

Study of Cu, Cu-Ni and Rh-modified Cu porous electrodeposits as electrode materials for the electroanalysis of nitrate and nitrite ions

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Abstract

Three porous materials (Cu, a Cu-Ni alloy with 70 at% Cu and Rh-modified Cu) have been tested as electrodes for the electroanalysis of nitrate and nitrite ions, in either neutral or basic media, using mainly a flow injection technique. Porous Cu and Cu-Ni were prepared by electrodeposition at high current density, exploiting the transient template action of hydrogen bubbles. Rh-modified Cu electrodes were obtained from porous Cu, through a galvanic displacement reaction. All materials had a linear response for both nitrates and nitrites, at concentrations up to 10^{-3} M, at least. Sensitivities, detection limits and stability were determined. Compared with Cu, used as a benchmark, (i) Rh-modified Cu had higher sensitivity for nitrates, comparable sensitivity for nitrites, lower or comparable detection limits and overall better stability; (ii) Cu-Ni had lower sensitivity, but exhibited lower detection limits and more stable performance for most analyte/medium combinations.

Keywords electrocatalysis, electrodeposition, flow injection, galvanic displacement, hydrogen template.

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Introduction

The concentration of nitrate and nitrite ions in soils, fresh water and sea water tends to increase as a result of various human activities, mainly agriculture and, to a lesser extent, combustion processes that form NO_x species, then converted to nitrite. Owing to their negative impact on human health, the levels of nitrate and nitrite ions in the environment need to be monitored, to ensure that they do not exceed the thresholds established by the World Health Organization and by various governments. Although the most commonly used analytical methods for the determination of nitrates and nitrites are derived from the classical Griess test, implying derivatization followed by colorimetric analysis, electroanalytical procedures are also intensively investigated (for reviews see [1-3]).

Requirements for the use of bare electrodes in nitrate/nitrite electroanalysis are strong catalytic activity in the reduction of these ions, and good stability under the test conditions. After screening several cathode materials, various investigators have converged to identify copper [4-10] or its alloys, especially Cu-Ni [11,12], as the most suitable ones. To cope with the intrinsic tendency of Cu to become deactivated upon nitrate reduction, in most cases Cu layers were formed *in-situ*, just before the analyses, by reducing Cu ions deliberately added to the analytical samples. The Cu deposition conditions were optimized to produce macroporous materials [7], with large and fresh surfaces, or especially active sites [9].

In recent papers [13-15], our group has shown that electrodeposited Cu-Ni alloys are more active than Cu in the reduction of nitrates and that, when prepared with an appropriate bimodal porosity [14,15] they withstand poisoning better than Cu or compact Cu-Ni alloys. The porous Cu-Ni deposits have been prepared according to methods previously reported for other porous metals [16-23] and alloys [23-25], i.e. by exploiting the transient template action of hydrogen bubbles. Electrolyses performed at high current density cause simultaneous metal ions reduction and

hydrogen evolution, leading to the formation of deposits with both macropores and micropores, at the tens of microns and sub-micron scales, respectively. These features are favourable to run electrochemical processes occurring under mixed kinetic control, like nitrate reduction, as the macropores allow enhanced mass transport, while the micropores ensure large surface area.

Rh is known to be a very active electrode material for nitrate reduction [26] and we have shown that Cu-Rh alloys are also good catalysts for the same reaction [27]. Therefore, it is interesting to compare a porous electrode containing Cu and Rh with porous Cu and Cu-Ni. Rather than attempting the hydrogen-assisted electrodeposition of porous Cu-Rh alloys, we have preferred to deposit Rh onto porous Cu, through a galvanic displacement reaction, thus obtaining a material henceforth called Rh-modified Cu, in which the expensive noble metal is present only at the surface of the porous Cu.

In the present paper, we describe an investigation aimed at assessing the potential of porous Cu-Ni and Rh-modified Cu as electrode materials for nitrate determination, using Cu electrodes of comparable morphology as a benchmark. The study addresses mainly nitrate, because it is substantially more inert than nitrite [1-3], and therefore less easy to detect. Most results reported in the following concern flow injection analysis, because this technique is simple and has potentially a high sample throughput. They may be interesting also from the viewpoint of end column detectors.

Experimental

Chemicals and materials. All chemicals used in this investigation were commercially available and were employed as received. Two kinds of working electrodes were used: (i) Cu RDEs (0.283 cm²) and (ii) Screen-Printed Gold Electrodes (0.125 cm²), henceforth called Au-SPE, purchased from DropSens, Oviedo, Spain. These electrodes comprise an Au counter electrode and an Ag reference

electrode. The latter was converted to an Ag/AgCl electrode by anodization in a chloride medium [28], to render its potential more stable under the flow injection conditions.

Electrodepositions were performed in a conventional, single-compartment glass cell, bearing a Pt wire counter electrode. Other electrochemical experiments involving RDEs were performed in two-compartment cells. The working electrode and a Pt wire counter electrode were located in the main compartment and appropriate reference electrodes (Hg/HgO/1M KOH or Hg/Hg₂SO₄/0.5M K₂SO₄ in basic and neutral media, respectively) were inserted in a side compartment connected to the main one through a Luggin capillary.

A DropSens FLWCL flow cell, with an internal capacity of 50 μ L, was used in flow injection analyses. In this cell, the analyte solution impinges perpendicularly onto the working electrode. The diameter of the nozzle is ca. one fifth of that of the electrode, and the distance between the nozzle mouth and the electrode is 0.25 mm.

Electrodeposition and other electrochemical experiments were performed using an Autolab PGSTAT 302 N potentiostat/galvanostat, equipped with a booster providing currents up to 10 A. SEM images and EDS analyses were obtained with a Fei-Esem FEI Quanta 200 FEG instrument, equipped with a field emission gun, operating in high vacuum conditions. Na₃RhCl₆ solutions were analysed with a Perkin-Elmer Lambda 15 UV/VIS Spectrophotometer.

Procedures. Porous Cu or Cu-Ni layers were deposited onto either Cu disc electrodes, rotated at 2500 rev min⁻¹, or stationary Au-SPE electrodes, under galvanostatic conditions. Cu was deposited from solutions containing 0.40 M CuSO₄, 1.5 M H₂SO₄ and 0.050 M HCl [16], with a -3 A cm⁻² current density for Cu RDEs and a -6 A cm⁻² current density for Au-SPE. Cu-Ni was deposited from solutions containing 0.125 M CuSO₄, 0.125 M NiSO₄, 0.30 M Na citrate and 1.0 M (NH₄)₂SO₄, pH 4.5 [15], with a -3 A cm⁻² current density. For both Cu and Cu-Ni, the transferred charge was 40 C cm⁻², leading to the deposition of ca. 6 mg cm⁻² of metal or alloy, with a current efficiency around 50% [14,15]. The

solutions were kept at 20°C, and were vigorously stirred when Cu or Cu-Ni were deposited onto Au-SPE.

Rh-modified Cu electrodes were obtained by immersing porous Cu electrodes in deaerated solutions containing 10^{-3} M Na_3RhCl_6 , 1 M NaCl and HCl to adjust the pH at 2.0. The Rh/Cu galvanic exchange reaction was allowed to occur, at open circuit, typically during 2 h. This procedure was previously used by our group for modifying Ni foams with Rh nanoparticles [29]. When Rh-modified Cu electrodes were prepared on Au-SPE, AgCl was grown on the Ag electrode ahead of the galvanic displacement reaction. The Rh content of the Rh-modified Cu electrodes was estimated from the decrease in the concentration of Rh(III) ions in the solutions used for the galvanic exchange [29], determined by UV-Visible spectroscopy. Cyclic voltammetry in 1.0 M NaOH (50 mV s^{-1} scan rate) was used to estimate the Rh surface area from the H desorption charge [29, 30]

Electroanalytical experiments were carried out with RDEs coated with porous Cu, Cu-Ni or Rh-modified Cu layers, by immersing them in either 0.10 M NaOH or 0.10 M Na_2SO_4 (pH =7.0), polarizing the electrodes at an appropriate potential and measuring the chronoamperometric response caused by additions of NaNO_3 dissolved in the same basic or neutral solutions. All solutions were deaerated and kept at 20°C.

Au-SPE electrodes coated with porous Cu, Cu-Ni or Rh-modified Cu layers, and the same 0.10 M NaOH or 0.10 M Na_2SO_4 background solutions were used in flow injection experiments, by making additions of either NaNO_3 or NaNO_2 samples. The electrolyte flow was fixed at 1.0 ml min^{-1} . The sample loop capacity was 0.50 mL.

Results and discussion

Preparation and SEM characterization of the porous electrodes. Porous Cu and Cu-Ni layers were prepared at large cathodic current densities, under conditions causing vigorous hydrogen evolution.

Deposition baths and experimental conditions were those described in previous articles by our group [13-15] and by others [16,17,19,20], with possible minor variations aimed at adapting the procedures to rotating disc or screen printed electrodes. Rh-modified Cu electrodes were obtained by modifying porous Cu electrodes through a spontaneous deposition reaction in which Rh(III) chloride complexes displaced a part of the Cu electrodeposits.

Fig. 1a-d show SEM images of Cu and Cu-Ni (Cu 70 at%, determined by EDS) porous layers electrodeposited onto Au-SPE electrodes. The Cu-Ni images are essentially identical to those obtained with the same material deposited onto an RDE, reported in [14,15]. The morphologies of Cu layers electrodeposited onto Au-SPE and Cu RDE (not shown) were also undistinguishable, and very close to those shown by Shin and Liu [16]. Both materials exhibit a bi-modal porosity, where one can recognize pores with quasi-circular mouths and typical diameters between 10 and 40 μm , due to the growth of the electrodeposits around the hydrogen bubbles, and much tinier, less deep, irregular pores separating assemblies of metal dendrites. The larger features are very similar for both Cu and Cu-Ni, depending mainly on the number of H_2 bubbles per unit surface and on their size at the departure, primarily imposed by the current density. Instead, the fine structure is significantly more open for Cu than for Cu-Ni, because the two materials are likely to have somewhat different kinetics of electrocrystallization and dendritic growth.

The Rh-modified Cu images in Fig 1e-f show that the Rh/Cu galvanic exchange occurred without altering the larger features of porous Cu. The larger magnification allows to appreciate some coarsening of the dendrites and an enlargement of the interstices between crystallite assemblies, as already reported for Ru/Ni and Ir/Ni exchanges [31]. EDS analyses performed at different positions along the layer thickness, after fracturing the Rh-modified Cu deposit, showed small fluctuations in the Rh/Cu ratio, compatible with the experimental uncertainty, but no definite increasing or decreasing trends. These observations suggest that the cathodic and anodic partial

reactions of the galvanic displacement reactions were randomly distributed, not localized in specific areas, thus leading to a rather homogeneous distribution of Rh on the Cu surface.

Rh-modified Cu electrodes prepared with a reaction duration of 2 h had Rh loadings in the range 0.10 to 0.13 mg cm⁻². Assuming the Rh(III) reduction to be quantitatively compensated by Cu dissolution, the amount of displaced Cu was 0.09 to 0.12 mg cm⁻², if Cu²⁺ was formed, or twice as much if dissolution as Cu⁺ was preferred, as expected in chloride solution where CuCl₂⁻ is the predominating species [32]. The largest amount (0.24 mg cm⁻²) corresponds to only 4% of the Cu initially present. Therefore, it is not surprising that the Rh-modified Cu electrodes retained the geometry of porous Cu.

The Rh surface area was estimated by measuring the hydrogen desorption charge in 1 M NaOH, as described in [29,30]. Using Rh-modified Cu layers deposited on either Cu RDEs or Au-SPEs, the Rh surface area was found to be ca. 40 times their geometric area. In a recent paper [33], we have shown the porous Cu roughness factor to be 125±5. Therefore, the Rh surface area was about one third of the surface area of the Cu layers submitted to galvanic exchange. This result may be due to two convergent causes: (i) at the sub-micron scale, the Rh morphology was coarser than that of Cu (Fig. 1, parts b and e); (ii) Rh did not cover the whole Cu surface. Thus, it is probable that Rh-modified Cu electrodes had both Rh and Cu surface sites.

Chronoamperometry. Fig. 2a compares the current transients measured with rotating Cu, Cu-Ni or Rh-modified Cu electrodes, upon three successive additions of 5 × 10⁻⁴ M NaNO₃ to 0.1 M Na₂SO₄, pH 7. For each electrode material, Fig. 2a shows two curves obtained with two independent but nominally identical electrodes, to provide an indication on the reproducibility of the tests. Minor differences were found for Cu and Cu-Ni, while the traces relevant to Rh-modified Cu almost perfectly overlapped. In the absence of nitrate ions, after a 900 s potentiostatic polarization (only partially shown), stable background currents were measured at the selected potential (-1.5 V vs.

Hg/Hg₂SO₄/0.5M K₂SO₄). These currents increased in the order Cu < Cu-Ni < Rh-modified Cu, according to the activity ranking of these materials in the hydrogen evolution reaction. Each addition of NaNO₃ caused an increase in the reduction current, roughly comparable for the three materials. The transitions were not very sharp because the nitrate concentration took some time to homogenize in the solution volume (ca. 50 mL). Between two successive additions, the reduction current underwent some drift towards smaller (in modulus) values, more pronounced for Cu than for Cu-Ni or Rh-modified Cu, due to progressive electrode deactivation.

Fig. 2b shows that the current ($I_{0+\Sigma\Delta I}$) varied linearly with the NaNO₃ concentration. ($I_{0+\Sigma\Delta I}$) is defined as the sum of the stationary current measured in the absence of nitrates (I_0), plus the appropriate number of current jumps (ΔI) caused by the additions. Each ΔI value was evaluated by approximating the 60-second portions of the I-time curves recorded just before and just after the additions with straight lines, and taking the current difference at the time of the addition. The quantity ($I_{0+\Sigma\Delta I}$) was preferred to the current values measured either just after the addition or at the end of each 300-second period when nitrate concentration remained constant, because the former was noisy and the latter was affected by electrode deactivation.

The slopes of the best-fitted straight lines in Fig. 2b allowed the assessment of the sensitivities of the electrodes, summarized in Table 1, together with those determined in comparable experiments performed in basic solutions (0.1 M NaOH). In neutral media, the sensitivity for nitrate, measured at the same potential, increased in the order: Cu (9.5 A cm⁻² M⁻¹) < Cu-Ni (10.9 A cm⁻² M⁻¹) < Rh-modified Cu (12.0 A cm⁻² M⁻¹). For basic media, Table 1 reports, for Cu, Cu-Ni and Rh-modified Cu electrodes, data obtained at different potentials which provided a good compromise between sensitivities and detection limits. The detection limits in Table 1 were estimated as 3 times the average peak-to-peak noise [12]. In most cases, they varied between 2 ×

10^{-6} and 7×10^{-6} , with the exception of Rh-modified Cu in neutral medium (2×10^{-5} M). The review of Moorcroft et al. [1] reports values comprised between 4×10^{-7} and 1×10^{-5} M.

Flow injection – Sensitivity and linearity. In preliminary tests, performed with both Cu and Cu-Ni, the effect of the electrode morphology was investigated by comparing porous and compact electrodeposits. The responses were found to be ca. five times larger for the former than for the latter, showing that a significant part of the inner pore surface area was active, and highlighting the advantage of using porous electrode materials.

Different flow injection experiments were performed to assess linearity, sensitivity, stability and reproducibility of the measurements. Fig. 3a shows, as an example, the result of an experiment aimed at evaluating the minimum linear range and the sensitivity of porous Cu in neutral solution. A continuous flow of 0.1 M Na_2SO_4 solution was maintained in the cell and solutions with NaNO_3 concentrations varying between 0 and 10^{-3} M were injected. Fig. 3a shows that the response increased with the NaNO_3 concentration, but there was a response even when a nitrate-free solution was injected. The resulting peak currents, measured for three successive injections for each concentration, were averaged and plotted vs. the nitrate ion concentration. The insert in Fig. 3a shows that, in the explored concentration range, a straight line fitted well all data points, including that corresponding to the injection of a solution with no nitrates. This means that the hydrodynamic perturbation caused by injection of nitrate-free 0.1 M Na_2SO_4 solution provided a constant additive contribution to the peak current. This artefact was an intrinsic limitation of the device used for the experiments, not related with the nature of the working electrode.

Experiments similar to those shown in Fig. 3 were performed for several combinations of electrode material, analyte (nitrate or nitrite) and solution pH, to determine the effect of the potential of the working electrode. Examples are shown in Fig. 4. Fig. 4a-b compare the calibration curves obtained for both analytes with a Cu-Ni electrode, in basic media. The sensitivity for nitrates

increased slightly as the potential became more negative, whereas the plots recorded with nitrite at different potentials overlapped. These results agree with the behaviour reported in [13] for compact Cu-Ni alloys, where it was shown that the peak reduction current was somewhat higher for nitrate than for nitrite, and that a better defined diffusion plateau was observed for the latter than for the former. Fig. 4c-d shows that the sensitivity of Rh-modified Cu electrodes in the reduction of either nitrates or nitrites, in neutral media, went through maxima at -1.1 V vs. Ag/AgCl. These examples show that the potential dependence is not unique for different electrode-analyte-pH combinations, and that the E value selected for analyses must be optimized for each combination.

Table 2 summarizes the main results concerning sensitivity and detection limit for nitrates and nitrites in both neutral and basic media. For each electrode-analyte-pH combination, this table reports data only for the potential affording the highest sensitivity, among those investigated. It must be noted that potentials negative enough to cause significant hydrogen evolution were not suitable because the formation and detachment of hydrogen bubbles prevented the background current from becoming stable. The following sensitivity rankings were observed:

- Nitrate in neutral medium: Rh-modified Cu > Cu > Cu-Ni
- Nitrate in basic medium: Rh-modified Cu > Cu > Cu-Ni
- Nitrite in neutral medium: Cu > Rh-modified Cu > Cu-Ni
- Nitrite in basic medium: Cu > Rh-modified Cu > Cu-Ni

Thus, the sensitivity ranking for the same analyte did not depend on the medium. Rh-modified Cu had a significantly improved sensitivity for nitrate, but not for nitrite, as compared with Cu. The sensitivity of Cu-Ni, lower than that of Cu, agrees with the lower peak current of the former, though at a less negative potential, as previously reported [13].

Flow injection – Stability and reproducibility. Fig. 5 shows examples of the experimental response obtained by testing the stability of Rh-modified Cu electrodes in either neutral or basic media. In both cases, the peak currents measured by successively injecting 0.5 mL volumes of 5×10^{-4} M NaNO_3 became somewhat lower. Although the decrease of the peak current was caused partially by a declining background current, this result pointed to some deactivation of the electrodes.

Fig. 6 summarizes the results of stability tests for twelve electrode/analyte/medium combinations, showing the ratio ($I_{\text{peak}}^n/I_{\text{peak}}^1$) plotted vs. the progressive number of the injections. I_{peak}^n and I_{peak}^1 are the peak currents measured at the n^{th} and first injection of each series, respectively, both corrected for the background current. To assess the performance loss of each system, the data in Fig. 6 were fitted with straight lines which slopes were used as quantitative parameters to establish the following stability ranking:

- Nitrate in neutral medium: Cu-Ni [-0.32] > Rh-modified Cu [-0.49] > Cu [-0.90]
- Nitrate in basic medium: Cu [-0.03] > Rh-modified Cu [-0.47] > Cu-Ni [-0.55]
- Nitrite in neutral medium: Cu-Ni [-0.10] > Cu [-0.57] > Rh-modified Cu [-0.62]
- Nitrite in basic medium: Cu-Ni [-0.20] > Rh-modified Cu [-0.43] > Cu [-1.3]

The figures in brackets were the average percent signal loss per injection. They underwent some variations when nominally identical experiments were repeated with different electrodes of the same kind, but the above rankings were respected. In most cases, Cu-Ni provided the most stable response.

Conclusions

Porous Cu, Cu-Ni and Rh-modified Cu electrodes have been prepared by hydrogen evolution assisted electrodeposition, combined when necessary with galvanic displacement, obtaining materials with

comparable morphologies characterized by a bimodal porosity. These materials have been compared as cathodes for nitrate and nitrite electroanalysis, in neutral and basic media. Linear ranges up to 10^{-3} M molar were obtained for all of them. Detection limits in the range 2.5×10^{-6} M to 1.2×10^{-5} M were estimated in flow injection analyses. As compared with the Cu benchmark, Rh-modified Cu exhibited 25 to 50% higher sensitivity for nitrate, but a lower stability, especially in basic media. Cu-Ni was the most stable electrode under most conditions, although it was generally less sensitive than the other electrode materials.

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Table 1. Sensitivity and detection limit of porous Cu, Cu-Ni and Rh-modified Cu RDEs, with respect to nitrate ions in 0.1 M Na₂SO₄ or 0.1 M NaOH.

Electrode	Medium	Potential ^a / V	Sensitivity / A cm ⁻² M ⁻¹	Detection Limit ^b / M × 10 ⁻⁶
Cu	Na ₂ SO ₄	-1.5	9.4±0.2	4.5
Cu-Ni	Na ₂ SO ₄	-1.5	10.9±1.0	2
Rh-modified Cu	Na ₂ SO ₄	-1.5	12.3±0.3	20
Cu	NaOH	-1.2	9.1±0.1	5
Cu-Ni	NaOH	-1.0	5.1±0.3	7
Rh-modified Cu	NaOH	-0.8	6.0±0.1	6

a: Potential was measured vs. Hg/Hg₂SO₄/0.5M K₂SO₄ in neutral media and vs. Hg/HgO/1M KOH in basic media.

b: Detection limit is defined as 3 times the peak-to-peak noise level.

Table 2. Sensitivity and detection limit of porous Cu, Cu-Ni and Rh-modified Cu electrodes, with respect to nitrate or nitrite ions in 0.1 M Na₂SO₄ or 0.1 M NaOH, determined with flow injection experiments.

Electrode	Medium	Potential ^a / V	Analyte	Sensitivity / A cm ⁻² M ⁻¹	Detection Limit ^b / M × 10 ⁻⁶
Cu	Na ₂ SO ₄	-1.3	NO ₃ ⁻	2.81±0.07	8.5
Cu-Ni	Na ₂ SO ₄	-1.2	NO ₃ ⁻	2.38±0.08	10
Rh-modified Cu	Na ₂ SO ₄	-1.1	NO ₃ ⁻	4.2±0.1	8.5
Cu	NaOH	-1.3	NO ₃ ⁻	3.83±0.08	12
Cu-Ni	NaOH	-1.2	NO ₃ ⁻	3.02±0.05	2.5
Rh-modified Cu	NaOH	-1.125	NO ₃ ⁻	4.86±0.09	5
Cu	Na ₂ SO ₄	-1.3	NO ₂ ⁻	3.54±0.02	10
Cu-Ni	Na ₂ SO ₄	-1.2	NO ₂ ⁻	2.53±0.02	8
Rh-modified Cu	Na ₂ SO ₄	-1.1	NO ₂ ⁻	3.16±0.08	8
Cu	NaOH	-1.3	NO ₂ ⁻	3.81±0.007	9
Cu-Ni	NaOH	-1.2	NO ₂ ⁻	2.56±0.01	4
Rh-modified Cu	NaOH	-1.125	NO ₂ ⁻	3.55±0.15	7

a: Potential was measured vs. Ag/AgCl (AgCl was formed by anodization on the screen-printed Ag electrode).

b: Detection limit is defined as 3 times the peak-to-peak noise level.

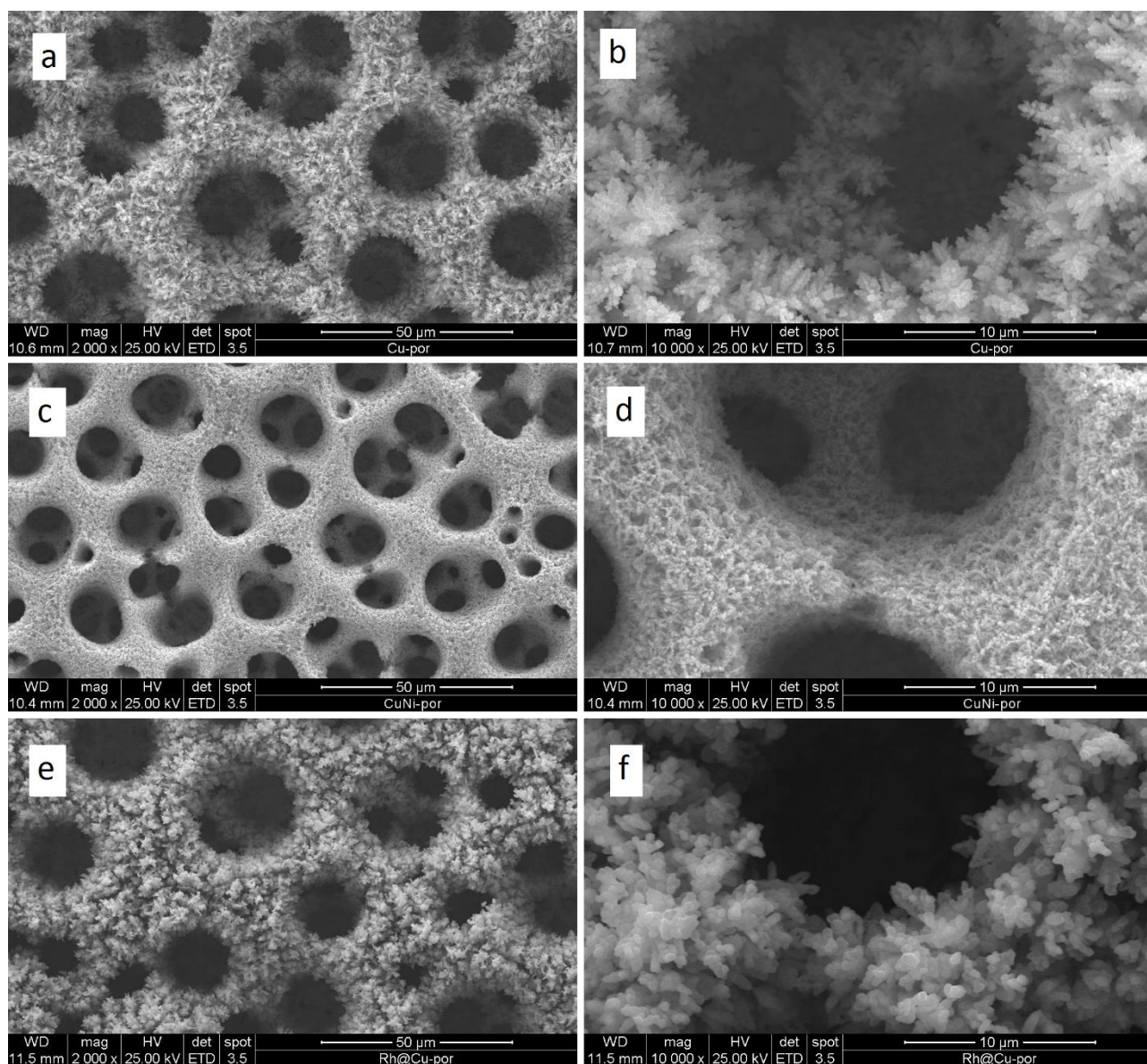


Fig. 1 SEM images of Cu (a, b), Cu-Ni (c, d) and Rh-modified Cu (e, f) porous layers deposited onto Au-SPE electrodes. Cu was deposited from 0.40 M CuSO₄, 1.5 M H₂SO₄ and 0.050 M HCl; Cu-Ni (Cu 70 at%) was deposited from 0.125 M CuSO₄, 0.125 M NiSO₄, 0.30 M Na citrate and 1.0 M (NH₄)₂SO₄, pH 4.5; Rh-modified Cu was obtained from porous Cu through a Rh/Cu galvanic exchange.

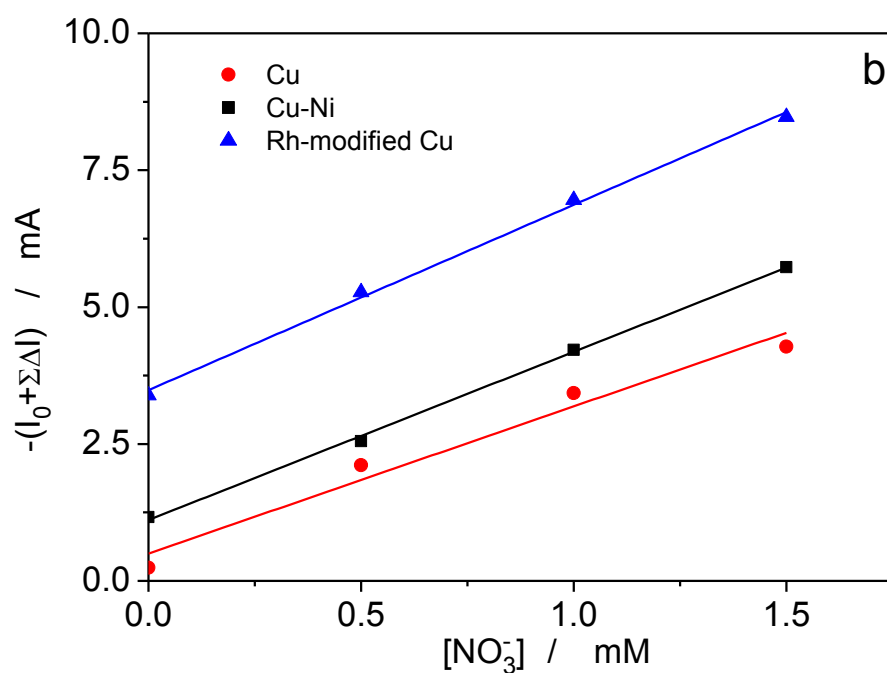
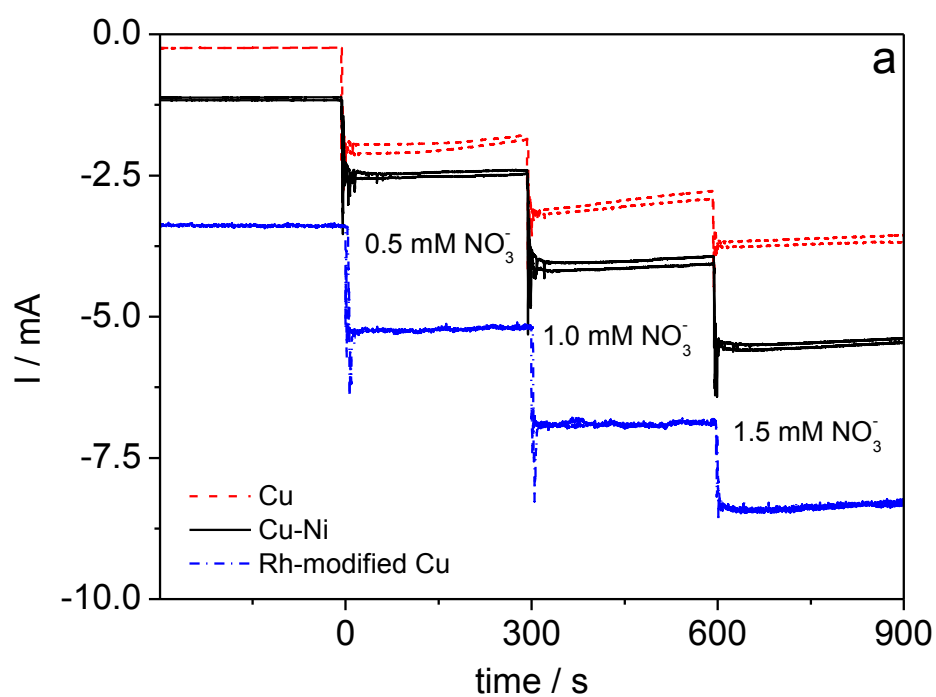


Fig. 2 a Chronoamperometric curves recorded with Cu, Cu-Ni and Rh-modified Cu rotating disc electrodes (0.283 cm^2 geometric area) in $0.1 \text{ M Na}_2\text{SO}_4$, pH 7, and after successive additions of $5 \times 10^{-4} \text{ M NaNO}_3$. Angular speed $2500 \text{ rev min}^{-1}$, $E = -1.5 \text{ V vs. Hg/Hg}_2\text{SO}_4/0.5\text{M K}_2\text{SO}_4$. **b** Plots of the quantity $(I_0 + \Sigma\Delta I)$ as a function of the nitrate concentration.

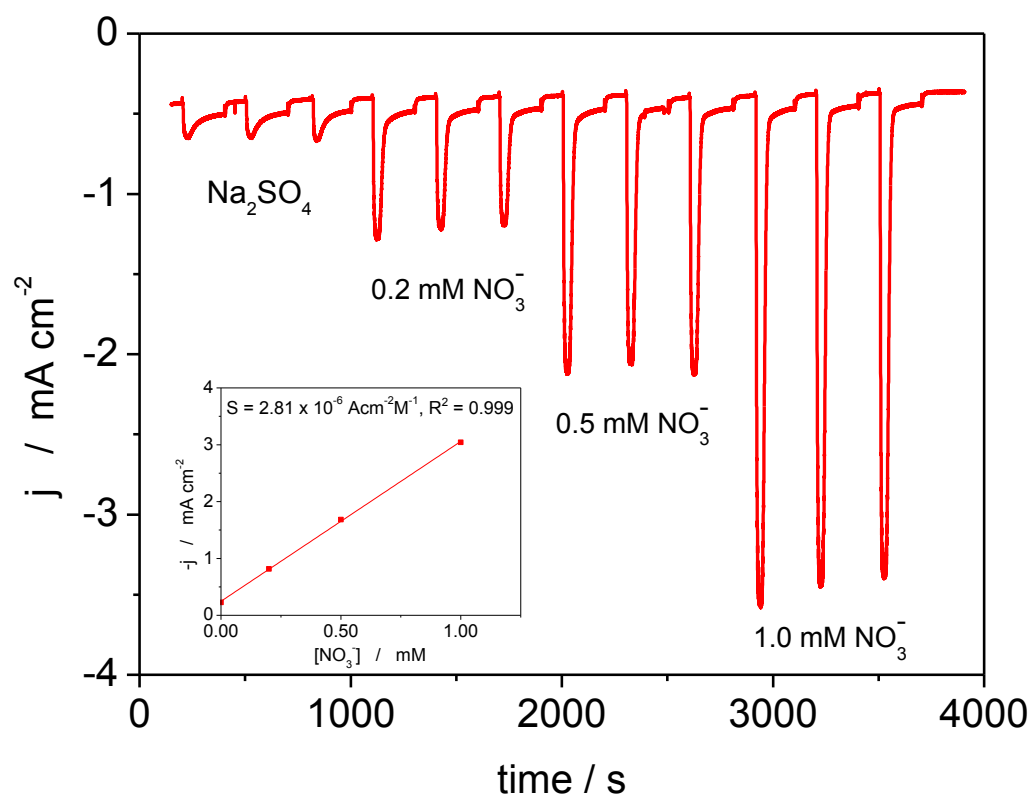


Fig. 3 Response of a porous Cu electrode, kept at -1.30 V vs. Ag/AgCl, to successive injections of 0.1 M Na_2SO_4 alone or with NaNO_3 at the concentrations indicated on the figure. The insert shows the dependence of the peak current (averaged over three tests) on the nitrate ion concentration.

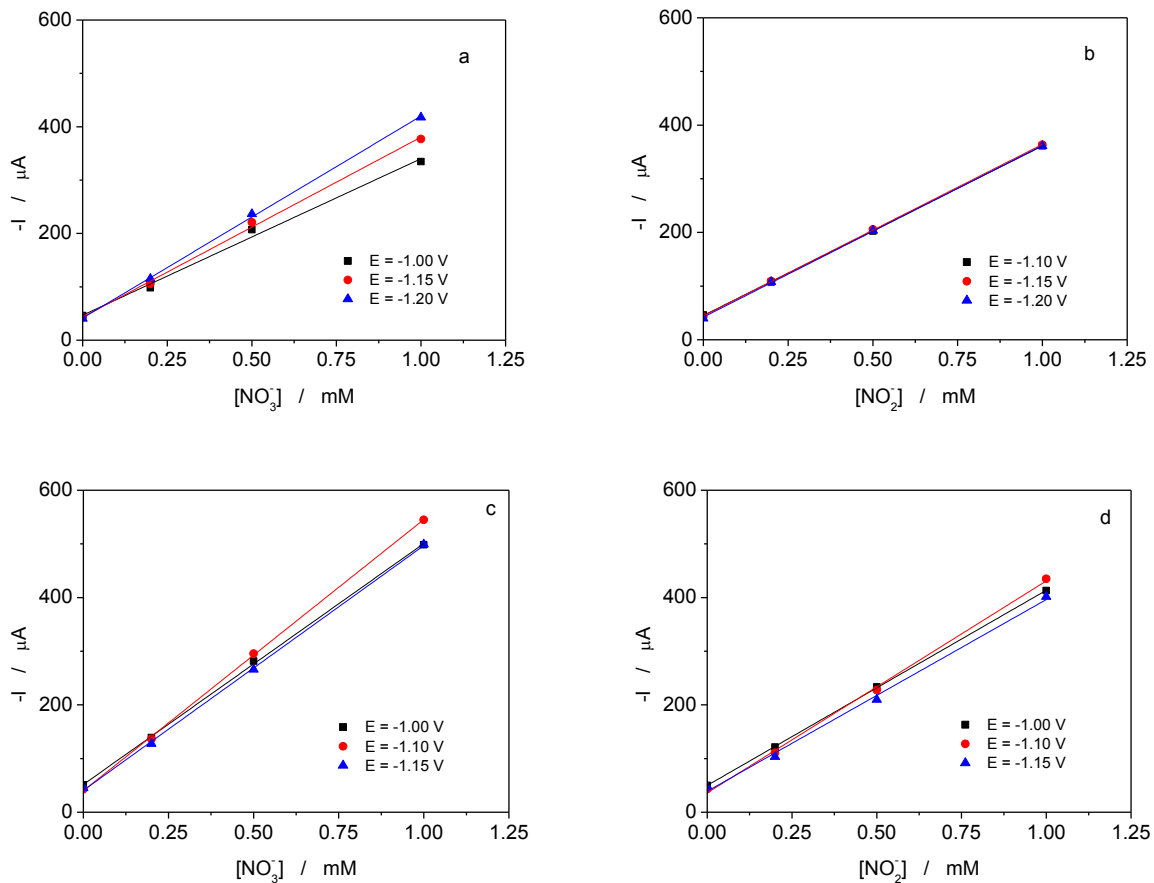


Fig. 4 Effect of potential on the calibration curve for the following systems: (a) porous Cu-Ni/nitrates/NaOH; (b) porous Cu-Ni/nitrites/NaOH; (c) Rh-modified Cu/nitrates/Na₂SO₄; (d) Rh-modified Cu/nitrites/Na₂SO₄.

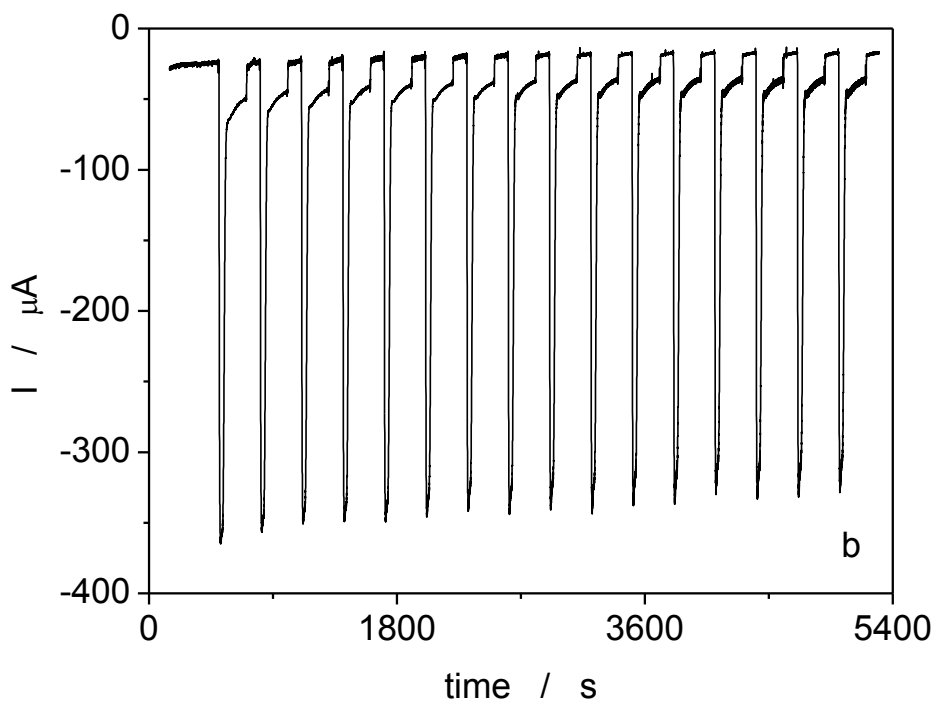
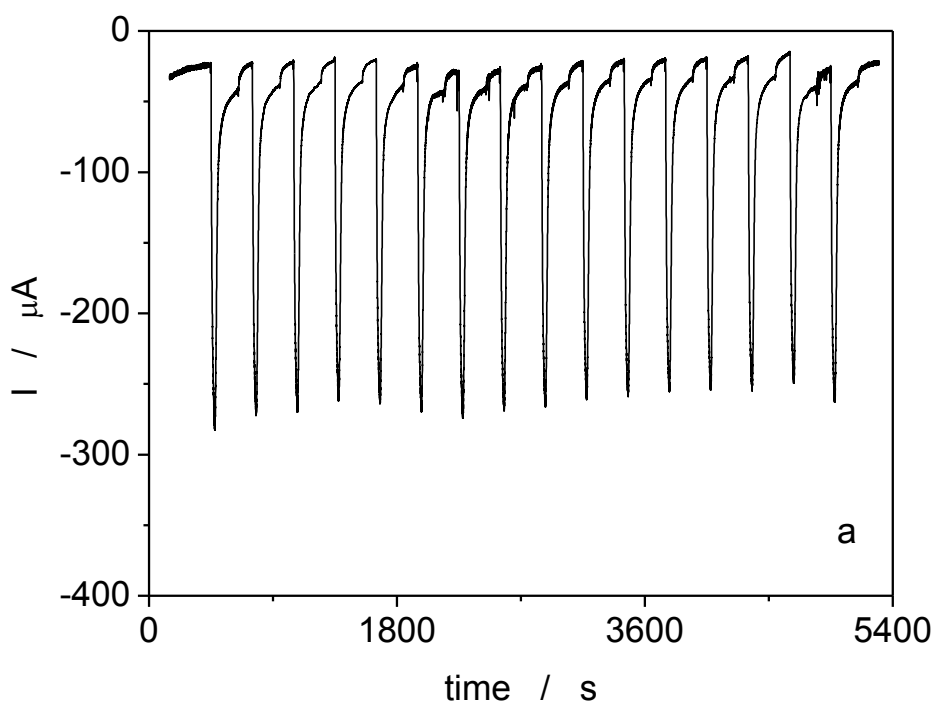


Fig. 5 Response of a Rh-modified Cu porous electrode, kept at -1.10 V vs. Ag/AgCl, to successive injections of 5×10^{-4} M NaNO_3 (a) in 0.1 M Na_2SO_4 and (b) in 0.1 M NaOH .

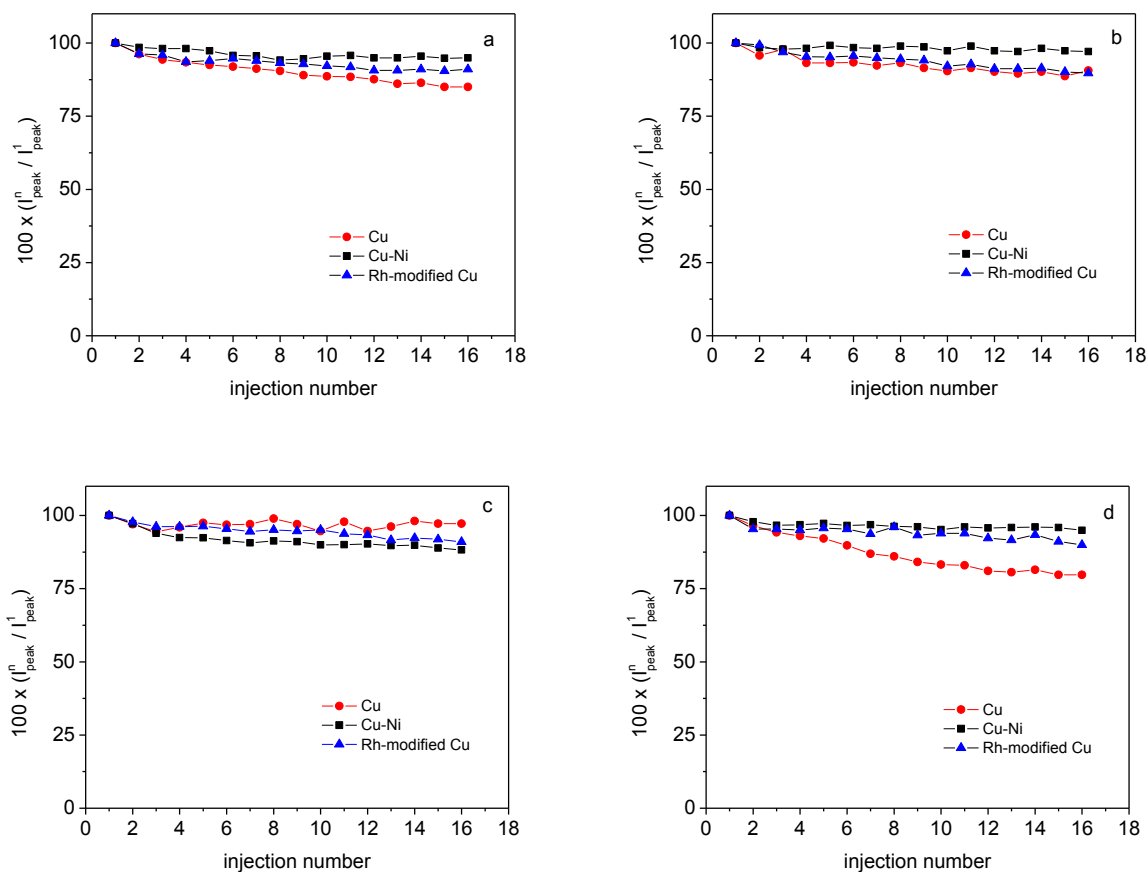


Fig. 6 Evolution of the response of porous Cu, Cu-Ni and Rh-modified Cu electrodes with successive injections of 5×10^{-4} M analyte for the following systems: (a) nitrates/Na₂SO₄; (b) nitrites/Na₂SO₄; (c) nitrates/NaOH; (d) nitrites/NaOH. The response of the n^{th} injection of each series is normalized with respect to the first injection.