

Study of the role of sodium hypophosphite in electroless nickel bath solution

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Abstract. Cyclic voltametric investigations have been made to understand the electrochemical behaviour of sodium hypophosphite in electroless plating bath solution. The possible reaction steps at the anode and cathode have been identified. An ECE type of mechanism appears to be operative in the overall reaction during electroless plating. Both organic and inorganic species in the bath solution influence the voltammetric pattern of the hypophosphite. Temperature enhances the peak currents and changes the reaction mechanism. The oxidation potentials of the reaction steps vary with temperature and also the presence of organic components in the bath solution.

Keywords. Electroless plating; cyclic voltammetry; electrochemical behaviour; sodium hypophosphite.

1. Introduction

In recent years, electroless nickel (EN) coating technology has attained considerable significance in metal-finishing industries. However, the problems associated with the process continue to draw the attention of researchers owing to the lack of comprehensive and basic understanding of the system (Mallory and Hajdu 1990; Ridel 1991).

In electroless plating, the metal reductant plays a significant role in driving the plating process. Polarisation (Flis and Duquette 1984; Crousier *et al* 1993) and voltammetric (Podesta *et al* 1990) studies have been made with sodium hypophosphite as reducing agent in EN plating bath solutions. However, the proposed mechanisms are not adequate for explaining the overall reaction. Hence, an attempt is made here to study the possible reactions of sodium hypophosphite (SHP) in the presence of bath constituents through the cyclic voltammetric technique.

2. Experimental

Solutions were prepared using distilled water and analytical grade chemicals. Experiments were carried out using acidic ($pH\ 5$) $0.15\ M\ NaH_2PO_2$ solution at ambient temperature. The composition of each solution component was varied as and when required. The solution of sodium hypophosphite being a good electrolyte, the need for using other supporting electrolytes did not arise. The detailed experimental

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procedures adopted in the present investigations were similar to those given earlier (Mimani *et al* 1993).

An all-glass single compartment cell was used, wherein the working and counter electrodes were platinum foils (0.5 cm^2) with saturated calomel electrode as the reference. The solutions were deaerated by bubbling pure nitrogen gas before every run. A PAR model Scanning Potentiostat 362 was used to record the data. Reproducible voltammograms were obtained on repeated scanning.

3. Results

The electrochemical reactions of 0.15 M sodium hypophosphite (SHP) at $\text{pH } 5$ were obtained by cycling the potential from -0.25 V to 1.20 V at different scan rates (figure 1). The voltammograms show an anodic hump i_{pa}^1 followed by a large anodic peak i_{pa}^2 and a small cathodic peak i_{pc} . From the results obtained at different scan rates, a plot of i_p values of peak i_{pa}^2 versus $\gamma^{1/2}$ is made. A straight line passing through the origin depicts the irreversible nature of the reaction as observed earlier (Podesta *et al* 1990). The peak i_{pc} appeared only if the potential is scanned to the region of i_{pa}^2 which indicated the inter-relationship between i_{pa}^2 and i_{pc} .

Most of the developed EN baths containing SHP operate at higher temperature ranges. Hence, it was felt that it was necessary to study the effect of temperature on the

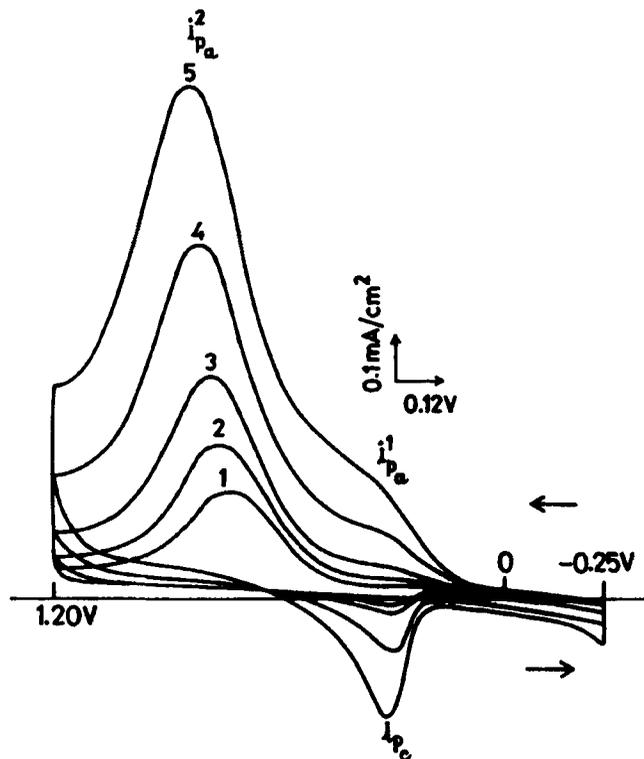


Figure 1. Cyclic voltammograms obtained on platinum with 0.15 M SHP at $\text{pH } 5$ in the potential range -0.25 to 1.20 V , as a function of sweep rate: (1) 100 , (2) 50 , (3) 20 , (4) 10 and (5) 5 mVs^{-1}

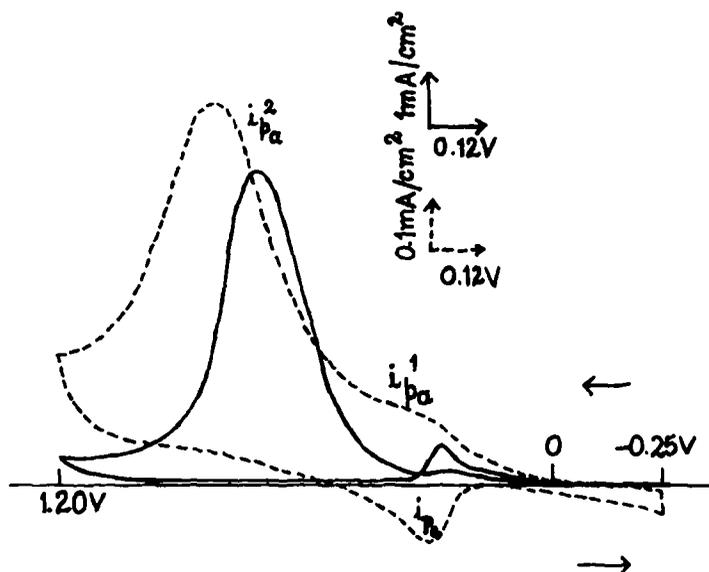


Figure 2. Cyclic voltammograms obtained on platinum with 0.15 M SHP at pH 5 in the potential range -0.25 to 1.20 V at a scan rate 50 mVs^{-1} (----- 298 K; ——— 343 K)

voltammetric pattern. A typical voltammogram with 0.15 M SHP at pH 5 and temperature 343 K is shown in figure 2. The voltammetric behavior in the anodic cycle is almost similar to that at ambient temperature. However, peak current is increased nearly tenfold and peak potential i_{pa}^2 shifts to lower values. In the cathodic cycle, the i_{pc} current is initially cathodic and then inverts to the anodic side at more negative potentials.

Experiments were conducted in the presence of additives which are commonly used in plating bath solutions. Boric acid (BA), sodium sulphate (SS) and sodium chloride (SC) at 0.5 M each and nickel sulphate (NS) at 0.1 M were added individually to 0.15 M SHP at pH 5. Some of these commonly present ions in the EN bath were found to affect the reaction of the SHP by varying either the peak potentials or the current (table 1).

The influence of organic acids or salts on the cyclic voltammogram was also studied. Sodium acetate (SA), lactic acid (LA), sodium potassium tartrate (SPT) and sodium citrate (SCI) with a concentration of 0.4 M were added individually to 0.15 M SHP at pH 5. Change in the i_p 's and E_p 's with evolution of gas at the extreme positive potential values is noticed (table 1). The shift in potential is in the order,

$$(\text{SCI}) > (\text{SA}) > (\text{SPT}).$$

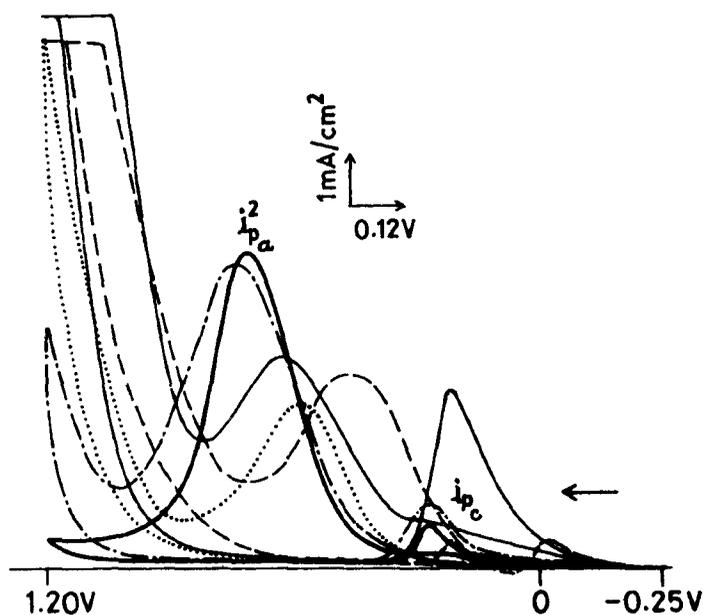
Further, the additives BA (0.5 M), SPT (0.4 M), SC (0.5 M), NS (0.1 M) and SCI (0.4 M) when added at pH 5 in various combinations affected the i_p 's and E_p 's to different extents (figure 3).

4. Results and discussion

It is known that hypophosphite can be oxidized chemically to phosphate (Van Wazer 1958). The voltammetric pattern (figure 1), however, shows a hump i_{pa}^1 and a broad peak

Table 1. The variation of peak currents (i_p) and peak potentials (E_p) in 0.15 SHP at pH 5 and 303 K in the presence of different additives at a scan rate of 50 mVs⁻¹.

Peak	Inorganic components				Organic components				
	BA	SS	SC	SHP	SA	LA	SCI	SPT	
i_{pa}^2	i_p^*	0.650	0.920	0.460	0.740	0.360	0.370	0.320	0.360
	$E_{p/v}^+$	0.786	0.750	0.900	0.774	0.636	0.684	0.636	0.774
i_{pc}	i_p^*	0.080	0.090	0.050	0.120	0.240	0.210	0.190	0.020
	E_p^+	0.324	0.324	0.396	0.280	0.204	0.216	0.216	0.216

*in mA/cm²; + in V**Figure 3.** Cyclic voltammograms obtained on platinum with 0.15 M SHP at 343 K and pH 5 in the potential range -0.25 to 1.20 V at a scan rate 50 mVs⁻¹ (— SHP; - - - BA + SC; - · - NS + BA + SC + SCI; ···· BA + SPT; - - - - BA + SC + SPT).

i_{pa}^2 confirming that the oxidation is not a single-step process but involves an intermediate. Based on the observed results, the following mechanism for the oxidation process can be proposed.

occurs to produce phosphorus (De Bethane *et al* 1961). Based on the above reactions, an overall mechanism scheme for the role of hypophosphite in the electroless plating baths could be proposed.

The feasibility of a direct mechanism as reported earlier (De Bethane *et al* 1961; Gafin and Orchard 1992) appears to be less relevant, because in such a case, the process would begin with hypophosphite reduction giving either an equal or an even larger amount of phosphorus content in the deposit than nickel. This is contrary to the observed results. In the case of the ECE mechanism, the process begins with the oxidation step to initiate the electrochemical reduction of the nickel ion. Because of the slow chemical reaction after the phosphate stage, the formation of phosphorus gets kinetically controlled.

In the presence of the organic ions, the influence on the oxidation of the SHP is more distinct. The hydroxy carboxylic acids are known to form acyl phosphates or esters with hypophosphites (Burt and Simpson 1969),



The electrochemical process then proceeds from the hypophosphite ester to the phosphate ester (Kazlauskas and Whitesides 1985) in a manner proposed in the above mechanism.



At the positive end, the evolution of oxygen or carbon dioxide takes place due to the presence of hydroxyl and carboxylate groups. The lowering of potentials of i_{pa}^2 by ~ 150 mV shows the ease of oxidation of SHP in the presence of these organic acids.

The CV pattern is not affected at ambient or higher temperatures in presence of (BA) or (SC) in the SHP solution. But the addition of (SPT) or (SCI) or (NS) reduces the peak potential of i_{pa}^2 , while (NS) increases the i_p of i_{pc} to a considerable extent. The peak potential which is lowered in the presence of boric acid and tartrate is further lowered in the presence of sodium chloride. Thus, the role of the chloride ion in enhancing the oxidation of the hypophosphite is clearly seen. The increase of i_p of i_{pc} supports the earlier findings that nickel ions catalyze the co-deposition of phosphorus in EN bath solutions (Brenner 1963; Harris and Dang 1993).

5. Conclusions

From these studies it is concluded that in the EN plating systems the bath constituents not only influence the reaction of the metal ion but also the reducing agent. The effect of pH and temperature on the oxidation potential of the phosphate formation suggests the need to carefully control the pH value and temperature during the EN process specially in the acid baths. The proposed mechanism explains the incorporation of phosphorus in the EN deposits. The organic acids which are thought to be behaving as complexing agents for the metal ion, have a greater role to play by way of enhancing the oxidation of the hypophosphite. The individual effect of the additive appears to be less pronounced when compared to the combined effect.

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