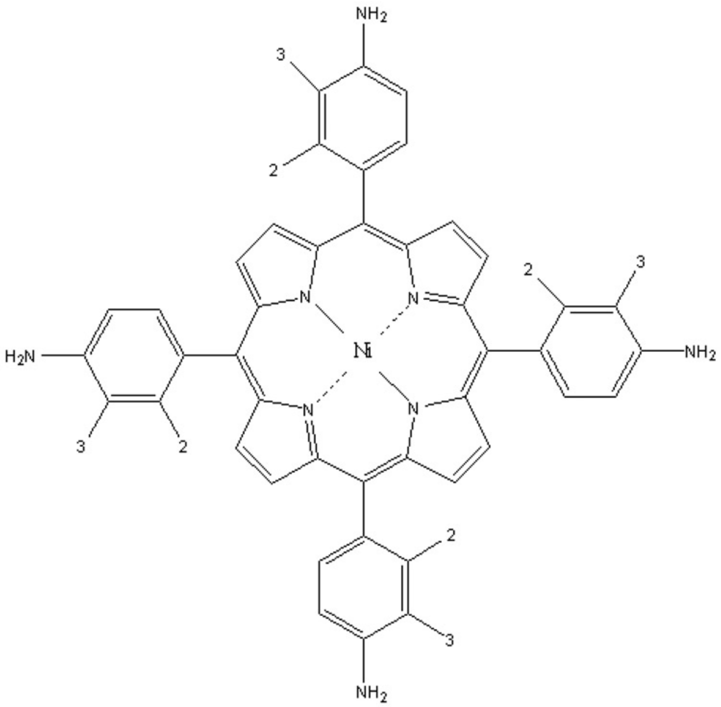

Figure 1. Structure of Ni-para-tetraaminophenylporphyrin.

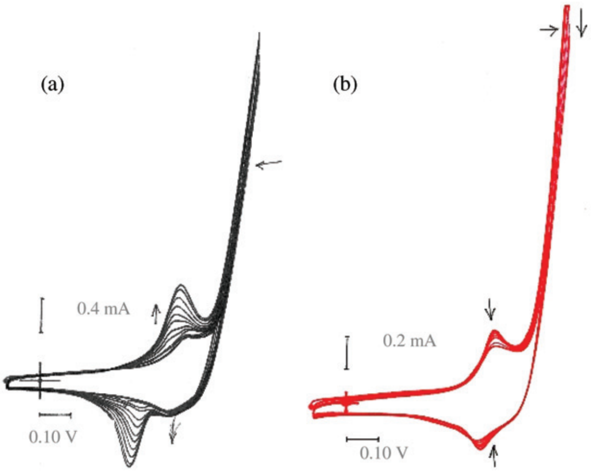

Figure 2. (a) Cyclic voltammogram of Co_3O_4/NiTAPP (type 3 electrode). Scan rate: $100\,mV\,s^{-1}$. Electrolyte: 1 M KOH. 400 cycles; (b) cyclic voltammogram of Co_3O_4 glass electrode. Scan rate: $100\,mV\,s^{-1}$. Electrolyte: 1 M KOH. 400 cycles.

interaction with the porphyrin. The current of the redox couple of figure 2(a) increases with the number of cycles. The current increase can be due to the electrolyte going into the layers formed by the porphyrin, to the formation of a nickel hydroxide [40] that permits the interaction of the porphyrin with the Co of the cobaltite, or to the rearrangement of supramolecular assemblies formed during reflux [41]. The UV-vis spectra of the different electrodes only show in each case the presence of the porphyrin but not if it is metalled, or the order of the adsorbed layers. On the other hand, the same surface modified with Co-porphyrin (method 1) is not a good electrocatalyst for the oxidation of hydrazine, and no linear relationships are obtained between current or open circuit potential and hydrazine concentration. The same occurs when the free-ligand is used. This indicates that when cycled, the Ni porphyrin forms nickel hydroxide that plays an important role in the electrocatalysis, or more realistically, a supramolecular assembly is formed. In fact, if the electrode surface is modified with the free ligand (method one) and $Ni(OH)_2$, a potentiometric sensor is not obtained. The characteristics of the ligand are probably drastically changed if a supramolecular system is formed, because the main interactions will be between the ligands (π–π interactions) and hydrogen bonds between the amino groups of different porphyrins. However, further studies are required to elucidate the reason for the different behavior of the porphyrin refluxed on the surface compared to the same porphyrin adsorbed or polymerized. The influence of the formation of a supramolecular arrangement on the electrocatalysis is very important, as can be see in the case of the electroreduction of CO_2 by a Co-tetrabenzoporphyrin/glassy carbon electrode. In this case the modified electrode is capable of electroreducing carbon dioxide only if a supramolecular assembly is previously formed, otherwise there is no electroactivity [41]. In the case of the Co-tetrabenzoporphyrin, the adsorbed complex or the supramolecular arrangement catalyzes equally the electroreduction of molecular oxygen, indicating that the ligand is responsible for the different behavior in each reduction, because the electroreduction of CO_2 is assisted by the ligand [42] and the electroreduction of oxygen is metal-centered [43].

The electropolymerization of the porphyrin on the conducting glass electrode is shown in figure 3, where no redox couples are seen and only an ill-defined oxidation wave appears at positive potentials. The growth of the polymer is very low, but the UV-vis spectrum of the modified electrode reveals the presence of the polymer in the widening of the Soret and Q bands (not shown).

Under the same conditions we tested the three modified electrodes and also the bare electrode, but no relation was found between hydrazine concentration and the open circuit potential (OPC) except for the type 3 electrode. In fact, this electrode can be washed with doubly distilled water and immersed in a different solution containing a different amount of hydrazine, and its behavior is linear (see figure 4, which shows the real data and the linear fit), and its response is very fast. After two or three minutes it reaches a constant value that is maintained until the end of the experiment (10 min). This behavior is comparable to the response of a pH meter. The bare electrode or other modified electrodes, show erratic behavior, and the OCP changes constantly without any noticeable trend. Figure 5 is a detail of figure 4 showing a good linear relationship at low hydrazine concentrations. However, the electrode is not very stable and loses its capacity after 3 or 4 days. Efforts to inmprove its stability are under way.

It is not clear why only the type 3 electrode has good behavior as a potentiometric sensor. However, this behavior confirms that the active site of this electrode is different than the others, even though all are formed by the same substrate and the same porphyrin. We attribute this behavior to the formation of a supramolecular assembly in the case of the type 3 electrode. On the other hand, OPC values are very negative, corresponding to a redox couple of the ligand. If an adduct between the ligand and

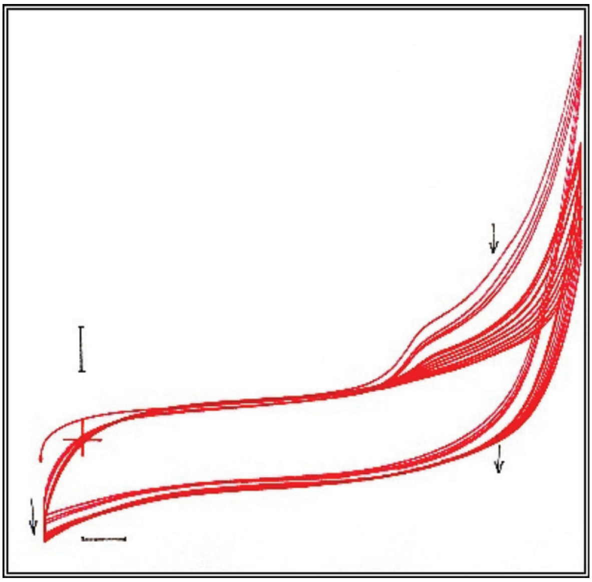

Figure 3. Electropolymerization of NiTAPP on Co_3O_4 glass electrode. 1 mM NiTAPP/dimethylformamide/0.1 M TBAP. 100 mV s^{-1}, 140 cycles.

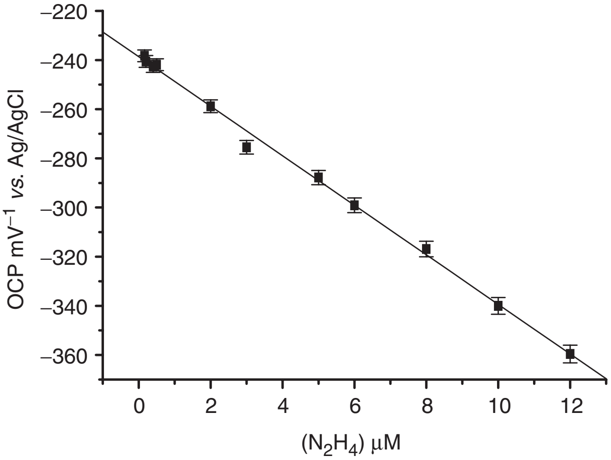

Figure 4. Plot of open circuit potential of electrode 3 in the presence of a solution containing hydrazine. Response taken at three minutes of contact.

hydrazine is responsible for the changes in the OCP values, type 1 and type 2 electrodes do not modify the electronic characteristics of the ligand to the same extent as type 3 electrode. In the case of a conducting glass formed by SnO_2:F modified with Co-tetraaminophthalocyanine, [25] or its free-ligand, changes in the OCP are obtained in the presence of hydrazine, showing that two adducts are formed with the metal or the ligand. Therefore it is possible that in the cases of type 1 and type 2 electrodes the formation of an adduct between the nickel metal center of the porphyrin and the hydrazine takes place, and the more stable adducts do not allow electrooxidation

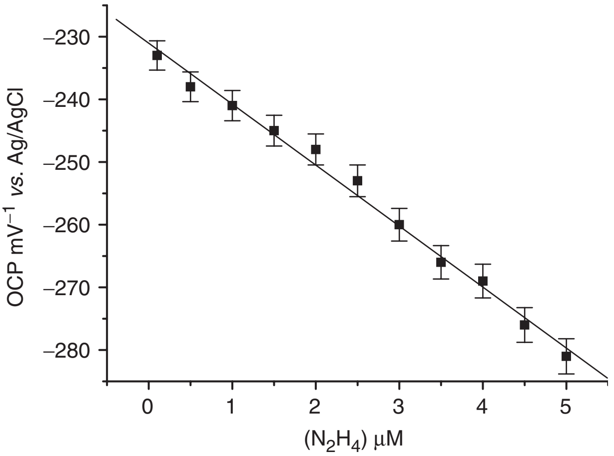

Figure 5. Plot of the first part of figure 2 showing the good relationship obtained at low hydrazine concentrations.

of hydrazine. If this is true, no relationship between current or OCP and hydrazine concentration can appear because of the slow kinetics of the oxidation. In fact, here we show that in the case of the OCP there is no relationship, and in a previous communication we had shown that there is no correlation between current and concentration for those electrodes. In the case of the type 3 electrode, the formation of an adduct between the metal of the porphyrin and the hydrazine is hindered and only the ligand can react.

4. Conclusions

We found that a *p*-Ni-tetraaminophenylporphyrin/Co-cobaltite/SnO_2:F electrode modified by refluxing in DMF is capable of acting as a potentiometric sensor of hydrazine in basic medium. It was tested in a hydrazine concentration range of 1.6 to 12 μM, showing good linearity and fast response. In order to obtain this potentiometric sensor, the bare Co-cobaltite/SnO_2:F electrode was immersed for 6 h at 150°C in a solution containing the porphyrin. Other ways of modifying the same surface (immersing the electrode for 15 min at 20°C or electropolymerizing the porphyrin on the surface) do not produce a potentiometric hydrazine sensor. The reason is not yet understood, but it is probably related to formation of two different kinds of adducts. In the case of the refluxed porphyrin, the adduct may be produced by hydrazine and the ligand due to formation of a supramolecular assembly; in the other cases the adduct may be formed between the nickel and the hydrazine.

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