An Electrochemical Quartz Crystal Microbalance Study of Adsorption on a Platinum Electrode in Sulfuric Acid

Youngran Lim and Euijin Hwang*

Electrochemistry Group, Korea Research Institute of Standards and Science, Taejon 305-340, Korea
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The adsorption phenomena on platinum substrates have been extensively studied and some reviews can be found elsewhere.[1,2] In order to understand the interfacial structure between platinum electrodes and sulfuric acid solutions, many attempts have been made by applying different techniques such as IR spectroscopy,[3-10] sum frequency generation,[11-13] radiotracer labeling,[14,15] scanning tunneling microscopy (STM),[16] and electrogravimetry.[17,18]

The electrochemical quartz crystal microbalance (EQCM) has been adopted as an *in situ* gravimetric tool for investigation of electrosorption phenomena in sulfuric acid.[17,18] Shimatzu and Kita[17] explained their Pt-EQCM results in sulfuric acid as a mass increase is mainly due to adsorption of water during the potential sweep from hydrogen adsorption region to oxygen adsorption region. They also suggested the possibility of the specific adsorption of (bi)sulfate (SO_4^{2-} and/or HSO_4^-) on the platinum surface in the double layer region. Their opinion about water adsorption has been, however, contested by Watanabe and his coworkers.[18] They claimed that the mass change in the double layer region was not due to the water adsorption but due to the specific adsorption or co-adsorption of sulfate and/or bisulfate from the relation between the mass change and the charge in the double layer region.

In our experiments the background behaviors of platinum electrodes in sulfuric acid solutions were carefully examined using our low noise EQCM[19] to clarify the above controversy. Optically polished AT-cut quartz crystals with 6 MHz resonance frequencies (Valpey-Fisher) were used for all experiments. The electrodes on both sides of a quartz crystal were prepared by RF plasma sputtering from titanium (Cerac, 99.995 %) and platinum (Cerac, 99.95 %) targets. Titanium undercoating (50 nm thick) was followed by platinum coating (200 nm thick). The prepared platinum electrodes were so rough that the surface roughness factor calculated from the hydrogen adsorption was about 16. The sensitivity of the Pt-EQCM derived from the coulometric dissolution of silver was − 12.1 ng/Hz cm², which was in good agreement with the theoretical value20 of − 12.3 ng/Hz cm².

Sulfuric acid solutions were prepared from concentrated sulfuric acid (Aldrich, 99.999 %) and doubly distilled water that was prepared by distillation of deionized water firstly from a dilute alkaline permanganate bath and finally through a droplet trap. 1 M perchloric acid (Aldrich, double distilled, PPB/Teflon grade) was also prepared for comparison. All the solutions were deaerated by bubbling argon gas of 99.99+ % purity for 30 minutes before used. All the data represented in this paper were collected in steady state.

A typical cyclic voltammogram of a Pt-EQCM in 0.1 M

sulfuric acid and the simultaneously recorded frequency change are shown in Figure 1. In the positive-going potential scan the frequency decreased continuously in the whole potential range from − 0.3 to 1.2 V *vs*. SCE and in the reverse scan of the potential the frequency returned reversibly to the initial value as reported by other authors.[17,18,21] The same trends were also observed in 0.01 and 1 M sulfuric acid solutions. In the hydrogen adsorption region at potentials below 0.1 V (*vs*. SCE) the well-known hydrogen adsorption and desorption peaks were recorded in the voltammogram. The frequency, however, increased, *i.e.*, the mass decreased, as hydrogen atoms were adsorbed on the platinum surface. It means that desorption of some heavier adsorbates, which had been already adsorbed on the surface, occurred concurrently with hydrogen adsorption. The increase of electrode mass was observed as expected in the so-called oxygen adsorption or oxide formation region at the potentials above 0.5 V.

Figure 2(a) shows three voltammograms in sulfuric acid solutions of various concentrations. The voltammograms shifted to the positive direction as the acid concentration increased. The corresponding frequency changes were differentiated with time and converted to the mass change (ΔM)
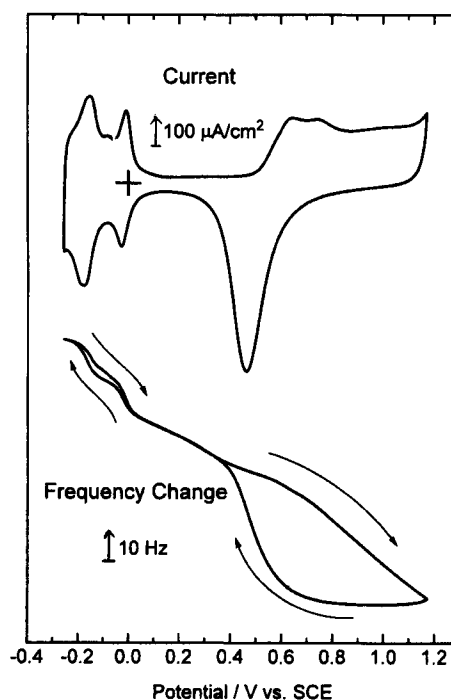

Figure 1. A Pt-EQCM response in 0.1 M sulfuric acid. Sweep rate, 10 mV/s; sampling interval, 0.2 s; gating time of frequency counter, 0.1 s.

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rates, $d\Delta M/dt$, which are shown in Figure 2(b). In the hydrogen adsorption region it is clearly observed that the mass changes occur predominantly at the potentials of current peaks. It denotes that the precedent adsorbates, which could be water,[3] are expected to be replaced with and repelled by hydrogen atoms at the instant of reduction of hydrogen ions.

In the positive-going potential scan above 0.1 V in Figure 2(b), remarkable small humps were observed in the double layer regions of the $d\Delta M/dt$ curves while the corresponding current curves were almost flat in this region as shown in Figure 2(a). It is noticeable that the potentials and the sizes of these humps were almost not affected by varying concentrations of sulfuric acid (or pH). On the basis of this result it can be assumed that this hump is only corresponding to a potential dependent specific adsorption and the point of zero charge is independent of pH, though it has been controversial.[2] According to the common concept of two research groups[17,18] mentioned above and some results using the other methods such as FT-IR,[4,6,9,10] radiotracer,[14,15] and STM,[16] this hump should be corresponding to the specific adsorption of (bi)sulfate. While some authors suggested only (bi)sulfate adsorption in double layer region from their FT-IR results,[4,6,10] a STM image was interpreted as a coadsorbate of (bi)sulfate and water.[16] To clarify the above assumption of (bi)sulfate adsorption the same experiment has been done in 1 M perchloric acid. As shown in Figure 3, no significant change in $d\Delta M/dt$ was observed in the double layer potential region. Even though it is not a decisive proof, the above assumption is believed to be quite within the realms of possibility.
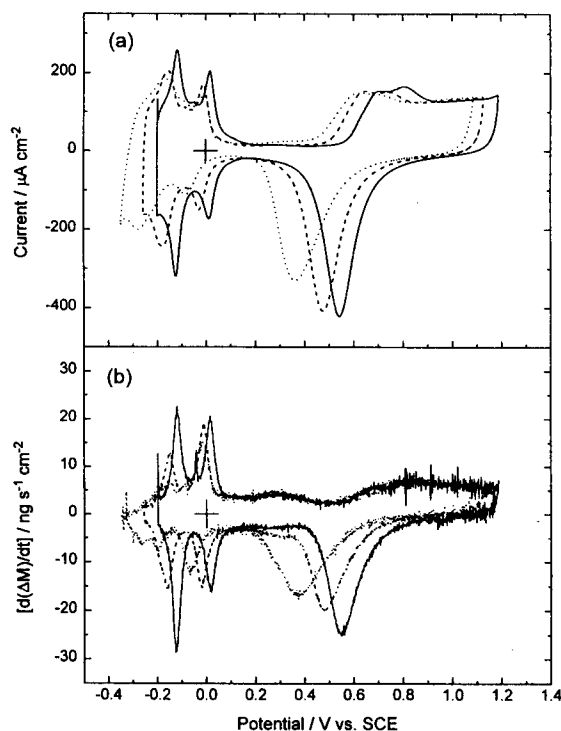
Watanabe *et al.* concluded that the increase in mass in the double layer region was only due to the (bi)sulfate adsorption from the inspection of the relation between the mass increase and the charge in the double layer region.[18] However, they have not shown any quantitative result. Shimatzu and Kita ignored the double layer charging current in their calculation assuming that the minimum current in the double layer region was taken as the potential independent charging
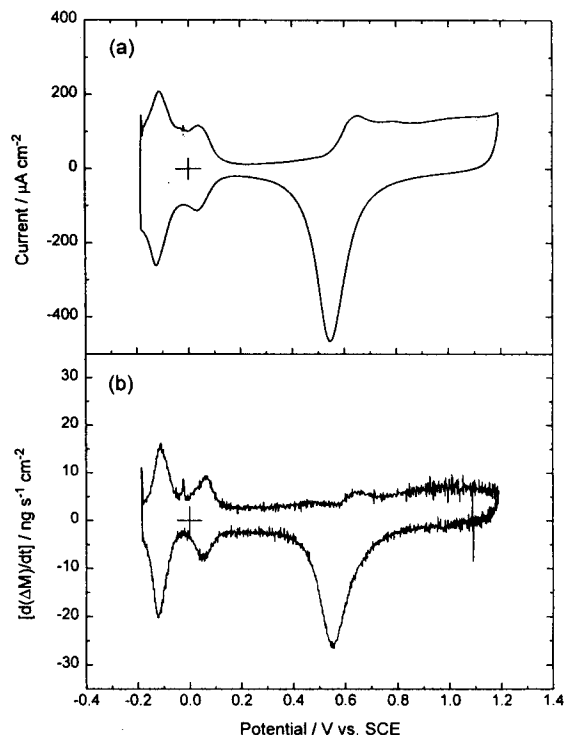

Figure 3. A Pt-EQCM response in 1 M perchloric acid. Sweep rate, 10 mV/s; sampling interval, 0.2 s; gating time of frequency counter, 0.1 s. (a) Cyclic voltammogram and (b) the corresponding mass change rate.

Figure 2. Pt-EQCM responses in 1 M (-), 0.1 M (---), and 0.01 M (···) sulfuric acid solutions. Sweep rate, 10 mV/s; sampling interval, 0.2 s; gating time of frequency counter, 0.1 s. (a) Cycl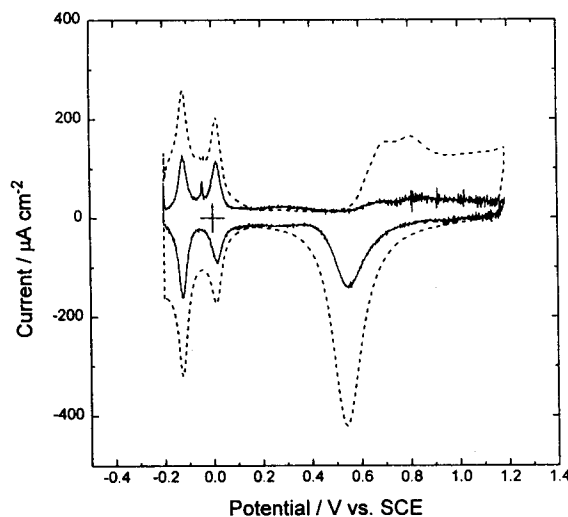ic voltammograms and (b) the corresponding mass change rates without any data processing such as signal averaging or smoothing.

Figure 4. An estimated current-potential curve (-) assuming 17 g for an electrochemical equivalent and a real current-potential curve (---) in 1 M sulfuric acid. Sweep rate, 10 mV/s; sampling interval, 0.2 s; gating time of frequency counter, 0.1 s.

current.[17] But, the charging current accumulates negatively charged species in the double layer in this potential region,[2] which makes the *effective* mass increase because the charged species should be bound at the surface weakly or strongly in the electric field unlike those in the bulk solution.

We have calculated the charging current contribution of (bi)sulfate adsorption according to the Watanabe's opinion. The estimated charging current converted from $d\Delta M/dt$ was so small that the specific adsorption of (bi)sulfate in the double layer potential region could not explain the charging current. We took the hydroxide adsorption as an alternative choice. The current estimated from $d\Delta M/dt$ is described in Figure 4 with the assumption of the electrochemical equivalent of 17 g, where both estimated and real charging currents are comparable in magnitude. Although the assumption of hydroxide adsorption has no scientific evidence, we can say that the mass increase associated with the charging current in the double layer potential region is mainly due to adsorption of a species that has approximately 17 g of the *effective* equivalent weight in the sense of a quartz crystal.

Another remarkable thing shown in Figure 4 is that the estimated currents corresponding to the formation and the stripping of (hydr)oxides are much less than the real currents. It means that the oxidation reactions in the oxide formation region occur not only by getting hydroxides from solution but also with the hydroxides (or water according to Shimatzu and Kita[17]) already bound on the surface. The real current could not be also explained only with the formation of Pt-O where the equivalent weight of oxygen is 8 g. Even though the estimated current increases almost twice in this case, it is still much less than the real current.

Although many questions still remain, it was demonstrated that a low noise EQCM and its capability getting frequency derivatives can tell more details about electrochemical surface phenomena.

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Unusual Poling Behavior of Poly(p-phenylene terephthalates) with a Nonlinear Optical Sidegroup

Suck-Hyun Lee, Won-Seok Song, Myeong-Jo Jung, Il-Cheol Jeon*, Byung-Goo Ahn**, and Seog-Jeong Song**

Department of Applied Chemistry, University of Ajou, Suwon 441-749, Korea
**Department of Chemistry, Jeonbuk National University, Jeonju 560-756, Korea*
***Kolon Group Central Research Institute, Yongin-gun, Kyunggi-do 449-910, Korea*

Nonlinear optical (NLO) effects arise when light causes changes in frequency, phase or other optical properties of a material. Substances allowing us to manipulate photonic signals efficiently are of great interest in technologies for opt-