

## In-Situ Scanning Tunneling Microscopy of Platinum Electrode in Sulfuric Acid

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An in-situ scanning tunneling microscope (STM) was applied to clean Pt surfaces in aqueous sulfuric acid solutions. An electrochemical pretreatment was employed for a Pt electrode. It was suggested that the migration of ad-atoms of Pt produced by the oxidation and reduction cycles should occur towards a particular crystallographic direction.

Scanning tunneling microscope (STM) is a powerful tool for in-situ electrode surface characterization.<sup>1-5)</sup> Electrochemically deposited gold<sup>2)</sup> and silver<sup>3)</sup> have been imaged in an electrochemical cell. Our recent paper described fine structures of semispherical platinum (Pt) particles deposited on a HOPG electrode with an atomic resolution in a sulfuric acid.<sup>5)</sup> The importance of the characterization of Pt surface is well recognized in both the fields of electrocatalysis and chemicalcatalysis.

STM has been already applied for Pt surfaces in UHV.<sup>6)</sup> Vázquez et al. have recently described an ex-situ observation of the topography of electrochemically activated Pt electrodes in air.<sup>7)</sup> Fan and Bard have also examined Pt electrodes in air after different pretreatments.<sup>8)</sup> However, application of in-situ STM to electrodes in liquid solutions promises to give more information on the electrochemical mechanisms.

The present paper reports, for the first time, an in-situ observation of Pt electrodes before and after an electrochemical pretreatment with atomic resolutions in aqueous sulfuric acid solutions. An electrochemical cell illustrated in the insert, Fig. 1, was attached on a spring plate in our apparatus reported previously.<sup>5)</sup> A Pt wire and well-polished Pt or Ag wires were

used for a counter and quasi-reference electrodes. The working electrode was a platinum plate (99.99%) whose surfaces were mechanically polished using successively finer grades of alumina down to  $0.1\ \mu\text{m}$ . The mechanically polished Pt plate was then annealed in a gas-oxygen flame near  $1100\text{--}1200\ ^\circ\text{C}$  for 1 h. After this prolonged annealing, the crystal grains could be clearly observed under an optical microscope, indicating that the sample could be classified as a well-crystallized polycrystalline Pt. The final surface treatment was carried out following a procedure employed for electrochemical studies of single crystals of Pt described by Clavilier et al.,<sup>9)</sup> and Motoo and Furuya.<sup>11)</sup> The Pt electrode was annealed in a gas-oxygen flame near  $1100\ ^\circ\text{C}$  for 1 min and then quickly brought in contact with ultra-pure water (Millipore-Q) saturated with hydrogen.

Figure 1 shows typical cyclic voltammograms of the Pt electrode in a  $0.1\ \text{M}\ \text{H}_2\text{SO}_4$  solution. Curve (A) was obtained when the positive electrode potential was limited in the double-layer region. The amount of hydrogen adsorbed on the Pt electrode can be calculated as ca.  $0.21\ \text{mC}/\text{cm}^2$  by an integration of peaks. Note that this value is almost identical to a value calculated for a polycrystalline Pt.<sup>11)</sup> The above result is sufficient proof that the surface of Pt was clean and probably is flat on an atomic scale. Curve (B) was recorded after 50 cycles at  $v = 0.2\ \text{V/s}$  between the electrode potentials where hydrogen and oxygen were slightly evolved. The shape of the voltammogram seems to be typical for polycrystalline Pt electrodes. Note that the actual surface area was slightly increased only about 10-20% after the 50 potential cycles between 0 and 1.4 V as shown in Fig. 1.

Figure 2 shows a typical image of the virgin Pt surface observed in a  $0.1\ \text{M}\ \text{H}_2\text{SO}_4$  solution. Near-to-atomically flat surfaces were observed with a few shallow multiatomic steps ( $1\text{--}10\ \text{\AA}$  in height) for all specimens with different positions examined here. This indicates directly that the annealing procedure in a gas-oxygen flame produces near-to-atomically flat surfaces in consistent with the result discussed in Fig. 1. In contrast, Vázquez et al. reported more irregular structures for untreated Pt specimens observed in air.<sup>7)</sup> Such differences might

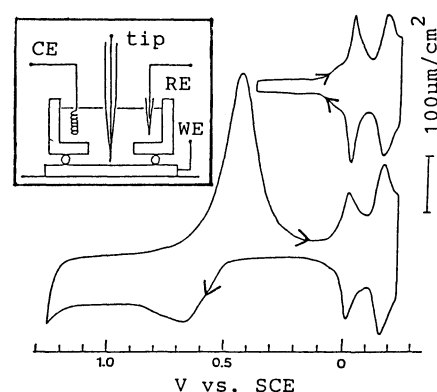


Fig. 1. Cyclic voltammograms of thermally treated Pt in its initial (A) and after 50 cycles (B).  $v = 0.1\ \text{V/s}$ . The potential was referenced to a SCE.

be due to the difference in the pretreatment.

After observations of STM images at the same area shown in Fig. 2, the tip (glass coated Pt) was left up only about  $1000 \text{ \AA}$  from the surface of Pt and then disconnected from the STM feed back circuit. Then, the Pt electrode potential was cycled for 50 times at a scan rate of  $0.2 \text{ V/s}$  as shown in Fig. 1-B. Figure 3 shows STM images after the electrochemical treatment described above. Note that these images were taken at the same position as that for Fig. 2. Surprisingly,

large differences from the virgin state can be seen for the images after the potential cycles. Relatively smooth terraces spaced of the order of  $5\text{--}20 \text{ \AA}$  and parallel-ridges can clearly be seen in Fig. 3-A. Figure 3-B shows another image observed near the area of Fig. 3-A. In this case, very regular parallel-terrace structures separated by ca.  $150 \text{ \AA}$  were observed. It is noteworthy that the direction of the steps and ridges observed in Figs. 3-A and -B is exactly the same as that of the shallow atomic steps shown in Fig. 2. This result gives a very important aspect for the direction of the migration of ad-atoms of Pt produced by the oxidation and reduction cycles under the potential scans described above. The migration of Pt ad-atoms should occur towards the direction perpendicular to that of the steps.

Similar ridges have been observed in air after applying a square wave signal between 0 and  $2.3 \text{ V}$ .<sup>7)</sup> It is known that application of such an unusual high

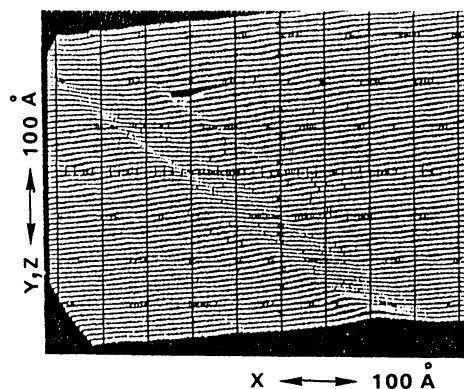


Fig. 2. STM image of the near-to-atomically flat Pt in  $0.1 \text{ M H}_2\text{SO}_4$ . The current was  $6 \text{ nA}$ . The tip was  $+90 \text{ mV}$ .

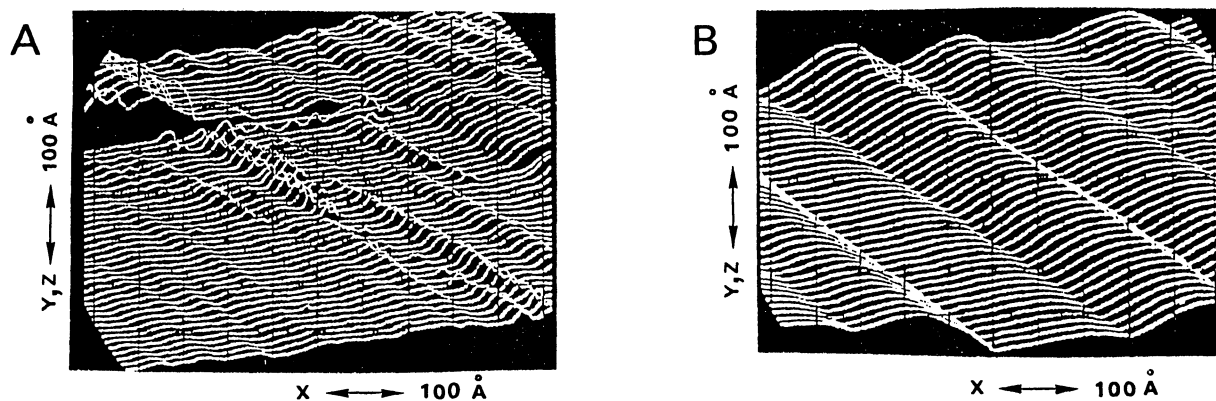


Fig. 3. STM images of the Pt surfaces obtained in  $0.1 \text{ M H}_2\text{SO}_4$  after 50 potential cycles between  $-0.22 \text{ V}$  and  $+1.25 \text{ V}$  vs. SCE at  $0.2 \text{ V/s}$ . The tunneling current was  $6 \text{ nA}$ . The tip was  $+90 \text{ mV}$  with respect to the Pt electrode.

anodic potential (2.3 V) causes a very large increase in the surface area. However, the increase in the surface area caused by the present activation procedure was quite small as shown in Fig. 1. It is very surprising to observe such a large change in the morphology under the potential cycle applied in this study.

We have carried out similar observation at different portions of the specimen. In these cases, parallel-ridges were not clearly observed. Instead of these structures shown in Fig. 3, semi-spherical domains have predominantly been observed. The diameter and height of semi-spheres are in a range of ca. 50 and 10 Å, respectively. Similar semi-spherical domains, namely, dome-like or pebble-like structures were also distinguished in air.<sup>7)</sup> Different morphologies observed at different portions should be caused by the crystallographic orientation of each small single crystals composed in the specimens.

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