

Short communication

Electrochemical corrosion of platinum electrode in concentrated sulfuric acid

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Abstract

We report on the electrochemical corrosion of a Pt electrode in strong sulfuric acid. The electrochemical measurements were conducted using a Pt-flag working electrode, Ag/Ag₂SO₄ reference electrode and Pt counter electrode at 25 °C. The measured cyclic voltammograms significantly changed in the H₂SO₄ concentration range of 0.5–18 mol dm⁻³, especially from 14 to 18 mol dm⁻³. After successive potential sweeps for 15 h in 16 mol dm⁻³ H₂SO₄, a weight loss of the Pt-flag electrode was realized. In contrast, a controlled potential electrolysis by cathodic polarization caused a weight gain, which was attributed to sulfur deposition by the H₂SO₄ reduction. The subsequent anodic polarization produced corrosion of the deposited sulfur. Consequently, the alternating polarization generated platinum corrosion, resulted in the production of platinum and sulfur composite particulates in the solution.

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1. Introduction

Platinum is one of the most resistive metals to corrosion, and its high stability has been validated for many applications in electrochemistry fields [1]. The durability of the platinum-based electrode is one of the key issues for the practical application of polymer electrolyte fuel cells (PEFCs). PEFC performance deterioration during long-time power generation is attributed in part to a reduction in the electrochemically active surface area of the platinum electrocatalyst. One of the proposed mechanisms for the reduction of the electrochemically active surface area is platinum dissolution at the high potentials typical of the PEFC cathode [2,3]. The dissolved platinum will either deposit on neighboring Pt particles to form larger particles (Ostwald ripening) [4] or diffuse to an electrochemically inactive portion of the membrane-electrode assembly to form Pt particles (Pt band) [5].

When we consider the theoretical stability, Pourbaix's diagram suggests that platinum metal will dissolve as Pt²⁺ during

anodic polarization in a strong acidic solution of pH < 0 [6]. However, the actual Pt corrosion does not occur according to the theoretical prediction. For instance, in the presence of Cl⁻ ion, Pt anodically dissolves as the PtCl₄²⁻ or PtCl₆²⁻ complex [7–11]. However, in a sulfuric acid or nitric acid solution, the electrolyte enhances the passivation of platinum, which participates in the corrosion reaction [7,12–15]. Especially, in 0.5–5 mol dm⁻³ sulfuric acid, the Pt oxide layer formed by anodic polarization induces corrosion under an inverse cathodic polarization condition; the extent of the corrosion is considered to be dependent on the formed Pt oxide [13–15].

Based on the previous reports [7–15], the platinum corrosion mechanism seems to strongly depend on the electrolytic species. The proton exchange membrane (PEM) for use in PEFCs has a functional group of –CF₂–SO₃H which could be representative of a strong protic acid. In the present study, we selected H₂SO₄ as a strong protic acid to investigate the electrochemical corrosion of the Pt electrode. First, the corrosion phenomenon in 0.5–18 mol dm⁻³ sulfuric acid was studied by cyclic voltammetry (CV) in combination with gravimetric measurements. As a result, the CV profiles markedly changed in 14–18 mol dm⁻³ sulfuric acid. A sulfur deposition on the surface of the electrode by cathodic polarization, which induces the Pt corrosion

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under anodic polarization, was then realized by an SEM–EDS analysis.

2. Experimental

The electrolytic solutions were prepared using extra pure sulfuric acid (Wako Pure Chemical) and Milli-Q water (Millipore). The electrochemical measurements were conducted using a potentiostat (BAS, ALS-600) and involved cyclic voltammetry and controlled potential electrolysis. For the electrochemical measurement in the strong sulfuric acid, Pt-flag [16,17] (5 mm diameter and 0.3 mm thick), Ag/Ag₂SO₄ [18] and Pt coil electrodes were employed as the working, reference and counter electrodes, respectively. A 2-compartment glass cell, each separated by a glass frit, was used to ensure that the products at the working electrode and counter electrode remained separated. The working electrode was pretreated in 0.5 mol dm⁻³ sulfuric acid by a cyclic potential sweep for 15 min at the rate of 50 mV s⁻¹ in the potential range shown in Fig. 1 [19]. All the electrochemical experiments were performed under deaerated conditions at 25 ± 1 °C. Unless otherwise noted, the listed potentials are versus Ag/Ag₂SO₄. A microbalance (MX5, Mettler Toledo), a microscope (Inf-500-DA, Scopeman), and a scanning electron microscope in combination with an energy dispersive X-ray analyzer (SEM–EDS; JEOL, JSM-6060A and JED-2300)

were also used to study the Pt-corrosion mechanism. After polarization of the Pt-flag electrode, it was carefully washed three times with Milli-Q water, and then dried in a vacuum chamber at room temperature, for the purposes of the gravimetric analysis and surface microscope observation. Since the resolution of the microbalance is 0.5 μg, it ensured a 1.1 μg cm⁻² change for the 5 mm-diameter Pt-flag electrode.

3. Results and discussion

The cyclic voltammograms (CVs) measured in the concentration range of 0.5–18 mol dm⁻³ sulfuric acid are shown in Fig. 1. The CVs were measured in the potential window range and the 2nd–10th cycles of the successive potential sweeps recorded. From this figure, the CV shapes are seen to markedly change in the electrolyte concentration range of 14–18 mol dm⁻³. The proton-desorption peaks, i.e., the anodic current observed in the potential < -0.3 V, decreases with an increase in the sulfuric acid concentration, and the peaks disappeared at around 18 mol dm⁻³. This suggests that the H-desorption as well as the H-adsorption do not occur in the strong sulfuric acid. When the sulfuric acid concentration is greater than 16 mol dm⁻³, a new reduction wave is observed at -0.2 V when the anodic reverse potential is greater than +0.3 V.

In the 14 and 16 mol dm⁻³ sulfuric acid solutions, successive potential sweeps for 15 h were carried out in the potential range as shown in Fig. 1. As a result of seven weight change measurements, a significant weight change with a good reproducibility occurred as listed in Table 1. These results revealed that the Pt electrode corroded more in the 16 mol dm⁻³ sulfuric acid due to the successive potential sweeps.

The upper diagram of Fig. 2 shows a CV measured by 10 successive potential sweeps in the potential range of -0.69 and +1.38 V in the 16 mol dm⁻³ sulfuric acid. In this figure, the anodic current observed at the potential < -0.5 V gradually decreased with the number of successive potential sweeps. When the potential sweep is further repeated, the anodic and cathodic current peaks at +0.6 and -0.2 V gradually increased; whereas, the anodic current peak at +0.75 V disappeared and the cathodic current peak at +0.23 V decreased. The final CV waveform in the < -0.2 V region was a similar to the one obtained in the 18 mol dm⁻³ sulfuric acid as seen in Fig. 1.

When we compared the CVs obtained in the 0.5 and 16 mol dm⁻³ sulfuric acid solutions shown in Fig. 1, the anodic and cathodic current peaks at +0.75 and +0.23 V in the 16 mol dm⁻³ sulfuric acid seem to be the platinum oxide formation and its reduction to produce Pt, respectively [15]. As seen in Fig. 2, due to the successive potential sweeps, the magnitudes of the coupled reactions decreased; therefore, it is presumed that

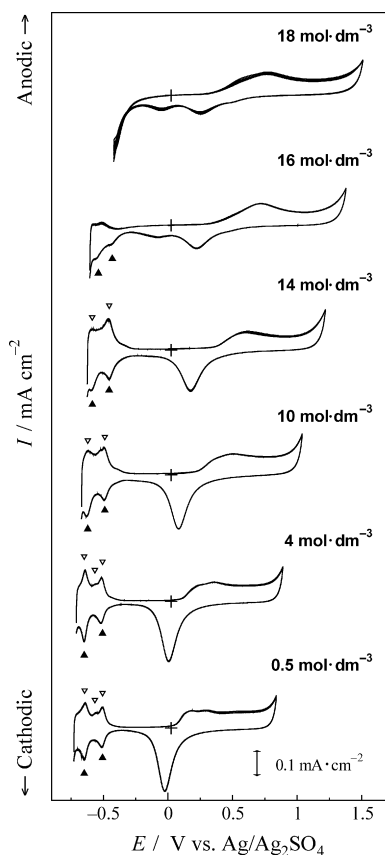


Fig. 1. Cyclic voltammograms of Pt-flag electrode in various sulfuric acid concentrations. Sweep rate: 50 mV s⁻¹. (▲) proton adsorption wave, (▼) proton desorption wave. CVs were recorded from the 2nd–10th cycles of the successive potential sweeps.

Table 1

Weight change of Pt-flag electrode in 14 and 16 mol dm⁻³ sulfuric acid solutions

H ₂ SO ₄ (mol dm ⁻³)	14	16
Weight change (μg cm ⁻² h ⁻¹)	-0.15	-6.7

The potential sweep range corresponds to that given in Fig. 1. The potential sweep time was 15 h.

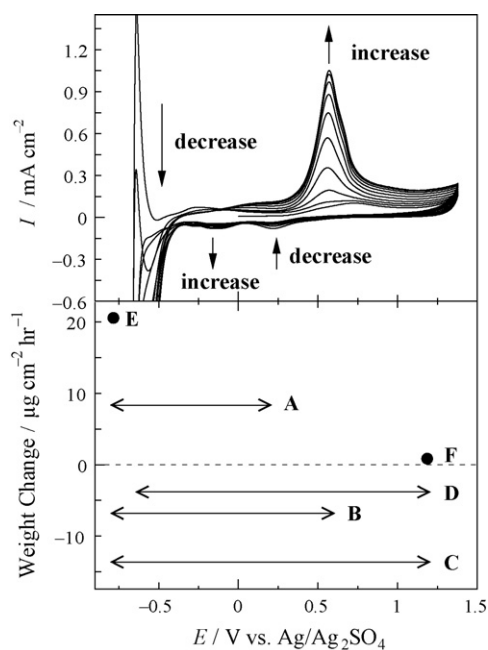


Fig. 2. Upper diagram: cyclic voltammogram of the Pt-flag electrode in 16 mol dm^{-3} sulfuric acid during successive potential sweeps at the rate of 50 mV s^{-1} . Lower diagram: weight change of the Pt-flag electrode in 16 mol dm^{-3} sulfuric acid. Lines A–D denotes successive potential sweeps in the potential range and, E and F denote controlled potential electrolysis, each for 3 h.

the newly appeared anodic peak at +0.6 V is due to platinum corrosion.

In order to validate this assumption, a gravimetric analysis was conducted by changing the potential-sweep range in the 16 mol dm^{-3} sulfuric acid. The observed weight changes are illustrated in the lower diagram of Fig. 2, in which lines A–D denote the 3-h potential sweep in the potential range denoted by the lines.

First, the weight changes of the Pt electrodes after the 3-h potential sweep were measured for a cathodic potential limit of -0.8 V . These results are shown in Fig. 2 as lines A–C. For line A obtained in the potential sweep range of -0.8 to $+0.2 \text{ V}$, no weight loss was observed, while a weight loss was seen for the anodic reverse potential $>+0.6 \text{ V}$ as expressed by lines B and C.

Moreover, line C showed a higher weight loss than that for line B. This supports the assumption that the anodic current peak at $+0.6 \text{ V}$ is related to the platinum corrosion.

Next, the weight change in the Pt electrode after the -0.64 to $+1.2 \text{ V}$ potential sweep for 3 h was measured and expressed as line D in order to compare the result of line C. As seen in Fig. 2, the weight loss of the electrode as demonstrated by line C is much greater than that represented by line D. Accordingly, the cathodic polarization is known to be an indispensable factor for the platinum corrosion in strong sulfuric acid.

When we look at lines A–D in Fig. 2, a weight gain is observed only for line A. This strongly suggests that an adsorption or deposition occurs during the cathodic polarization. To clarify this, the static electrolysis of the Pt electrode for 3 h was independently performed at -0.8 and $+1.2 \text{ V}$. These results are shown in Fig. 2 as points E and F. Point E confirms that the weight of the Pt electrode increases as a result of the cathodic polarization. However, the anodic polarization at $+1.2 \text{ V}$ produced no weight change as indicated by point F. These data also showed a good reproducibility. Based on these results, it is deduced that the cathodic reaction accompanying the weight gain induces the Pt corrosion by the following anodic polarization.

Fig. 3 shows camera images of the Pt electrode; photograph (a) is the electrode after a 3-h polarization at -0.8 V , and photograph (b) is that of the same electrode electrolyzed for an additional 3 h at $+0.8 \text{ V}$. Both were electrolyzed in 16 mol dm^{-3} sulfuric acid. It was observed from the figure that the Pt surface is colored gray by the preceding -0.8 V polarization, while the original metallic luster and the original weight occurred by the following $+0.8 \text{ V}$ polarization.

Fig. 4(a) and (b) shows the results of the SEM–EDS analysis of the electrodes showed in Fig. 3(a) and (b), respectively. In Fig. 4, an SEM image and EDS mappings of the platinum, sulfur and oxygen are represented. By comparing Figs. 3(a) and 4(a), a gray deposited material, which caused the weight increase as a result of the cathodic polarization, is found to have a $5\text{--}20 \mu\text{m}$ diameter. The deposited material consists of sulfur and a slight amount of oxygen. However, in Fig. 4(b), the sulfur-based dotted image disappeared after the subsequent anodic polarization. Moreover, an X-ray photoelectron spectroscopy (XPS; JEOL, JPS-100SX) analysis of the electrode (a) showed only an

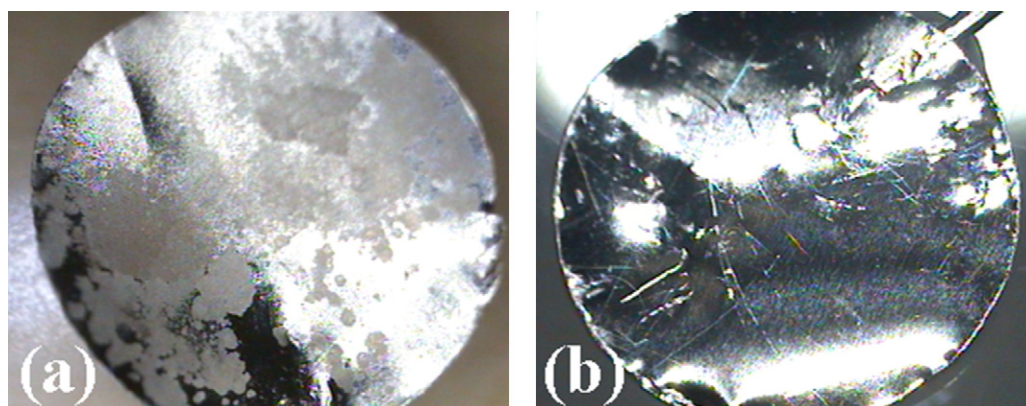


Fig. 3. CCD camera images of Pt-flag electrode (5 mm diameter). (a) Electrolyzed at -0.8 V in 16 mol dm^{-3} sulfuric acid for 3 h. (b) The electrolyzed electrode (a) at $+0.8 \text{ V}$ in 16 mol dm^{-3} sulfuric acid for 3 h.

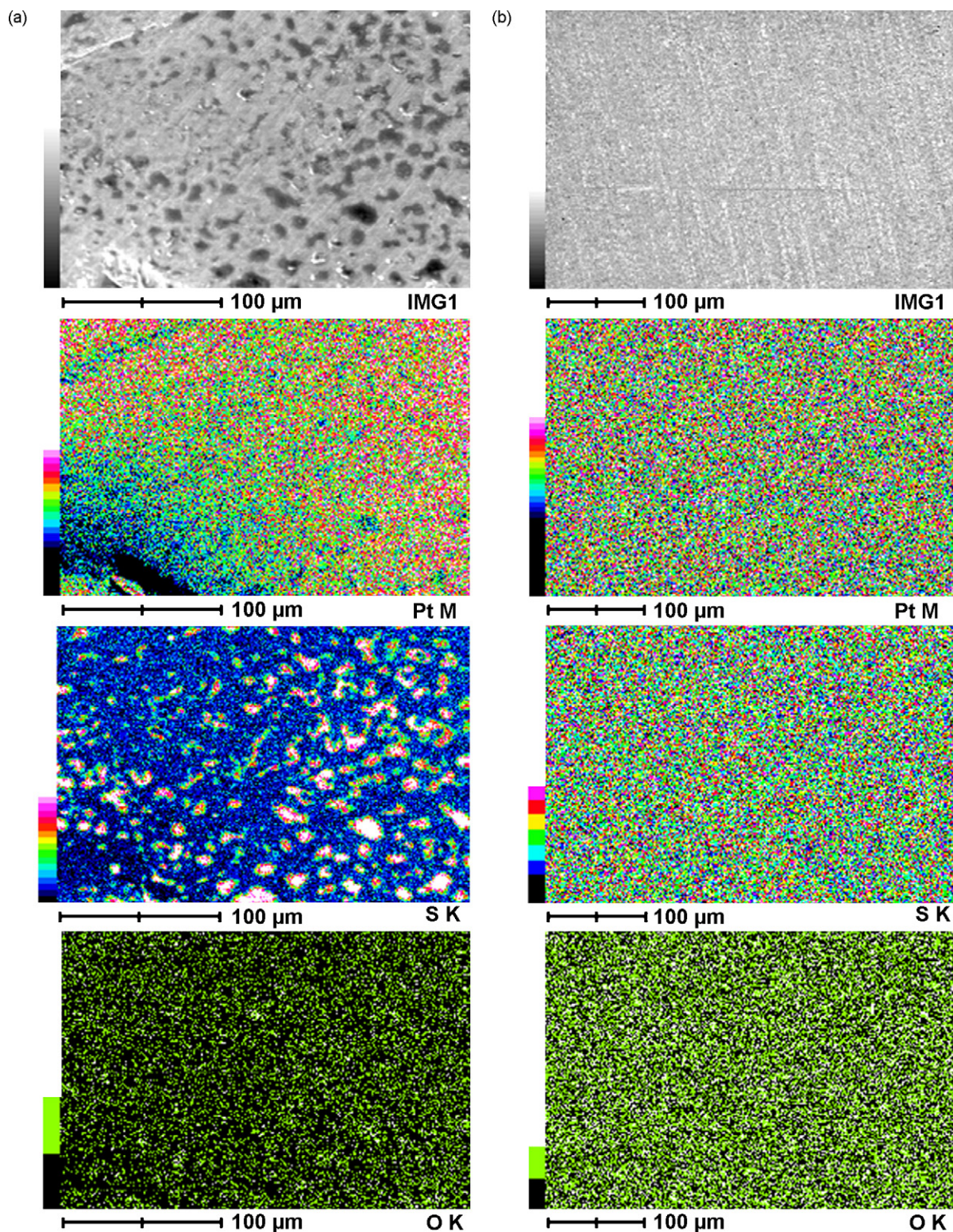
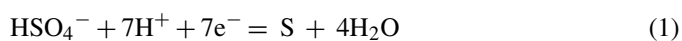


Fig. 4. SEM and EDS elemental analyses of Pt-flag electrode. (a) and (b) correspond to those shown in Fig. 3.

absorption peak at 162.5 eV, which corresponds to atomic sulfur; whereas, the peak at 166 eV, which comes from molecular sulfur, was not found [20]. According to the results demonstrated in Figs. 3 and 4, it was determined that the atomic sulfur deposited by the cathodic polarization at -0.8 V almost dissolves due to the following anodic polarization at $+0.8$ V. The

deposition/corrosion behavior of the sulfur correlated to the Pt dissolution. The estimated sulfur-deposition reaction could be expressed as [21]



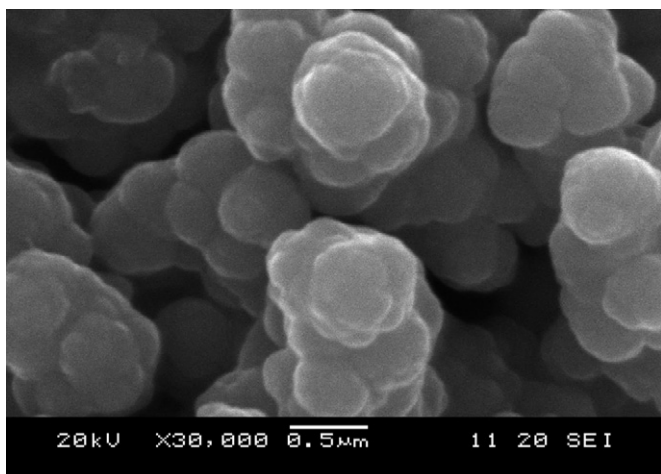


Fig. 5. SEM image of the material deposited on a 15 cm² Pt working electrode in 18 mol dm⁻³ sulfuric acid.

and



In order to ensure the Pt corrosion rate, an electrolysis confirmation experiment in 18 mol dm⁻³ sulfuric acid was conducted by employing a 15 cm² Pt-flag electrode immersed in a 50 cm³ electrolytic solution and the potential sweep rate of 100 mV s⁻¹ between -0.8 and +0.2 V. After a 30-h electrolysis, black particulates were found to be electrodeposited on the Pt electrode. The deposited particulates were easily dispersed in pure water by swinging the Pt electrode. Subsequently, the particulates were washed with pure water and then dried in a vacuum chamber at room temperature for the SEM-EDS analysis. The SEM photograph shown in Fig. 5 indicates that spherical particles of approximately 0.5 μm diameter aggregate to form the particulates. The EDS analysis revealed that the deposited material consists of 10 wt.% platinum, 90 wt.% sulfur and a negligible small amount of oxygen.

In addition, the above-electrolyzed 18 mol dm⁻³ sulfuric acid solution was diluted for examination using an Inductively Coupled Plasma Spectrometer (SPS4000, Seiko), which resulted in no detection of Pt-based ions in the solution. The 30-h electrolyzed sulfuric acid solution was diluted to 0.5 mol dm⁻³. If the corroded platinum was entirely dissolved in the 18 mol dm⁻³ sulfuric acid, the platinum concentration in the diluted sulfuric acid was calculated to be 0.068 mg dm⁻³, which exceeds the equipment detection limit of 0.015 mg dm⁻³. This fact indicates that the corroded platinum almost exists in the black particulates.

Based on these results, it was deduced that the platinum corrosion mechanism comprises (i) sulfur deposition due to the cathodic polarization at -0.7 to -0.8 V, and (ii) its dissolution accompanying platinum corrosion due to the subsequent anodic polarization at +0.6 to +0.8 V. Taking into account the result shown in Fig. 2, the deposited sulfur is considered to prevent the anodic formation of the platinum oxide. This could induce the platinum corrosion based on the electrode oxidation,



which is predicted by the Pourbaix diagram [6]. The presented mechanism is different from that in dilute sulfuric acid [13–15].

Next, a CV measurement was carried out in H₃Pt(SO₃)₂OH-containing 14 mol dm⁻³ sulfuric acid. As a result, a cathodic current peak at -0.2 V, which is based on the reduction of the Pt-complex ion, was observed. Based on this observation, the cathodic current peak at -0.2 V observed in Fig. 2 seems to be attributed to the reduction of the dissolved Pt species. It is considered that almost all of the dissolved platinum or its reductant does not diffuse into the bulk of the electrolyte, but reacts with the sulfur at the surface of the electrode to form the black particulates shown in Fig. 5.

4. Conclusion

This report described the electrochemical corrosion of the Pt electrode in strong sulfuric acid. The measured cyclic voltammograms significantly changed in the H₂SO₄ concentration range of 14–18 mol dm⁻³. After successive potential sweeps for 15 h in 16 mol dm⁻³ H₂SO₄, a weight loss of the Pt-flag electrode was realized. In contrast, a controlled potential electrolysis by cathodic polarization caused a weight gain, which was attributed to sulfur deposition by the H₂SO₄ reduction. The subsequent anodic polarization produced dissolution of the deposited sulfur. Consequently, the alternating polarization generated platinum corrosion, thus resulting in the platinum and sulfur composite particulates in the solution.

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