Supporting Information

Atomic-Level Observation of Electrochemical Platinum Dissolution and Redeposition

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MEMS chips for electrochemical cells.

We employed a liquid electrochemical TEM specimen holder (Poseidon, Protochips Inc.) with liquid flow and electrical biasing capabilities\(^1\). The electrochemical cell was mounted at the tip of the holder. The electrochemical cell consisted of a large MEMS chip (approximately 6 × 4.5 mm) fitted with a SiN viewing window and three electrodes and a small MEMS chip (approximately 2.1 × 2.1 mm) with only a SiN viewing window. The electrolyte is encapsulated by the two MEMS chips and O rings. Both MEMS chips were designed and manufactured within our group. The SiN viewing windows, polycrystalline Pt thin film electrodes for electrochemical measurement and a SiO\(_2\) spacer that defines the minimum liquid thickness on the Si substrate were fabricated by photolithography techniques. The size of the SiN viewing window on the large MEMS chip was approximately 200 × 15 μm and 10 nm thick. Polycrystalline Pt thin film electrodes were fabricated by spatter deposition to a thickness of 25 nm. The edge of the spattered Pt electrode was tapered and this edge was observed during the in situ TEM observation (Figure S10). The Pt reference electrode on the large MEMS chip (indicated as “(RE)” in Figure 1a) was not used during the in situ TEM observation and was only used for confirmation of potential stability (Figure 3a). The size of the SiN viewing window on the small MEMS chip was approximately 200 × 30 μm and 10 nm thick. Each MEMS chip was hydrophilized by plasma cleaning (JIC-410, JEOL) for 5 min before assembling the MEMS chips at the tip of the holder. The large MEMS chip and the small MEMS chip were arranged so that the long sides of the SiN windows intersect with each other to minimize bowing at the corners\(^2\).
TEM observation conditions.

An environmental TEM with an image Cs-corrector (Titan ETEM, FEI Company) and an energy filter (GIF Tridiem, Gatan) was employed, operating at an accelerating voltage of 300 kV. High-resolution TEM images were obtained using the energy filtered mode. The energy slit with a 30 eV slit width was set to zero loss. The in situ liquid TEM observation conditions are summarized in Table S1.

Estimation of electrochemical cell thickness.

The cell thickness was estimated from the electron energy-loss spectrum obtained at the viewing windows using the energy filter. The cell thickness (t) was defined as \( t = \lambda \times \ln(I_t/I_0) \), where \( \lambda \) is the inelastic mean free path of the specimen and \( I_t \) and \( I_0 \) are the total and zero-loss areas under the electron-energy loss spectrum \(^3\). The inelastic mean free path of the amorphous SiN thin film \( (\lambda_{SiN}) \) was investigated using commercial SiN thin films (ALLIANCE Biosystems) with various thicknesses (5, 10, 20, 50 and 100 nm) as standard samples. A \( \lambda_{SiN} \) value of 153.8 nm was obtained using a calibration curve derived from commercial SiN thin films.

Electrochemical measurement conditions.

An electrolyte comprising 0.1 M HClO\(_4\) was prepared by diluting HClO\(_4\) (Super Special Grade, Wako Pure Chemical) with pure water. Electrochemical measurements were performed using a potentiostat (VSP-300, Biologic). The electrolyte was flowed using a syringe pump (Pump 11 Elite, Harvard Apparatus) at a flow rate of 300 \( \mu \)L/h. All experiments were performed at room temperature (approximately 298 K). The surface of the polycrystalline Pt thin film electrode was electrochemically cleaned before the in situ liquid electrochemical TEM observation using
approximately 1,000 potential cycles between 0.05 $V_{\text{RHE}}$ and 1.2 $V_{\text{RHE}}$ at a scan rate of 0.5 V/s. The cleaning was repeated until the Pt reduction peak was clearly visible (Figure 3d).

**Avoidance of abnormal Pt redeposition via electron beam irradiation.**

We confirmed that an excessive electron beam current density causes abnormal Pt redeposition without the application of a potential (Figures S3 and S4). To avoid abnormal Pt redeposition, the electron beam current density was set to $6.0 \times 10^3$ A/m$^2$. Furthermore, we also considered abnormal redeposition of Pt electrochemically dissolved under electron beam irradiation (Figures S5 and S6). We avoided the abnormal Pt redeposition by employing a potential step voltammetry technique, blanking the electron beam before the potential steps and resuming beam irradiation 1 min after the potential changes with flowing electrolyte to flush the dissolved Pt. In addition, confirmation of the electron beam effect without applying a potential is shown in Figure S11.

**Figure S1.** Problems encountered with controlling the liquid thickness in conventional electrochemical cells. (a–e) Schematic cross-section diagrams of cell structure. (a) An ideal cell
layout. The edge of the electrode is located at the edge of the SiN viewing windows where the bowing of the SiN windows is minimized. However, the actual liquid thickness is increased due to the phenomena illustrated in (b–e). (b–d) Effect of increase and decrease of SiN window size due to errors in the etching of the Si substrate during the fabrication of SiN windows. If the SiN window size is increased as depicted in (b), both the SiN window and the electrode are bowed into the vacuum. Conversely, if the SiN window size is decreased as depicted in (c), the Si substrate obstructs the beam path. As actual MEMS chips need to avoid this situation, the electrode size must have a margin that is larger than the fluctuation of the SiN window size, as depicted in (d). In practice, however, even if the ideal position of the electrode and the SiN window shown in (a) is achieved, misalignment of the two MEMS chips still increases the liquid thickness, as depicted in (e).

**Figure S2.** An overview of the developed RHE with a liquid junction.
Figure S3. Abnormal Pt redeposition upon excessive electron beam irradiation. (a, b) A series of high-resolution energy filtered TEM images of a Pt thin film electrode in 0.1 M HClO$_4$ during electron beam irradiation. Excessive irradiation ($1.6 \times 10^4$ A/m$^2$) causes abnormal Pt redeposition without the application of potential, as depicted in (b). We confirmed that the abnormal Pt redeposition could be avoided by reducing the electron beam current density to $6.0 \times 10^3$ A/m$^2$. 
Figure S4. Confirmation of the crystal structure of the abnormal Pt redeposition generated by the excessive electron beam irradiation used in the observation shown in Figure S3. (a, b) TEM images of the Pt thin film electrode under vacuum after the in situ observation. The used MEMS chip was rinsed using pure water and dried before the TEM observation. (a) Normal Pt thin film. (b) Pt thin film covered by the abnormal Pt redeposition. (c, d) Electron diffraction patterns obtained from the red circles in (a, b), respectively. The abnormal Pt redeposition showed a similar polycrystalline diffraction pattern (d) compared to that of the normal Pt thin film (c).
Figure S5. Significant abnormal Pt redeposition under electron beam irradiation during Pt reduction. (a–c) Liquid electrochemical TEM observation images of a Pt thin film electrode in 0.1 M HClO₄ during CV analysis over the potential range 0.05–1.20 V_RHE at a scan rate of 0.5 V/s. Abnormal Pt redeposition only occurs beyond the Pt reduction potential at the beam irradiated area, as depicted in (b, c). We presumed the following process for abnormal Pt redeposition: (1) Pt dissolved by oxidation and reduction is redeposited under the electron beam; (2) additional dissolved Pt diffuses from the electrolyte bulk to the irradiated area along the resultant concentration gradient; and (3) a large amount of Pt is redeposited locally under the beam-irradiated area.
Figure S6. Confirmation of the crystal structure of the abnormal Pt redeposition generated during the Pt reduction process shown in Figure S5. (a, b) TEM images of the Pt thin film electrode under vacuum after the in situ observations. The observed MEMS chip is the same as shown in Figure S4. (a) Normal Pt thin film. (b) The Pt thin film with the abnormal Pt redeposition. (c, d) Electron diffraction patterns obtained from the red circles in (a, b), respectively. The abnormal Pt redeposition shows a similar polycrystalline diffraction pattern (d) compared to that of the normal Pt thin film (c).
Figure S7. Simulated TEM images for confirming the effects of defocus and sample tilts. (a–l)

Simulated high-resolution TEM images of a Pt grain surface with a step edge. The simulation was performed using a multislice code\textsuperscript{4} with following conditions: accelerating voltage of 300 kV, no aberration, and a uniform Pt grain thickness of 10 nm. Dashed lines on the images indicate the original position of the topmost surface in (a). (a) Pt<110> zone axis illumination at
just focus. (b) The Pt grain was tilted to +9.6 mrad along the X direction from (a) to simulate the in situ TEM observation results shown in Figures 4 and 5. Only the Pt(111) lattice fringes parallel to the X direction become visible. (c–h) A defocus series from (b). In both under- and over-focus conditions, the lattice fringes shift to the outside of the Pt surface, keeping the step edge. Therefore, the structural changes in the step edges observed during the in situ TEM experiments were not caused by defocusing. In addition, these simulation results show that the delocalization of the topmost surface appears uniformly. Thus, the observed partial (non-uniform) decrease and increase in the Pt surface lattice fringes could be interpreted as the changes in the Pt surface structure. (i–l) A series of sample tilts from (b). By tilting the Pt grain along the Y direction, the lattice fringes shift to outside the Pt surface keeping the step edge. Thus, we confirmed that sample tilt did not cause the changes for the step edge structure or the partial decrease and increase of the Pt surface lattice fringes observed in Figures 4 and 5.

**Figure S8.** Schematic of Pt dissolution and redeposition behavior observed during liquid electrochemical TEM observation in Figures 4 and 5.
**Figure S9.** Measurement results of the lattice distance at the topmost surface of the Pt electrode shown in Figure 5e. The Pt(111) lattice distance increased by around 5% at the topmost layer of the Pt grain compared to the inside of the Pt grain.
Figure S10. TEM image of a polycrystalline Pt thin film electrode. The edge of the Pt electrode is tapered for approximately 160 nm, and the tapering area consists of Pt crystal grains with diameters of 3 to 10 nm. The crystal grain at the edge of the Pt electrode was observed during in situ liquid electrochemical TEM experiments.
Table S1. Summary of the in situ liquid TEM observation conditions.

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<th>Current density (A/m²)</th>
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Figure S11. Confirmation of the electron beam effect. (a–c) A series of high-resolution energy filtered TEM images of the Pt thin film electrode in 0.1 M HClO₄ during continuous electron beam irradiation without applying potential. The beam current was set to 6.0 × 10³ A/m², the same value used in the observations shown in Figures 4 and 5. The observed Pt grain is the same as in Figure 5. The triangles in the images indicate surface step edges. At first, there were no significant changes in the positions of the step edges during 2 min of beam irradiation (from (a) to (b)). Next, 5 min of beam irradiation led to changes in the positions of the step edges (decrease of surface lattice fringes’ length) (from (a) to (c)). However, in the cases of the in situ TEM observations shown in Figures 4 and 5, beam irradiation was limited to within 2 min at each 3 min potential step (the remaining time was used for beam blanking). Therefore, it is interpreted that the observed Pt surface structural changes shown in Figures 4 and 5 mainly originate from
the electrochemical reaction.

References


