EQCM Study on Pulse Current Pt Electrodeposition

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Electrochemical Quartz Crystal Microbalance (EQCM) was used to investigate the events occurring during current-on (T_on) and current-off (T_off) for pulse current electrodeposition of Pt in both air and Ar atmospheres. The EQCM profiles indicated a transient mass loss when the current was turned on, followed by a linear mass gain associated with the Pt electrodeposition from the H₂PtCl₆ plating bath. During the T_off, the mass revealed a steady increase until it leveled off after 10 sec. The minute transient mass loss during the initial stage of T_on was attributed to the reduction of the adsorbed PtCl₆²⁻ whereas the mass gain during the T_off was due to the absorption of PtCl₆²⁻ onto the freshly-deposited Pt surface. In air atmosphere, the parasitic oxygen reduction reaction consumed part of the reduction current and thus, reduced the Pt plating efficiency by 6%. In addition, smaller mass gains during T_off and T_on were observed for the Pt plating in air atmosphere.

**Keywords:** Pulse Current Electrodeposition, EQCM, Platinum, Electrodeposition Efficiency

1. INTRODUCTION

Pt is a noble metal known for catalytic activities toward a variety of chemical and electrochemical reactions. [1-4] In electrochemical systems, the Pt reveals desirable attributes in corrosion resistance and exchange current density. [5] For example, in polymer electrolyte fuel cells, the Pt is used for the oxidation of hydrogen at the anode and the reduction of oxygen at the cathode. [6-9] In general, the catalytic performance of Pt depends on its composition, morphology, and surface structure. In the literatures, Pt in cubic, tetrahedral, and cubotahedral shapes has been synthesized and evaluated for catalytic performances. [10-12] So far, the widely used methods to synthesize Pt are chemical reduction and electrodeposition. The chemical reduction route is often employed to form Pt
in nanoparticulate forms. For electrochemical application, however, the most straightforward approach is to electroplate the Pt directly onto the current collector because the electrodeposition enables the formation of Pt at the surface so the catalyst utilization rate can be significantly enhanced. [13-16]

The electrodeposition can be conducted in direct-current or pulse mode. Between these two, the pulse mode allows for multiple events of nucleation and growth, as well as sufficient resting time to replenish the electrolyte. To date, the pulse plating technique has been demonstrated for depositing materials within sub-micrometer trenches and producing deposits in unique shapes. [17-19] In pulse electrodeposition, independent parameters, such as current density (J\text{a}), current-on time (T\text{on}), and current-off time (T\text{off}) are adjusted to obtain deposits with different particle sizes and distributions. [20, 21] In addition, the events occurring during T\text{on} and T\text{off} play significant roles in determining the deposit morphology and coulombic efficiency. For example, Chen et al. studied the current efficiency under various pulse current conditions and observed a significant morphology change by simply adjusting the T\text{on} in Pb/Sn plating bath. [22] It is anticipated that the chemical species in the plating bath or produced during T\text{on} would adsorb and interact with the freshly-deposited metal surface during T\text{off}, and thus participates in the reduction reaction during subsequent T\text{on}.

The electrochemical quartz crystal microbalance (EQCM) is a powerful tool to investigate the events occurring at the working electrode. The operation principle of EQCM and the critical factors affecting the EQCM data have been reviewed in details. [23-25] The EQCM detects the change in the resonance frequency of the working electrode during electrochemical reaction, and correlated the frequency change to the variations in the mass of the deposit, the viscosity of the electrolyte, and temperature. [26-28] Based on the information obtained via EQCM, relevant electrochemical steps can be identified and analyzed, such as electrodeposition, dissolution, adsorption/desorption, and coulombic efficiency. [29-34] In the case of electroplating, the mass change can be determined using the Sauerbrey equation. [35] In short, the mass change caused by the chemical and physical reactions on the working electrode can be monitored in-situ, along with the corresponding potential or current. The mass sensitivity of the EQCM is in the order of ng/cm\textsuperscript{2} and therefore, even a subdued mass change on the electrode surface can be detected accurately.

Earlier, the EQCM has been utilized to study the electrodeposition of Pt using potential-controlled methods such as constant potential, pulse potential, and cyclic voltammetric (CV) scans. [25, 36-41] However, none of them discussed the electroplating behavior using pulse galvanostatic deposition via EQCM. In this study, we employed the EQCM to investigate the events occurring during pulse current Pt electrodeposition in both air and Ar atmospheres. The EQCM recorded the variations in mass and potentials during T\text{on} and T\text{off} in order to identify the chemical reductions, adsorption/desorption, and the role of dissolved oxygen.

2. EXPERIMENTAL

The EQCM instrument consisted of a Research Quartz Crystal Microbalance (RQCM; INFICON) and a potentiostat (VersaSTAT 4; Princeton Applied Research). The resolutions of the RQCM and the potentiostat were 50 and 10 ms per data point. The working electrode was a standard 9
MHz polished Au-coated AT-cut quartz crystal (INFICON) with a geometric area of 1 cm$^2$. The Ag/AgCl and Pt foil (8 cm$^2$) were served as the reference and counter electrodes, respectively. The distance between the working electrode and the counter electrode was 6 cm, and the volume of the electrolyte was 100 ml.

Prior to the EQCM calibration and Pt electrodeposition, the working electrode was subjected to multiple CV scans between -0.4 and 1.2 V (vs. Ag/AgCl) in a 0.1 M aqueous H$_2$SO$_4$ solution at a scan rate of 50 mV/s. The purpose of the CV scans was to remove any contaminant on the Au surface. Subsequently, the sensitivity of the working electrode was determined using a mixture of 0.01 M AgNO$_3$ and 0.5 M HNO$_3$ aqueous solutions in which a potentiostatic plating at 50 mV (vs. Ag/AgCl) was conducted for 5 sec. The plating of Ag produced a minute weight increment which resulted in a slight reduction of the resonance frequency of the quartz crystal. The Ag plating was repeated for five consecutive times and assuming its coulombic efficiency was 100%, the sensitivity factor for the Au-coated quartz crystal was 5.799 ng/Hz·cm$^2$, based on the Saubrey equation. After the calibration, the working electrode was immersed in a 0.1 M aqueous H$_2$SO$_4$ solution for multiple CV scans from -0.4 to 1.2 V (vs. Ag/AgCl) at 50 mV/s until the resonance frequency remained unchanged. At this stage, the deposited Ag was stripped completely from the Au surface.

The Pt plating electrolyte was prepared by dissolving 99.9 wt% H$_2$PtCl$_6$ (UniRegion Bio-Tech) in deionized water. The resulting concentration was 10 mM and the pH value of the electrolyte was 1.78. The Pt electrodeposition was performed in both air and Ar atmospheres. For the experiments in Ar atmosphere, the plating bath was purged with Ar for 1 hr to remove any dissolved oxygen, and the electrodeposition was carried out in a sealed system saturated with Ar. The Pt electrodeposition was conducted in a pulse current mode in which the current density was -5 mA/cm$^2$, the T$_{on}$ was 1 sec, and the T$_{off}$ was 50 sec. In total, 20 pulses were imposed and their corresponding variations in mass and potentials were recorded. All the electrochemical process was conducted at 25°C, and the electrolyte was unstirred throughout the entire experiments. Since the pH of the Pt plating bath was 1.78, the potential for the reversible hydrogen electrode (RHE) became -0.305 V (vs. Ag/AgCl) as RHE = [-0.200 − 0.0591×(pH)]. All the potentials in the figures were plotted against the RHE.

3. RESULTS AND DISCUSSION

The OCV for the working electrode in the Pt plating bath was 1.058 V (vs. RHE). This value reflected the interfacial structure between the Au surface and the Pt ions in the electrolyte. Once the pulse plating was performed, and the Au surface was fully covered by the Pt deposit (after 1 pulse), the OCV became 0.981 V (vs. RHE). Fig. 1(a) displays the EQCM results from pulses #5~#9 for the Pt electrodeposition in air atmosphere. Among these pulses, the OCV at T$_{off}$ maintained a constant value and a sharp drop to -0.272 V was observed once the current was switched on. This indicated a potential drive of 1.253 V for the reduction reaction. During T$_{on}$, the OCV rose up quickly and continued increasing until it leveled off after 10 sec. As expected, considerable mass gain was recorded during T$_{on}$, which was attributed to the deposition of Pt from the electrolyte. These EQCM results demonstrated a consistent pattern of successive Pt deposition in every pulse.
Table I. Possible reduction reactions and their respective redox potentials during pulse current electrodepositions ($T_{on}$) in air atmosphere.

<table>
<thead>
<tr>
<th>Reduction reaction</th>
<th>Redox potential estimated from Nernst equation (V vs. RHE) $^a$</th>
<th>Redox potential in standard state (V vs. RHE)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2H^+ + 2e \rightarrow H_2$</td>
<td>0</td>
<td>0</td>
<td>41</td>
</tr>
<tr>
<td>$O_2 + 4H^+ + 4e \rightarrow 2H_2O$</td>
<td>N/A $^b$</td>
<td>1.334</td>
<td>41</td>
</tr>
<tr>
<td>$PtCl_6^{2-} + 4e \rightarrow Pt + 6Cl^{-}$</td>
<td>0.819</td>
<td>0.849</td>
<td>41</td>
</tr>
<tr>
<td>$PtCl_6^{2-} + 2e \rightarrow PtCl_4^{-} + 2Cl^{-}$</td>
<td>N/A $^b$</td>
<td>0.831</td>
<td>41</td>
</tr>
<tr>
<td>$PtCl_4^{2-} + 2e \rightarrow Pt + 4Cl^{-}$</td>
<td>N/A $^b$</td>
<td>0.863</td>
<td>41</td>
</tr>
</tbody>
</table>

$^a$ we assume that the activity coefficient is 1 so the value of activity is equal to the concentration.

$^b$ the exact concentrations of dissolved $O_2$ and $PtCl_4^{2-}$ are unknown.

Table I lists the possible electrochemical reactions during $T_{on}$ and their corresponding redox potentials. In principle, these reactions were likely to occur to various degrees contingent on their respective concentrations and overpotentials.

Figure 1. (a) The EQCM profiles from pulses #5–#9 for the Pt electrodeposition in air atmosphere ($T_{on}$ = 1 sec; $T_{off}$ = 50 sec; current density = $-5$ mA/cm$^2$). (b) The enlarged EQCM profile from a single pulse (#7).
Fig. 1(b) exhibits the EQCM profile from a single pulse (#7) so the detailed responses of in mass and OCV can be better distinguished. During T_off, the OCV reading was 0.981 V. Once the current started flowing (T_on), the potential decreased sharply at the beginning, followed by a slow decline. We realized that the former was caused by the double-layer charging and parasitic ohmic drop whereas the latter was associated with the activation and concentration polarizations of possible reactions listed in Table I. Once the current was switched off (T_off), the potential rebounded immediately reflecting the removal of ohmic drop. However, the potential continued rising for a few seconds during T_off, suggesting the dynamic reconstruction of electrode/electrolyte interface. Table II lists the possible reactions occurring during the initial stages of T_off and T_on, as well as their expected variations in the mass and OCV.

Table II. Possible reactions during the initial stage of T_off and initial stage of T_on, as well as their expected variations in the mass and OCV (↓: Decrease; ↑: Increase; —: No change).

<table>
<thead>
<tr>
<th>Possible Reactions</th>
<th>Mass</th>
<th>OCV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtCl$_6^{2-}$(aq) → PtCl$_6^{2-}$(ad)</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>PtCl$_4^{2-}$(aq) → PtCl$_4^{2-}$(ad)</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>PtCl$_6^{2-}$(ad) + H(ad) → Pt</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>PtCl$_4^{2-}$(ad) + H(ad) → Pt</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>H(ad) + H(ad) → H$_2$(g)</td>
<td>↓</td>
<td>—</td>
</tr>
<tr>
<td>H$_2$O(aq) → H$_2$O(ad)</td>
<td>↑</td>
<td>—</td>
</tr>
<tr>
<td>PtCl$_6^{2-}$(ad) → Pt(s)</td>
<td>↓</td>
<td>—</td>
</tr>
<tr>
<td>PtCl$_4^{2-}$(ad) → Pt(s)</td>
<td>↓</td>
<td>—</td>
</tr>
<tr>
<td>H$_2$O(ad) → H(ad) → H$_2$(g)</td>
<td>↓</td>
<td>—</td>
</tr>
<tr>
<td>H$^+$ (aq) → H(ad) → H$_2$(g)</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>O$_2$ + 4H$^+$ → 2H$_2$O</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

For the mass variation, a slight mass loss was observed during the start of T_on, which was due to the reduction of the adsorbed PtCl$_6^{2-}$ on the freshly-deposited Pt surface. Afterwards, a sizeable mass gain was recorded owing to the deposition of Pt from the Pt ions in the electrolyte, i.e., the electrochemical reduction of PtCl$_6^{2-}$ and PtCl$_4^{2-}$. Interestingly, during T_off, a moderate mass increment was also recorded which was attributed to the adsorption of PtCl$_6^{2-}$ from the electrolyte. According to earlier studies of Pt (111) film immersed in an aqueous solution containing 0.6 mM H$_2$PtCl$_6$ and 50 mM HClO$_4$, the adsorbed species on the Pt (111) surface at potential between 0.7 ~ 0.95 V (vs. RHE) was exclusively PtCl$_6^{2-}$. [42] Therefore, in our case we believed that once the current was turned off, the PtCl$_6^{2-}$ was adsorbed preferentially to the fresh Pt surface, leading to a steady rise of the OCV to 0.981 V (vs. RHE). It is noted that this 0.981 V was more positive than the redox potential of PtCl$_6^{2-}$/Pt which was 0.819 V (vs. RHE) for 10 mM H$_2$PtCl$_6$ electrolyte from Nernst equation. Hence, thermodynamics favored the formation and stability of PtCl$_6^{2-}$ adsorption onto the fresh Pt surface.

An alternative explanation for the mass gain during T_off might be the formation of Pt(OH)$_x$ or the adsorption of Cl$^-$ ions. In the literatures, the Pt surface was prone to form Pt(OH)$_x$ at potential up to 0.85 V (vs. RHE) in acidic solutions. [43, 44] In our case, the OCV during T_off was 0.981 V (vs. RHE),
and thus the presence of Pt(OH)$_x$ was likely. However, the H$_2$PtCl$_6$ was not used in those studies but in our plating bath the PtCl$_6^{2-}$ was the predominant constituent. In theory, the mass gain associated with the Pt(OH)$_x$ during T$_{off}$ should be equal to the transient mass loss during T$_{on}$ because the reduction current was expected to reduce the adsorbed species first. However, in our case the EQCM profiles indicated a different pattern; the transient mass loss during T$_{on}$ was merely 13% of the mass gain during T$_{off}$. Therefore, we concluded that the formation of Pt(OH)$_x$ was not the principal contributor to the mass gain during T$_{off}$. Likewise, the amount of adsorbed Cl$^-$ during T$_{off}$ was likely to be relatively low. It is also possible that during T$_{off}$, the adsorbed hydrogen engaged in a displacement reaction with the PtCl$_6^{2-}$ ions from the electrolyte, resulting in a mass gain. However, according to Solla-Gullon et al. and Nutariya et al., the adsorbed hydrogen can only exist on the fresh Pt surface in a potential range between 0.12 and 0.27 V (vs. RHE). [45] Therefore, we concluded that the mass gain during T$_{off}$ was not caused by the formation of Pt(OH)$_x$, the adsorption of Cl$^-$, and the displacement reaction of the adsorbed hydrogen.

The Pt is an electocatalyst for oxygen reduction reaction (ORR) and the pulse plating inevitably induces the ORR in conjunction with the deposition of Pt.

![EQCM profiles](image)

**Figure 2.** (a) The EQCM profiles from pulses #5~#9 for the Pt electrodeposition in Ar atmosphere (T$_{on}$ = 1 sec; T$_{off}$ = 50 sec; current density = $-5$ mA/cm$^2$). (b) The enlarged EQCM profile from a single pulse (#7).
To investigate the effect of dissolved oxygen in the electrolyte, we performed the EQCM experiments in deaerated bath. Fig. 2(a) displays the EQCM results from pulses #5~#9 for the Pt electrodeposition in Ar atmosphere. In general, the EQCM results were rather similar to those shown in Fig. 1(a). The OCV at T_{off} was 0.981 V (vs. RHE), and the potential experienced a sharp drop when the current was turned on. Likewise, during T_{on}, a transient mass loss was observed followed by a notable mass gain. Once the current was switched off, both the OCV and mass continued increasing and leveled off after 10 sec. Fig. 2(b) shows an enlargement of pulse #7 which revealed a similar pattern as that of Fig. 1(b).

![EQCM results from pulses #5~#9 for the Pt electrodeposition in Ar atmosphere.](image)

**Figure 3.** Comparison of EQCM profiles from pulse #7 in air and Ar atmospheres; (a) voltage vs. time, and (b) mass gain vs. time.

Fig. 3 provides the EQCM profiles in potentials and mass gains from the pulse #7 in both air and Ar atmospheres, respectively. As shown in Fig. 3(a), the OCVs during T_{off} in both samples exhibited values of 0.981 V (vs. RHE), suggesting identical electrode/electrolyte structures. During T_{on}, their potentials revealed an instantaneous drop to 0.221 V, and became increasingly negative with plating time. In a galvanostatic mode, the potential response can be explained by chronopotentiometric behavior in which the flux of PtCl$_6^{2-}$ at the electrode surface (x = 0) can be deduced at any given time by the Fick’s first law;
where the \( J_0 \) is the flux of PtCl\(_6^{2-}\) toward the working electrode, the \( D_0 \) is the diffusion coefficient of PtCl\(_6^{2-}\) in the plating bath, the \( A \) is the microscopic area of the deposited Pt, the \( F \) is the Faraday’s constant, and the \( i(t) \) is the input current. Because the \( i(t) \) was kept constant, the flux or the concentration gradient at the working electrode surface remained unchanged throughout the plating process. This behavior agreed well with the linear mass gain shown in Fig. 1(b) and Fig. 2(b).

The concentration of PtCl\(_6^{2-}\) at the working electrode surface \( (C_0(0,t)) \) can be obtained by the following equation: [46]

\[
C_0(0,t) = C_0^\circ - \frac{2i t^{1/2}}{n F A D_0^{1/2} \pi^{1/2}}
\]

where the \( C_0^\circ \) is the bulk concentration of PtCl\(_6^{2-}\), and the \( t \) is the plating time. According to equation (2), the \( C_0(0,t) \) was expected to fall steadily with plating time. Because the mass increased linearly during \( T_{on} \), a constant deposition rate was anticipated. Therefore, the \( C_0(0,t) \) did not fall to zero; if the \( C_0(0,t) \) did fall to zero, the potential was expected to drop significantly to a more negative value in order to initiate an alternative reduction reaction. It is realized that the potential was related to the surface concentration of PtCl\(_6^{2-}\), as dictated by the Nernst equation. Because of the steady reduction in the surface PtCl\(_6^{2-}\) concentration as plating time progressed during \( T_{on} \), the potential became increasingly negative, a typical behavior known as concentration polarization. As shown in Fig. 3(a), the potential drop in air atmosphere was relatively smaller as compared to that in Ar atmosphere. This inferred that at any given time the surface concentration of PtCl\(_6^{2-}\) in air atmosphere was higher. We realized that in air atmosphere part of the reduction current was consumed by the ORR which was facilitated by the presence of freshly-deposited Pt. This led to a relatively slow decrease in the concentration of surface PtCl\(_6^{2-}\). The occurrence of ORR also reduced the coulombic efficiency and as a result, rendered a smaller amount of Pt deposition in air atmosphere, as shown in Fig. 3(b). During the \( T_{off} \), the OCV rose faster in air atmosphere because of the relatively abundant PtCl\(_6^{2-}\) on the surface. This produced a more positive potential as predicted by the Nernst equation.

**Figure 4.** The amount of mass gain for 20 consecutive pulses during \( T_{on} \) and \( T_{off} \) in both air and Ar atmospheres.
Fig. 4 demonstrates the amount of mass gain for 20 consecutive pulses during $T_{\text{on}}$ and $T_{\text{off}}$ in both air and Ar atmospheres, respectively. To cover the entire Au surface, the necessary Pt amount was 0.484 $\mu$g/cm$^2$ for a monolayer of Pt (111). Therefore, from the mass gain during $T_{\text{on}}$, the Au surface was fully covered by the Pt after the first pulse, which was consistent with the OCV observation during $T_{\text{off}}$. For both samples, the mass gains during $T_{\text{on}}$ were much greater than those during $T_{\text{off}}$. In addition, the mass gain during $T_{\text{on}}$ in Ar atmosphere was consistently larger than that in air because the absence of dissolved oxygen for the ORR in the latter case. On the other hand, the mass gain due to the adsorption of PtCl$_6^{2-}$ was larger in Ar atmosphere than that in air atmosphere. Except for the first few pulses, the amount of mass gain during $T_{\text{on}}$ for both samples exhibited a decreasing trend whereas the mass gain due to the surface PtCl$_6^{2-}$ adsorption revealed an opposite pattern. We believed that an increasing microscopic surface area of the Pt with increasing pulses allowed for more adsorption of PtCl$_6^{2-}$. The adsorbed PtCl$_6^{2-}$ was subsequently reduced when the current was turned on, so the current left for reducing the PtCl$_6^{2-}$ in the electrolyte became less and the amount of Pt deposit became smaller with increasing pulses.

![Coulombic efficiency vs. Pulse](image.png)

**Figure 5.** The coulombic efficiencies of Pt deposition during $T_{\text{on}}$ for both air and Ar atmospheres.

Fig. 5 exhibits the coulombic efficiencies of Pt deposition during $T_{\text{on}}$ for both air and Ar atmospheres. The coulombic efficiencies in Ar case were consistently larger than those in air. Except for the first few pulses, the coulombic efficiencies were around 52% in air whereas in Ar case the coulombic efficiencies were improved to 58%. It was therefore concluded that approximate 6% of the pulse current was consumed by the ORR, and the remaining 40% pulse current was utilized to reduce
PtCl$_6^{2-}$ to PtCl$_4^{2-}$, and engaged in the parasitic hydrogen evolution reaction. It is noted that the PtCl$_4^{2-}$ was not adsorbed on the working electrode and hence was not responsible for the mass loss during $T_{on}$.

4. CONCLUSION

The EQCM was utilized to study the events occurring during $T_{on}$ and $T_{off}$ in pulse current electrodeposition of Pt. For both air and Ar atmospheres, during $T_{on}$, the EQCM profiles indicated a transient mass loss, followed by a linear mass gain. The transient mass loss was caused by the reduction of the adsorbed PtCl$_6^{2-}$ whereas the linear mass gain was associated with the Pt plating from the electrolyte. During $T_{off}$, the mass revealed a steady increase until it leveled off after 10 sec which was due to the absorption of PtCl$_6^{2-}$ onto the freshly-deposited Pt surface. In air atmosphere, the parasitic ORR reduced the Pt plating efficiency by 6%. In addition, smaller mass gains during $T_{off}$ and $T_{on}$ were observed for the Pt plating in air atmosphere.

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