- The variations of the peaks potentials with increasing purine concentration of cyclic voltammograms. The ratios $\Delta Ep/\Delta \log\ [XH_2^+]$ determined for purine concentrations varying in the range (10^{-3} - 10^{-1}) mol dm^{-3} were close 60 mV, proving that one purine molecule is bound.

- The variations of the peak potentials with pH. The ratios $\Delta Ep/\Delta pH$ determined were close 60 mV, proving processes of one proton and one electron.

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ELECTROCATALYTIC BEHAVIOUR OF DIFFERENT SUBSTRATES FOR THE ELECTROOXIDATION OF $NaBH_4$ IN ELECTROLESS METAL DEPOSITION

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INTRODUCTION

The catalytic activity of a given substrate for the electroless metal deposition (EMD) is determined by its ability to promote the adsorption of the reductant species and to originate an anionic radical which will be involved in the metal ion reduction; it can be evaluated by measuring the open circuit potential. It is well known that the involved mechanism is highly dependent on the substrate nature, solution pH and composition[1-3].

Sodium borohydride is a reducing agent widely used in industrial electroless plating. It is highly unstable in acid or neutral medium, undergoing fast hydrolysis[4] and if nickel ions are present, nickel boride will be precipitated with consequently bath decomposition; when the pH is maintained above 12, the hydrolysis of borohydride ions can be avoided and good quality Ni-B deposits are produced[5]. However, the mechanism of EMD employing this reductant is not established.

In this work the electrooxidation of borohydride ion (BH_4^-) on Ni and Cu electrodes, in the absence of traditional complexing agents and in metal ions free media, has been studied by cyclic voltammetry and potential time measurements using stationary and rotating electrodes. The results are analysed using the "Intermediate Radical Mechanism"[6] approach.

EXPERIMENTAL

Cyclic voltammetry and potential/time measurements were performed in conventional electrochemical cells. Specpure Nickel and Copper rods have been used to prepare the working electrodes, being a disk of 0.196 and 0.388 cm² area, respectively, exposed to the electrolyte. The electrodes were polished to a mirror finishing and before each experiment a new surface was regenerated by manual polishing with alumina 0,3 μm; as counter electrode a platinum foil was employed and all electrode potentials were controlled with respect to a saturated calomel electrode by an EG & G potentiostat/galvanostat model 273A. Rotating

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electrode experiments were performed with equipment from Oxford Electrodes. The results were collected by XY-t recorder, Yokogawa, model 3023.

The solutions were prepared with Analar grade reagents and de-ionised bidestilled water and deaerated with N_2 (99,999 %) before each experiment. All measurements were carried out at 25,0 ± 0,1 °C.

RESULTS AND DISCUSSION

Ni and Cu appear to be non catalytic for the electrooxidation of borohydride ion, since the open circuit potential in metal ions free media, for both electrodes, does not reach the value correspondent to the deposition (≈ 1,25 V)[7] in useful time (figure 1a and b).

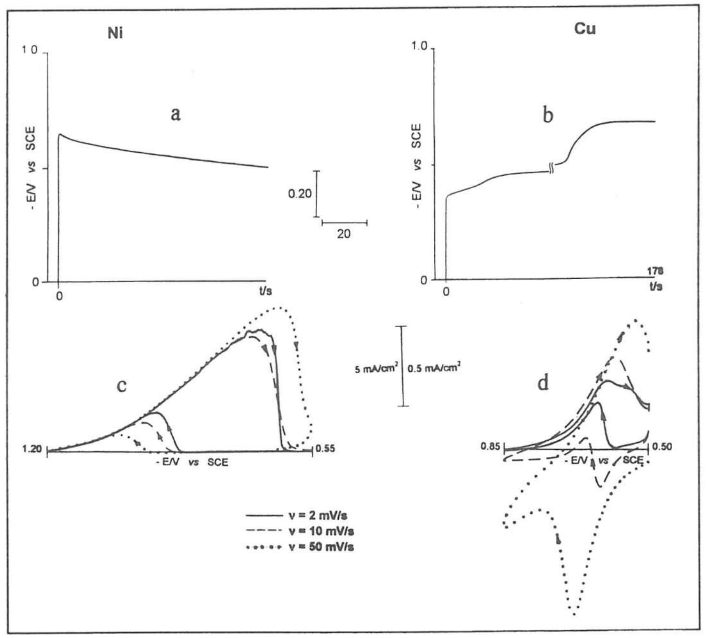

Fig. 1 - Evaluation of catalytic activity of Ni and Cu substrates in 0.05 M $NaBH_4$, 1.00 M NaOH; pH = 13.3, T = 298 K.

When the potential of the electrode is controlled and swept on the cathodic direction (fig. 1c and d), the conditions for the interaction substrate/reductant species are created and an anodic current peak is observed denoting the oxidation of the borohydride ion during the cathodic potential scan. It is likely that a mechanism similar to the one described for hypophosphite ion[6] applies:

$$BH_4^- \longrightarrow \dot{B}H_{3\,ads}^- + \dot{H}_{ads} \qquad (1)$$

$$\dot{B}H_{3\,ads}^- + OH^- \longrightarrow BH_3OH^- + e \qquad (2).$$

The assumption is well supported by the shift of the potential where current peak occurs with the increase of the sweep rate, showing that the adsorption/desorption processes are potential and time dependent. Taking into account the nature of the species formed in reaction (2), the following steps may occur:

$$BH_3OH^- \longrightarrow \dot{B}H_2OH_{ads}^- + \dot{H}_{ads} \qquad (3)$$

$$\dot{B}H_2OH^-_{ads} + OH^- \longrightarrow BH_2(OH)_2^- + e \qquad (4)$$

$$BH_2(OH)_2^- \longrightarrow \dot{B}H(OH)_{2\,ads}^- + \dot{H}_{ads} \qquad (5)$$

$$\dot{B}H(OH)_{2\,ads}^- + OH^- \longrightarrow BH(OH)_3^- + e \qquad (6)$$

$$BH(OH)_3^- \longrightarrow \dot{B}(OH)_{3\,ads}^- + \dot{H}_{ads} \qquad (7)$$

$$\dot{B}(OH)_{3\,ads}^- + OH^- \longrightarrow B(OH)_4^- + e \qquad (8)$$

When the adsorption is hindered, *e. g.* by electrode rotation, the global rate of the process is e[illegible]ted to decrease. Indeed, a lower open circuit potential for both electrode materials is ob[illegible] rotation rates (figures 2a and b).

Nevertheless, the effect of electrode rotation is complex, since it enhances the access of borohydride ion to the interface but it also contributes for the decreasing of the "residence time" for an effective adsorption. As it can be observed on the cyclic voltammograms presented in figures 2c and d, with the rotation of the electrode, there is a lowering of the current peaks on both scans, being the effect more marked for the Ni surface. Only at high rotation rates, *e.g.* over 500 rpm, the two effects appear to be balanced and the electrode rotation will facilitate the diffusion of the new species away from the electrode, leaving the electrode surface available for new adsorption and oxidation processes. Then the "critical potential", E_d, can be observed for the case of Nickel (figure 2a) but Copper remains non-catalytic for the electrooxidation of BH_4^- (figure 2b).

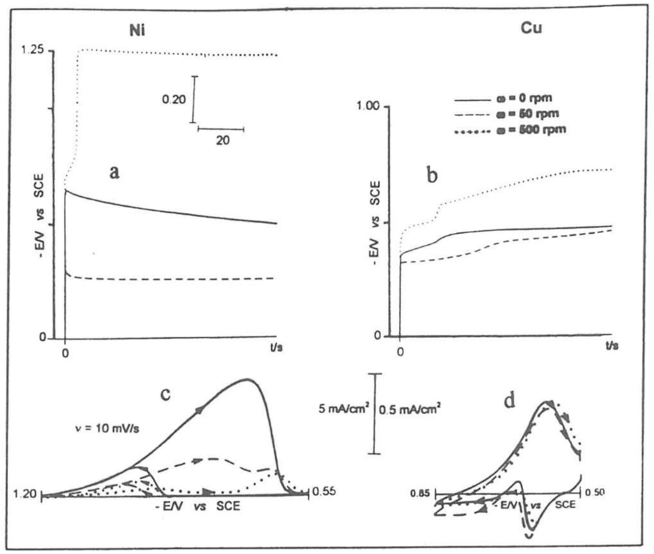

Fig. 2 - Effect of electrode rotation on the catalytic activity of Ni and Cu substrates. Solution composition: 0.05 M $NaBH_4$ containing 1.00 M NaOH; pH = 13.3, T = 298 K.

Further support of a mechanism as described by equations (1) to (8) for the electrooxidation of BH_4^- on Ni and Cu, is given by comparing the effect of rotating the electrode on the observed current during the anodic scan. As illustrated by figure 3a the magnitude of the current peak II, is non dependent of the electrode rotation, suggesting that there is an important contribution from the intermediate radicals oxidations, reactions (4), (6) and (8).

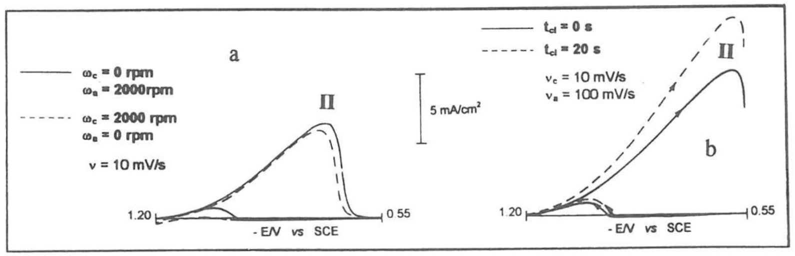

Fig. 3 - Cyclic voltammetry of the system Ni/BH_4^-. Solution composition: 0.05 M $NaBH_4$, containing 1.00 M NaOH; pH = 13.3, T = 298 K.

As in the case of the first steps of adsorption/oxidation, reaction (1) and (2), there is some time requirement for the occurrence of the subsequent adsorptions, denoted by increase in peak II, after holding the electrode potential at the cathodic limit for 20 s (figure 3b).

Both substrates can behave as catalytic after appropriate induction. For instance, a -900 mV/5 s potential step is enough for the observation of the "critical potential", E_d, for nickel in alkaline media. The role of induction to create the interfacial conditions for the occurrence of the processes described by steps (3) - (8) will be discussed in a separate paper.

CONCLUSIONS

In spite of the evident non catalytic ability of the Nickel and Copper substrates to promote the electrooxidation of BH_4^-, controlling the electrode potential, the reductant adsorption, radicals formation and their oxidation occur. The cyclic voltammetric information and data on the potential evolution with time, discussed in the present work, reveal that the process can be described by the "Intermediate Radicals Mechanism".

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