

Kinetic Model of Hypophosphite Oxidation on a Nickel Electrode in D₂O Solution

Yue ZENG^{1*}, Hui Xian WANG², Shang Ci YU¹, Xin De WU¹, Xue Qiang CAO¹

¹Department of Chemistry, Hunan Normal University, Changsha, Hunan 410006

²Department of Chemistry, Jishou University, Jishou, Hunan 416000

Abstract: Kinetic model of hypophosphite oxidation on a nickel electrode was studied in D₂O solution in order to reach a better understanding of the oxidation mechanism. In the model the electrooxidation of hypophosphite undergo a H abstraction of hypophosphite from the P-H bond to form the phosphorus-centered radical $\cdot\text{PHO}_2^-$, which subsequently is electrochemically reacted with water to form the final product, phosphite. The kinetic equations were derived, and the kinetic parameters were obtained from a comparison of experimental results and the kinetic equations. The process of hypophosphite electrooxidation could be well simulated by this model.

Keywords: Kinetic model, hypophosphite oxidation, mechanism, nickel electrode.

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 deflection¹, electrochemistry, *in situ* IR^{2,3} and electrochemical mass spectroscopy^{4,5}. The kinetic model study provides a powerful means of characterizing kinetics and mechanism of electrodic processes. In our recent paper the kinetic model of the Ni-Mo alloy codeposition has been studied⁶. In the present study a kinetic model of hypophosphite oxidation on a nickel electrode was presented in order to reach a better understanding of the oxidation mechanism.

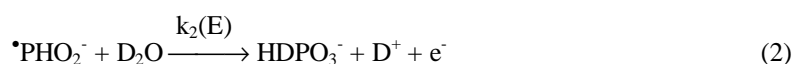
Experimental

The experiments were carried out in D₂O (D content 99.8 mol%) solution containing 0.19 mol·L⁻¹ NaH₂PO₂ (anhydrous, prepared according to reference 7) and 0.15 mol·L⁻¹ CH₃COONa (anhydrous, p.a.). The pH of solution was adjusted to 4.5 with CH₃COOD (D content 98%). The detailed description of the electrochemical mass spectrometry measurements has been reported in a previous paper⁵. Two large platinum electrodes served as the counter electrode. The electrode potential was measured vs. a saturated calomel electrode (SCE). The temperature was kept at 353±1K.

Kinetic model

In our recent paper the mechanism of hypophosphite oxidation on a nickel electrode has

been studied by means of *in situ* UV-Vis spectroscopy^{8,9}. The experimental results indicated that the electrooxidation of hypophosphite undergo a H abstraction of hypophosphite from the P-H bond to form the phosphorus-centered radical, $\bullet\text{PHO}_2^-$, which subsequently is electrochemically reacted with water to form the final product, phosphite. In D_2O solution this process could be expressed as



Taking into account the fact that the probability of HD molecule formation is twice as high as either H_2 or D_2 ¹⁰, a reasonable assumption, *i.e.*, $2k_4 = 2k_5 = k_6$, can be proposed for the reactions 4, 5 and 6.

For simplification, C_P , C_{D^+} and Q represent the concentrations of H_2PO_2^- and D^+ , and the fractional coverages on the surface of the electrode, respectively. According to the material balance for intermediates (H^\bullet , D^\bullet and $\bullet\text{PHO}_2^-$) and the pseudo-steady-state assumption, the expressions of Q_{H^\bullet} , Q_{D^\bullet} and $Q_{\bullet\text{PHO}_2^-}$ can be written as, respectively,

$$Q_{\text{H}^\bullet} = \frac{k_1 C_P}{(2k_1 k_4 C_P + 2k_3 k_4 C_{\text{D}^+})^{1/2}} \quad (7)$$

$$Q_{\text{D}^\bullet} = \frac{k_3 C_{\text{D}^+}}{(2k_1 k_4 C_P + 2k_3 k_4 C_{\text{D}^+})^{1/2}} \quad (8)$$

$$Q_{\bullet\text{PHO}_2^-} = k_1 C_P / k_2 \quad (9)$$

The content (in mol%) of H_2 , HD and D_2 in the evolving gas can be calculated from Eq. 4, 5 and 6, respectively,

$$\text{H}_2\% = \frac{1}{1 + 2K + K^2} \cdot 100 \quad (10)$$

$$\text{HD}\% = \frac{2K}{1 + 2K + K^2} \cdot 100 \quad (11)$$

$$\text{D}_2\% = \frac{K^2}{1 + 2K + K^2} \cdot 100 \quad (12)$$

where
$$K = \frac{k_3 C_{D^+}}{k_1 C_P} \quad (13)$$

$k_2(E)$ in Eq.2 and $k_3(E)$ in Eq.3 are electrochemical rate constant. The expressions are, respectively,

$$k_2(E) = k_{20} \exp(\alpha_2 n_2 FE/RT) \quad (14)$$

$$k_3(E) = k_{30} \exp(-\beta_3 n_3 FE/RT) \quad (15)$$

where k_{10} and k_{30} are electrochemical rate constants at E (applied potential)=0. α and β are anodic and cathodic transfer coefficient. E is potential referred to SCE.

Results and Discussion

Kinetic parameters were obtained from a comparison of experiment results and the kinetic equation using SigmaPlot software for windows.

The effect of the scan rate on the peak current of the hypophosphite oxidation was shown in **Figure 1**. In the lower scan rate range, the oxidation peak current depended linearly on $v^{1/2}$. In the higher scan rate range, the oxidation peak current decreased with the scan rate. This result indicated that a time dependent step precedes the electrooxidation step. As the scan rate increases the time spent for the time dependent step is lower, which results a lower oxidation current and more negative potential of the oxidation peak. These electrochemical characterisation were in agreement with that radical formation is a time dependent step¹¹.

Figure 1 The effect of the scan rate on the peak current of the hypophosphite oxidation

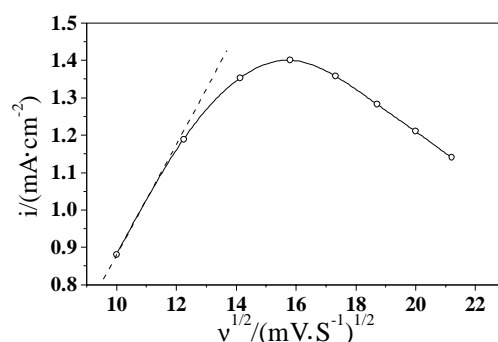
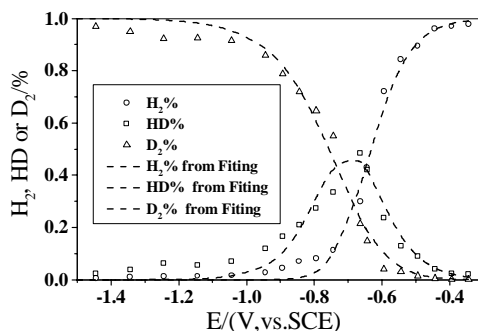


Figure 2 shows the comparison between predicted and experimental distribution of H₂, HD and D₂ in the evolving gas. It can be seen from **Figure 2** that the distribution of H₂, HD and D₂ in the evolving gas can be well simulated in the potential range from -0.3 V to -1.5 V. At the potentials more negative than -0.9 V the main content in the evolving gas is D₂, while at the potentials more positive than -0.5 V, H₂ is a main content in the evolving gas. In the potential range from -0.9 V to -0.5 V the evolving gas was a mixture gas composed of H₂, HD and D₂. The content of HD increased, then decreased, with the increase in the potential. At the open circuit potential (-0.45 V) the maximum

of HD content was obtained.

Figure 2 The comparison between predicted (Dotted lines,) and experimental (○-H₂, □- HD and △-D₂, according to reference 5)



The kinetic model of the hypophosphite oxidation on a nickel electrode was studied using the cyclic voltammogram and the electrochemical mass spectrometry measurements. The experimental data were fitted according to $K=1.11 \times 10^{-3} \exp(-0.455FE/RT)$. The results shown the validity of the electrocatalytic oxidation mechanism in which the phosphorus-centred radical $\cdot\text{PHO}_2^-$ was formed as the reaction intermediate. Then it can be further concluded that the electrocatalytic oxidation of hypophosphite involves 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.

Acknowledgment

The work was supported by the Natural Science Foundation of the Education Commission of Hunan Province (No. 99C57)

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Received 2 January, 2001