



Electrochemical Behavior of Thin Platinum(111) Films Deposited on Mica Surfaces

Hsue-Yang Liu, Fu-Ren F. Fan, and Allen J. Bard*

Department of Chemistry, The University of Texas, Austin, Texas 78712

Atomically smooth Pt electrode surfaces are usually prepared from single crystals and are, of necessity, of limited area. It is possible to prepare "smooth" electrode surfaces by mechanical polishing with a fine polishing agent (e.g., 0.1 μm alumina), but such surfaces are only macroscopically smooth (e.g., with asperities $>1000\text{\AA}$). An alternative approach is to deposit a thin film onto a smooth substrate such as flat glass or quartz. One problem with this approach is the weak adhesion of a thin metal film to the substrates, especially when the electrode is immersed in liquid and subjected to an applied electrode potential. Mica is a naturally occurring material that can be cleaved to produce an atomically smooth surface. It has been used to prepare epitaxially grown single-crystal films (1-9) for UHV experiments, and films of Ag and Au on mica have been applied to electrochemical measurements (8, 9). Thin Ag(111) films have been prepared to study electroreflectance (9a) and to investigate the migration of complexes (8) at electrode/electrolyte interfaces. Au(111) (9b) films were utilized to examine the hydrogen adsorption isotherm in acidic solutions. In this paper, we report the preparation of smooth Pt(111) films grown on freshly cleaved mica surfaces and the electrochemical behavior of such films in aqueous and non-aqueous solutions.

The thin platinum films were prepared by RF sputtering at 2×10^{-4} torr under Ar flow with a Materials Research Corporation Model MRC 8620 triple shutter RAD sputtering module. Films 1000\AA thick were prepared at a deposition rate of $10\text{\AA}/\text{s}$. Before deposition, a thin sheet was first peeled off from a thick mica plate (grade 2, ruby c.c.s. mica sheet, United Mineral and Chemical) in air. Mica has been used frequently for surface studies (1-7), and techniques like multiple beam interferometry (10)

can be used to confirm the perfect cleavage and smooth surface.

The crystallography of the resulting platinum film deposited on the mica surface was examined using x-ray diffraction techniques. Figure 1 shows spectra obtained at bare (B) and Pt-deposited (A) mica surfaces. Although the background spectrum (Fig. 1B) due to the bare mica surface is relatively complicated, a peak at $2\theta = 39.5^\circ$ (Fig. 1A) that arises from Pt(111) (ASTM no. 4-0802) can be clearly identified. No peaks associated with other crystal phases were found, so that the crystal phase of the resulting platinum film is clearly (111). Scanning electron microscopy (SEM) was used to check the smoothness of the thin Pt(111) film. There were no distinguishable island features at up to $40,000\times$ magnification. These results indicate that a smooth thin Pt(111) film can be readily prepared on the mica surface (1, 2a).

For electrochemical measurements, the thin platinum film was connected with conductive silver paint (Acme Chemicals and Insulation Company) to a copper wire lead in a glass tube. The electrode surface was masked by 5 min epoxy and silicone rubber cement, except for the area to be examined. The cyclic voltammogram (CV) obtained at the thin platinum film in a solution of $0.5M$ H_2SO_4 is shown in Fig. 2A. The nature of hydrogen adsorption and oxide film formation on platinum single-crystal electrodes have been the subject of many studies (11-16). As shown in Fig. 2A, at the Pt/mica electrode in the hydrogen adsorption region, only a single peak at $-0.2V$ is observed. These results, when compared with those reported previously under similar experimental conditions (11, 13a), show that the thin platinum film used in the present study behaves as a Pt(111) surface. Therefore, the electrochemical results as consistent with the assignment of the Pt(111) surface as deduced from the

* Electrochemical Society Active Member.

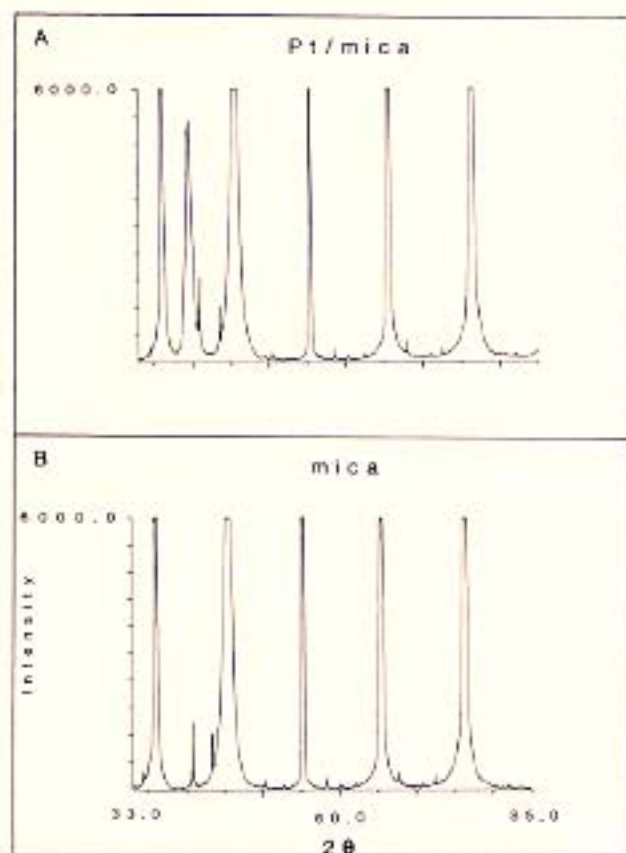


Fig. 1. X-ray diffraction spectra of Pt-deposited mica surface (A) and bare mica surface (B).

x-ray diffraction data. The thin Pt film became flaky if the electrode potential was repeatedly scanned over the hydrogen evolution region. This probably can be attributed to penetration by hydrogen into the platinum lattice.

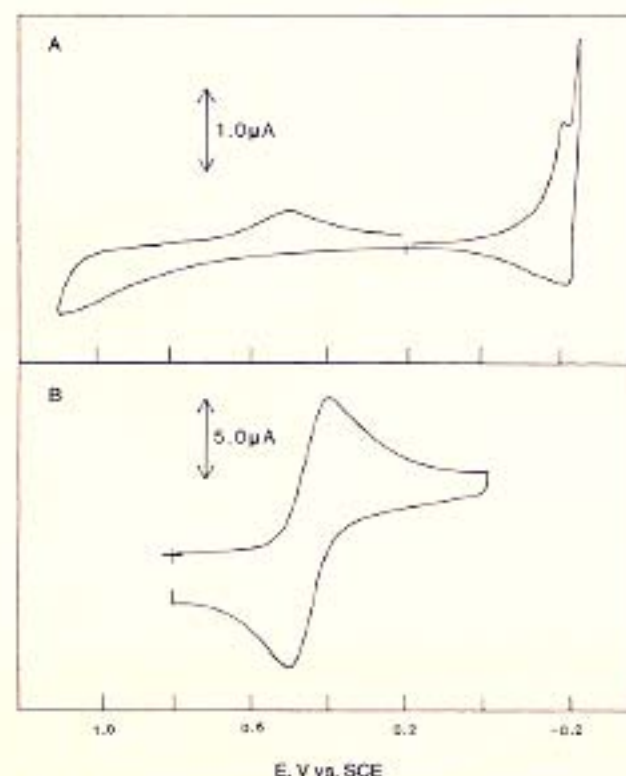


Fig. 2. A: Cyclic voltammogram of thin Pt(111) film in 0.5M H_2SO_4 . Electrode area: 0.08 cm^2 , Scan rate: $10 \text{ mV}\cdot\text{s}^{-1}$. B: Same as A, except the solution containing $1.4 \text{ mM Fe(CN)}_6^{4-}$, Scan rate: $50 \text{ mV}\cdot\text{s}^{-1}$.

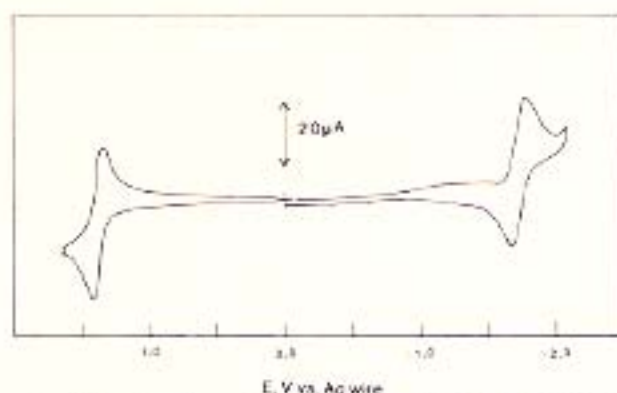


Fig. 3. Cyclic voltammogram of 1 mM DPA in 0.1 M TBAF/MeCN solution at 0.12 cm^2 thin Pt(111) film. Scan rate: $100 \text{ mV}\cdot\text{s}^{-1}$.

However, this thin film was very stable if the electrode potential was not allowed into the hydrogen adsorption or evolution region. The response of Fe(CN)_6^{4-} at this thin platinum film is given in Fig. 2B. The electrode could be scanned repeatedly over these potentials without loss of Pt from the surface. The observed behavior is similar to that found with bulk Pt electrodes.

To demonstrate the usefulness of this smooth thin Pt(111) film in nonaqueous media, cyclic voltammetry of 9,10-diphenylanthracene (DPA) carried out in MeCN-0.1M tetrabutylammonium fluoroborate (TBAF) solution (Fig. 3). Both reversible reduction ($\text{DPA} \rightarrow \text{DPA}^-$) and oxidation ($\text{DPA}^- \rightarrow \text{DPA}$) reactions were observed. The thin platinum film was stable in the solution on repeated scanning of the electrode potential between +1.65 and -2.1V vs. Ag wire. Electrogenerated chemiluminescence (ECL) was also observed with this thin platinum film in the same solution for potential steps (50 ms) between +1.65 and -2.1V. In past studies, we found that Pt films sputtered on glass would peel from the substrate when subjected to such large potential excursions, presumably because of the significant changes of surface tension at the Pt/solution interface.

The possible application of thin Pt films deposited on mica as optically transparent electrodes (OTE) (17) was also examined. A 500Å Pt film on mica is transparent in the visible region with relatively constant absorbance (ca. 1.0) with an associated sheet resistance of about $15 \Omega/\square$. These results are comparable to those reported for Pt deposited on quartz (17). However, as demonstrated above, the Pt film on mica appears to show better mechanical stability.

In conclusion, the experiments described here indicate that smooth thin Pt(111) films can be easily prepared on cleaved mica surfaces. Our results also show that these thin films are stable in aqueous and nonaqueous media during electrochemical experiments. Mica surfaces can be used as smooth templates to prepare a wide range of thin film electrodes. We are especially interested in such electrodes for the construction of an ultrathin layer electrochemical cell using mica balance techniques (18). Studies of this application and further characterization of these films are currently under investigation in this laboratory.

Acknowledgment

The support of the National Science Foundation (CHE8402135) and IBM is gratefully acknowledged.

Manuscript submitted June 7, 1985; revised manuscript received Aug. 27, 1985.

The University of Texas assisted in meeting the publication costs of this article.

REFERENCES

1. J. W. Matthews, "Epitaxial Growth, Part B," Chap. 9, Academic Press, New York (1975).
2. (a) R. L. Palmer and J. N. Smith, Jr., *J. Chem. Phys.*, **60**,

- 1453 (1974); (b) D. G. Welke, M. G. Lagally, and R. L. Palmer, *J. Vac. Sci. Technol.*, **17**, 453 (1980).
3. M. Barkai, E. Grunbaum, and G. Deutscher, *Thin Solid Films*, **90**, 85 (1982).
4. J. Koshy, *ibid.*, **41**, 1, 13 (1977).
5. M. H. B. Stiddard, *ibid.*, **94**, 1 (1984).
6. A. I. Dawar, A. Kumar, R. P. Mail, and P. C. Mathur, *ibid.*, **112**, 107 (1984).
7. J. Caballero, G. Kremer, and L. A. Moraga, *ibid.*, **117**, 1 (1984).
8. (a) R. Waser and K. G. Weil, *J. Electroanal. Chem.*, **150**, 89 (1983); (b) R. Waser and K. G. Weil, *Z. Phys. Chem. N. F.*, **139**, 203 (1984).
9. (a) D. M. Kolb and R. Kotz, *Surf. Sci.*, **64**, 96 (1977); (b) D. A. Scherson and D. M. Kolb, *J. Electroanal. Chem.*, **176**, 353 (1984).
10. S. Tolansky, "Multiple-Beam Interferometry of Surfaces and Films," Oxford University Press, London (1949).
11. A. T. Hubbard, *Acc. Chem. Res.*, **13**, 177 (1980).
12. K. Yamamoto, D. M. Kolb, R. Kotz, and G. Leimpfuhl, *J. Electroanal. Chem.*, **96**, 233 (1979).
13. (a) W. E. O'Grady, M. Y. C. Woo, P. L. Hagans, and E. Yeager, *J. Vac. Sci. Technol.*, **14**, 365 (1977); (b) A. S. Homa, E. Yeager, and B. D. Cahan, *J. Electroanal. Chem.*, **150**, 181 (1983).
14. (a) F. T. Wagner and P. N. Ross, Jr., *ibid.*, **150**, 141 (1983); (b) P. N. Ross, Jr., *ibid.*, **76**, 139 (1977).
15. B. E. Conway, H. Angerstein-Kozolowska, and F. C. Ho, *J. Vac. Sci. Technol.*, **14**, 351 (1977).
16. F. Will, *This Journal*, **112**, 451 (1965).
17. W. R. Heineman, F. M. Hawkridge, and H. N. Blount, in "Electroanalytical Chemistry," Vol. 13, A. J. Bard, Editor, Marcel Dekker, New York (1984).
18. (a) J. N. Israelachvili and G. E. Adams, *Nature*, **262**, 774 (1976); (b) J. N. Israelachvili, *J. Colloid. Interface Sci.*, **44**, 259 (1973); (c) J. N. Israelachvili and G. E. Adams, *J. Chem. Soc. Faraday Trans. 1*, **74**, 975 (1978); (d) H. K. Christenson, *J. Chem. Phys.*, **78**, 6906 (1983); (e) P. F. Luckham and J. Klein, *J. Chem. Soc. Faraday Trans. 1*, **80**, 865 (1984); (f) H. K. Christenson and R. G. Horn, *J. Colloid Interface Sci.*, **103**, 50 (1985).