

## **Electrochemical Quartz Crystal Microbalance Study on Electrodeposition of Pt on Au-QCM**

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### **Abstract**

Platinum was electrodeposited on an Au-QCM in 40 mM  $\text{H}_2\text{PtCl}_6$  solution using an electrochemical quartz crystal microbalance. At 0.2 V vs. SHE, a 4-electron reduction of Pt-ion took place. On the other hand, at 0.6 V a mixture of 2-electron and 4-electron reduction took place.

### **Introduction**

There are growing interests in the fuel cell as an alternate energy conversion and efficient power sources due to its environmentally clean working condition. Among fuel cells, PEFC is considered to be one of the most attractive energy conversion devices for applications such as automobile and stationary power supplies, which require it to be durable and inexpensive. Platinum is well known for its electrochemical stability in most medium and hence it has been used as catalyst in PEFC. However, it has been found that Pt dissolves under potential cycling conditions in operating PEFCs<sup>1,2</sup>. The commercialization of PEFC requires that the loading capacity of Pt is reduced among others, which means the degradation behavior of Pt should be well understood<sup>3-5</sup>. In order to gain full understanding at the degradation mechanism of Pt catalyst in PEFC, it is important to do fundamental research on the stability of Pt under conditions that suits its application. The catalytic activity of Pt depends on its particle size, the shape and dispersion<sup>6-10</sup>. In order to effectively utilize the limited resource of the noble metals, there is a need to have a simple and low cost method of preparing Pt nanoparticle for studying its degradation behavior.

Electrochemical deposition (ECD) offers the efficient way of producing metal nanoparticles with easy control over the deposition parameters. Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) is used for the ECD of Pt on various substrates. Uosaki et al. used the same solution to epitaxially grow Pt on Au(111) and discussed the growth mechanism on atomic scale<sup>11</sup>. Zangari et al. have reported on the ECD of Pt on highly oriented pyrolytic carbon (HPOG)<sup>12</sup>. The authors have made a detail characterization on the electrochemistry of Pt ECD from  $\text{H}_2\text{PtCl}_6$  based electrolytes, focusing in particular on the effect of Pt concentration, the supporting electrolyte, and complexation effects by chlorides on the kinetics and mechanism of Pt electrocrystallization. In the second part of their works, the authors have reported on the optimum conditions for the growth of Pt nanoparticles with uniform dispersion and narrow size distribution<sup>13</sup>. Similarly, Zoval et al. have reported on the electrochemical preparation of Pt nanocrystallites on basal oriented graphite surface by using a pulsed potentiostatic method<sup>14</sup>.

There is a need to have more study on the electrodeposition mechanism of Pt. In this study, electrochemical quartz crystal microbalance (EQCM) was used to electrodeposit Pt on Au-QCM from  $\text{H}_2\text{PtCl}_6$  solution. The focus of the study was the mechanism of electrodeposition of Pt.

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## Experimental Section

### *Electrodeposition of Pt*

The EQCM is a unique method that enables simultaneous and in-situ determination of nanoscale mass change related to electrochemical phenomenon by measuring a change of the resonant frequency. Mass change per unit area,  $\Delta m$ , is calculated from the changes in resonance frequency,  $\Delta f$ , using the Sauerbrey equation<sup>15</sup>:

$$\Delta m = -\left(A_{\text{piezo}} \sqrt{\rho_q \mu_q} / 2f_0^2\right) \Delta f = -C_f \cdot \Delta f \quad (1)$$

where  $f_0$  is the resonant frequency of the quartz resonator,  $\mu_q$  is the shear modulus of the quartz ( $2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$ ), and  $\rho_q$  is density of the quartz ( $2.648 \text{ g cm}^{-3}$ ). The terms in the bracket represent the sensitivity factor,  $C_f$ , of the QCM.

The deposition process was studied by cyclic voltammetry and mass change by EQCM and analyzed by current-time (i-t) transients. A 6 MHz AT-cut Au QCM with geometrical area of  $1.33 \text{ cm}^2$  was used as a substrate and a 40 mM  $\text{H}_2\text{PtCl}_6$  solution as the electrolyte. From CV and mass change response, a suitable potential for electrodeposition of Pt was chosen. Prior to electrodeposition, the solution was deaerated by passing purified  $\text{N}_2$  for 15 min through the solution and it was not stirred during the measurements. All the measurements were made at 298 K in a one-compartment Teflon cell with 50 mL capacity. The cell had a special Teflon cover with holes designed to host the auxiliary and reference electrodes and degassing tubes. KCl-saturated silver/silver chloride electrode (SSE) with a lugging capillary was used as a reference electrode and Pt wire was used as the counter electrode. All the potential values are referred to a SHE.

## Results and Discussion

### *EQCM investigation of Pt deposition on an Au-QCM*

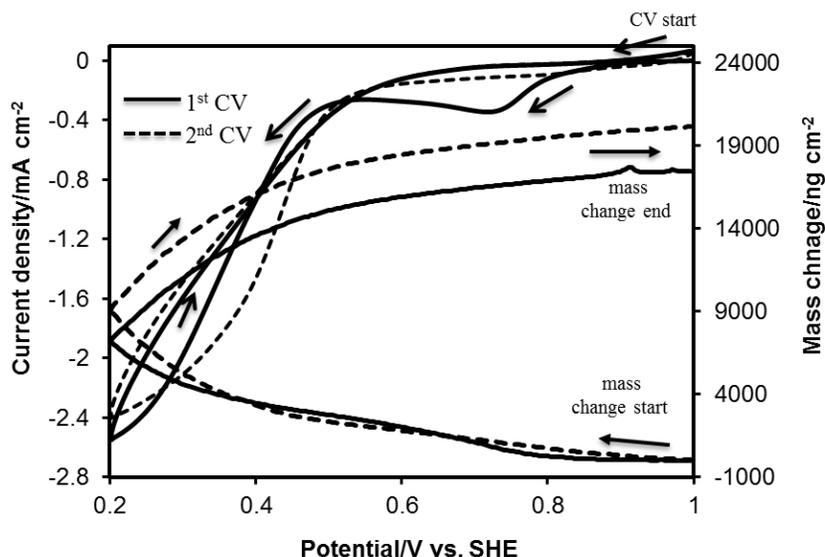
Figure 1 shows the voltammogram of Au-QCM in deaerated 40mM  $\text{H}_2\text{PtCl}_6$  solution for 2 potential cycles between 1.0 and 0.2 V. The corresponding mass change during potential cycle is shown together in the same plot. The potential scan was started from 1.0V towards cathodic direction at 20mV/s. A cathodic current started to flow around 0.8 V with the simultaneous increase of surface mass. With the increase of potential in cathodic direction, a sharp increase in cathodic current was observed with a similar increase in the surface mass on EQCM. When the sweep direction was reversed at 0.2 V, a cathodic current still flowed and the surface mass continued to increase until the potential reached to 0.8 V. In the 2nd potential cycle, the current response was similar to 1st cycle except the absence of current rise at 0.8 V. On the other hand, the mass change during 2nd potential cycle was similar to 1st potential cycle. This difference in the current response can be related to the change of surface state from Au to Pt after 1st CV cycle. A similar behavior has been reported elsewhere<sup>12</sup>.

The appearance of two slopes in surface mass change in Fig.1 makes it necessary to quantify the deposition process at 0.6 V and 0.2 V.

According to Feltham et al. electrodeposition of Pt from  $\text{H}_2\text{PtCl}_6$  solutions involves three steps<sup>16</sup>:



and/or



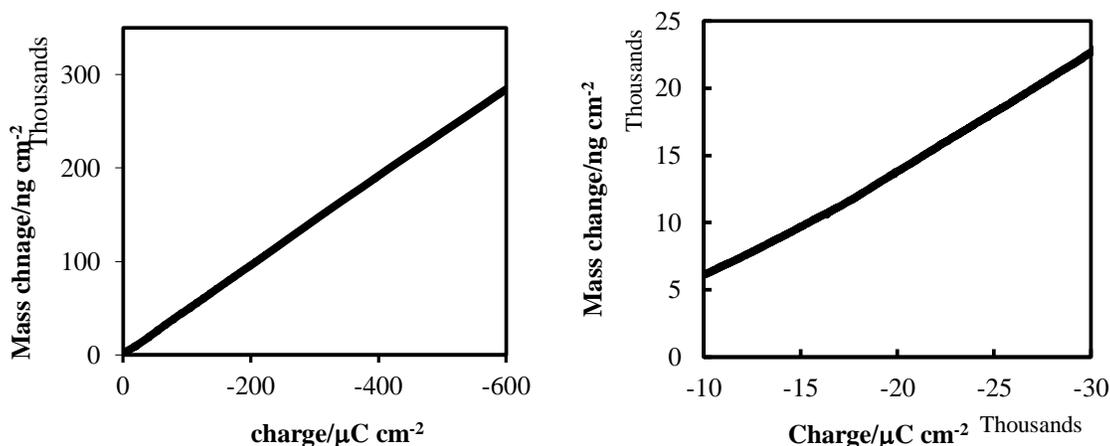
**Figure 1:** CV of Au-QCM in 40mM  $\text{H}_2\text{PtCl}_6$ , scan rate 20mV/s

Both 2-electron reduction and 4-electron reduction reactions can take place at almost same potential range. Since slopes of mass change in Fig.1 at 0.6 V and 0.2 V are different it seems that different reduction processes occur at these two potentials. A convenient way of verifying this is to make a plot of mass change (QCM) against charge density (Voltammogram) and find the mass change per mole electron from its slope according to the relation:

$$\Delta m = \Delta q M / nF \quad (5)$$

Where  $\Delta m$  is mass change per unit area,  $\Delta q$  is charge density,  $M$  is molar mass,  $n$  is the number of electrons transferred and  $F$  is the Faraday's constant. Fig.2 shows a plot of mass change and cathodic charge density at 0.6 V and 0.2 V, respectively. The mass change per mole electron calculated from the slopes at 0.6 V and 0.2 V comes around 81.5 and 45.6 g/(mol electron), respectively. If a 4-electron reduction of Pt-complex (equation 2) is considered, the slope should be 48.7 g/(mol electron) and that for 2-electron reduction (equations 1 and 3), the slope should be 97.5 g/(mol electron). Therefore, at 0.2 V, a 4-electron reduction took place since we have found a slope of 45.6 g/(mol electron). On the other hand, at 0.6 V a mixture of 2-electron and 4-electron reduction could take place since the slope is more than that needed for 4-electron transfer and less than that needed for 2-electron reduction. From this result, electrodeposition of Pt should be carried out at 0.2 V vs. SHE.

Uosaki et al. have reported a 4-electron reduction at 0.6V in very low concentration of  $\text{H}_2\text{PtCl}_6$  solutions<sup>11</sup>. This difference can come from the adsorption of  $\text{Cl}^-$  at high concentration of  $\text{H}_2\text{PtCl}_6$  used in this study which can shift the overpotential towards more cathodic direction.



**Figure 2:** mass change and charge density plot for (a) 0.6 V and (b) 0.2V potential steps

## Conclusion

The electrodeposition of Pt in 40mM  $H_2PtCl_6$  solutions was characterized by a 4-electron reduction at 0.2 V vs. SHE and a mixture of 2-electron and 4-electron reduction at 0.6 V.

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