

Electrocatalytic Oxidation of Hypophosphite on Nickel Electrode ——*In Situ* UV-Vis Spectroscopic study

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Abstract: The electrocatalytic oxidation of hypophosphite on a nickel electrode has been studied by means of *in situ* UV-Vis subtractive reflectance spectroscopy. An absorbency band around 245 nm, which was ascribed to the formation of an intermediate, $\cdot\text{PHO}_2^-$, was observed in the electrocatalytic oxidation process. Accordingly, the electrocatalytic oxidation of hypophosphite might undergo a H abstraction of hypophosphite from the P-H bond to form the phosphorus-centred radical $\cdot\text{PHO}_2^-$, which is subsequently electrooxidized to the final product, phosphite.

Keywords: *In situ* UV-Vis subtractive reflectance spectroscopy; electrooxidation; hypophosphite; mechanism.

The fact that hypophosphite is one of the most widely used reducing agents in the Ni-electroless deposition has stimulated the study of anodic oxidation of hypophosphite on nickel¹⁻¹⁰. This anodic reaction, which is important for the understanding of the Ni-electroless deposition mechanism, is expected to be one of the important reactions in the Ni-electroless process. Recently, the role and oxidation mechanism of hypophosphite in electroless deposition of Ni-P alloy have been studied in detail using the probe beam deflection⁸, electrochemistry and *in situ* IR^{9,10}. However, some particulars are still imperfect. For example, the intermediate on the electrode surface during electrocatalytic oxidation could not be detected even though *in situ* IR technique was used^{9,10}.

In situ UV-Vis spectroscopy provides a powerful means of characterizing the electrodic processes such as adsorption¹¹ and reaction¹² occurring in the vicinity of an electrode at the molecular level. In this study the electrocatalytic oxidation of hypophosphite on the nickel electrode was investigated by means of *in situ* surface UV-Vis subtractive reflectance spectroscopy to obtain the information about the anodic oxidation mechanism of hypophosphite.

In situ UV-Vis spectroscopic measurements were performed with UV-Vis spectrometer (Shimadzu UV-240) and the combined spectroelectrochemical measurement system¹³. The visible light source was a 36 W tungsten-halogen lamp and the ultraviolet light was a 10 W deuterium discharge lamp. EG&G PARC M175

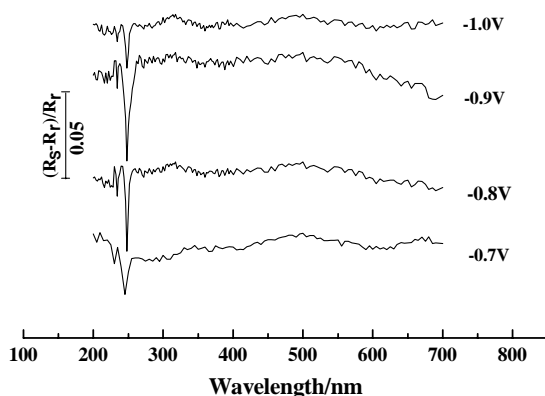
potentiostat was used to control the applied potential. The working electrode was polycrystalline Ni rod with geometric surface area of 0.1 cm^2 embedded in a Teflon sheath. A large platinum ring served as the counter electrode. A cell with the quartz window set for an angle of incidence of 45° was employed to minimize optical contributions from effects at the double layer of the electrode/electrolyte solution interphase. More detailed descriptions of the spectroelectrochemical measurements have been reported in previous papers¹².

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 and discussion

Figure 1 presents the *in situ* UV-Vis subtractive reflectance spectra on the nickel electrode. In order to minimize the effects of the hydrogen evolution and hydroxide formation on subtractance reflective spectra experiments the scan range was chosen in the potential range between -600 to -1000 mV, and the reference potential was monitored at $E_r = -600$ mV. It is obvious from **Figure 1** that the spectra change with the potential. Two absorption bands emerged around 245 nm and 234 nm at the potential of more negative than -700 mV. As the change in the potential from -700 mV to -1000 mV, the intensity of these bands increased, then decreased, the maximum was reached at the potential of about -900 mV due to the effect of the hydrogen evolution on the reflectance spectra at the potential more negative than -900 mV. If the solutions were deaerated by nitrogen before the experiments the band at 234 nm disappeared.

Figure 1 The *in situ* UV-Vis subtractive reflectance spectra on the nickel electrode, $E_r = -0.6 \text{ V}$

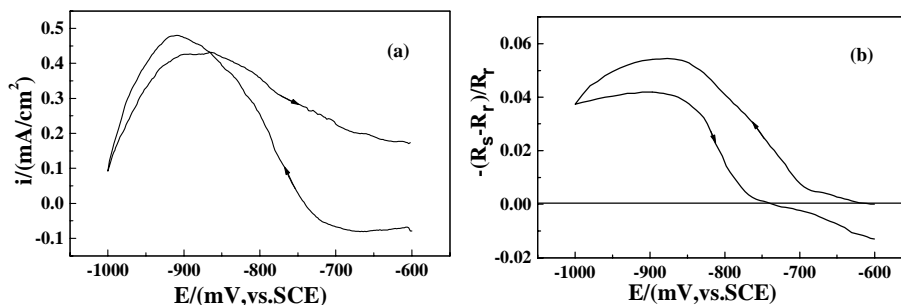


Shastri *et al*¹⁴ have reported that $\cdot\text{PHO}_2^-$ radical can be formed by pulse radiolysis of N_2O -saturated solution of hypophosphite and exhibits an optical absorption with λ_{max}

240 nm and ϵ_{\max} 3400 M⁻¹ cm⁻¹. And the reaction of $\cdot\text{PHO}_2^-$ with O₂ 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 M⁻¹ cm⁻¹. It is entirely possible that the maximum absorption wavelength of $\cdot\text{PHO}_2^-$ will have small change because it has different chemical environment in the solution and on the electrode surface. Therefore the appearance of the band at 245 nm and 234 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.

The existence of $\cdot\text{PHO}_2^-$ was confirmed by a comparison between linear scan voltammetry (a in **Figure 2**) and linear scan absorptiometry (b in **Figure 2**), in the latter the absorbency at a particular wavelength being monitored while the electrode potential was changed linearly with time. It is shown in **Figure 2** clearly that the absorbency at 245 nm by $\cdot\text{PHO}_2^-$ increased as the potential entered the range of the oxidation, reached a maximum at the potential of about -850 mV, then decreased with the negative scan of potential. In the potential range of -900 mV to -1000 mV the intensity of the absorption bands decreased, which might be due to hydrogen adsorbed on the electrode surface weakening the UV-Vis signal.

Figure 2 The comparison of between linear scan votammetry(a) and linear scan absorptiometry(b), the scan rate: 5mV·s⁻¹, E_r = -600mV, λ=245nm



The phosphorus-centred radical $\cdot\text{PHO}_2^-$ as an intermediate in the homogeneous was suggested during the hypophosphite oxidation by diperiodatocuprate(III)¹⁵. Similarly a few intermediates, such as PO₂⁻ (metaphosphite)¹⁶, $\cdot\text{PHO}_2^-$ (phosphorus-centred radical)⁶, HOPO (metaphosphorus acid)² and so on, have been reported during electrocatalytic oxidation of hypophosphite occurring on the nickel electrode. Gutzeit *et al* proposed a two-step mechanism¹⁸, in which the oxidation of hypophosphite occurs on the nickel electrode through two distinctive steps with PO₂⁻ as an intermediate, i.e., the hypophosphite undergoes firstly a 2H abstraction from the P-H bonds to form a metaphosphite(PO₂⁻) intermediate, which was subsequently hydrated to final product, phosphite. However, as Electrochemical Mass Spectrometry studies have shown that the product of the electrocatalytic oxidation of hypophosphite on the nickel electrode in D₂O solution is HDPO₃⁻ rather than D₂PO₃⁻⁴, the mechanisms, involved PO₂⁻ or HOPO as an intermediate, can not be accepted.

The intermediate, $\cdot\text{PHO}_2^-$, was first suggested by Oliveira *et al*¹⁷, and subsequently the systematic studies were performed by Abrantes *et al* using a classical

electrochemical technique⁷, a probe beam deflection study⁸ and *in situ* IR^{9,10}. However this intermediate, $\bullet\text{PHO}_2^-$, was not be observed even though *in situ* IR technique was used^{9,10}. By means of *in situ* UV-Vis spectroscopy we have detected the intermediate $\bullet\text{PHO}_2^-$ during the electrocatalytic oxidation of hypophosphite for the first time. The experimental results confirmed the validity of the electrocatalytic oxidation mechanism in which the phosphorus-centred radical $\bullet\text{PHO}_2^-$ was formed as the reaction intermediate. Accordingly, it can be unequivocally concluded that the electrocatalytic oxidation of hypophosphite involves a H abstraction of hypophosphite from the P-H bond to form the phosphorus-centred radical $\bullet\text{PHO}_2^-$, which is subsequently electrooxidized to the final product, phosphite.

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