

Electrodeposition of PbO₂ Thin Films at the Interface of Two Immiscible Liquids

Eiji Tada and Hiroyuki Kaneko

Department of Materials Science and Engineering, Faculty of Engineering and Resource Science, Akita University,
Tegata Gakuen-cho, Akita 010-8502

(Received August 7, 2000; CL-000753)

PbO₂ thin films were electrodeposited by anodic oxidation at the *n*-decane / lead(II) acetate(aq) interface. SEM observations and X-ray analyses revealed that the film consisted of two layers, one the organic-side layer less than 1 μm thick and the other the aqueous-side thicker layer, which were different in the crystal orientation each other. A film of PbO₂ grew along the interface by anodic deposition, similarly to the metallic film by cathodic deposition.

Previously, the authors reported that film-like metal deposits were prepared electrochemically at the interface of an organic liquid and an aqueous solution, immiscible each other.¹⁻⁵ Therefore, this electrodeposition using the interface of two immiscible liquids as a reaction field is expected to become a novel preparation of thin films.

This electrodeposition method has two big advantages for the preparation of thin films. First, no solid substrate is necessary for the deposition, because a liquid-liquid interface is considered to play a role of a virtual substrate. Secondly, filmy deposits preferentially grow along the interface and then thin films are easily obtained.

So far, the authors have succeeded in obtaining metallic films such as Zn,^{1,2} Co,³ Cu,⁴ Au⁵ etc. It is interesting whether thin oxide films can be also prepared at the interface of two immiscible liquids by anodic deposition, instead of cathodic metal deposition. In this paper, the preparation of filmy PbO₂, as a typical conductive oxide, is challenged and the films obtained are investigated electrochemically and metallographically.

The electrolytic cell used in this study was a glass beaker with a water-jacket to circulate thermostated water.⁵ All electrochemical experiments were carried out by the three-electrode method. The working electrode was a platinum wire of 0.5-mm diameter. The counter electrode was a platinum disk of 30-mm diameter, positioning under the working electrode. The reference electrode was a Ag-AgCl electrode in a sat'd KCl. A Luggin capillary connected to the reference electrode was positioned closely to the working electrode.

The interface of two immiscible liquids consisted of a non-conductive organic liquid and an electrolyte solution containing Pb(II) ion. As a preliminary experiment, a possibility of the PbO₂ formation was investigated with some combinations of an organic liquid and an aqueous solution of lead salts; an organic liquid, *n*-decane and an electrolyte solution, 1 kmol/m³ Pb(CH₃COO)₂ were chosen as a desirable combination in this study. The working electrode was positioned exactly at the interface with a micro-manipulator. The electrolytic cell was maintained at 25 °C.

Cyclic voltammogram of Pb(II) at the interface showed that the electrodeposition of PbO₂ was initiated above 0.9 V. Higher overpotentials prevented a thin smooth film from grow-

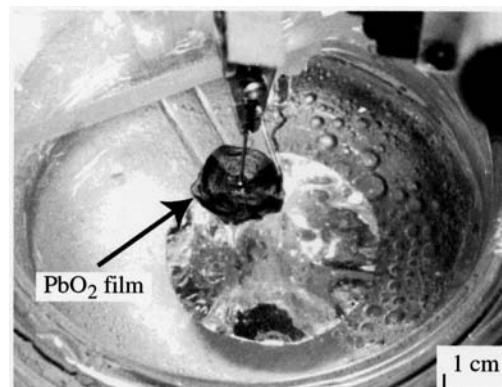


Figure 1. Growth feature of a PbO₂ thin film electrodeposited for 60 min at 1.25 V at the interface of two immiscible liquids. (Air bubbles in the water jacket are seen on the right-hand side.)

ing along the interface and enhanced the growth of deposits toward the bulk solution. Then the electrode potential for the deposition of a thin film should be settled at a lower overpotential. On the other hand, at potentials near 0.9 V, the growing rate was too slow to confirm a film formation. Consequently, the electrodeposition was carried out at a potential of 1.25 V.

Figure 1 shows the growing feature of a PbO₂ deposit. The deposit grew concentrically from the tip of the electrode along the interface. The deposit was filmy and dark-brown. There are some circular and radial stripes on its surface.

Figure 2(a) shows SEM photographs of a PbO₂ film: the film had a very flat surface with a uniform thickness. As shown in Figure 2(b), the film consisted of two layers: a very thin layer

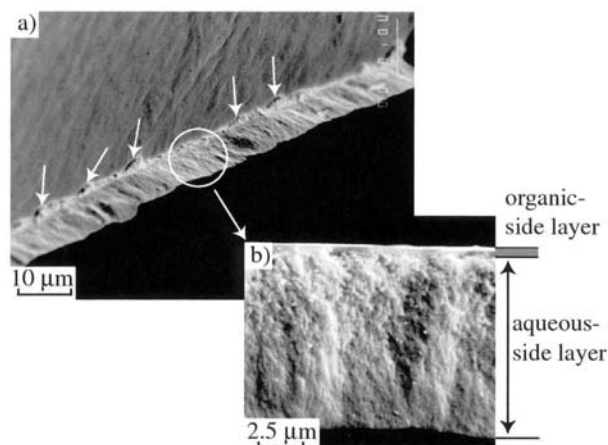


Figure 2. SEM micrographs of a PbO₂ thin film prepared at 1.25 V: (a) a view from the organic side of the film and (b) a cross-sectional view.

(less than 1 μm thick) on the organic side and a layer (about 10 μm thick) on the aqueous side. Furthermore, Figure 2(a) showed that the organic-side layer peeled away here and there (as indicated by the white arrows). The occurrence of the peeling areas was attributed to the difference in the structure between both sides of layers. Also, the authors^{2,5} confirmed that metal films electrodeposited at the liquid-liquid interface had two layers. These observations coincide with the results in this study: filmy deposit grows along the interface by both anodic and cathodic depositions.

Figure 3 shows the X-ray diffraction patterns of the film. As a reference, the diffraction pattern of deposit on a platinum plate is shown in Figure 3(c). Figures 3(a) and (b) were measured by incidence of X-ray on the surfaces of organic- and aqueous sides of the film, respectively. All the diffraction patterns shown in Figure 3 are generally consistent with the pattern for powdered $\beta\text{-PbO}_2$.⁶ However, each of the fractions of the relative peak intensity was different from those fractions of the powdered $\beta\text{-PbO}_2$. Figure 3(b) showed strong (200) reflection. This pattern is almost consistent with that on the Pt plate. As shown in Figure 3(a), (200) reflection was weakened, but (110) and (101) reflections were strengthened. Reflections indicated at low angles are considered to reflect the orientation near the surface because of the large absorption coefficient of PbO_2 .⁷ Therefore, the whole film deposited at the interface is identified as $\beta\text{-PbO}_2$, while there is a significant difference in the crystal orientation between both sides of the film.

SEM observations and X-ray diffraction patterns revealed that PbO_2 film consisted of two oriented layers. The crystal ori-

entation of organic-side layer was different from that of the aqueous-side layer. Growth mechanism of the PbO_2 thin film at the interface of two immiscible liquids may be considered as follows. By applying a cell voltage, a very thin layer preferentially grows along the interface continuously. Then, this layer plays a role of a usual solid substrate, and the nucleation and the formation of deposits proceed on the aqueous side of the substrate into the bulk solution. Preferential growth of the layer along the interface is attributed to the change in the surface energy by means of an immiscible two-liquid interface. A detailed study on the role of organic liquid is in progress. Trenouth et al.⁸ carried out the electrodeposition of copper at the interface between air and an electrolyte containing an organic reagent, and observed that initial nucleation occurred at the interface and that followed by growth of the deposit downward to the bulk solution. These suggest that the difference in the growth mechanisms of organic-side and aqueous-side layers of the PbO_2 film brings about the difference in the crystal orientation of both layers.

As indicated in this paper, application of low overpotentials made the PbO_2 film smooth and concentric circle morphology. Although deposition current increases by applying higher overpotential, many deposits nucleate and grow on the aqueous-side layer. Furthermore, on the organic-side layer, the morphology of the growing front changes from concentric circle to branching tip. Branch morphology of the growing front can be explained by DLA (Diffusion Limited Aggregation) model on the electrodeposition in the Hele-Shaw cell⁹ and at the immiscible two-liquid interface.¹⁰ On the other hand, on applying lower overpotentials charge transfer limited condition would be maintained at the growing front. Consequently a radially uniform growth rate is obtained, resulting in a smooth and concentric circle morphology of the film. This study showed that the oxide film as well as metallic films was electrodeposited at the interface between two immiscible liquids. A PbO_2 thin layer was obtained on the organic side. Therefore, this method is expected to be developed to make thin films, by clarifying the conditions of the preferential interfacial growth.

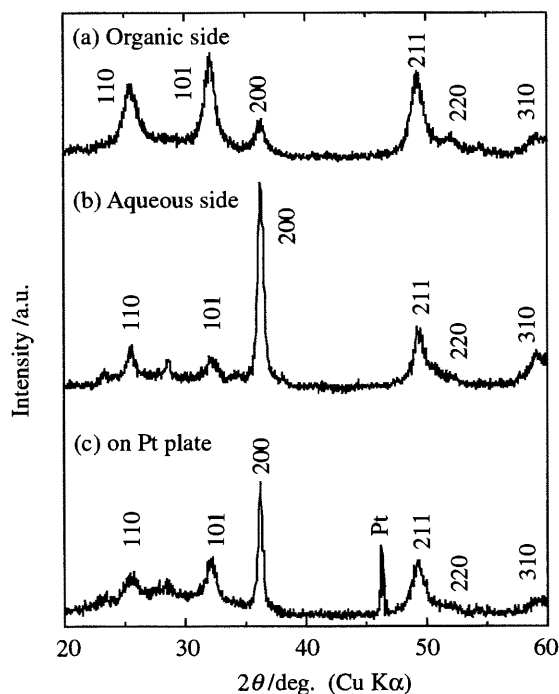


Figure 3. X-Ray diffraction patterns of a film electrodeposited at 1.25 V: (a) organic side of the film, (b) aqueous side of the film and (c) a deposit prepared on a Pt plate at the same potential in the same aqueous solution.

References and Notes

- 1 R. Tamamushi and H. Kaneko, *Electrochim. Acta*, **25**, 391 (1980).
- 2 H. Kaneko, H. Taimatsu, and H. Sakahara, *Met. Trans., JIM*, **34**, 732 (1993).
- 3 H. Kaneko, H. Taimatsu, and T. Takahashi, *Denki Kagaku (presently Electrochemistry)*, **61**, 838 (1993).
- 4 H. Kaneko, H. Taimatsu, and E. Otsuki, *Shindo Gijyutsu Kyokai Shi*, **33**, 175 (1994).
- 5 T. Mitsui and H. Kaneko, *J. Appl. Electrochem.*, **27**, 1100 (1997).
- 6 Joint Committee on Powder Diffraction Standards 351222.
- 7 R. G. Barradas and A. Q. Contractor, *J. Electroanal. Chem.*, **138**, 425 (1982).
- 8 J. M. Trenouth, R. A. Dilorio, and A. J. Sukava, *J. Electrochem. Soc.*, **122**, 43 (1975).
- 9 For example, G. L. M. K. S. Kahanda and M. Tomkiewicz, *J. Electrochem. Soc.*, **136**, 1497 (1989).
- 10 M. Matsushita, M. Sano, Y. Hayakawa, H. Honjo, and Y. Sawada, *Phys. Rev. Lett.*, **53**, 286 (1984).