

Anodic and cathodic process of hypophosphite on a Ni-Ag electrode

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The reduction and the oxidation of hypophosphite on a Ni-Ag electrode have been studied to provide the information about the phosphorus incorporation mechanisms during the electroless deposition and the electrodeposition of Ni-P alloys. In the electrooxidation process, an absorbency band around 240 nm, which was ascribed to the formation of an intermediate $\cdot\text{PHO}_2^-$, was observed by *in situ* UV-Vis subtractive reflectance spectroscopy. Accordingly, the electrooxidation of hypophosphite might undergo an H abstraction of hypophosphite from the P—H bond to form the phosphorus-centred radical $\cdot\text{PHO}_2^-$, which was subsequently electrooxidized to the final product, phosphite. In the reduction process Ni-phosphine compound $\text{Ni}-(\text{PH}_3)_n$ was observed by *in situ* surface Raman spectroscopy. The results from the Raman experiments show that, in the NiSO_4 -free solution, hypophosphite was reduced only to Ni-phosphine compound, while in the case where NiSO_4 coexisted in the solutions, the Ni-phosphine compound, as an intermediate, was oxidised by Ni^{2+} to elemental phosphorus in alloys with nickel acting as the catalyst.

Keywords *In situ* Raman spectroscopy, *in situ* UV-Vis spectroscopy, hypophosphite, electrooxidation, electroreduction, mechanism

Introduction

It is very necessary that the oxidation and the reduction of hypophosphite should be meticulously studied. On the one hand, hypophosphite is one of the most widely used reducing reagents in the Ni-electroless deposition, in which the oxidation of hypophosphite is expected to be one of the most important reactions. On the other hand, the codeposition of phosphorus with nickel is

a very important reduction process of hypophosphite during the electrodeposition of Ni-P alloys. Thus the studies on both anodic and cathodic processes of hypophosphite could help us in throwing a light on the phosphorus incorporation mechanisms during the electroless deposition and the electrodeposition of Ni-P alloy.

It is well known that the reductant for Ni-electroless deposition in hypophosphite solutions is not the H_2PO_2^- ion, according to proposed mechanisms, atomic hydrogen, H ,¹⁻³ or the hydride ion, H^- .^{4,5} For the oxidation of hypophosphite a two-step oxidation mechanism with the formations of a metaphosphite (PO_2^-) and two atomic hydrogens was suggested by Gutzeit.¹ However, as Electrochemical Mass Spectrometry studies have shown that the product of the electrocatalytic oxidation of hypophosphite on the nickel electrode in D_2O solution is HDPO_3^- rather than D_2PO_3^- ,⁶ the oxidation mechanism, involving PO_2^- as an intermediate, can not be accepted. A multi-step-oxidation mechanism was proposed by Abrantes and co-workers.³ In this proposed mechanism, the hypophosphite is first adsorbed on nickel surface and followed by the cleavage of a P—H bond to form the adsorbed atomic hydrogen and the adsorbed phosphorus compound radical ($\cdot\text{PHO}_2^-$), and the latter reacts with water to phosphite. Recently, the role and the oxidation mechanism of hypophosphite in the electroless deposition of Ni-P alloy have been studied in detail using the probe beam deflection,⁷ electrochemistry and *in situ* IR.^{8,9} However, phosphorus codeposition with nickel under the inducing effect of nickel was not described in detail in previous

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Phosphorus can not be electrodeposited by itself, but it can be readily codeposited with iron-group metals from aqueous electrolytes. Two proposed mechanisms, *i. e.*, the direct and the indirect mechanisms, for the codeposition of phosphorus with nickel have been proposed. In the direct mechanism, first suggested by Brenner,¹⁰ the hypophosphite in the bath is reduced only to elemental phosphorus. However, as phosphorus can not be electrochemically produced in pure state from aqueous solutions, this mechanism can not be accepted widely. The second mechanism, *i. e.*, the indirect mechanism, was first proposed by Ratzker *et al.*¹¹ In this mechanism, the hypophosphite is first reduced to phosphine (PH₃), which subsequently undergoes a chemical reaction with Ni²⁺ to produce both elemental nickel and phosphorus in alloy.

After the indirect mechanism was proposed, many experiments have been attempted to support its validity.^{9,10} So far the indirect mechanism seems to have been accepted completely. However, very recently Marikawa *et al.*¹² reported that the nickel phosphide was formed on the surface of Ni electrode cathodized in H₂PHO₃ solution, and it was concluded that alloy was formed through a direct deposition mechanism. Thus more detailed information is necessary for an understanding of the phosphorus incorporation mechanisms during the electroless deposition and the electrodeposition of Ni-P alloys.

In situ spectroscopic studies provide a powerful means of characterising the electrodic processes such as adsorption and reaction occurring in the vicinity of an electrode at the molecular level. In present study the oxidation and the reduction of hypophosphite on a Ni-Ag electrode were investigated using *in situ* surface Raman spectroscopy and *in situ* UV-Vis subtractive reflectance spectroscopy in conjunction with electrochemical techniques to obtain the information about the phosphorus incorporation mechanisms during the electroless deposition and the electrodeposition of Ni-P alloy.

Experimental

All electrochemical measurements were carried out on an EG&G PARC M263A potentiostat using conventional three-electrode cell. The electrode potential was measured vs. a saturated calomel electrode (SCE). The working electrode matrix was polycrystalline Ni rod with

geometric surface area of 0.1 cm² embedded in a teflon-sheath. The working electrode surface was covered by the Ni-Ag alloy by potentiostatic electrodeposition at the potential of -1.2 V for 1 min in the bath containing 0.1 M Ni(NO₃)·6H₂O + 3 × 10⁻³ M AgNO₃ + 0.5 M K₄P₂O₇·3H₂O + 6 × 10⁻³ M KCN. As is well known the surface enhanced Raman spectroscopy (SERS) can be performed only on certain metals such as Ag, Au and Cu, and only when the surface of the metal has been roughened. The presence of the Ag component on the nickel substrate caused a strong surface enhancement and high-quality surface Raman spectra could be observed. A large area platinum served as the counter electrode. The solutions were prepared just before the experiments from twice distilled water and analytical grade reagents.

Raman measurements were performed with a confocal micprobe Raman system (Lan Ram I) with a holographic notch filter and a CCD detector. The excitation line was 514.5 nm from an Ar⁺ laser delivered at the sample point with about 12 mW. The spectra were obtained with the collection time of 30 s. An EG&G PAP M173 potentiostat was used to control the applied potential during Raman measurements. A more detailed description of the spectroelectrochemical measurements was reported in a previous paper.¹³

In situ UV-Vis spectroscopic measurements were performed with a UV-Vis spectrometer (shimadzu UV-240) and the combined spectroelectrochemical measurement system.¹⁴ The visible light source was a 36 W tungsten-halogen lamp and the ultraviolet light was a 10 W deuterium discharge lamp. An EG&G PARC M175 potentiostat was used to control the applied potential. A cell with the quartz window set for an angle of incidence of 45° was employed to minimise optical contributions from effects at the double layer of the electrode/electrolyte solution interphase.

The *in situ* UV-Vis subtractive reflectance spectra were calculated as $(R_s - R_r)/R_r$ where R_s and R_r are the reflectance of the electrode at the sample and reference potential, E_s and E_r , respectively. Taking into account this sign convention, the negative going bands correspond to species present in greater quantity at the sample than at the reference potential, and the positive going bands represent the opposite change in the vicinity of the electrode surface.

Results

Electrochemical characteristic

The voltammogram of Ni-Ag electrode is shown in Fig. 1 (curve 1) in 0.1 M NaH_2PO_2 solution in the potential range from 0 V to -1.2 V. For a comparison the corresponding voltammogram in 0.1 M NaNO_3 solution is also shown in Fig. 1 (curve 2). The cyclic voltammogram in 0.1 M NaNO_3 solution presents the non-occurrence of any oxidation and any reduction processes other than the hydrogen evolution at the potentials more negative than ca. -1.1 V. In 0.1 M NaH_2PO_2 solution an oxidation peak at ca. -0.14 V is a voltammetric feature of the hypophosphite oxidation to phosphite.¹⁵ Another small reduction peak at -0.84 V could be ascribed to the reduction of hypophosphite to Ni-phosphine compound, which has been detected by Raman spectroscopic experiment.

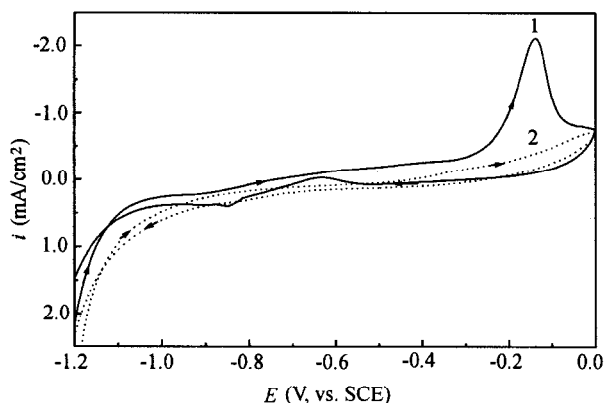


Fig. 1 Cyclic voltammograms of Ni-Ag electrode in 0.1 M NaH_2PO_2 (curve 1) and in 0.1 M NaNO_3 (curve 2), $v = 100 \text{ mV/s}$.

In order to examine the electrooxidation behaviour of hypophosphite the cyclic voltammetric experiments were carried out in the potential range from -0.4 V to 0.1 V using various electrodes in 0.1 M NaH_2PO_2 solution and the current response is shown in Fig. 2. The voltammograms on both Ni electrode (curve 1) and Ni-Ag electrode (curve 2) reveal a feature peak corresponding to the oxidation of hypophosphite to phosphite.¹⁵ The peak current of Ni-Ag electrode is greater than that of Ni electrode and the peak potential of Ni-Ag electrode is more positive than that of Ni electrode. For a comparison the corresponding voltammograms of both Ag electrode

(curve 3) and Cu electrode (curve 4) are also shown in Fig. 2. The oxidation of hypophosphite does not take place on Ag electrode nor on Cu electrode. The oxidation and reduction peaks attributed to the $\text{Cu}/\text{Cu}(\text{OH})_2$ couple can only be seen from the voltammograms of Cu electrode at ca. 0.07 V and at ca. -0.02 V, respectively. However in addition to the redox current of the $\text{Cu}/\text{Cu}(\text{OH})_2$ couple, the Cu electrode, on which three cycles of voltammetric experiments have been completed in 0.1 M $\text{NaH}_2\text{PO}_2 + 0.1 \text{ M NiSO}_4$ mixture solution, has a greater oxidation current (curve 5) and low potential (< -0.4 V) for the oxidation of hypophosphite. As three cycles of voltammetric experiments have been completed the Ni-P alloy is electrodeposited on the partial surface of Cu electrode, then the outstanding catalytic activity for the oxidation of hypophosphite stems from the active Ni-P alloy deposited freshly.

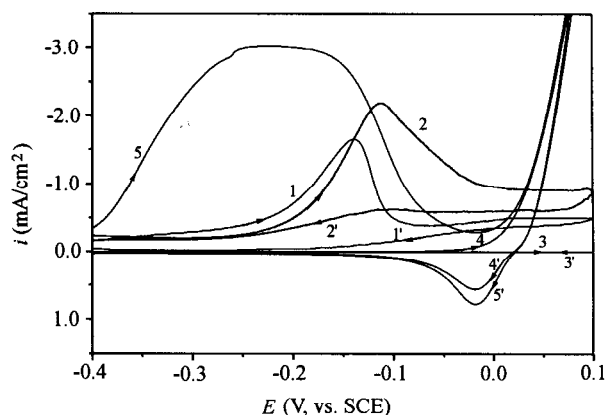


Fig. 2 Voltammograms of various electrodes in 0.1 M NaH_2PO_2 (curves 1, 2, 3 and 4 represent Ni, Ni-Ag, Ag, and Cu electrode, respectively, curve 5, Cu electrode covered partially by Ni-P alloy on electrode surface, $v = 100 \text{ mV/s}$).

Fig. 3 shows the cyclic voltammograms of Ni-Ag electrode in 0.1 M $\text{NaH}_2\text{PO}_2 + 0.1 \text{ M NiSO}_4$ mixture solution, and curves 1, 2, 3 and 4 present the 1st, 2nd, 3rd and 4th circles, respectively. By comparison with the NiSO_4 -free case, two remarkable characteristics can be observed: (i) Two new reduction peaks at ca. -0.95 V and at ca. -0.85 V, which are attributed to the electrodeposition of Ni-P alloy and to the reduction of hypophosphite to Ni-phosphine, respectively, appear. (ii) The electrochemical activities of the reaction corresponding peaks, *i. e.*, the oxidation of hypophosphite to phosphite (-0.14 V), the reduction of hypophosphite to Ni-phosphine (-0.85 V), the electrodeposi-

tion of Ni-P alloy (-0.95 V) and hydrogen evolution reaction, are much greater on Ni-P alloy surface than on Ni-Ag alloy surface because the electrodeposition of Ni-P alloy takes place in the reverse sweep at the potential more negative than -0.7 V and all peak's intensities increase with the number of circulation.

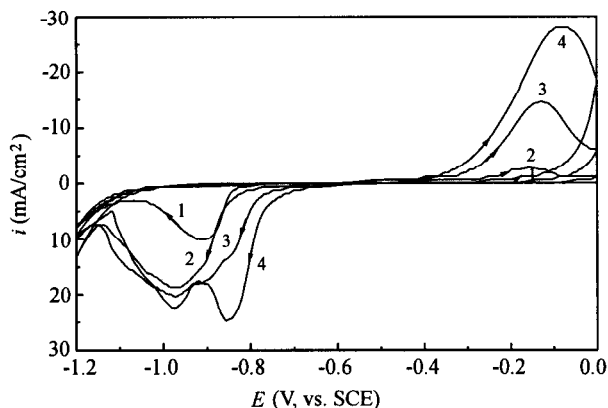


Fig. 3 Voltammograms of Ni-Ag electrode in 0.1 M NaH_2PO_2 + 0.1 M NiSO_4 (curves 1, 2, 3 and 4 represent the 1st, 2nd, 3rd and 4th cycles, respectively, $v = 100$ mV/s).

These cyclic voltammetric experiments show that Ag and Cu electrodes have no catalytic activity, Ni and Ni-Ag electrodes have good catalytic activity and Ni-P alloy deposited freshly has outstanding catalytic activity for the oxidation of hypophosphite.

In situ surface Raman spectra

Raman spectra obtained from the surface of the electrodeposited Ni-Ag alloy electrode in 0.1 M NaH_2PO_2 solution are shown in Fig. 4 as the potential was varied stepwise from -0.3 V to -1.0 V. At open-circuit potential (OCP, -0.3 V) the appearance of a band at 559 cm^{-1} in the spectra, which can be attributed to phosphite ($A_1\delta(\text{PO}_3)$, 590 cm^{-1} ,¹⁶ 550 cm^{-1} ¹⁷), indicate that hypophosphite can be oxidised spontaneously to phosphite on the electrode surface. As the potential was changed from -0.3 V to -1.0 V, the intensity of the band at 559 cm^{-1} decreased, and that of the band at 461 cm^{-1} , which is the spectral characteristic of hypophosphite ($\delta(\text{PO}_2)$, 465 cm^{-1} ,¹⁶ 467 cm^{-1} ¹⁷), increased.

An interesting aspect is that a new band at 360 cm^{-1} appeared at potentials more negative than -0.7 V, which shows that a new substance was formed on the surface of electrode by the electrochemical process. We as-

signed it to a Ni-phosphine compound, $\text{Ni}(\text{PH}_3)_n$ (ν (Ni-P), 350 – 390 cm^{-1}).^{18,19}

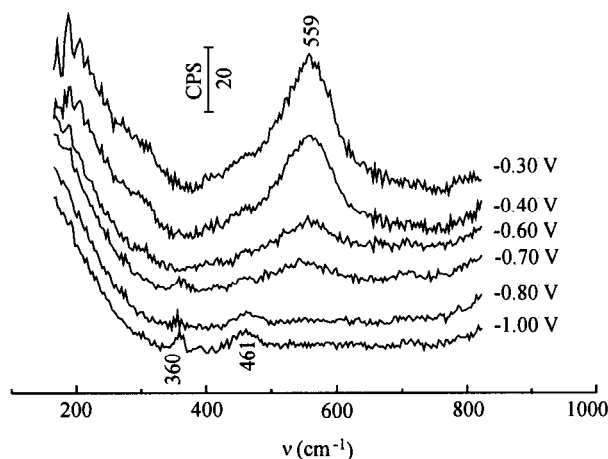


Fig. 4 Surface Raman spectra on Ni-Ag electrode in 0.1 M NaH_2PO_2 solution.

Raman spectra obtained from the surface of the electrodeposited Ni-Ag alloy electrode in the solution containing 0.1 M NaH_2PO_2 + 0.1 M NiSO_4 are shown in Fig. 5 at various potentials. At the potentials more positive than -0.4 V, there was a band at 565 cm^{-1} , indicating the existence of phosphite on the surface of the electrode. Consequently hypophosphite can also be oxidised spontaneously to phosphite on the electrode surface in the solution containing NiSO_4 . As the potential was changed from -0.25 V (OCP) to -0.80 V, the intensity of the band at 565 cm^{-1} decreased, and that of the band at 467 cm^{-1} increased then decreased, the maximum being reached at the potential of -0.6 V, which means that the reduction and the oxidation of hypophosphite occurred at potentials more negative or more positive than -0.6 V, respectively, on the electrode.

There was another new band at 377 cm^{-1} at the potential of -0.7 V, at which electrodeposition starts. We assigned our 377 cm^{-1} band to $\nu(\text{Ni-P})$ in Ni-P alloy. Two facts, *i. e.*, the absence of the bands attributed to a Ni-phosphine compound, $\text{Ni}(\text{PH}_3)_n$, and the appearance of a new band at 377 cm^{-1} , possibly mean that $\text{Ni}(\text{PH}_3)_n$ reacted with Ni^{2+} to form the Ni-P alloy. In the potential range from -0.6 V to -0.8 V the intensities of all bands decreased, which might be due to hydrogen evolution and the electrodeposition of Ni-P alloy on the surface of the electrode. As a result of vigorous electrodeposition occurring at the potential of -0.8

V, the surface of the electrode was entirely covered by the Ni-P alloy, whose surface enhancement of Raman scattering was so weak that the surface Raman bands disappeared.

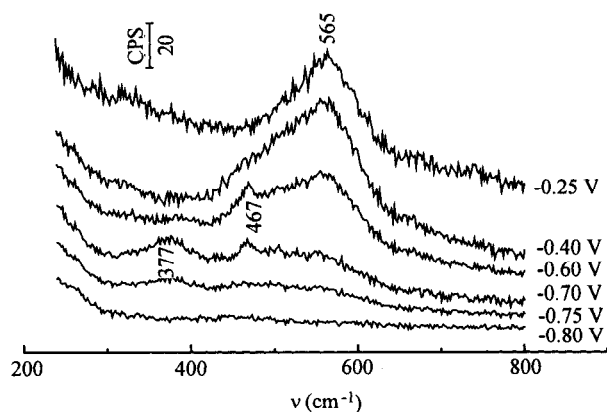


Fig. 5 Surface Raman spectra on Ni-Ag electrode in 0.1 M NaH_2PO_2 + 0.1 M NiSO_4 solution.

In situ UV-Vis subtractive reflectance spectra

Fig. 6 presents the *in situ* UV-Vis subtractive reflectance spectra on the Ni-Ag electrode. The reference potential was monitored at $E_r = -0.6$ V. In order to examine the characteristic of hypophosphite oxidation on the Ni-Ag electrode the sample potential was collected at $E_s = -0.15$ V. It is obvious from Fig. 6 that when oxygen existed in the solution (curve 1) two absorption bands emerged around 240 nm and 225 nm. However after the solution was deaerated with high pure nitrogen the peak at ca. 225 nm disappeared nearly and the peak at ca. 240 nm existed still in the spectrum though there

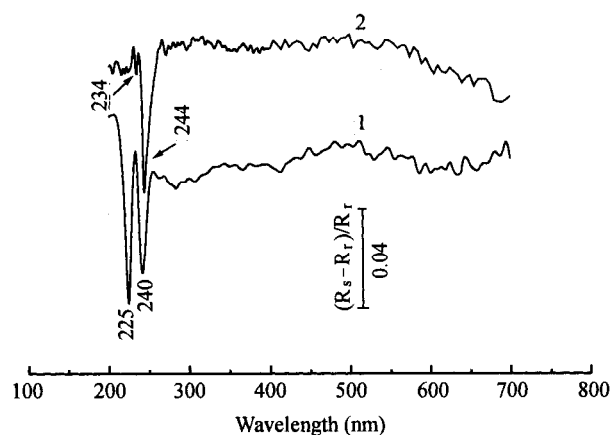


Fig. 6 *In situ* UV-Vis subtractive reflectance spectra on Ni-Ag electrode (curve 1: oxygen exists in the solution; curve 2: the solution was deaerated. $E_r = -0.6$ V, $E_s = -0.15$ V)

were small shifts at their positions.

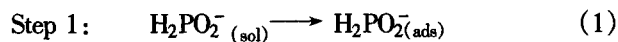
Shastri *et al.*²⁰ reported that $\cdot\text{PHO}_2^-$ radical could be formed by pulse radiolysis of N_2O -saturated solution of hypophosphite and exhibited an optical absorption with λ_{max} 240 nm and ϵ_{max} $3400 \text{ M}^{-1} \cdot \text{cm}^{-1}$. And it could react with O_2 to form peroxy radical ($\cdot\text{O}_2\text{PHO}_2^-$), whose spectrum has a maximum at 230 nm with molar absorptivity ϵ_{max} $1700 \text{ M}^{-1} \text{ cm}^{-1}$. Therefore the appearances of the bands at 240 nm and at 225 nm could be attributed to the formation of the intermediates, $\cdot\text{PHO}_2^-$ and $\cdot\text{O}_2\text{PHO}_2^-$, in the electrochemical process, respectively.

Conclusions and discussion

$\text{Ni}-(\text{PH}_3)_n$ and $\cdot\text{PHO}_2^-$ were detected as the intermediates during the reduction and the oxidation of hypophosphite on a Ni-Ag electrode using *in situ* surface Raman spectroscopy and *in situ* UV-Vis subtractive reflectance spectroscopy for the first time, respectively. The IR characteristic of hypophosphite on Ni electrode was studied by Abrantes *et al.*⁸ It was concluded that the hypophosphite anion is adsorbed on the electrode surface via the two hydrogen atoms in the P—H bonds. Taking into account these considerations and the results obtained in this work, a reasonable mechanism can be proposed for the reduction and the oxidation of hypophosphite on a Ni-Ag alloy electrode. This overall reaction mechanism is represented in Fig. 7, and can be described as follows depending on the electrode potential E :

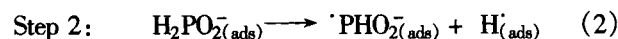
- $-0.7 \text{ V} < E < -0.4 \text{ V}$, the adsorption range

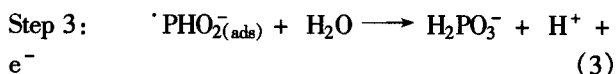
In this potential range, hypophosphite is stable, *i. e.*, the oxidation and reduction can not take place other than the adsorption as represented by step 1 in Fig. 7.



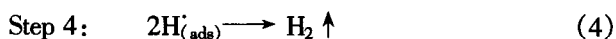
- $E > -0.4 \text{ V}$, the oxidation range

A P—H bond in the hypophosphite is cleaved to form both the adsorbed atomic hydrogen and phosphorus-centered radical, $\cdot\text{PHO}_2^-$, *i. e.*, step 2 in Fig. 7. This radical can react with water to produce phosphite and hydrogen ion and throw simultaneously an electron to the electrode as reported in Ref. 7, *i. e.*, step 3 in Fig. 7.

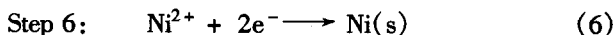
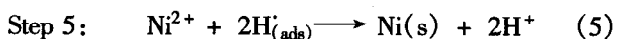




It is known that the hypophosphite oxidation occurs simultaneously with the evolution of hydrogen. It rises from the combination of two atomic hydrogens, *i. e.*, step 4 in Fig. 7.



When Ni^{2+} coexists with hypophosphite in the solutions, the atomic hydrogen adsorbed on the surface of electrode or electron from reaction (3) can result in the reduction of Ni^{2+} to elemental nickel in Ni-electroless deposition, *i. e.*, step 5 and step 6 in Fig. 7. As the steps 2, 5 and 6 can spontaneously take place at the open circuit potential (-0.25 V), the Ni-electroless deposition can also spontaneously proceed in the solution with Ni^{2+} .



• $E < -0.70$ V, the reduction range

The hypophosphite, adsorbed on the surface of electrode, can be reduced to Ni-phosphine, $\text{Ni}-(\text{PH}_3)_n$, *i. e.*, step 7 in Fig. 7. In NiSO_4 -free solution Ni-phosphine could be decomposed to result in the phosphine evolution under the suitable condition as reported by a previous paper,²¹ *i. e.*, step 8 in Fig. 7. While in the case where NiSO_4 coexisted in the solution the Ni-phosphine compound as an intermediate can be oxidized by Ni^{2+} to elemental phosphorus in the Ni-P alloy under the catalysis of nickel, simultaneously Ni^{2+} is reduced to elemental nickel in the Ni-P alloy, *i. e.*, step 9 in Fig. 7.

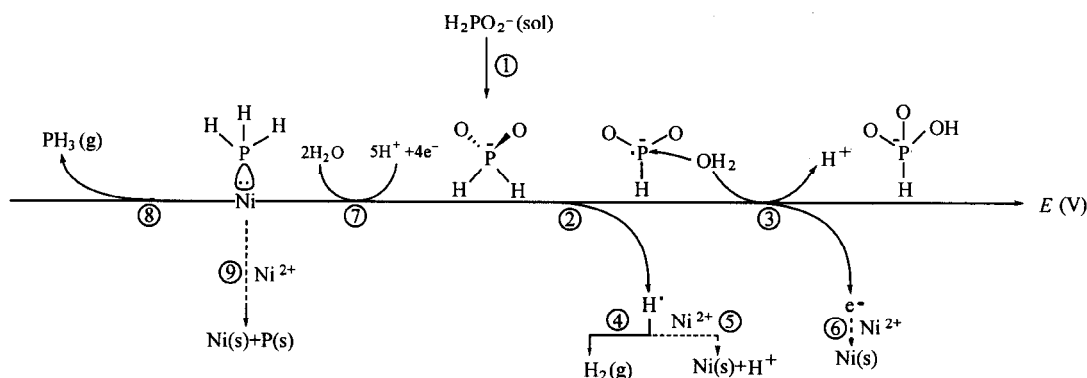
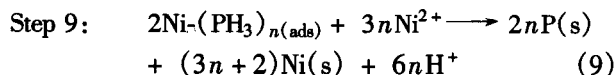
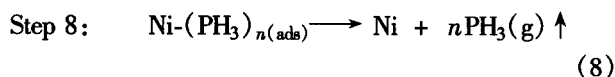
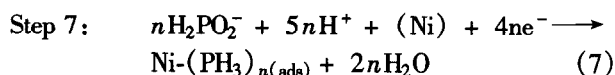


Fig. 7 Scheme of the electrodic process of hypophosphite on a Ni-Ag electrode.

Acknowledgements

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