Chinese Chemical Letters Vol. 15, No. 12, pp 1483-1486, 2004
http://www.imm.ac.cn/journal/ccl.html

The Deactivation of Nickel Hydroxide to Hypophosphite Electrooxidation on a Nickel Electrode

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Abstract: The deactivation of nickel hydroxide to the electrooxidation of hypophosphite on a nickel electrode was studied by means of *in situ* UV-Vis subtractive reflectance spectroscopy. The experimental results show that when the potential is lower than –1.0 V (SCE), the surface on nickel electrode is free of nickel hydroxide, on which hypophosphite is active. When the potential moves positively to about –0.75V, two absorbency bands around 300 nm and 550 nm, which were ascribed to the formation of α-nickel hydroxide, were observed, nickel is oxidized to α-nickel hydroxide. Severe deactivation of the surface occurs when the nickel surface is covered with nickel hydroxide, which separates the hypophosphite ion from nickel substrate.

Keywords: Hypophosphite, electrooxidation, deactivation, nickel hydroxide, *in situ* UV-Vis spectroscopy.

Hypophosphite is one of the most widely used reducing agents in the Ni-electroless deposition. This fact has stimulated the study of anodic oxidation of hypophosphite on a nickel electrode using the probe beam deflection[1], electrochemistry, *in situ* IR[2,3] and electrochemical mass spectroscopy[4,5]. It is well evidenced that when the nickel is immersed in an alkaline bath it becomes spontaneously covered by α-$Ni(OH)_2$ film. This film affect directly the oxidation of hypophosphite on the surface of electrode and further affect the Ni-electroless deposition. In the present study the deactivation of nickel hydroxide to the electrooxidation of hypophosphite on a nickel electrode was studied by means of *in situ* UV-Vis subtractive reflectance spectroscopy.

Experimental

All electrochemical measurements carried out on CHI660A electrochemical workstation (USA) using conventional three-electrode cell. The working electrode was polycrystalline Ni rod with geometric surface area of 1.5×0.5 cm^2 embedded in a Teflon sheath. The exposed surface was polished on fine emery abrasion paper. A platinum electrode served as the counter electrode. The electrode potential was measured *vs*. a saturated calomel electrode (SCE). The solution was prepared just before the experiment with double

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distilled water and analytical grade reagents. The temperature was kept at about 19℃.

In situ UV-Vis reflectance spectroscopy measurement was performed with RF5301-PC spectrofluorophotometer (Japan) using the synchronous spectrum function. A cell with the quartz window set for an angle of incidence of 45^o was employed to minimize optical contributions from effects at the double layer of the electrode/ electrolyte solution interphase. CHI660A electrochemical workstation was used to control the applied potential.

In situ UV-Vis subtractive reflectance spectra were calculated as $\Delta R/R = (R_s - R_r)/R_r$ 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 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 shows the cyclic voltammograms and reflectograms of a nickel electrode in 0.1 $mol\cdot L^{-1}$ NaOH solution. In **Figure 1a t**he peaks A and A' observed in the potential range –1.1 V to –0.6 V are related to the process $Ni + 2OH^- \Leftrightarrow \alpha\text{-}Ni(OH)_2 + 2e^-$. The corresponding reflectogram (**Figure 1b**) at λ = 550 nm reveals the change in the relative reflectivity ($\Delta R/R$) during the redox process of nickel. Owing nickel hydroxide has great absorptivity at λ = 550 nm (seen below), the relative reflectivity decreases during the growing of the nickel hydroxide. When the potential sweep is reversed the relative reflectivity increases with the reduction of nickel hydroxide to nickel, as shown by the cyclic voltammogram. If the upper limit of potential is increased to 0.6 V, the redox of nickel hydroxide to oxyhydroxide, $Ni(OH)_2 + OH^- \Leftrightarrow NiOOH + H_2O + e^-$, takes pace in the potential range of 0.3 V to 0.5 V, as seen from peaks B and B' in **Figure 1c**. The corresponding reflectogram (**Figure 1d**) at λ = 550 nm shows that the relative reflectivity ($\Delta R/R$) decreases with the increase of the potential. In the potential range of the oxyhydroxide, the remarkable increase and decrease of $\Delta R/R$ can be observed during the positive and negative scan, respectively, which could be begotten by the form of nickel oxyhydroxide and the oxygen evolution.

Figure 2 shows the cyclic voltammograms of a nickel electrode in 0.2 $mol\cdot L^{-1}$ NaH_2PO_2 + 0.1 $mol\cdot L^{-1}$ NaOH solution. It can be seen from **Figure 2** that the distinct difference is the appearance of the hypophosphite oxidation peak (peak C and C') at about the potential of -0.98 V, simultaneously, the comparing with **Figure 1,** when the potential sweep is reversed (*i.e.*, the negative scan) the high of this oxidation peak (*i.e.*, peak C') changes with the upper limit of potential. When the upper limit of the sweep potential is ower than the potential of -0.75 V (**Figure 2a**), at which nickel do not be oxidized to the nickel hydroxide. The surface of nickel electrode is free of nickel hydroxide or oxyhydroxide, the electrode possesses the same activity during the positive and negative scan. If the upper limit of potential is increased to the potential of the oxidation nickel to nickel hydroxide (*e.g.*, -0.45 V, **Figure 2b**) or oxyhydroxide (*e.g.*, 0.6 V, **Figure 2c**), the electrode surface was partially covered by nickel hydroxide or by oxyhydroxide, which

Figure 1 Voltammograms and reflectograms of a nickel electrode simultaneously recorded at $\nu = 10\ mV\cdot s^{-1}$, $\lambda = 550\ nm$, and $E_r = -1.0\ V$

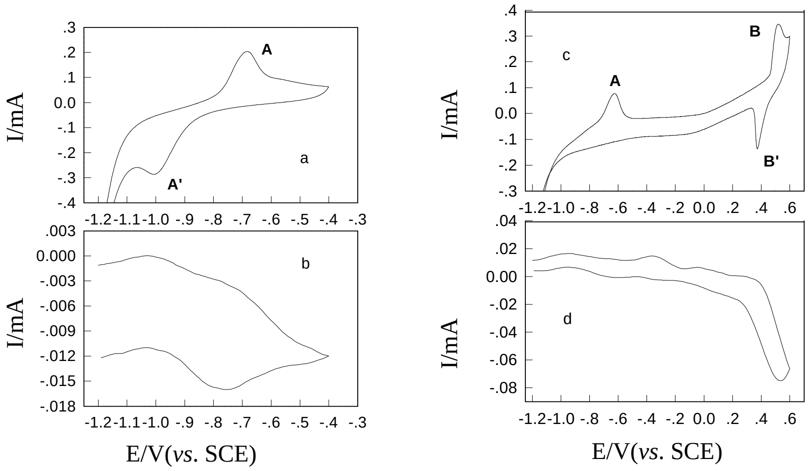


Figure 2 Voltammograms of a nickel electrode in $0.2\ mol\cdot L^{-1}\ NaH_2PO_2 + 0.1\ mol\cdot L^{-1}\ NaOH$ solution at $\nu = 100\ mV\cdot s^{-1}$

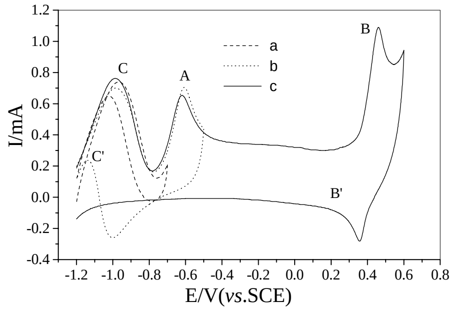
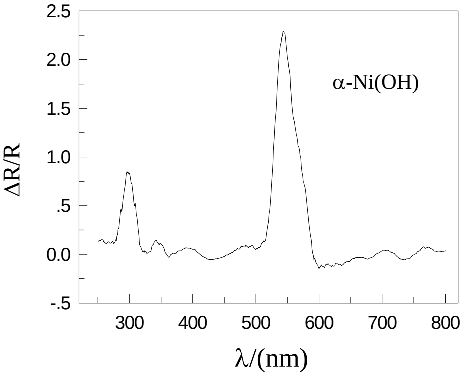


Figure 3 Reflectogram of a nickel electrode in $0.1\ mol\cdot L^{-1}$ NaOH solution at potentiostatic potential of -0.45 V for 1000 s, and $E_r = -1.0$



separates the hypophosphite ion from nickel substrate, and results in the deactivation for the oxidation of hypophosphite on nickel surface during the reverse scan.

Figure 3 shows the relative reflectivity of working electrode pretreated at potentiostatic potential of -0.45 V for 1000 s in 0.2 mol·L^{-1} NaH_2PO_2 + 0.1 mol·L^{-1} NaOH solution before the experiments. It is obvious from **Figure 3** that two absorption peaks emerged around 300 nm and 550 nm, which could be attributed to the formation of α-$Ni(OH)_2$[6]. After the working electrode was pretreated by the same method above mentioned the hypophosphite oxidation peak disappears on the cyclic voltammograms during the positive and negative scan. It is well evidenced that at the potential of -0.45 V the nickel on electrode surface is oxidized to α-$Ni(OH)_2$. It is the surface hydroxide that separates the hypophosphite ion from nickel substrate and results in severe deactivation of hypophosphite electrooxidation.

Acknowledgment

The work was supported by the Natural Science Foundation of Hunan Province (No. 01JJY3017).

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Received 9 February, 2004