Short communication

Study of Pt electrode dissolution in H_2O_2-containing H_2SO_4 solution using an electrochemical quartz crystal microbalance

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ABSTRACT

Pt electrode dissolution has been investigated using an electrochemical quartz crystal microbalance (EQCM) in H_2O_2-containing $0.5\,mol\,dm^{-3}$ H_2SO_4. The Pt electrode weight-loss of *ca.* $0.4\,\mu g\,cm^{-2}$ is observed during nine potential sweeps between 0.01 and 1.36 V vs. RHE. In contrast, the Pt electrode weight-loss is negligible without H_2O_2 ($<0.05\,\mu g\,cm^{-2}$). To support the EQCM results, the weight-decrease amounts of a Pt disk electrode and amounts of Pt dissolved in the solutions were measured after similar successive potential cycles. As a result, these results agreed well with the EQCM results. Furthermore, the H_2O_2 concentration dependence of the Pt weight-decrease rate was assessed by successive potential steps. These EQCM data indicated that the increase in H_2O_2 accelerates the Pt dissolution. Based on these results, H_2O_2 is known to be a major factor contributing to the Pt dissolution.

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1. Introduction

In various electrochemical reactions, Pt is well known to have high catalytic activities. For that reason, Pt catalysts are widely used in applications such as fuel cells [1,2], biosensors [3], and electrochemical analyses [4]. Although Pt metal only slowly and slightly corrodes, Pt dissolution reportedly occurs under various circumstances [5–9]. This phenomenon engenders the decline of the Pt catalytic activities. Therefore, many researchers have examined the effects of the electrode potential and the acidic solution concentration on the Pt dissolution based on results obtained in a deaerated atmosphere [7–9].

The O_2 reduction at the Pt electrode is an important reaction in polymer electrolyte fuel cells (PEFCs) [10–12]. In the PEFCs, cathode catalysts used for the O_2 reduction are reportedly degraded because of Pt dissolution during long-term operation [2,13,14]. Consequently, to achieve a long lasting PEFC, it is worthwhile to correctly understand the Pt dissolution phenomenon in an O_2 atmosphere. However, no reports in the related literature describe the Pt dissolution in an O_2 atmosphere.

We previously investigated Pt corrosion using a solid-state electrochemical cell composed of a membrane electrode assembly (MEA) [15]. Results showed that the rate of decrease of the Pt electrochemical surface area (ESA) obtained by successive potential cycling in an O_2 atmosphere was greater than that in an N_2 atmosphere. Moreover, one factor contributing to the Pt ESA decrease is known to be the electrode potential region, where a large amount of H_2O_2 is generated during the O_2 reduction [16]. Based on this known factor, we measured the change in the Pt ESA in the presence of H_2O_2, from which the decrease in Pt ESA was known to be accelerated by the added H_2O_2. From cross-sectional observations of the MEA after successive potential cycles, the decrease in the Pt ESA is considered to be the Pt dissolution. However, the relation between the presence of H_2O_2 and the Pt dissolution remains uncertain.

For this study, we conducted electrochemical quartz crystal microbalance (EQCM) measurements in a $0.5\,mol\,dm^{-3}$ H_2SO_4 solution in order to semiquantitatively investigate factors controlling the solubility of Pt. Specifically, the Pt electrode weight change was measured by changing the H_2O_2 concentration. Results showed that the weight of the Pt electrode drastically decreased in the presence of H_2O_2, even after nine potential sweeps. Next, to support the EQCM data, the weight-loss of a Pt disk electrode and Pt dissolved in the solutions were measured after the successive potential cycles. The obtained mass-balance between them well agreed. Furthermore, when successive potential steps are conducted while changing the H_2O_2 concentration, the Pt electrode-decrease rate estimated from the EQCM data increases with the increasing H_2O_2 concentration. These results indicate that H_2O_2 participates in the Pt dissolution.

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2. Experimental

In this study, the Pt dissolution was evaluated using an EQCM (9 MHz, QCM922, Model 283; Princeton Applied Research) in a deaerated atmosphere [17]. The 0.5 mol dm^{-3} H$_2$SO$_4$ that was used as the electrolytic solution was prepared by diluting conc. H$_2$SO$_4$ (Wako Pure Chemical Industry, Ltd.) with Milli-Q water. For the electrochemical measurements, ϕ5 mm Pt-EQCM electrode (QA-A9M-PT; Seiko EG&G Co., Ltd.), Pt plate, and Ag/Ag$_2$SO$_4$ electrode [15,17] were used, respectively, as the working, counter, and reference electrodes. All the electrode potentials in this report are related to the reversible hydrogen electrode potential (RHE). Before the measurements, the Pt-EQCM electrode was cleaned by potential cycling at the sweep rate of 50 mV s^{-1} in the electrochemical window of 0.5 mol dm^{-3} H$_2$SO$_4$ (0.01–1.41 V vs. RHE) for 60 min. The profile of the cyclic voltammogram obtained using the potential cycles was identical to the reported profile [18], which confirmed that the Pt electrode surface was clean. The electrode potential was controlled using a potentiostat. The 0.05 and 0.98 mol dm^{-3} H$_2$O$_2$-containing electrolyte solutions used to adjust the H$_2$O$_2$ concentrations were prepared by adding 30% H$_2$O$_2$ (Wako Pure Chemical Industry, Ltd.) to 0.5 mol dm^{-3} H$_2$SO$_4$. The measured currents and weight changes were normalized by the geometric surface area of the Pt-EQCM electrode.

Furthermore, to support the EQCM data, the weight-losses of a Pt disk electrode and amounts of Pt dissolved in the solutions after successive potential cycling were measured using a microbalance and inductively coupled plasma-optical emission spectrometry (ICP-OES). The successive potential cycles were conducted in a H$_2$O$_2$-containing 0.5 mol dm^{-3} H$_2$SO$_4$ solution using a two-compartment glass cell, in which a Nafion 117 membrane (2.5 × 2.5 cm^2, Dupont) was used as a septum. The Nafion membrane was pretreated by boiling in 0.5 mol dm^{-3} H$_2$SO$_4$ and then washing twice by boiling in pure water for 1 h each [15,19]. The Pt disk electrode (1 × 1 cm^2, thickness: 0.03 mm), Au plate, and Ag/Ag$_2$SO$_4$ electrode were used as the working, counter, and reference electrodes, respectively. The electrode potential was controlled using a potentiostat (Model 600, ALS). The experimental procedure is described as follows [9,17,20]. The Pt electrode was carefully washed in pure water, then in methanol using ultrasonic agitation. After drying in a vacuum chamber at 80 °C, the weight of the Pt electrode was measured by the microbalance (accuracy: 1 μg, MX5, Mettler Toledo). The Pt electrode was then introduced in one compartment of the electrochemical cell with the Ag/Ag$_2$SO$_4$ and the Au plate was introduced in the other compartment. Each compartment contained 10 ml of N$_2$-saturated 0.5 mol dm^{-3} H$_2$SO$_4$. Before the measurements, the Pt electrode was cleaned by potential cycling under the same conditions as those used for the EQCM measurement. Subsequently, the solution in the working electrode-compartment was replaced with 10 ml of a 294 mmol dm^{-3} H$_2$O$_2$ + 0.5 mol dm^{-3} H$_2$SO$_4$ solution, and the successive potential cycles were conducted at the sweep rate of 50 mV s^{-1} between 0.61 and 1.36 V vs. RHE in a deaerated atmosphere. After the potential cycles, the Pt electrode was washed and dried under the conditions described above and its weight was measured using the microbalance. It should be noted that the electrolytic solution after the potential cycling was measured by ICP-OES (determination limit: 0.136 mg dm^{-3}, SPS4000, Seiko) to assess the amount of the dissolved Pt.

3. Results and discussion

3.1. Pt dissolution in 0.5 mol dm^{-3} H$_2$SO$_4$ in the presence of H$_2$O$_2$

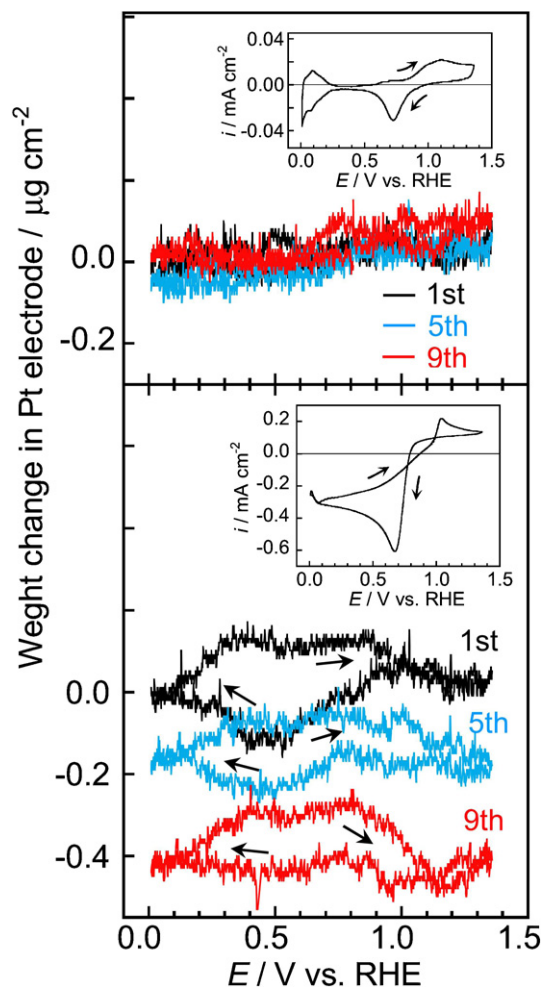First, to clarify the effect of H$_2$O$_2$ on the Pt dissolution, the weight change of the Pt disk electrode during a potential sweep

Fig. 1. Weight change of a Pt disk electrode obtained by a potential sweep at 10 mV s^{-1} in N$_2$-saturated 0.5 mol dm^{-3} H$_2$SO$_4$ (upper figure) and N$_2$-saturated 89 mmol dm^{-3} H$_2$O$_2$ + 0.5 mol dm^{-3} H$_2$SO$_4$ (lower figure). The insets show cyclic voltammograms of the Pt electrode measured during the potential sweep.

at 10 mV s^{-1} in an N$_2$ atmosphere was measured using the EQCM. Additionally, the measurement in the presence of H$_2$O$_2$ was also conducted. Fig. 1 shows the results obtained for the potential sweep in the 0.5 mol dm^{-3} H$_2$SO$_4$ (0.01–1.36 V vs. RHE). The insets show the cyclic voltammograms of the Pt electrode. In the N$_2$ atmosphere, a typical voltammogram of Pt is observed in the inset of the upper panel, [18]. In this case, a slight weight change in the Pt disk electrode, which is attributed to the Pt-oxide formation and its reduction [21], is measured between 0.5 and 1.36 V vs. RHE in the upper panel. In addition, the weight change obtained during each potential cycle shows a similar behavior. Based on this result, a negligible amount of Pt dissolution is found to occur during at least nine potential sweeps in the N$_2$ atmosphere.

As the inset in the lower panel of Fig. 1 shows, from the cyclic voltammogram measured in the N$_2$-saturated electrolytic solution including 89 mmol dm^{-3} H$_2$O$_2$, the oxidation current of H$_2$O$_2$ is observed between *ca.* 0.9 and 1.36 and its reduction current is measured between *ca.* 0.8 and 0.5 V vs. RHE. In this case, the lower panel shows that the weight-gain and weight-loss of the Pt electrode are observed during one cycle. However, when the potential cycles are repeated nine times, the Pt electrode weight irreversibly decreases with the potential cycles. The decreased weight obtained at 0.01 V vs. RHE after the nine potential cycles in the presence of H$_2$O$_2$ is extremely high at *ca.* 0.4 μg cm^{-2}, whereas that in the N$_2$-saturated electrolytic solution is negligible at <0.05 μg cm^{-2}. This

Table 1
Weight change of Pt disk electrode and Pt amount in the solution obtained by successive potential cycling in 294 mmol dm^{-3} H$_2$O$_2$ + 0.5 mol dm^{-3} H$_2$SO$_4$.[a]

Time (h)	Electrode weight change (μg)	Pt concentrations in solution measured by ICP-OES (mg dm^{-3})	Pt amount in solution (μg)
12	−14	1.173	11.73
16	−17	1.360	13.60

[a] The successive potential cycling was conducted between 0.61 and 1.36 V vs. RHE at a sweep rate of 50 mV s^{-1}.

result suggests that the Pt easily dissolves in the presence of H$_2$O$_2$, under continuous potentiodynamic polarization for nine potential sweeps.

3.2. Pt weight-loss and Pt dissolution amounts after successive potential cycling in the presence of H$_2$O$_2$

To support the Pt dissolution in the presence of H$_2$O$_2$ observed by EQCM, successive potential cycling was conducted in the H$_2$O$_2$-containing 0.5 mol dm^{-3} H$_2$SO$_4$ using a Pt disk electrode, after which the weight-losses of the Pt electrode and the amounts of Pt dissolved in the solutions were measured using the microbalance and ICP-OES. Table 1 shows the results obtained by the successive potential cycling between 0.61 and 1.36 V vs. RHE at 50 mV s^{-1} in 294 mmol dm^{-3} H$_2$O$_2$ + 0.5 mol dm^{-3} H$_2$SO$_4$. As shown in the table, the Pt electrode weight-loss is observed after the successive potential cycles for 12 and 16 h. The weight-loss amount increases with the increasing potential cycling time. When the solutions after the potential cycles were measured by ICP-OES, Pt was detected. From Table 1, the Pt concentration is found to increase according to the increase in the potential cycling time. It should be noted that from the ICP-OES data and the solution volume, the amounts of Pt dissolved in the solutions are estimated at 11.73 μg for 12 h and 13.60 μg for 16 h (see Table 1). These values are almost the same as the Pt disk electrode weight-loss amounts of 14 and 17 μg, indicating that most of the Pt dissolved by the successive potential cycling remained in the solutions. In other words, this result implies that the Pt electrode weight decrease is only caused by the Pt dissolution. According to this, the Pt weight decrease in the presence of H$_2$O$_2$ measured by EQCM in the lower panel of Fig. 1 was proved to be attributed to the Pt dissolution.

3.3. H$_2$O$_2$ concentration dependence of Pt dissolution amount

The results described above underscore a widely acknowledged phenomenon: Pt dissolution easily occurs in the presence of H$_2$O$_2$. In order to investigate the effect of H$_2$O$_2$ concentration on the Pt dissolution, a potential step was employed. First, the cyclic voltammogram was taken at 50 mV s^{-1} in the N$_2$ atmosphere to demonstrate that the surface is clean (upper panel of Fig. 2). Subsequently, the potential step was conducted at 0.36 and 1.36 V vs. RHE. The potential step cycle number and holding time at each electrode potential were, respectively, 12 cycles and 85 s. The Pt weight change measured by the potential step without H$_2$O$_2$ is denoted by line (a) in the lower panel of Fig. 2. From this result, the Pt electrode weight is inferred not to change during the measurement. Next, in 14 mmol dm^{-3} H$_2$O$_2$ + 0.5 mol dm^{-3} H$_2$SO$_4$, the same potential step was conducted. This result is denoted by line (b) in the lower panel of Fig. 2. The Pt electrode weight slightly increases to *ca.* 400 s, which might result from the formation of Pt-oxide such as a precursor to the Pt dissolution [17]; it then decreases linearly. In this case, although the Pt electrode weight increases by the potential step of 0.36 → 1.36 V vs. RHE, it decreases by 1.36 → 0.36 V vs. RHE. The results show that the Pt dissolution occurs by the cathode potential step, as induced by the added H$_2$O$_2$.
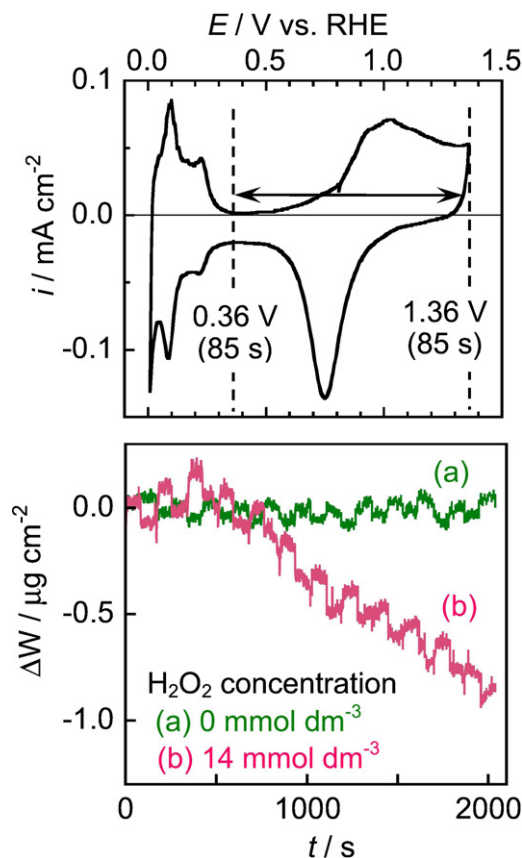

Fig. 2. Upper: cyclic voltammogram of Pt disk electrode in N$_2$-saturated 0.5 mol dm^{-3} H$_2$SO$_4$ obtained at a sweep rate of 50 mV s^{-1}. Lower: weight change of Pt disk electrode measured by repeating the potential step between 0.36 and 1.36 V vs. RHE. Potential step cycle number and potential holding time: 12 cycles and 85 s.

Subsequently, the Pt weight change was measured using successive potential steps between 0.36 and 1.36 V vs. RHE for the various H$_2$O$_2$ concentrations. Fig. 3 shows the rates of weight change in the Pt electrode, as estimated from the slope of the linear weight change, vs. the H$_2$O$_2$ concentrations. This graph demonstrates that the rate of weight decrease of the Pt electrode concomitantly increases with the increasing H$_2$O$_2$ concentration, showing that the Pt dissolution depends on the amount of H$_2$O$_2$ included in
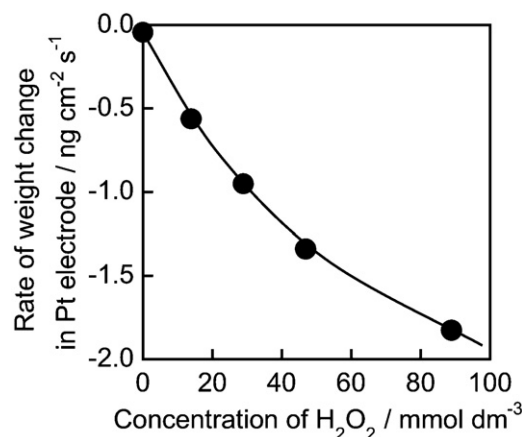

Fig. 3. Rate of weight change in Pt-EQCM electrode obtained using a potential step vs. H$_2$O$_2$ concentration in N$_2$-saturated 0.5 mol dm^{-3} H$_2$SO$_4$. The potential step was conducted between 0.36 and 1.36 V vs. RHE. Potential step cycle number and potential holding time: 12 cycles and 85 s.

$0.5\,\text{mol}\,\text{dm}^{-3}$ H_2SO_4. This result reveals that H_2O_2 is a major factor contributing to the Pt dissolution.

When we compare the results of Table 1 and Fig. 3, the weight decrease rate of the Pt electrode calculated from Table 1 is *ca.* $-0.16\,\text{ng}\,\text{cm}^{-2}\,\text{s}^{-1}$, which is smaller than those of Fig. 3. This result is considered to be dependent on the concentration-change of H_2O_2 added to the electrolyte, which is consumed during the potential cycling for 12 and 16 h; however the Pt weight decrease rate in Table 1 is sufficiently larger than that at $0\,\text{mmol}\,\text{dm}^{-3}$ in Fig. 3 ($-0.04\,\text{ng}\,\text{cm}^{-2}\,\text{s}^{-1}$).

As mentioned in the lower part of Fig. 1, the Pt electrode irreversibly decreases in the presence of H_2O_2 while its weight-gain and weight-loss are repeated. In Fig. 2, the Pt electrode weight increases by the anode potential step and the Pt dissolution occurs by the cathode potential step. These results are similar to those observed for the Pt dissolution in H_2SO_4 [7,17]. In Refs. [7,17], the formation of Pt-oxide and its reduction have been reported concerning the Pt dissolution. According to these results, the existence of H_2O_2 is considered to contribute to the formation of Pt-oxide or its reduction. However, it remains uncertain how H_2O_2 participates in these reactions. To clarify this, we plan to investigate the detailed Pt dissolution mechanism in the presence of H_2O_2.

4. Conclusions

In this study, we investigated the Pt dissolution in the presence of H_2O_2 by EQCM using a Pt disk electrode. The obtained results are summarized as follows:

(1) When the electrode potential is swept in the electrochemical window of $0.5\,\text{mol}\,\text{dm}^{-3}$ H_2SO_4, the Pt electrode weight decreases with potential cycles, decreasing by *ca.* $0.4\,\mu\text{g}\,\text{cm}^{-2}$ after nine successive cycles. For the electrolytic solution without H_2O_2, the decreasing amount of the Pt electrode in the N_2 atmosphere is negligible at $<0.05\,\mu\text{g}\,\text{cm}^{-2}$. From this result, the Pt electrode dissolution is considered to be accelerated by the presence of H_2O_2.
(2) The results obtained by the successive potential cycling between 0.61 and 1.36 V vs. RHE in the presence of H_2O_2 showed that the weight-loss amounts of the Pt disk electrode well agree with the amounts of Pt dissolved in the solutions. These results support the fact that the weight decrease of the

Pt electrode in the presence of H_2O_2 obtained by EQCM is attributed to the Pt dissolution.
(3) The rate of decrease of the Pt weight obtained using a successive potential step between 0.36 and 1.36 V vs. RHE increases with an H_2O_2 concentration in $0.5\,\text{mol}\,\text{dm}^{-3}$ H_2SO_4, which indicates that the Pt dissolution depends on the amount of H_2O_2 in the electrolyte. This result strongly demonstrates that H_2O_2 is a major factor contributing to the Pt dissolution.

Acknowledgement

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