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Pt Dissolution in Acidic Medium: Suitability of EQCM and ICP-MS Techniques

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This study reports on the suitability of EQCM and ICP-MS techniques for studying the dissolution of Pt in acidic medium. For a 6 MHz QCM, the difference in the EQCM and ICP-MS results were pronounced when CV was carried out at $0.1 Vs^{-1}$. At such high scan rate of the CV, the frequency response of EQCM does not follow the Sauerbrey equation due to heterogeneous distribution of current on the QCM surface. The active surface area of Pt and its mass loss decreases with the cycle number of CV.

Keyword: Polymer electrolyte fuel cell; electrochemical quartz crystal microbalance; Platinum dissolution; Frequency response; Scan rate

1. Introduction

There is a growing interest in the study of dissolution of Pt in acidic medium due to its use as a catalyst in polymer electrolyte fuel cell (PEFC). Platinum is well known for its electrochemical stability in most medium. However, it has been found that Pt dissolves under potential cycling conditions in operating PEFCs [1, 2]. The commercialization of PEFC requires that the loading capacity of Pt is reduced among others, which means the degradation behavior; Pt should be well understood [3-5]. Since the amount of Pt dissolved in most mediums is very small it requires a technique that can detect a trace amount of Pt. Among the techniques used for determining the trace amount of Pt dissolved during electrochemically induced condition, electrochemical quartz crystal microbalance (EQCM) and inductively coupled plasma mass spectroscopy (ICP-MS) are most sensitive.

The EQCM is a unique method that enables simultaneous and in-situ determination of nanoscale mass change related to an electrochemical phenomenon by measuring a change of the resonant frequency. Mass change per unit area, Δm, is calculated from the changes in resonance frequency, Δf, using the Sauerbrey equation [6]:

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

Where f_0 is the resonant frequency of the quartz resonator, μ_q is the shear modulus of the quartz (2.947×10^{11} g cm^{-1} s^{-2}), and ρ_q is the density of the quartz (2.648 g cm^{-3}). The terms in the bracket represent the sensitivity factor, C_f, of the QCM.

The EQCM has been widely used in the investigations of various electrode processes, including noble metals and their alloys [7-9]. It has been only recently that the dissolution of Pt is being studied by EQCM [10-12] under the condition of cyclic voltammetry. The results of EQCM have been mainly analyzed based on the mass change associated with oxide formation and its reduction during CV with a little information on the amount of dissolution. While EQCM gives valuable information regarding the surface state of a metal under applied potential, the quantitative estimation of amount of dissolution is still not mentioned. On the contrary, ICP-MS has been used to determine the amount of dissolution of metals by analyzing the test solution [10, 11, 13, 14].

This study presents the results of both EQCM and ICP-MS analyses regarding the quantitative estimation of the amount of Pt dissolution in acidic medium. The purpose is to find if the results of both the techniques can be used as a quantitative tool for the study of the dissolution of Pt under potential cycle conditions.

2. Experimental

A Hokuto Denko EQCM system was used in this study, which consisted of an oscillating circuit (HQ-304C), a frequency counter (HQ-101D) and a potentiostat (HZ-5000) controlled by a personal computer through a GPIB interface. An AT-cut Au quartz crystal with a fundamental frequency of 6 MHz in air was used as a mass sensor. Each quartz crystal had a 1.33 cm^2 circular area on each side. One side of the QCM was electroplated with Pt in 40 mM H_2PtCl_6 solution at 0.2 V vs. SHE. The Pt layer thickness was fixed at about 65 nm. The XRD pattern of the Pt layer showed the formation of a dominant (111) oriented Pt bulk phase with the average particle size of 40-60 nm [11]. The theoretical sensitivity factor of this QCM was 16.30 ng Hz^{-1}, which changed to about 18.10 ng Hz^{-1} (12.47 ng Hz^{-1} cm^{-2}) in electrolyte solution after depositing Pt. A frequency resolution of 0.2 Hz was obtained at the sampling gate time of 1 s in the present system.

The Pt-plated Au quartz crystal was used as a working electrode. The frequency change measured by the oscillating circuit was recorded simultaneously with the potential and current in a personal computer. All the measurements were made in a one-compartment Teflon cell with 25 ml of 0.5 M H_2SO_4 solution open to air. A KCl-saturated silver/silver chloride electrode (SSE) with a double junction was used as a reference electrode and Au wire was used as the counter electrode. The potential values are referred to the SHE. All the measurements were made at 298 K with solutions prepared in triply distilled water.

To make sure that the all the samples used have almost similar initial surface conditions, an electrochemical cleaning was carried out by running cyclic voltammetry in between 0.0-1.4 V at 0.1 V s^{-1} for 100 cycles. It was found that 100 cycles of CV gave a very reproducible current-potential profile. After cleaning process, the solution was changed and real measurement was started, where CV was recorded at a scan rate of 0.1 Vs^{-1} in potential range 0.0-1.4 V.

From the last cycle of the CV, electrochemically active surface area (ECA) was determined by integrating the charge in the underpotential deposition region of H (UPDH) in 0.0-0.4 V. All the results here are reported with respect to ECA. At the end of the CV, the test solutions were analyzed for the amount of dissolved Pt with the help of a high-resolution inductively coupled plasma-mass spectrometer (ICP-MS, SPQ 9000 Seiko Instruments Inc.) with a detection limit of 1 ppt for platinum. The amount of Pt dissolution was also calculated from the difference in the frequency change of QCM at 0.45 V in between last cycle and first cycle of the CV by using equation 2 and it was compared with the result obtained from ICP-MS.

Amount of dissolution (EQCM) =

$$-\left(\Delta f_{last} - \Delta f_{first}\right)C_f / EASA \dots\dots\dots\dots\dots\dots\dots\dots 2$$

3. Results and Discussion
3.1 Cyclic voltammetry of Pt

Fig 1 shows the voltammetric and frequency-change responses of Pt in 0.5M H_2SO_4 recorded at 0.1V s^{-1}. The potential was scanned from a hold potential of 0.45 V for 5 min towards anodic direction. The voltammetric curve in Fig 1 qualitatively resembles those reported in the literature for polycrystalline Pt in sulfuric acid solutions [12, 15, 16]. For discussing the result of frequency change of the EQCM, the voltammogram can be divided into three regions; spanning from 0.0-0.4V is the region of hydrogen adsorption and desorption, from 0.4-0.75 V is the double layer region and from 0.75-1.4 V corresponds to surface oxidation and reduction of Pt. In the positive-going scan, a rise of the current was observed at 0.75 V indicating the beginning of the surface oxidation. In the negative-going scan, a cathodic peak at 0.75V was observed due to reduction of surface oxide formed during anodic scan.
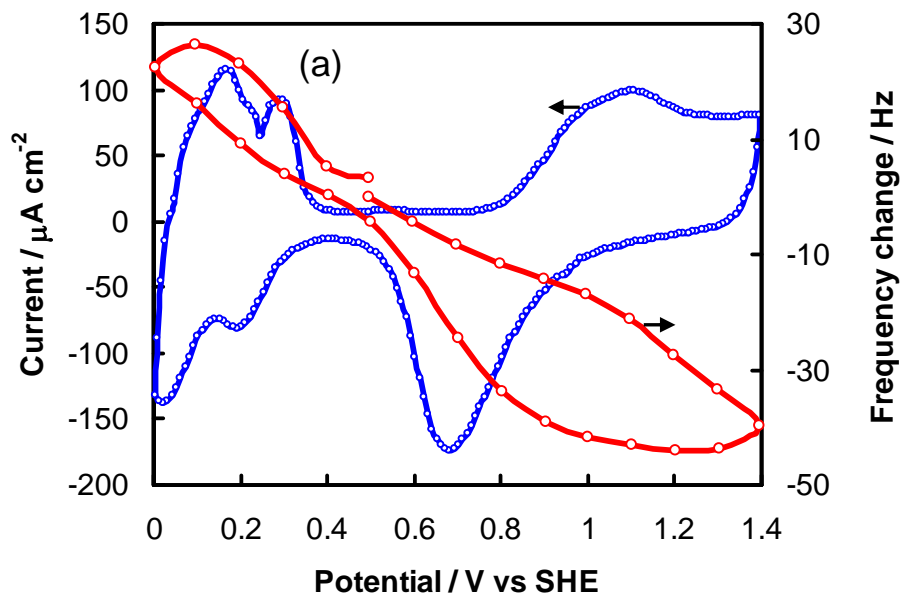
Fig 1: Cyclic voltammogram and corresponding frequency change response of an electrodeposited Pt-QCM in 0.5 M H_2SO_4 solutions at (a) 0.1 Vs^{-1}

The frequency-change response of the EQCM during CV is related to surface phenomenon occurring at the electrode surface leading to mass change. It should be mentioned that an increase of mass on the QCM leads to decrease in the frequency, whereas a decrease of mass leads to an increase of frequency. In 0.0-0.4 V of the CV, the hysteresis in the frequency change response due to hydrogen adsorption-desorption process. In the double layer region, 0.4-0.75 V, where no faradic reaction responsible for frequency change should take place, the frequency change response is attributed to the adsorption and desorption phenomenon of water molecules and/or sulfate ions [17, 18]. Hysteresis indicates that the adsorption-desorption equilibrium was not established quickly.

In 0.75-1.4 V of the CV, the hysteresis in the frequency change response was due to the formation and reduction of platinum oxide [12].

3.2 Estimation of amount of dissolution of Pt from EQCM and ICP-MS

The ICP-MS analysis of the test solution after running CV was carried out in order to determine the amount of Pt dissolved during potential cycling (CV). All the ICP-MS analyses were made under similar condition so as to avoid the experimental error. Here the results are presented in per active surface area of each sample as mentioned above. **Fig 2** shows the bar plot of the amount of Pt dissolved during potential cycling as estimated from ICP-MS analysis of the test solution and change in the frequency response of EQCM in between first and last cycle of CV. These plots are the representative of many such measurements at all the three scan rates. In **Fig 2**, results of the experiments No. 1-3 are from the same sample and rest others are from another sample. This was done to avoid a large difference in the surface roughness of the samples.
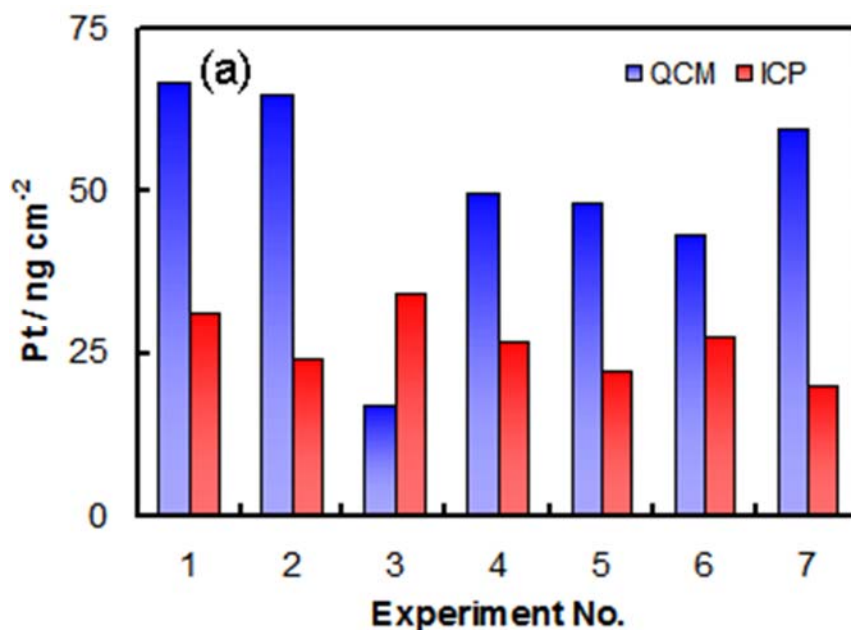
Fig 2: Bar plot showing the amount of Pt dissolved as estimated from EQCM and ICP-MS after (a) 100 cycles of CV at scan rate of 0.1V s^{-1} in 0.5 M H$_2$SO$_4$ solution.

Fig 2 shows that when CV was performed at 0.1 Vs^{-1}, the difference in the ICP-MS and EQCM results was very large irrespective of the type of samples used. Because of the nature of the experiments we cannot find the standard deviation of the measurements. However, we can calculate how close the two results were at different scan rates. It can be found that at 0.1 Vs^{-1}, for experiment No.6, the ICP-MS result was about 63.1 % of the EQCM result, EQCM gave a higher amount of Pt dissolution compared to ICP-MS. The reason for this difference needs to be analyzed further.

However, EQCM has an advantage over ICP-MS as it can give the electrochemical information together with the amount of dissolution. For example, the change of active surface area with the progress of CV can be found from the UPD H region, which can be related to the loss of Pt and increase of particle size of the Pt nanoparticles

during CV. Such in-situ information cannot be obtained from ICP-MS. **Fig 3** shows the variation of active surface area and the mass loss against the cycle number of CV as obtained from EQCM and ICP-MS. In this experiment, sampling of the test solution was carried out at a specific cycle of CV and analyzed by ICP-MS. The mass loss of Pt as measured by ICP-MS follows the similar trend as estimated from the frequency-change response of EQCM, though the difference was obvious. It can be found that in the first few cycles the mass loss is large accompanied by large change in active surface area. As CV progresses, the mass loss becomes less and so the change in the active surface area. This shows that if EQCM is used properly, not only the dissolution of Pt can be studied quantitatively, but also qualitative information regarding the effect of dissolution on the active surface area can be extracted.
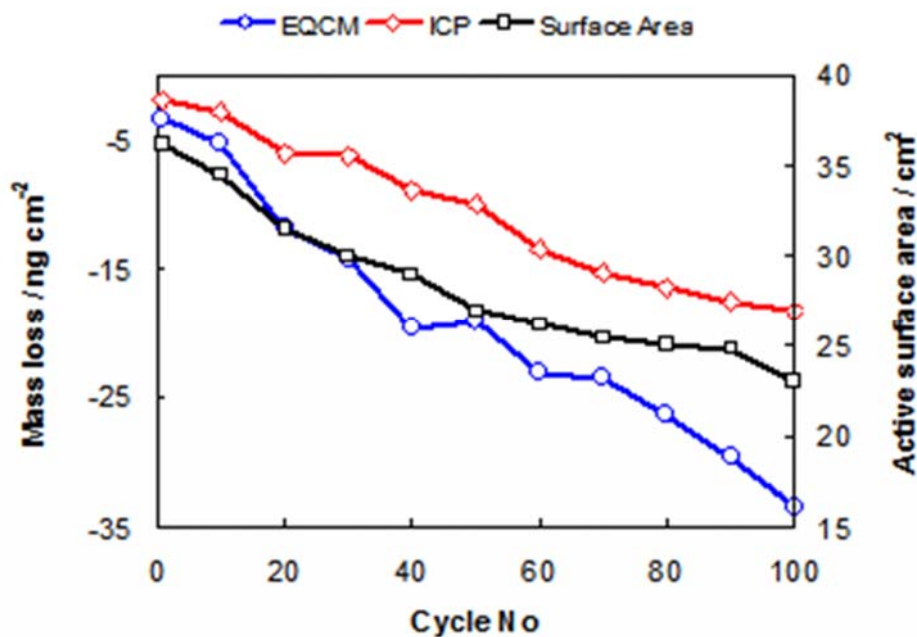
Fig 3: Mass loss change as estimated from EQCM and ICP-MS against cycle number of CV at scan rate of 0.1 Vs^{-1}. Shown together are the changes in the active surface area as estimated from UPD H region of CVs.

4. Conclusions
From this study on the suitability of EQCM and ICP-MS techniques for the study of the dissolution of Pt in acidic medium it was concluded that EQCM has an advantage over ICP-MS as it can give the electrochemical information together with the amount of dissolution. For a 6 MHz QCM, the difference in the EQCM and ICP-MS results were pronounced when CV was carried out at 0.1 Vs^{-1}. At a higher scan rate of the CV, the frequency response of EQCM does not follow the Sauerbrey equation due to heterogeneous distribution of current on the QCM surface.

5. Acknowledgements

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