Journal of Electrochemistry

Volume 8 | Issue 4

2002-11-28

Mechanistic Study of Oxidation of Hypophosphite on Pt Electrodes by SNIFTIRS

Tai-xiang JIANG

Hui-huang WU

Recommended Citation
Tai-xiang JIANG, Hui-huang WU. Mechanistic Study of Oxidation of Hypophosphite on Pt Electrodes by SNIFTIRS[J]. *Journal of Electrochemistry*, 2002 , 8(4): 376-380.
DOI: 10.61558/2993-074X.1467
Available at: https://jelectrochem.xmu.edu.cn/journal/vol8/iss4/1

第 8 卷 第 4 期
2002 年 11 月
电化学
ELECTROCHEMISTRY
Vol. 8 No. 4
Nov. 2002

Article ID:1006-3471(2002)04-0376-05

Mechanistic Study of Oxidation of Hypophosphite on Pt Electrodes by SNIFTIRS

JIANG Tai-xiang, WU Hui-huang *
(Dept. of Chem., State Key Lab. for Phys. Chem. of the Solid Surfaces, Xiamen Univ., Xiamen 361005, *China)*

Abstract: The oxidation of hypophosphite on a polycrystalline platinum electrode was studied by SNIFTIRS and cyclic voltammetry, the in-situ IR spectra were analyzed as a function of Pt electrode potentials in the solution of 0.5 mol/L H_2SO_4 + 0.1 mol/L NaH_2PO_2. It was found that the dissociative adsorption of hypophosphite ions occurs on Pt surface, and the oxidation product is H_3PO_4, rather than $H_2PO_3^-$ which was considered to produce on Ni electrodes, thereby a new insight into mechanism of hypophosphite oxidation on Pt in acidic media was provided.

Key words: Hypophosphite, Electro-oxidation, Electoless plating, Platinum electrode, SNIFTIRS

CLC Number: O 646 **Dccument Code:** A

Hypophosphite is one of the common reducing agents used in electroless plating particularly in Ni based alloy electroless plating. For understanding the mechanism of autocatalytic deposition of metal ions, the oxidation of hypophosphite has been investiged at different electrodes[1~7]. The mechanistic aspects presented so far, however, have need of the envidaces in molecular level, since the elctrooxidation was mostly studied with tranditional electrochemical methodes. Abrantes[6] reported recently that the electrooxidation of hypophosphite ions on polycrystalline nickel in alkaline solution using SNIFTIRS, (i. e. Subtractively Normalized Interfacial FTIR Spectroscopy) and gave a new insight into the oxidation process. In this work the same *in-situ* IR technique was utilized for investigation of the hypophosphite oxidation on polycrystalline Pt electrode in acidic solution, and the results show that the dissociative adsorption of hypophosphite occurs on Pt surface, and H_3PO_4 was detected as oxidation product rather than phosphite[6]. Ac-

---

Received date: 2002-06-26

* To whom correspoadence should be addressed, Tel: 0592-2183196, E-mail: hhwu@xmu.edu.cn

Foundation item: Supported by National Science Fundation of China (No 20073035)

cordingly, a new mechanism was proposed for the oxidation of hypophosphite.

1　Experimental

Cyclic voltammetry was carried out with a CHI 660 model electrochemical system, the structure of electrochemical cell used, the pretreatment of Pt elctrodes and of electrolytic solutions were the same as that in our previous work[7]. The electrode potentials were read with respect to a satuated calomel electrode (SCE).

The *in-situ* IR measurements were performed using Nicolet 730 spectrometer, a spectroelectrochemical cell with a CaF_2 window and experimental details regarding SNIFTIRS have been given elsewhere[8].

2　Results and Discussion

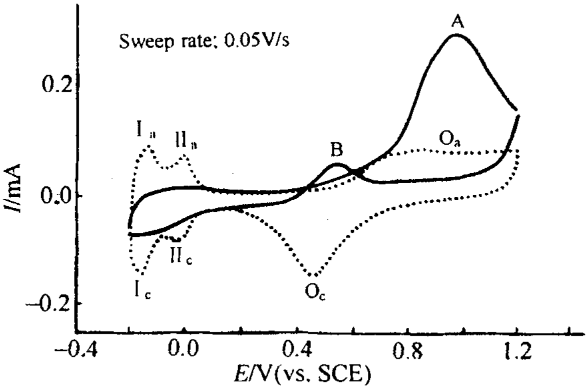

Fig. 1　Cyclic voltammetric curves of a Pt electrode in 0.5 mol/L H_2SO_4 without (dotted line) and with 0.1 mol/L NaH_2PO_2 (full line)

The cyclic voltammgram of a platinum electrode in 0.5 mol/L H_2SO_4 at 25 ℃is depected in Fig. 1 as a dotted line, which is quite in agreement with that shown in the the literature[9]. The two pairs of symmetric current peaks Ic, Ia and IIc, IIa, located at nearly - 0.2 V and 0.0 V (SCE), represent the adsorption and desorption of hydrogen (strongly adsorbed and weakly adsorbed states, respectively), on the other hand, the asymmetric current peaks Oa, Oc represent the formation and reduction of adsorbed oxygen on Pt. If the solution contains 0.1 mol/L NaH_2PO_2, the cyclic voltammetric curve is shown as the solid line in Fig. 1, as reported by Podesta et al.[3] An irreversible current peak, A, occurs in the potential sweep towards the more positive value, and an irreversible current peak, B, occurs in the reverse sweep. It is obvious that the presence of NaH_2PO_2 inhibites the adsorption of hydrogen and oxygen. Podesta et al. proposed that the mechanism for hypophosphite oxidation on Pt was as follows: the equilibrium

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- (ad) + 2H(ad) \tag{1}$$

is established on Pt in contact with a NaH_2PO_2 solusion, where $H_2PO_3^-$ (ad) and H(ad) are adsorbed species on Pt. The reaction (1) can be shifted to the right if the fast desorption of H-atoms can occur as molecular hydrogen. Podesta et al. assigned the peak B in Fig. 1 to an electrochemical reaction taking place on a Pt surface convered mainly by adsorbed $H_2PO_3^-$ ions, the product of the reaction being adsorbed H_3PO_4, and the peak A to electrooxidation of H_3PO_3 on fresh Pt since the inhibition caused by H_3PO_4 decreases in the potential range where the current peak located. These conclusions, however, were based on cyclic voltammetric experiments.

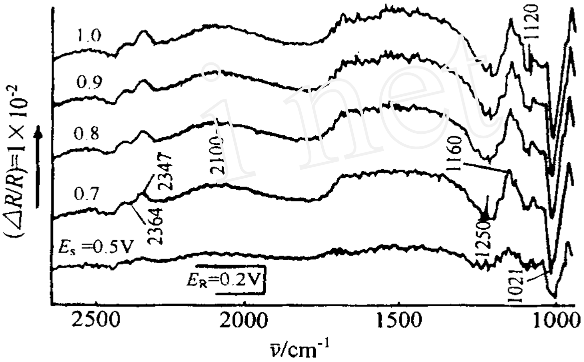

Fig. 2 SNIFTIRS spectra taken from a Pt electrode at various sample potentials in 0.5 mol/L H_2SO_4 + 0.1 mol/L NaH_2PO_2, E_R = 0.2 V

Fig. 2 shows the SNIFTIRS spectra at various sample potentials, which are the difference spectra, $\triangle R/R \equiv ([R(E_S) - R(E_R)]/R(E_R)$, where $R(E_S)$ and $R(E_R)$ represent the the reflectances at a sample potential E_S and at a reference potential E_R. For small values of $\triangle R/R$, this quantity is proportional to absorbance. Both positive (up-going) and negative (down-going) bands are observed in Fig. 2, positive bands are due to absorbances from species present at the reference potential E_R, while negative bands are due to absorbances from species present at the sample potential E_S. As seen in Fig. 2, where $E_R = 0.2$ V and is less positive than E_S, there are two negative bands at 1 020 cm^{-1}and 1 250 cm^{-1} and two positive bands at 1 160 cm^{-1}and 2 100 cm^{-1}, besides a bipolar band at 2 360 cm^{-1}. The vibrational modes and characteristic IR bands for hypophosphite and its possible oxidation products have been discussed in the literature[6,11]. The free hypophosphite ions in aqueous solution has a tetrahedral structure with a C_{2v} symmetry, hence exhibit 8 IR active bands, but they must not been obrerved in SNIFTIRS spectra owing to the limitation of surface selection rules. Similar to the *in-situ* IR experimental results of the hypophosphite electrooxidation on Ni in alkaline solution[6], 2 360 cm^{-1}and 1 160 cm^{-1} bands can be attributed to P—H and P—O stretching in hypophosphite, respectively, suggested that the adsorption of hypophosphite on Pt via two hydrogen atoms, otherwise the ν_{as}(P—O) and ν_{as}(P—H) mode bands at 1 180 cm^{-1}and 2 314 cm^{-1} would be present. When $E_R = 0.2$ V, the augmentation of the up-going band at 1 160 cm^{-1} with increasing positive potential of E_S, indicates the more hypophosphite ions were depleted at more positive potential. Bewick et al.[10] have examined the hydrogen adsorption by in situ IR technique, and found a 2 090 cm^{-1} band ascribed to M—H stresch of a hydrogen atom coordinated on top of the surface metal atom. It is reasonable to assign the broad band at 2 100 cm^{-1} in Fig. 2 to adsorbed hydrogen, the augmentation of this up-going band with increasing positive potential of E_S, indicates the less hydrogen atom on Pt at more positive potential, moreover, the absence of such a band on Ni electrodes[6] means the difference in the adsorbility of hydrogen on Ni from on Pt. In the work of Abrantes[6], a negative band at 1 020 cm^{-1} was also observed and considered due to the formation of oxidation product HPO_3^-, but there did not exist the negative band at 1 250 cm^{-1} as in Fig. 2. We believe that the latter band should be attributed to the presence of H_3PO_4 in solution as assigned by Nart[11], who studied the IR reflectance spectra of Pt elrctrodes in H_3PO_4 solution (pH 0.2 to 2.8) using both s- and p- polarized light. It is worth notice that Fig. 2 illustrates the absence of adsorbed undissociated H_3PO_4 on Pt, which exhibites a strong band at 1 055 cm^{-1}, while adsorbed $H_2PO_4^-$ is present from the 1 120 cm^{-1} band in Fig. 2 according to Nart[11].

As to the mechanism for hypophosphite oxidation on Pt electrodes in acidic solution two factors should be considered: firstly the predominant species of hypophosphite in acidic media, possibly it must be H_3PO_2 rather than $H_2PO_2^-$, secondly the influence of the surface states of Pt on the electrooxidation of hypophosphite. The peak potential of peak A in Fig. 1 is at about 1.0 V (SCE) where adsorbed oxygen layer is formed on Pt surface, and the peak potential of B is at about 0.5 V (SCE) located at the boundary between the double layer region and oxygen-adsorbed region. With these in mind the following mechanism is proposed for hypophosphite oxidation on Pt electrodes in acidic solution. In the oxidation process the dissociative adsorption of reactant takes place on Pt

$$H_3PO_2 \longrightarrow H_2PO_2(ad) + H(ad) \tag{2}$$

the fast desorption of resulting H(ad) may occur by chemical recombination into molecular hydrogen or by electrochemical oxidation into proton, then adsorbed H_2PO_2 may undergothe reactions:

$$H_2PO_2(ad) + H_2O \longrightarrow H_3PO_3(ad) + H^+ + e^- \tag{3a}$$

$$H_3PO_3(ad) + H_2O \longrightarrow H_3PO_4 + 2H^+ + e^- \tag{3b}$$

or

$$H_2PO_2(ad) + OH(ad) \longrightarrow H_3PO_3(ad) \tag{4a}$$

$$H_3PO_3(ad) + OH(ad) \longrightarrow H_3PO_4 + H^+ \tag{4b}$$

$$H_2O \longrightarrow OH(ad) + H^+ + e^- \tag{4c}$$

the reaction (3) occurs in the potential range where the oxygen-adsorbed layer can not be formed, and reaction (4) occurs in the potential range where the oxygen-adsorbed layer is formed, Trasatti[14] pointed out the posibility for the oxygen-adsorbed layer to take part in hypophosphite oxidation on Pd. Hence the peak A in Fig. 1 may be associated with the reaction (4), and the peak B with the reaction (3). It must be admitted that the mechanism shown in reaction (2) to (4) is simplistic, for instance, the anodic oxidation may occur via severral dehydrogenation steps (such as $H_3PO_2 \rightarrow H_2PO_2 \rightarrow HPO_2$), for more details of the mechanism new information is needed.

References:

[1] Trasatti S, Alberti A. Anodic oxidation mechanism of hypophosphorous and phosphrous acid on palladium [J]. J. Electroanal. Chem., 1966, 12: 236～249.

[2] Flis J, Duquette D J. Initiation of electroless nickel plating on copper, palladium-activated copper, gold and

platinum[J]. J. Electrochem. Soc., 1984, 132: 2 323～2 330.

[3] Podesta J J, Piatti R C V, Arvia A J. Voltammetric behaviour of platinum in aqueous solutions containing sodium hypophosphite[J]. J. Appl. Electrochem., 1990, 20: 245～251.

[4] Burke L D, Lee B H. Oxidation of some reducing agents used in electroless plating baths at gold anodes in aqueous media[J]. J. Appl. Electrochem., 1992, 22: 48.

[5] Abrantes L M, Oliveira M C, Bellier J P, et al. Electro-oxidation of hypophosphite ions on nickel single crystal electrodes[J]. Electrochim. Acta., 1994, 39: 1 915～1 922.

[6] Abrantes L M, Oliveira M C, Correia J P, et al. In situ IR study of electrooxidation of hypophosphite on a polycrystalline nickel electrode[J]. J. Chem. Soc., Faraday Trans., 1997, 93: 1 119～1 125.

[7] JIANG Tai-Xiang, WU Hui-Huang. Studies on electro-oxidation of hypophosphite ions $H_2PO_2^-$ at platinum electrodes[J]. J. Xiamen Univ. (Natural Sciences) (in Chinese), 2000, 39: 203～210.

[8] SUN Shi-Gang, YANG Dong-Fang, TIAN Zhao-Wu. In-situ FTIR reflectance spectroscopic studies of electrocatalytic processes[J]. Prog. Natural Sciences (in Chinese) 1991, 1: 40～44.

[9] Enyo M, Hydrogen Electrode Reaction on Electrocatalitically Active Metals[M]. Comprehensive Treatise of Electrochemistry, vol. 7 (eds. Conway B E, Bockris J O’M, Yeager E, et al.), New York: Plenum, 1983: 241～300.

[10] Bewick A, Russell J W. (a) Structural investigation by infrared spectroscopy of adsorbed hydrogen on platinum[J]. J. Electroanal. Chem, 1982, 132: 329～344, (b) Structural investigation by electrochemically modulated infrared spectroscopy of adsorbed hydrogen on rhodium[J]. J. Electroanal. Chem, 1982, 142: 337～343.

[11] Nart F C, Iwasita T. On the adsorption of $H_2PO_4^-$ and H_3PO_4 on platinum: an in-situ FTIR study[J]. Electrochim. Acta, 1992, 37: 385～391.

次亚磷酸根离子在铂电极上氧化的机理研究

蒋太祥，吴辉煌

(厦门大学化学化工学院，固体表面物理化学国家重点实验室，福建 厦门 361005)

摘要： 用 SNIFTIRS 和循环伏安法研究次亚磷酸根离子在多晶铂电极上的电氧化机理. 分析了 0.5 mol/L H_2SO_4 + 0.1 mol/L NaH_2PO_2 溶液中原位红外反射谱图与 Pt 电极电位的关系，发现次亚磷酸根离子在 Pt 上发生解离吸附，其氧化产物是 H_3PO_4，不同于在 Ni 上的氧化产物 $H_2PO_3^-$，据此提出了酸性溶液中次亚磷酸根离子在 Pt 上氧化机理的新看法.

关键词： 次亚磷酸根，电氧化，化学镀，铂电极，SNIFTIRS