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In situ STM imaging of surface dissolution and rearrangement of a Pt–Fe alloy electrocatalyst in electrolyte solution

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The formation of a Pt skin layer with predominantly (111)-oriented facets induced by dissolution of Fe atoms in a Pt–Fe alloy for fuel cell applications is investigated for the first time by using *in situ* electrochemical STM in 0.1 M $HClO_4$ solution.

Fuel cells are receiving much attention as a next-generation residential power source and as electric vehicle power sources.[1,2] The study of fuel cells has resulted in the rapid development of efficient catalytic electrode materials. Watanabe *et al.* have prepared many Pt-based alloys using the magnetron sputtering deposition method and investigated the catalytic properties of such alloys using cyclic voltammetry, EXAFS, XPS and other methods.[1] By using XPS, they found for a Pt–Fe alloy film that Fe atoms leached out into solution and formed a surface layer on the film with a modified electronic structure, which exhibits high CO-tolerance towards H_2 oxidation or O_2 reduction.[3–7] While electrochemical and other surface analysis techniques such as XPS, AES and EXAFS have been extensively used in the study of thin solid films, the information obtained from these methods is esssentially macroscopic and does not provide direct atomic-scale models for the film structures. On the other hand, scanning tunnelling microscopy (STM) is a powerful technique to obtain atomic resolution images in UHV and also electrolyte solutions.[8] STM has been extensively used to examine the surface structure of single crystals. Recently, Watanabe *et al.* initiated an *in situ* STM study on a sputtered Pt film in solution and revealed atomic features of the film to explore the interaction between electrodes and adsorbates.[9] However, no such study on Pt alloyed with non-precious metals has been reported. In order to decrease the cost of catalytic materials, understanding the microstructure of a variety of Pt-based d-transition metal alloy films is an important issue for fuel cell applications.

We thus have attempted to reveal the relationship between microstructure and electrocatalytic activity of films to hopefully develop more efficient electrode materials. In this paper, we report an *in situ* STM study of a Pt–Fe film in 0.1 M $HClO_4$ solution.

The samples of Pt–Fe were prepared by using rf-magnetron sputtering equipment (Anelva SPE-332H). In order to enhance the adhesion strength between the film and the flat glass substrate, and to increase the surface flatness, titanium and gold films were deposited as transitional layers prior to the Pt–Fe alloy film.[3,4,9] The Pt–Fe alloy film was prepared by simultaneously sputtering a Pt target (Tanaka Kikinzoku Kogyo, K. K. Japan, with a purity of 99.9%) and a Fe target (Nilaco, Japan, with a purity of 99.9%) in an Ar plasma (Ar: 5×10^{-1} Pa) after the chamber was evacuated to $< 5 \times 10^{-4}$ Pa. The thickness of the film is *ca.* 60 nm with a chemical composition of $Pt_{64}Fe_{36}$ confirmed by EDX analysis. The electrolyte solution was prepared from Reagent grade $HClO_4$ (Kanto Chemical Co. Japan) and Millipore-Q water. All electrode potentials are reported with respect to the reversible hydrogen electrode (RHE) in the same solution of 0.1 M $HClO_4$. The alloy film was characterised by cyclic voltammetry (CV) and STM. STM imaging was carried out under ambient conditions in the electrolyte solution. The *in situ* STM apparatus used was a Nanoscope III (Digital Instruments). The details for the STM measurement are the same as described in the literature.[10,11] To ensure general information, several different areas of the film were imaged. The measurements were carried out in a nitrogen-filled chamber.

The solid line shown in Fig. 1 is a steady-state CV on the Pt–Fe film in 0.1 M $HClO_4$ after 10 potential cycles between 0.05 and 0.95 V. The CV shows a feature similar to that of a polycrystalline Pt electrode.[12] The dashed line shows a CV recorded in the first scan toward positive direction from 0.5 V. From previous results using an *in situ* electrochemical quartz crystal nanobalance (EQCN), it is known that Fe and Pt atoms dissolve and Pt atoms are re-deposited on the surface when the film is immersed in solution.[13] The small peak at 0.71 V indicated by an arrow is assigned to the Fe^{2+}/Fe^{3+} redox process.[13] However, the peak decreased with each additional potential cycle and finally disappeared, resulting in a steady CV. This result shows that the potential cycles lead to increased dissolution of Fe and the rearrangement of Pt at the surface and formation of a Pt skin layer, protecting the underlying Pt–Fe alloy from corrosion.

Prior to STM imaging in the electrolyte solution, the fresh sputtered Pt–Fe film mounted in an electrochemical STM cell was observed under nitrogen atmosphere. Fig. 2A shows a typical STM image of the film with well-crystallized grains in a size range from 50 to 100 nm. Step-terrace structures are seen in the grains, although the width of terraces is usually less than 5 nm.

After recording the STM image shown in Fig 2A, a 0.1 M $HClO_4$ solution was injected into the electrochemical STM cell and the Pt–Fe film kept in the electrolyte solution for 5 min under potential control at 0.5 V, which is within the double-layer potential region. The surface morphology of the film (at the same manification) was found to change dramatically as shown in Fig. 2B with a rough surface with cauliflower-like features being observed rather than the more ordered surface seen in Fig. 2A.

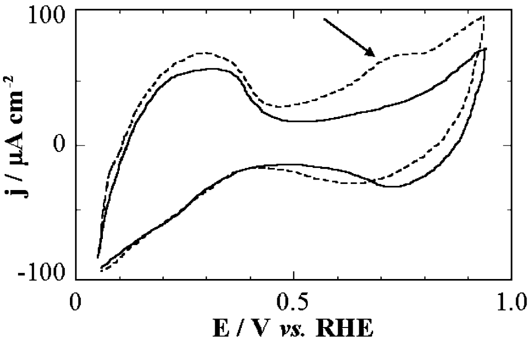

Fig. 1 Cyclic voltammograms for a Pt–Fe film in 0.1 $HClO_4$ at a scan rate of 20 mV s^{-1}. The solid line shows the steady-state CV while the dashed line is the first scan in positive direction from 0.5 V. The potential indicated by the arrow is *ca.* 0.71 V.

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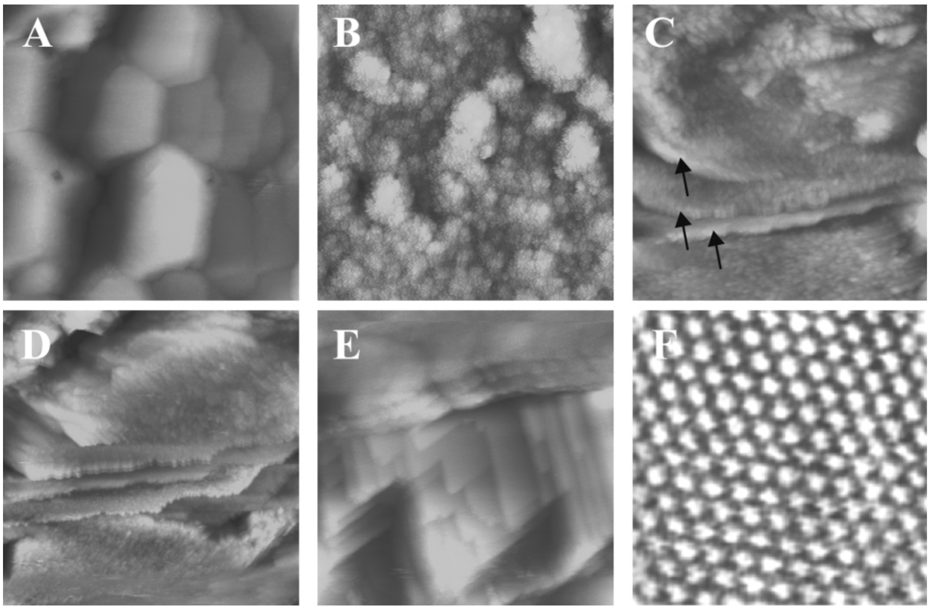

Fig. 2 (A) The surface morphology of a fresh Pt–Fe film in nitrogen-saturated ambient conditions. (B) The surface of a Pt–Fe film immersed for 5 min in 0.1 M $HClO_4$ at 0.5 V before the potential cycle. Images (C), (D) and (E) show changes of the surface on Pt–Fe films at 0.5 V after 10 potential cycles. The time interval from (C) to (D) is 40 min and 8 min from (D) to (E). The image (F) is an atomic image acquired at the terrace area of (E). The scan area for (A)–(D) is 300 × 300 nm, for (E) 68 × 68 nm and (F) 3 × 3 nm.

After recording the image of Fig. 2B, potential cycles were applied to the film as discussed above. Previous electrochemistry, XPS[3–7] and EQCN[13] experiments indicated that the Fe atoms leached out from the film in acid solution after a series of potential cycles and finally resulted in a pure Pt skin layer. In the present study, *in situ* STM was used to clarify the surface process.

After ten potential cycles between 0.05 and 0.95 V, the electrode potential was held at 0.5 V. A set of STM images was acquired at the same manification as in Fig. 2A and B. Fig. 2C–E show the change of surface morphologies with time. For example, the surface image shown in Fig. 2D is observed 40 min after that for Fig. 2C. It is clear that the edges which were formed occasionally on the film surface, as indicated by arrows in Fig. 2C, have become oriented crystalline steps. Several terraces also appear. After a further 8 min, Fig. 2D, an expanded image shown in Fig. 2E was acquired in which well-ordered (111)-oriented facets with terrace-step structure are observed. The step lines cross each other at 60 or 120° (width of the terraces is from several nm to more than 10 nm). Atomic resolution STM images can be acquired in the wide terraces as shown in Fig. 2F in which hexagonal structure can be seen. The atomic rows are in three-fold symmetry with the direction of the atomic rows being almost parallel to the step directions. The interatomic distances are measured to be *ca.* 0.28 ± 0.02 nm similar to the lattice of Pt(111). The characteristic image strongly indicates that the terrace surface has a close-packed structure, *i.e.* a Pt(111)-(1 × 1) structure.

The present result will shed new insight for electrode material study in fuel cells. Further studies on the Pt skin layer formed on the Pt–Fe alloy electrode, such as the adsorption and oxidation of CO, are now in progress by using STM from the viewpoint of electrocatalysis.

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