

## Electrochemical Study of Hypophosphite

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**Abstract:** Electrochemical behavior of hypophosphite was studied with cyclic voltammogram in acidic solution (pH = 4.6) at 80°C. Two anodic peaks were observed on gold electrode at -0.44V and -0.59V (SCE), respectively, and no corresponding cathodic peaks were obtained. The one at -0.44V was ascribed to the oxidation of tautomeric form of hypophosphite, the other at -0.59V was due to the oxidation of absorbed form of hypophosphite. The two oxidation reactions were believed to be the electron source of nickel ion reduction in electroless nickel processes.

**Key words:** cyclic voltammogram; electroless nickel plating; gold electrode; hypophosphite

Electroless nickel is extensively used in industry, but its reaction mechanism is incomplete. In the four kinds of theories that have been proposed, electrochemical mechanism is widely accepted. The theory proposes that electroless nickel proceeds along the electrochemical mechanism as the simultaneous reactions of cathodic nickel ion reduction and anodic oxidation of hypophosphite<sup>[1]</sup>. Oxidation of hypophosphite takes place on metals with enough catalytic activity and is the dominant step in electroless nickel<sup>[2]</sup>.

In the Ref. [3~5], alkaline solution was used, which can operate at low temperature and avoid the change of concentration. The results were extrapolated to real conditions in acidic electroless baths at elevated temperature. Polarization method was used, with which steady behavior was obtained. Thus no detailed mechanism could be obtained. This paper investigates hypophosphite oxidation with cyclic voltammogram in acidic solution on gold which has high catalytic activity and extensive double region.

### 1 Experimental

A three-compartment cell was placed in a water bath at 80°C. To avoid evaporation, the cell was filled with solution and sealed. A gold electrode was used as the working electrode. The counter electrode was a platinum foil with 4 cm<sup>2</sup> in area. Potentials were recorded with respect to saturated calomel electrode (SCE) in the experiment. The reference electrode was mounted

in a separate vessel at room temperature, a lugging capillary was used to minimize iR drop. The electrochemical equipment consisted of a EG&G PAR model 273 potentiostat with a microcomputer system capable of both controlling the experiments, collecting and plotting the data. The gold electrode was polished with various grades of Al<sub>2</sub>O<sub>3</sub> down to 0.05 μm on cloth, and then rinsed with water, distilled water prior to measurement.

Cyclic voltammogram were performed in solutions of 0.4 mol/dm<sup>3</sup> NaH<sub>2</sub>PO<sub>2</sub> + 0.1 mol/dm<sup>3</sup> NaCl electrolyte acetic buffer (pH = 4.6). The pH value was measured with a Model HM-20E pH meter (TOA electronics Ltd., Japan). The solutions used to measure the mixed potential consisted of 0.15 mol/dm<sup>3</sup> NiSO<sub>4</sub>, 0.4 mol/dm<sup>3</sup> NaH<sub>2</sub>PO<sub>2</sub>, 0.15 mol/dm<sup>3</sup> citric acid, 0.2 mol/dm<sup>3</sup> assistant ligand, 0.1 mol/dm<sup>3</sup> CH<sub>3</sub>COONa, CH<sub>3</sub>COOH (pH=4.6).

All chemicals were analytical grade. Solutions were made with double distilled water.

### 2 Results and Discussion

#### 2.1 Preliminary results

Electrode potentials for Au changed after immersion into electroless nickel plating solutions. The rest potential of the electroless nickel was approximately -0.7 V. According to the electrochemical mechanism, the rate of oxidation reaction is equal to that of reduction reaction at the rest potential, i. e., the oxidation of

hypophosphite and reduction of nickel ion take place at potential nearby  $-0.7$  V. The cyclic voltammogram of hypophosphite was obtained in the potential range of  $-0.75 \sim 0$  V.

Cyclic voltammograms from the solution containing the supporting electrolyte presented no background current at potentials between 0 and  $-0.6$  V. Below  $-0.6$  V, hydrogen evolved. After hypophosphite was added into the solution, hydrogen reduction was reduced greatly.

The voltammogram from solution containing hypophosphite is presented in Fig. 1. On the forward scan, two anodic peaks appeared at  $-0.59$  V and  $-0.44$  V, respectively. The scan was reversed at  $-0.2$  V. On the reverse scan, no corresponding cathodic peak appeared even potential scanned to  $-1.2$  V. When potential scan started at  $-0.5$  V, the anodic peak at  $-0.44$  V still appeared. If the potential scanned from  $-0.7$  to  $-0.2$  V firstly, no cathodic peak was obtained. On the reverse scan, two peaks at the same potential as above were observed. It is inferred that the reactions at the two peaks is independent.

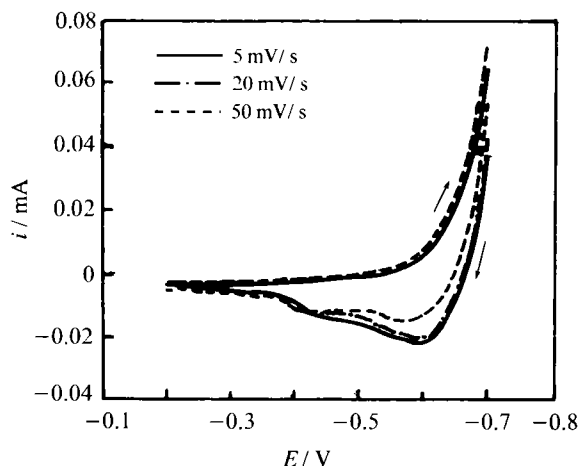


Fig.1 Cyclic voltammogram of  $\text{H}_2\text{PO}_2^-$  on gold

## 2.2 Oxidation reaction corresponding to peak at $-0.59$ V

There was only one obvious anodic peak at  $-0.59$  V (peak 1) on the cyclic voltammogram at low scan rate 5 mV/s. The peak potential did not change with scan rate. The peak current decreased when scan rate increased. This is the characteristic of irreversible oxidation process of adsorbed species.

Fig.2 shows the change of peak current with concentration of hypophosphite. The peak current increased

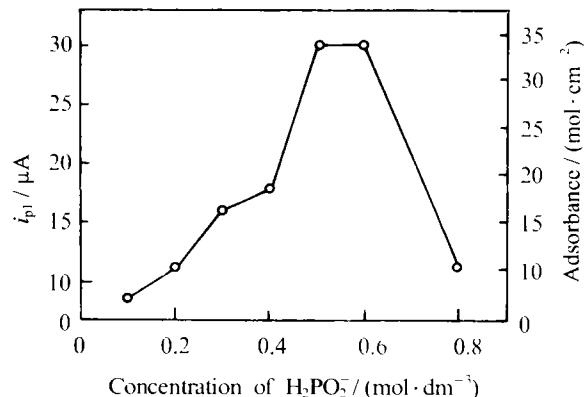
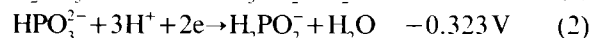
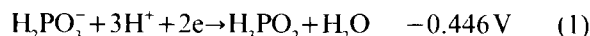


Fig.2 Effect of hypophosphite concentration on peak current and adsorbance (two curves overlap each other)

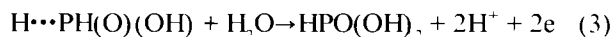
with increases of concentration of hypophosphite and reached a plateau at hypophosphite concentration of  $0.5 \sim 0.6 \text{ mol/dm}^3$ . With the further increases of  $\text{H}_2\text{PO}_2^-$  concentration, the peak current decreased. The adsorbance could be obtained according to Faraday's law. Thus, the adsorbance changed with concentration of hypophosphite and the isotherm of adsorption showed the same change as the peak current.

Calculations from thermodynamic data give the following standard redox potentials on the hydrogen scale<sup>[6]</sup>:



Purely on the energy grounds it might be expected that hypophosphite in acid would be oxidized very readily at an anode. In fact, hypophosphite is relatively inert toward anodic oxidation. The electroless nickel using hypophosphite as reductant can only take place on catalytic substrate. Gold is one of the catalytic substrate for electroless nickel. According to the results obtained, the following mechanism of hypophosphite oxidation at  $-0.59$  V is supposed.

Hydrogen atom in P—H bond is covalently adsorbed on active surface of gold. The "electron atmosphere" of P—H bond is attracted to the gold atom and the adsorbed state  $\text{H} \cdots \text{PH}(\text{O})(\text{OH})_{\text{ad}}$  formed. And it is readily oxidized



In electroless process, nickel ion accepts the electron from hypophosphite oxidation.

It has been proved<sup>[7]</sup> that hydrogen evolved during electroless deposition originated mainly from the reductant molecule. This phenomenon could be explained with the adsorbed state.

### 2.3 Oxidation reaction corresponding to the peak at $-0.44$ V

On the cyclic voltammogram (Fig. 1), there was a small peak at  $-0.44$  V (peak 2). The peak current increased with the increases of scan rate and the peak potential changed to positive direction. The peak current was proportional to the square root of scan rate, shown in Fig. 3. The current function  $i_{p2}/V^{1/2}$  decreased with the increases of scan rate, shown in Fig. 4. The results show that the oxidation at  $-0.44$  V proceeds along CE mechanism. The hypophosphite can exist in tauto-

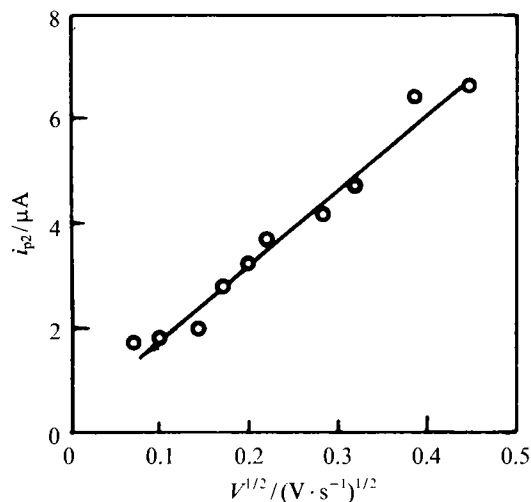


Fig.3  $i_{p2}-V^{1/2}$  curve

metric form in solution as suggested by Mitchell<sup>[8]</sup>:



The  $H_2PO(OH)$  is electro-inactive in solution. The tautomeric form is electro-active, it is readily oxidized at  $-0.44$  V on catalytic substrate



It appears that the reaction is irrelative to electroless deposition because it occurs at more positive potential than the rest potential of electroless deposition. Experiment shows that in the electroless deposition process, pH near the substrate surface fluctuates. Reaction (5) takes place more readily at high pH. It is believed that Reaction (5) is involved in the electroless process.

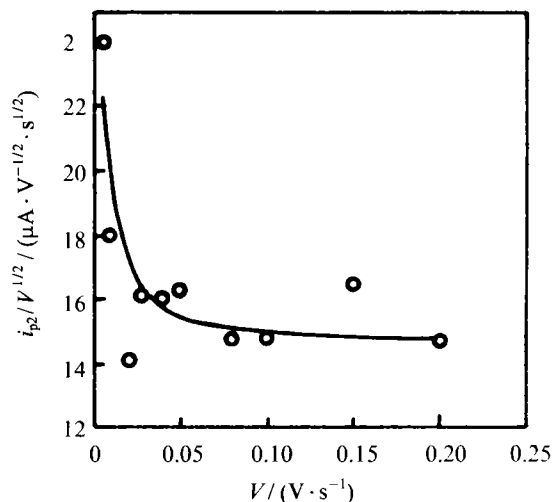


Fig.4  $i_{p2}/V^{1/2}-V$  curve

### 3 Conclusions

The cyclic voltammogram shows that hypophosphite can be oxidized in two forms. The adsorbed state is more readily oxidized than the tautomeric form. The two kinds of oxidation reactions are involved in electroless nickel.

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