



# ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE STUDY OF THE ELECTRODEPOSITION OF PLATINUM



Taizo HAGIHARA<sup>a,b</sup>, Kazumasa YAORI<sup>a</sup>, Keishiro IWAKURA<sup>a</sup>, Naoki FUKUMURO<sup>a</sup>, Shinji YAE<sup>a,1,\*</sup>

<sup>a</sup> Department of Chemical Engineering and Materials Science, Graduate School of Engineering, University of Hyogo 2167 Shosha, Himeji, Hyogo 671-2280, Japan

<sup>b</sup> Shinko Seiki co., Ltd., 1-35, 3-chome, Takatsukadai, Nishi-ku, Kobe 651-2271, Japan

## ARTICLE INFO

### Article history:

Received 19 March 2015  
Received in revised form 26 June 2015  
Accepted 26 June 2015  
Available online 2 July 2015

### Keywords:

electrochemical quartz crystal microbalance  
hydrogen adsorption  
tetrachloroplatinate(II)  
hexachloroplatinate(IV)

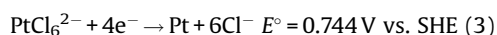
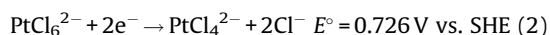
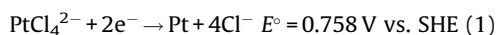
## ABSTRACT

The electrodeposition of Pt from aqueous solutions of  $K_2PtCl_4$  (Pt(II)),  $H_2PtCl_6$  (Pt(IV)), and a mixture of Pt(II) and Pt(IV) was studied using the electrochemical quartz crystal microbalance (EQCM) method. Pt deposition and cathode current flow began at the same potential in the Pt(II) solution. On the other hand, in the Pt(IV) solution, the cathode current increased at a more positive potential followed by Pt deposition at a more negative potential than in the Pt(II) solution. This difference in the potentials is due to the reduction reaction of Pt(IV) to Pt(II). Thus, Pt deposition in the Pt(IV) solution occurred in two potential ranges. In the first range, which was more positive than the second one, Pt was deposited via the reduction of Pt(II) to Pt(0). In the second range, direct deposition from Pt(IV) to Pt(0) proceeded, but was followed by hydrogen adsorption, which inhibited further Pt deposition.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Platinum (Pt) has been widely used as a catalyst in electrodes for various electrolysis systems, automotive catalytic converters, and fuel cells. Various studies of the electrochemical deposition of platinum have been reported [1–7]. We have been investigating the electrodeposition of platinum, gold, and palladium nanoparticles on n-type crystalline silicon substrates using a double potential step (DPS) method that involves the application of a single pulse potential (first step) and maintains a constant potential (second step) [8–10]. In this method, the particle density and size of the deposited metals can be controlled using the pulse potential during the first step and the electrical charges passed through the electrode during the second step, respectively. The particle density of the electrodeposited Pt was different between the aqueous solutions of tetrachloroplatinate(II) ( $PtCl_4^{2-}$ , hereafter Pt(II)) and hexachloroplatinate(IV) ( $PtCl_6^{2-}$ , hereafter Pt(IV)) differs [10,11]. Pt(II) and Pt(IV) can undergo three types of reduction reactions as follows:



where  $E^\circ$  is the standard electrode potential [12,13].

From a Pt(II) solution, metal deposition basically proceeds via Eq. (1). However, the chemical disproportionation reaction,  $2PtCl_4^{2-} \rightarrow Pt + PtCl_6^{2-} + 2Cl^-$ , should also be considered as another Pt deposition pathway for this solution [14]. From a Pt(IV) solution, the deposition of Pt is generally explained as a two-stage reduction [1,13]. In the first stage, the Pt(IV) is reduced to Pt(II) (Eq. (2)), and then, in the second stage, the generated Pt(II) is reduced to Pt(0) (deposition, Eq. (1)). It has been reported, however, that Pt can be directly deposited via the reduction of Pt(IV) to Pt(0) [15].

An electrochemical quartz crystal microbalance (EQCM) [16] can be used to measure *in situ* very small mass changes on the order of one ng. Therefore, EQCM is useful for the analysis of electrodeposition reactions [7,17]. In the present study, EQCM was used to analyze the electrodeposition of Pt from these two types of chloro complexes.

## 2. Experimental

The current-potential and resonant frequency-potential curves were measured using a QCM linked electrochemical measurement

\* Corresponding author. Tel.: +81 79 267 4911; fax: +81 79 267 4911.  
E-mail address: [yae@eng.u-hyogo.ac.jp](mailto:yae@eng.u-hyogo.ac.jp) (S. YAE).

<sup>1</sup> ISE member

system (Hokuto Denko, HQ-101D and HZ-5000). A quartz electrode coated with gold (geometric electrode area:  $0.07 \text{ cm}^2$ , resonant frequency: 10 MHz, Hokuto Denko, HX-Q1, HQ-601DK), a silver/silver chloride (Ag/AgCl) electrode, and a Pt wire were used as the working, reference, and counter electrodes, respectively. A glass cell which has fritted glass separation between two compartments for a working electrode and a counter electrode (Hokuto Denko, HX-601) was also employed. The working electrode surface was cleaned via cathodic electrolysis at a potential of  $-0.65 \text{ V}$  vs. Ag/AgCl in a pH 1.7 aqueous perchloric acid ( $\text{HClO}_4$ ) solution for 1 min prior to the experiment. Cyclic voltammetry experiment was performed at a sweep rate of  $20 \text{ mV s}^{-1}$  from the natural potential toward the negative potential. The mass change in the electrode was determined from the resonant frequency change. The sensitivity of the mass measurement was  $0.31 \text{ ng Hz}^{-1}$ , and the resonant frequency measurement resolution was set to one Hz ( $0.31 \text{ ng}$ ). Three types of aqueous metal salt solutions were used: a Pt(II) solution ( $5 \text{ mM}$  ( $M = \text{mol dm}^{-3}$ ) potassium tetrachloroplatinate(II) ( $\text{K}_2\text{PtCl}_4$ ), adjusted to pH 1.7 with  $\text{HClO}_4$ ); an acidic Pt(IV) solution ( $5 \text{ mM}$  hexachloroplatinic(IV) acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), adjusted to pH 1.7 with  $\text{HClO}_4$ ); and a neutral Pt(IV) solution ( $5 \text{ mM}$   $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $0.5 \text{ M}$  sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), adjusted to pH 7.0 using a phosphate buffer ( $0.1 \text{ M}$   $\text{K}_2\text{H}_2\text{PO}_4$  and  $0.1 \text{ M}$   $\text{NaOH}$ )).  $241 \text{ mM}$   $\text{K}_2\text{PtCl}_4$  and  $193 \text{ mM}$   $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solutions were used as mother liquors. The aqueous metal salt solutions were prepared by diluting the mother liquors and adjusting pH. Prior to each experiment, the aqueous metal salt solution was degassed by bubbling argon gas (Taiyo Nippon Sanso Corporation, 99.9999%, Class G1) for 30 min. During the measurement, bubbling and stirring were not performed. Each experiment was carried out using freshly prepared solution to avoid contamination of the metal salt solution with the products of counter electrode reaction. All the experiments were performed using reagent-grade chemicals (Wako Pure Chemical Industries) and ultra-pure water (Millipore, Simpli Lab-UV).

### 3. Results

Fig. 1 shows the current density ( $J$ : solid line) and the mass increase rate (Pt deposition rate ( $dm/dt$ ): broken line) versus electrode potential ( $E$ ) curves for the Pt(II) and acidic Pt(IV) solutions. The  $dm/dt$  scale was adjusted to 100% current efficiency for the two- and four-electron transfer reactions for the Pt(II) and Pt(IV) solutions, respectively. In the first sweep for the Pt(II) solution (Fig. 1(a)), the cathode current started increasing at  $0.29 \pm 0.05 \text{ V}$  vs. Ag/AgCl (average and standard deviation of nine experimental data), and the deposition rate increased with approximately 80% current efficiency. Peaks for the cathode current and deposition rate appeared at a potential of  $-0.19 \pm 0.001 \text{ V}$  (average and standard deviation of four experimental data). The peak for the cathode current was much larger than that for the deposition rate, and the current efficiency was approximately 60% at this peak. During the return sweep toward the positive potential from  $-0.05$  to  $+0.50 \text{ V}$ , the curves for the current density and deposition rate nearly overlapped. Pt deposition with 100% current efficiency continued until a potential of  $0.50 \text{ V}$  more positive than the onset potential of  $0.30 \text{ V}$  for the first negative sweep. In the second sweep (Fig. 1(b)), the cathode current started increasing at  $0.50 \text{ V}$ , the cathode current density monotonically increased towards a maximum at  $-0.20 \text{ V}$ , and the mass of the electrode increased with a current efficiency of approximately 80% up to a potential of zero V, as was observed in the first sweep. For the negative (forward) sweep between  $-0.05$  and  $-0.30 \text{ V}$  and the entire positive (return) sweep for the second sweep, the current density and deposition rate curves were similar to those for the first sweep, except that the current density of the two peaks at  $-0.20 \text{ V}$  for the negative sweep and  $-0.10 \text{ V}$  for the positive sweep were greater than those for the first sweep. The results for the third and higher sweeps were nearly the same as those for the second sweep.

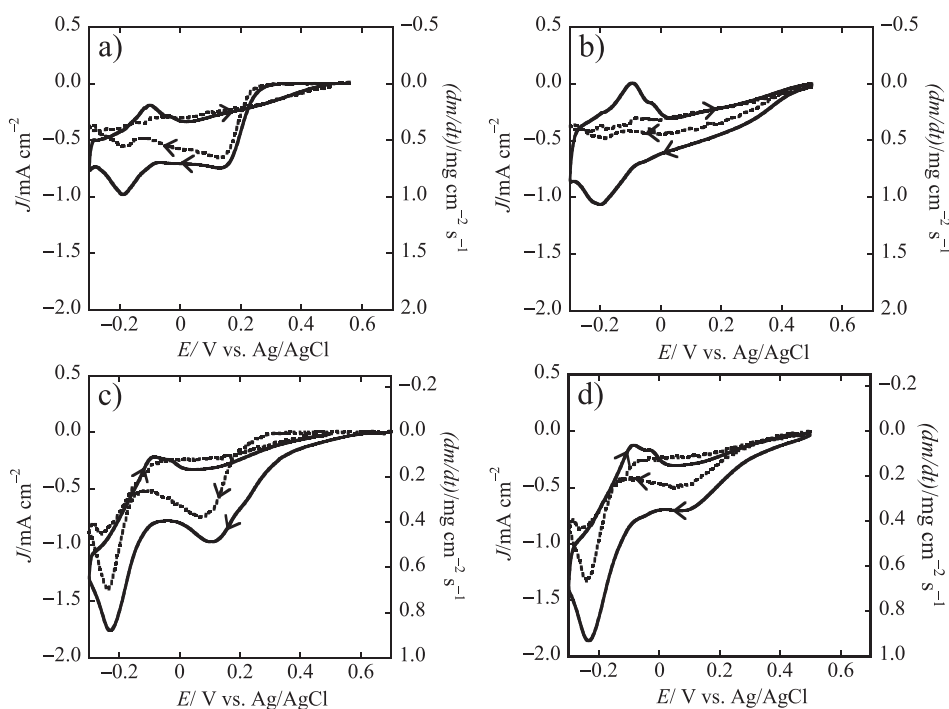


Fig. 1. Current density ( $J$ ) (solid line) and deposition rate ( $dm/dt$ ) (broken line) vs. potential ( $E$ ) curves for a gold coated quartz electrode in Pt(II) ( $5 \text{ mM}$   $\text{K}_2\text{PtCl}_4$ , pH 1.7 adjusted with  $\text{HClO}_4$ ) and Pt(IV) ( $5 \text{ mM}$   $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , pH 1.7 adjusted with  $\text{HClO}_4$ ) solutions. a) Pt(II) first sweep, b) Pt(II) second sweep, c) Pt(IV) first sweep, and d) Pt(IV) second sweep.

Download English Version:

<https://daneshyari.com/en/article/6610800>

Download Persian Version:

<https://daneshyari.com/article/6610800>

[Daneshyari.com](https://daneshyari.com)