THE PREPARATION OF PLATINUM AND GOLD SINGLE CRYSTAL SURFACES AND VOLTAMMETRIC BEHAVIOURS OF THESE ELECTRODES

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ABSTRACT

The surface crystal structures of polycrystalline electrodes that are not stable and the difficulties in obtaining reproducible results lead to several difficulties in working with such electrodes. For this reason especially in the recent years intensive search is being carried out. For this goal noble metal platinum is especially selected because of its high electrocatalytic effect. But obtaining single crystal surfaces and preparing electrode from these surfaces turn out to be difficult. During the thermal procedure, surface changes and due to the pretreatment that are adapted different current-potential curves are obtained.

In this review by giving the preparation methods of single crystal platinum and gold electrodes voltammetric studies have been explained with these electrodes.

1. INTRODUCTION

Electrocatalysis on single crystal surfaces has attracted the attention of those who work in this field of catalysis, as well as those who work in the field of chemical catalysis, because both types of catalysis are considered to be equally structure-sensitive. The study of electrocatalysis on well-defined single crystal surfaces is necessary to elucidate the structure dependence of this type of catalysis.

Platinum is a suitable material for single crystal study of electrocatalysis because of its high electrocatalytic activity for many reactions as shown by abundant information hitherto reported on polycrystalline samples. On the other hand gold has the widest double-layer region, among all the noble metals (37). This region covers 0.4-0.8 V in Pt, 0.3-0.5 V in Rh and 0.2-0.8 V in gold. That is why gold is the most suitable metal to investigate most of organic reactions.
However, the preparation and the conservation of well-defined single crystal surface encounter many difficulties. A surface of single crystal exposed by cutting to a direction parallel to the not plane having this index. The roughness factor of a true single crystal surface should ideally be unity.

Of course the kinetic parameters of the oxide growth could be dependent on the crystallographic orientation of the surface. Hence, measurements at polycrystalline metals are not very suitable for investigations of thin epitactic layers and monolayer effects, which could differ on different planes.

**EXPERIMENTAL**

Preparation of Pt and Au Single Crystals

A bead single crystal was prepared by the method of Kaischew (63) as modified by Clavilier et al (33). The crystallographic axes of the crystal were determined optically, using as a guide the laser beam spots on a wall, as reflected by the (111) facets on the bead surface. Then the crystal imbedded in resin was cut with a diamond cutting wheel to give the (111) face. This surface was then polished to optical flatness using a 0.1 µm diamond paste for the final finish. After the resin was removed, a Pt lead wire and Pt-Rh wire, which were used as a thermocouple for the exact measurement of temperature, were welded onto the sample at the opposite side of the surface. The (111) face thus obtained was annealed at 1100°C in a hydrogen-oxygen flame or in a small electric furnace specially designed for this purpose (74) (Fig 1) under an argon flow, and then cooled by a droplet of a ultrapure water in similar way to that used by Clavilier et al (33) or cooled in various atmospheres.

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**Fig. 1.** Electrode holder (part A) connected to the heat treatment furnace (part B), (C) inlet for atmospheric gas, (D) inlet for inert gas.
Figure 1 shows an electrode holder (part A) put in contact with a small furnace (part B; fused silica tube of 10 mm diameter); the narrow gap at the contact between the two tubes served as a gas exit. Atmospheric gas was introduced from the gas inlet of the furnace (C on the left), and inert gas was introduced from the gas inlet the electrode holder (D on the right).

The sample was supported by Pt and Pt-Rh wires, used as thermocouple wires, which were shielded in a Pyrex tube of 6 mm diameter, serving as a moving rod. After being cooled the sample was brought into the electrode holder tube by shifting the moving rod, and then the sample, together with the electrode holder, was transferred under the protection of an argon flow in the electrochemical cell. The Pt(111) surface was brought into contact the solution surface as schematically shows in Fig 2, in the way done by Clavilier et al (33).
Another way of the preparation of single crystals have been found by Faure (44). Roughly speaking, it consists in fusing a high purity platinum wire in H₂-O₂ low pipe, and in slowly cooling the spherical platinum droplet thus obtained, which solidifies as a single crystal. This crystal (about 3 mm in diameter), is X-ray oriented, then it is cut along a diametral plane. The surface is in turn, mechanically polished, to adjust accurately, its orientation, with 0.2°C. Finally, two platinum wires are welded at the back crystal to provide means of holding and heating it, together with the two wires of a platinum, platinum-rhodium thermocouple, and the crystal is carefully annealed in the low-pipe flame. The sample surface is cleaned in ultra high vacuum (UHV) by argon bombarding and annealing.

Gold single crystals (length 15 cm, diameter 4mm) are prepared from 99.999 % gold in a vacuum furnace using the Czochralski method (13). The crystals are electrolytically cut and planed using a spark erosion machine parallel to the (100) and (111) plane respectively, which is perpendicular to the axis of the crystal rod. Then the crystal surface is etched in aqua regia and polished electrolytically in a cyanide electrode. Finally, the crystals are annealed in a high vacuum at 830°C for 6h to minimize the number of dislocations. To examine the crystal surface, Laue back scattering diagrams are recorded using an X-ray diffractometer. It could be shown by these Laue diagrams that the spark erosion disturbed a thin surface layer only, which is removed completely by the subsequent etching and polished. Hence the Laue diagrams of the polished and annealed (111) and (100) planes have shown clearly-defined spots in a hexagonal or tetragonal symmetry, giving evidence for the correct orientation of the crystal plane (38,39). The crystals are fixed on a stainless steel holder by conducting glue containing graphite. To remove impurities from the surface, the crystals are washed in acetone, concentrated HNO₃, distilled water.

In single crystal experiments, it is always difficult to cover the planes of differing orientation, surrounding the working area. In general, teflon or epoxy resins are used. However, a teflon cover is not really tight and resins might contaminate the surface. Dickertmann et al (39) avoided these problems by the use of an usual cell the design, which is schematically shown in Fig 3. The nozzle of the syringe is situated some millimeters above the crystal surface to be examined (working electrode, WE). The syringe contains the electrolyte and the gold wire as counter (CE). At the beginning of the experiment, a few drops of the electrolyte are placed on the surface. The solution wets the exposed surface (about 0,12 cm²) completely. As there is a contact angle of about 50 degrees, the electrolyte can be kept on the plane and does not touch the sides of the crystals rod. Thus side effects and contamination are eliminated.
Fig. 3. Schematic diagram of the cell for single crystal surface experiments (WE) working electrode, (RE) reference electrode, (CE) counter electrode.
However, preparation and conservation of well-defined single crystal surfaces encounter many difficulties. Both rigorous cleaning and annealing in an ultra clean atmosphere are required. Structural changes caused by different cooling atmospheres bombardment with high energy particles.

Due to the simple preparation technique and stability of preferentially oriented electrode surface it appears to be interest i) to study the structural effects of these electrodes in electrocatalysis, ii) to prepare practical electrodes out of polycrystalline material with catalytic properties similar to single crystal structures.

However, an important in such studies is the accurate surface characterization. A knowledge of the surface topography is necessary in order to correlate surface structure with electrocatalytic activity. The most direct monitoring of surface structure is by means of optical techniques such as AES (Auger electron spectroscopy) and LEED (low energy electron diffraction) (1, 18, 19, 25, 26, 36, 40, 41, 43, 46-51, 57, 59, 60, 64, 66, 70-73, 76-83, 87, 88, 90, 96, 102, 103). But it is not possible interpret a LEED pattern obtained from faceted polycrystalline electrodes, which are of practical interest.

On the other hand, it was found recently that changes in the surface structure of a polycrystalline material can be produced by electrochemical procedures (16, 17, 20-24, 74, 93). Preferentially oriented polycrystalline platinum surfaces can be obtained by applying fast periodic potential perturbations under well-defined potential limits and frequency conditions. Especially Cervino et al (20) have made the fingerprints that the hydrogen adatom voltammetric fingerprints of platinum single crystal surface can be obtained via an electrochemical preparation of polycrystalline platinum material. The treatment consists in application of a very fast potential scan to the polycrystalline material in aqueous electrolytes. In a typical approach scan rates between 1000 and 15000 V/s and 1 M H$_2$SO$_4$ solution are used. Applying a fast potential scan in the range of 400 to 1600 mV (NHE) results in an electrode surface which according to the voltammogram in the same electrolyte at conventional sweep rates, e.g. 0.1 V/s exhibit the characteristics of that described for Pt (111) single crystal electrodes while at scan rates between 1 and 100 V/s a typical increase of the platinum surface is observed.

A voltammogram run immediately after the preparation of the platinum surface shown in Fig. 4a, by applying a symmetrical triangular potential scan of 100 mV/s in the 40-1500 mV range. (Fig 4b) shows a close resemblance with the characteristics of a Pt (111) single crystal surface. The mosaic structure of Fig 4 which includes step is obviously different from the surface morphology of the untreated sample (Fig. 5a). Fig 5b shows for comparison the voltammogram of the starting polycrystalline platinum electrode under the same conditions as in Fig. 4b.
Fig. 4. (a) Scanning electron micrograph (magnification 2300) for a polycrystalline platinum wire after a repetitive potential scan at 10000 V/s during 12 h between 420 and 1080 mV NHE in 1.0 M H₂SO₄ (b) the corresponding cyclic voltammogram in 1.0 M H₂SO₄ 100 corresponding cyclic voltammogram in 1.0 M H₂SO₄, 100 mV/s.

Fig. 5. (a) Scanning electron micrograph (magnification 2300) of a polycrystalline platinum wire and (b) the corresponding cyclic voltammogram in 1.0 M H₂SO₄, 100 mV/s.
Another micrograph was obtained for a polycrystalline Pt wire after the application of a 1400 V/s potential scan between 23 and 1320 mV for 12 h (Fig.6a). The surface appears to be smoother than after the first treatment and exhibits a parallel-channel-like structure. In this case, the voltammogram run at 100 mV/s between 40 and 1500 mV. (Fig. 6b), resembles closely that describes in the literature for the Pt (100) single crystal surface.

![Image](image_url)

**Fig. 6.** (a) Scanning electron micrograph (magnification 2200) of a polycrystalline platinum wire after a repetitive scan at 1400 V/s during 12h between 23 and 1320 mV NHE in 1.0 M H₂SO₄, (b) the corresponding cylic voltammogram in 1.0 M H₂SO₄, 100 mV/s.

Finally, it should be noticed that the preferentially oriented surfaces of polycrystalline platinum induced by fast potential perturbations correspond to structural changes in the surface which are comparable to those achieved from the thermal and chemical pretreatments, applied to either single or polycrystalline platinum and followed by voltammetry.

**RESULTS AND DISCUSSION**

The voltammetric curves with Pt and Au Single Crystal Electrodes.
The electrochemical behavior of platinum single crystal surfaces has been studied by several authors (8, 9, 11, 33, 87, 93, 104-106). On the other hand, electrochemical adsorption desorption of hydrogen has been shown to be a structure-sensitive reaction (12, 27, 30-33, 35, 60, 77, 85, 86, 92, 103). The kinetics of typical electrocatalytic reaction are likely to depend on the structure of the electrode surface. The influence of surface structure on the kinetics of an electrocatalytic reaction can be studied directly using single crystal surfaces. Clavilier and Armand (30) were investigated electrochemical induction of changes in the distribution of the hydrogen adsorption states on Pt (100) and Pt (111) in contact with sulfuric acid solution. They showed Pt(100) undergoes reversible electrochemical surface transformation while in contrast the Pt (111) surface, under the same conditions is changed irreversibility (Fig 7). According to Hubbard et al (60) Pt (100) surface is stable in aqueous electrolytes such as H₂SO₄, HClO₄ and HCl in the −0.2 V to, 1.2 V potential range. Similarly Pt (111) surface is stable in aqueous electrolyte. This has only recently been confirmed by reports of pronounced structural effects on the kinetics of formic acid (3, 4, 9, 15, 34, 67, 75), methanol (3, 29, 67) and formaldehyde (3) on single crystal platinum surfaces and of O₂ reduction on single crystal gold electrodes (4, 6, 7, 61, 91). On the other hand the adsorption and oxidation of carbon monoxide have been extensively studied in the gas phase on platinum single crystals (14, 43, 58, 67-69, 84, 89, 94).

![Figure 7](image.png)

Fig. 7. Cyclic voltammetry of a Pt (100) single crystal in 0.5 M H₂SO₄, (----) compared to the Pt (111) crystal (-----), 50 m V/s.
It has been recently pointed out (92) that the cyclic voltammogram of Au (111) in 0.5 M H₂SO₄ exhibits features bearing striking similarity to the anomalous peak found for Pt (111) in such a solution. In addition the charges under the peaks for Au (111) evaluated from I⁻ and SO₄²⁻ was found to range between 55-90 µC/cm², discharged univalent species. For instance, the case of Au (111) in 0.5 M H₂SO₄ is shown in Fig 8 (solid line) in which such a feature occurs at 0.72 V vs SCE. A spike is also observed in case of Au (111) in 0.01 M CsCl (dotted curve in Fig 8) at 0.68 V vs SCE which is precisely at the same potential where the capacitance as measured in a Cl⁻ containing electrolyte of a same concentration exhibit a sharp spike (56). Furthermore, the potential at which the spike occurs is a function of the anion concentration (28,52-56,92,97-101). A comparison of the voltammetric curves for Au (111) films grown epitaxially on mica, in solutions containing different anions (Fig 8) indicates that the spike shifts in the negative direction as the ability of the anion to undergo specific adsorption increases, i.e. SO₄²⁻ < Cl⁻ < Br⁻. This correlation is in complete agreement with the results obtained by Clavilier on Pt (111) referred to earlier if it is assumed that the ability of amino to undergo specific adsorption on this metal surface increases following the sequence ClO₄⁻ < SO₄²⁻ < Cl⁻. (27). The fact that the region of potentials involved in the voltammetric feature on Au (111) electrodes is greater than the Pt (111) (Fig. 9) may be due to differences in the adsorption isotherms for these surfaces in the case of Pt (111) with a region of potentials much narrower then for Au (111).

**Fig. 8.** Linear sweep voltammogram for Pt (111) in 0.5 M H₂SO₄, 50 m V/s.
Fig. 9. Linear sweep voltammograms for Au (111) on mica in 0.01M Cs Cl (----) and 0.01 M Cs Br (-----), sweep rate 50 m V/s (left-hand side current density axis), and 0.5 M H₂SO₄ (-----), sweep rate 10 m V/s (right-hand side axis).

For various metal adatoms, extensive work has been done by Pt and Au single crystal electrodes. For example, the under potential deposition (UPD) of lead on Pt (100) (2, 5, 41, 42, 45, 61, 62, 65) and gold single crystals (10). On the other hand electrocatalysis works of oxygen and hydrogen peroxide reduction single crystal gold electrodes have been made by several researches (4-8, 61, 62, 91).

In recent years studies concerning the effects of electrocatalysis and various metal atoms using gold and platinum single crystal electrodes have increased considerably.

REFERENCES


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