Commun. Fac. Sci. Univ. Ank. Series B
V. 45. pp. 67-84 (1999)

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

S. BİLGİÇ

Ankara University, Faculty of Science, Department of Chemistry, 06100 Tandoğan, Ankara, TURKEY

(Received May 20, 1999; Accepted June 24, 1999)

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 $1100\,^0$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.

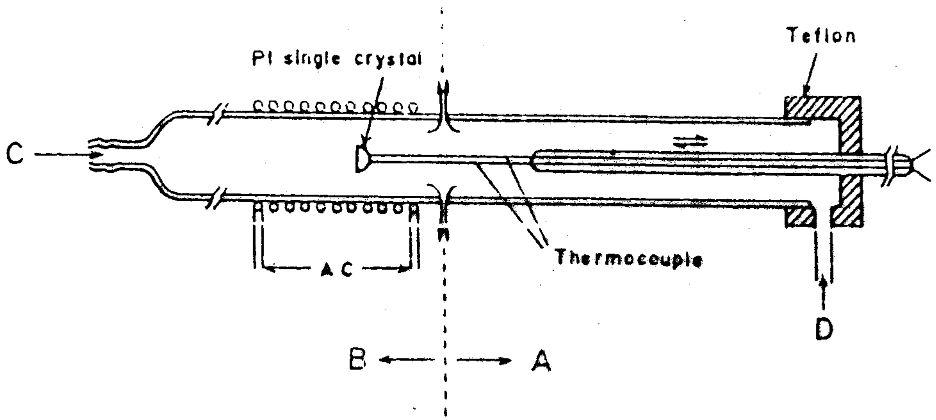

Fig. 1. Electrode holder (part A) connected to the heat treatment furnace (part B), (C) inlet for atmospheric gas, (D) inlet for inert gas.

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).

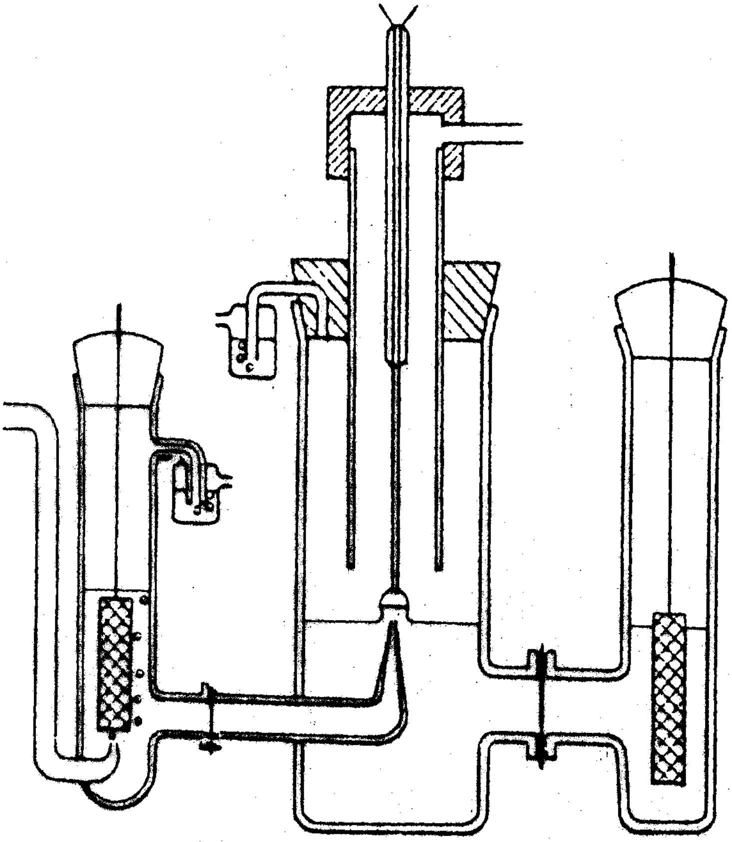

Fig. 2. Measurement cell assembly.

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 H_2-O_2 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 0.2^0C. 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 830^0C 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 HNO_3, 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 contamine 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 cm^2) 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.

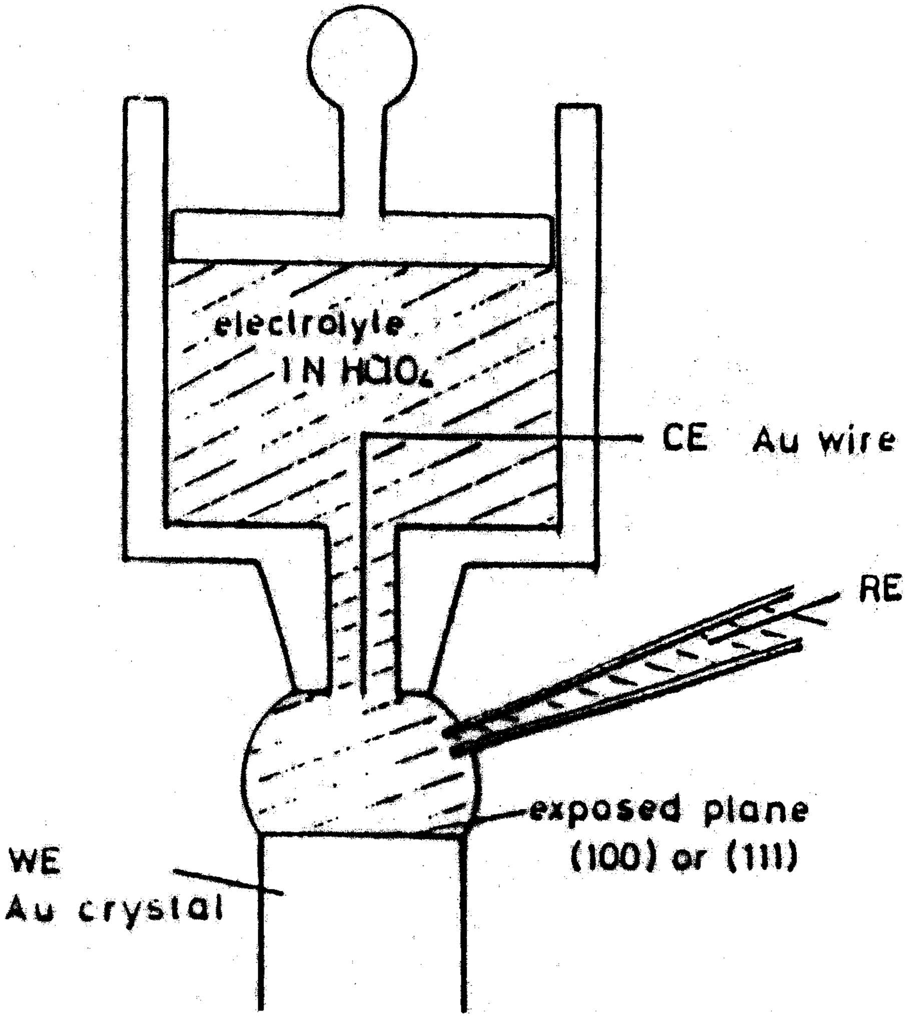

Fig. 3. Schematic diagram of the cell for single crystal surface experiments (WE) working electrode, (RE) reference electrode, (CE) counter electrode.

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_2SO_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 convential 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.

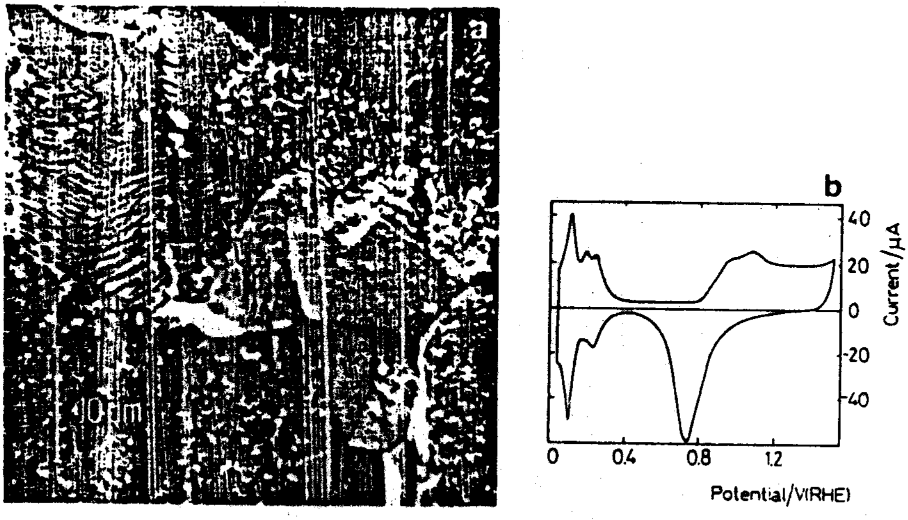

Fig. 4. (a) Scanning electron micrograph (magnification 2300) for a polycrystalline platinum wire after a repetitive potential scan at 10000 V/s during 12 h between 420 and 1080 mV NHE in 1.0 M $H_2 SO_4$ (b) the corresponding cylic voltammogram in 1.0 M $H_2 S O_4$ 100 corresponding cylic voltammogram in 1.0 M $H_2 S O_4$, 100 mV/s.

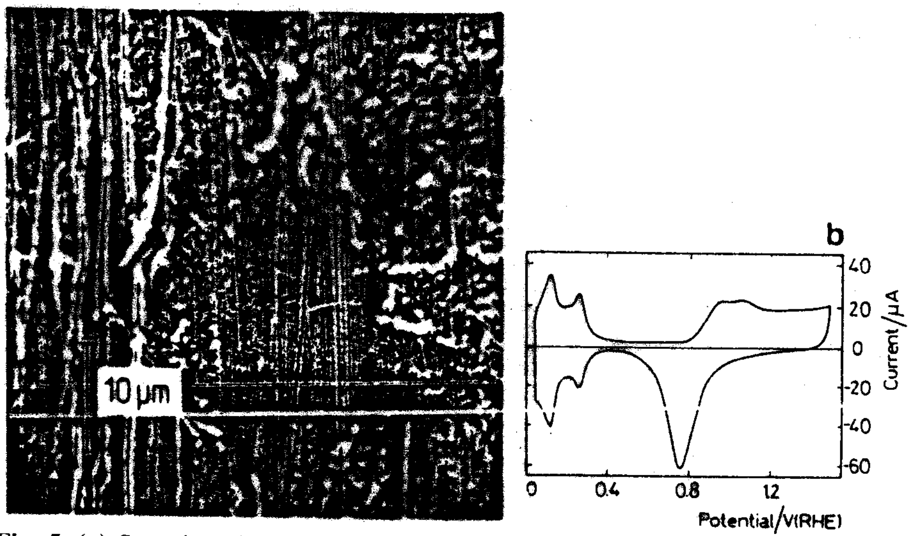

Fig. 5. (a) Scanning electron micrograph (magnification 2300) of a polycrystalline platinum wire and (b) the corresponding cyclic voltammogram in 1.0 M $H_2 SO_4$, 100 mV/s.

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

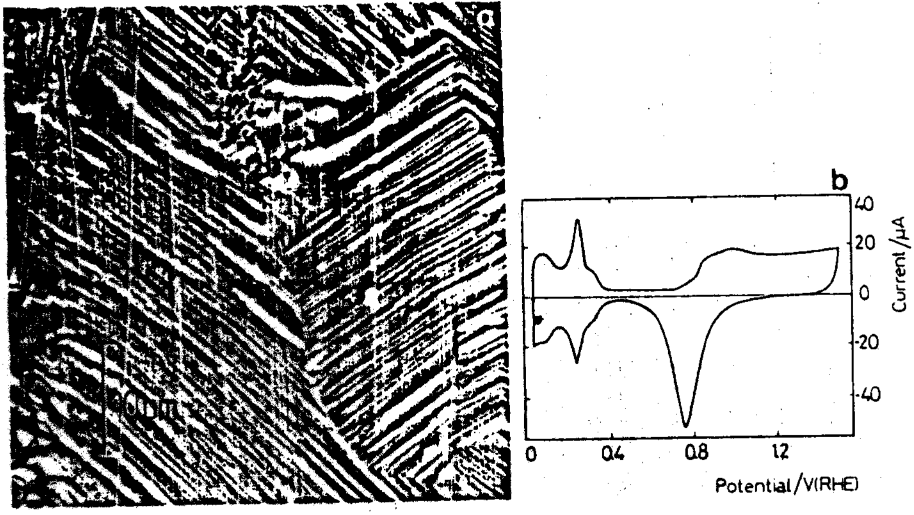

Fig. 6. **(a)** Scanning electron micrograph (magnification 2200) of a polycrystalline platinum wire after a repetitive scan at 1400 V/s during 12h between 23 and 1320 mV NHE in 1.0 M H_2 SO_4, (b) the corresponding cylic voltammogram in 1.0 M H_2 SO_4 , 100 m V/s.

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 these 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 H_2SO_4, $HClO_4$ and HCl in the –0.2 V to, 1.2 V potential range. Similarly Pt (111) surface is stable in aqeuous 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 O_2 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).

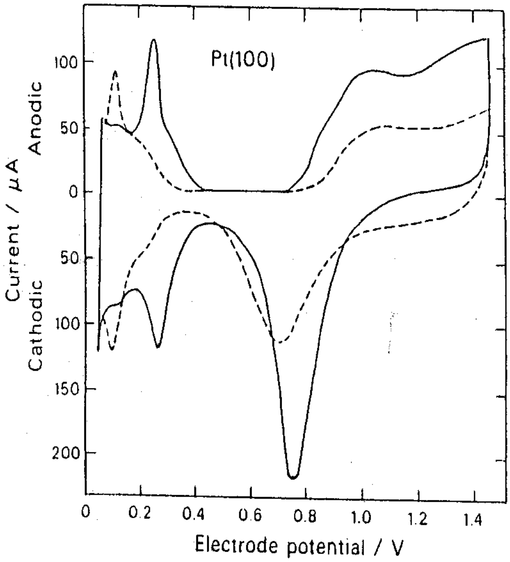

Fig. 7. Cylic voltammetry of a Pt (100) single crystal in 0.5 M H_2SO_4, (----) compared to the Pt (111) crystal (-----), 50 m V/s.

It has been recently pointed out (92) that the cyclic voltammogram of Au (111) in 0.5 M H_2SO_4 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 SO_4^{2-} was found to range between 55-90 μCcm^{-2}, discharged univalent species. For instance, the case of Au (111) in 0.5 MH_2SO_4 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 the undergo specific adsorption increases, i.e. SO_4^{2-}<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 ClO_4^- <SO_4^-<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).

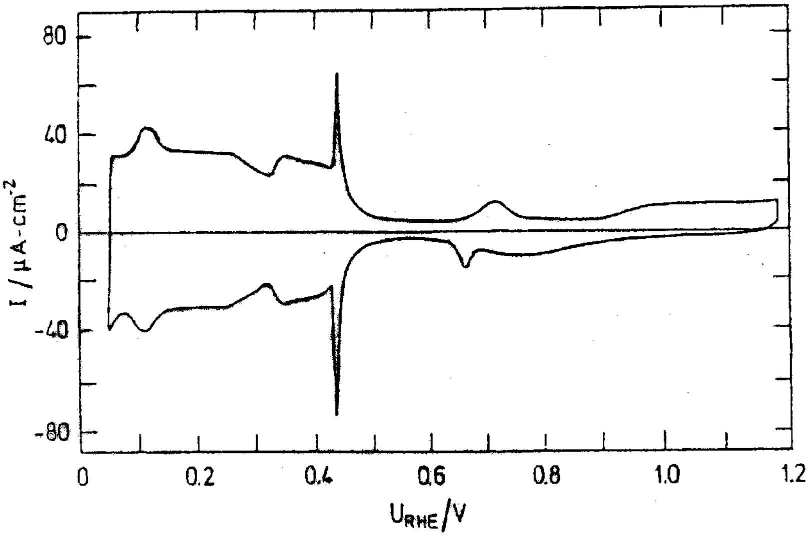

Fig. 8. Linear sweep woltammogram for Pt (111) in 0.5 M H_2SO_4, 50 m V/s.

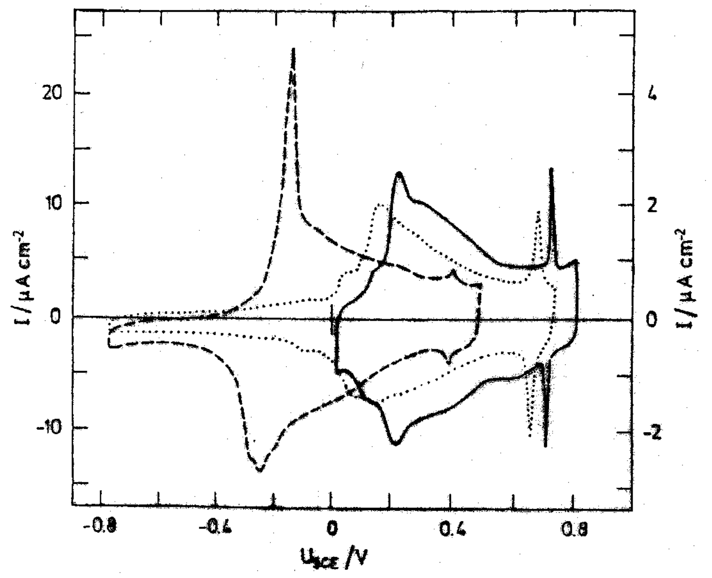

Fig. 9. Linear sweep voltammograms for Au (111) on mica in 0,01M Cs CI (----) and 0.01 M Cs Br (----), sweep rate 50 m V/s (left-hand side current density axis), and 0.5 M H_2SO_4 (----), sweep rate 10 m V/s (right-hand side axis).

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

[1] Aberdam D, Durand R, Faure R, El-Omar F: (1986), Structural Changes of Pt (111) Electrode Induced by Electrosorption of Oxygen in Acidic Solutions: A Coupled Voltammerty LEED and AES Study. Surf Sci 171: 303-330.

[2] Aberdam D, Traoré S, Durand R, Faure R: (1987) Ordered Overlayer of Lead Obtained by Underpotential Desorption on Pt (100), Surf Sci 180: 319-322.

[3] Adžić R R, Tripković A V, O'Grady W E: (1983), Structural Effects in Electrocatalysis. Nature 296: 137-138.

[4] Adžić R,R. Tripković A V, Markovic N M: (1983), Structural Effects in Electrocatalysis: Oxidation Of Formic Acid and Oxygen Reduction on Single Crystal Electrodes and the Effects of Foreign Metal Adatoms. J Electroanal Chem 150: 79-88.

[5] Adžić R, Yeager E, Cahan B D: (1974), Optimal and Electrochemical Studies of Underpotential Deposition of Lead an Gold Evaporated and Single Crystal Electrodes. J Electrochem Soc 121: 474-484.

[6] Adžić R R, Marković N M: (1982), Structural Effects in Electrocatalysis: Oxgen and Hydrogen Peroxide Reduction on Single Crystal Gold Electrodes and the Effects Of Lead Adatoms. J. Electroanal Chem 138:443-447.

[7] Adžić R R, Marković N M, Vesović V B: (1984), Structural Effects in Electrocatalysis Oxygen Reduction on the Au (100) Single Crystal Electrode. J Electroanal Chem 165:105-120.

[8] Adžić R R, Vesović V B: (1984), Structural Effects in Electrocatalysis Oxygen Reduction on the Gold Single Crystal Electrodes with (110) and (111) Orientations. J. Electroanal Chem 165:121-133.

[9] Adžić R R, O'Grady W E, Srinivasan S: (1980), Oxidation of Formic Acid on (100) and (111) Single Crystal Platinum Electrodes. Surf Sci 94: L191-L194.

[10] Alvarez-Rizatti M, Jüttner K: (1983), Electrocatalysis of Oxygen Reduction by UPD of Lead on Gold Single Crystal Surfaces. J Electroanal Chem 144: 351-363.

[11] Andricacos P C, Ross P N: (1984), The Underpotential Deposition of Cu on Pt Single Crystal Prepared in Ultra-High Vacuum System, J Electroanal Chem 167: 301-308.

[12] Bagotzky V S, Vassiliev Y B, I I Pyshnograeva: (1967), Role of Structural Factors in Electrocatalysis: I. Smooth Platinum Electrodes in H_2SO_4. Electrochim Acta 16:2141-2167.

[13] Barett W, Tetalman A S. The Principle of Engineering Material 12. Prentica-Hall, New Jersey, 1973, p 422.

[14] Barteau M A, Ko E I, Madix R J: (1981), The Adsorption of Carbon Monoxide, Molecular Oxygen and Molecular Hydrogen on Platinum (100), Surf Sci 102:99-117.

[15] Bittins-Cattaneo B, Santos E, Vielstich W: (1986), Voltammetry of UPD Copper and Formic Acid as Characterization of Preferentially Oriented Polycrystalline Platinum Surfaces Electrochim Acta 31:1495-1500.

[16] Carnullo J C, Triaca W E, Arvia A J: (1984), Changes in the Electrochemical Response of Polycrystalline Platinum Electrodes Promoted by Fast Repetitive Square Wave Potential Signals. J Electroanal Chem 175:337-340.

[17] Canullo J C, Triaca W E, Arvia A J: (1986), Electrochemical Faceting of Single Crystal Platinum Electrodes. J Electroanal Chem 200:397-400.

[18] Carroll Mc J: (1975), Surface Physics and Catalysis. Surf Sci. 53:297-316.

[19] Castiel D, Dobrzynski D, Spanjaard D: (1977), Surface Phonons and Superstructures, Some Applications, Surf Sci 63:21-32.

[20] Cerviño R M, Arvia A J, Vielstich W: (1985), Scanning Electron Microscopy and Voltammetry of Preferentially Oriented Polycrystalline Platinum Surfaces. Surf Sci 153B:623-628.

[21] Cerviño R M, Triaca W E, Arvia A J: (1985), Voltammetric Comparison Between Platinum with Preferred Orientation and Platinum Single Crystal Electrodes. Electrochim Acta 30:1323-1327.

[22] Cerviño R M, Triaca W E, Arvia A J: (1985), Electrochemical Preparation and Characteristics of Platinum Electrode Surfaces With Preferred Orientations. J Electroanal Chem 182:51-60.

[23] Cerviño R M, Triaca W E, Arvia A J: (1985), A Novel Effect. Changes in The Electrochemical Response of Polycrystalline Platinum Promoted by Very Fast Potential Perturbations. J Electrochem Soc 132:266-267.

[24] Chialvo A C, Triaca W E, Arvia A J: (1984), Changes in the Polycrystalline Gold Electrode Surface Produced by Square Wave Potential Perturbations. J Electroanal Chem 171: 303-316.

[25] Christman K, Ertl G: (1976), Interaction of Hydrogen with Pt (111), The Role of Atomic Steps. Surf Sci 60:365-384.

[26] Clarke T A, Mason R, Tescari M: (1973), The structure of the Pt (100) Surface, Surf Sci 40: 1-14.

[27] Clavilier J,: (1980), The Role of Anion on the Electrochemical Behavior of a (111) Platinum Surface An unusual Splitting of the Voltammogram in the Hydrogen Region, J Electroanal Chem 107:211-216.

[28] Clavilier J, Hamelin A, Valette G: (1967), Etude des Courbes Capacité-Différentielle-Potentiel et Intensité-Potentiel Surles Différents Plans Cristallins d'une Electrode d'or. CR Acad Sci. Paris Sér C 265_1:221-224.

[29] Clavilier J, Lamy C, Leger J M: (1981), Electrocatalytic Oxidation of Methanol on Single Crystal Platinum Electrodes. Comparison with Polycrystalline Platinum. J Electroanal Chem 125: 249-254.

[30] Clavilier J, Armand D: (1986), Electrochemical Induction of Changes in the Distribution of Hydrogen Adsorption States on Pt (100) and Pt (111) Surfaces in Contant with Sulphuric Acid Solution. J Electroanal Chem 199: 187-200.

[31] Clavilier J, Armand D, Wu B L: (1982), Electrochemical Study of the Initial Surface Condition of Platinum Surfaces with (100) and (111) Orientations. J Electroanal Chem 135:159-166.

[32] Clavilier J, Armand D, Sun S G, Petit M: (1986), Electrochemical Adsorption Behaviour of Platinum Stepped Surfaces in Sulphuric Acid Solutions. J Electroanal Chem 2053:267-277.

[33] Clavilier J, Faure R, Guinet G, Durand R: (1980), Preparation of Monocrystalline Pt Microelectrodes and Electrochemical Study of the Plane Surfaces Cut in the Direction of the (111) and (110) Planes. J Electroanal Chem 107: 205-209.

[34] Clavilier J, Parsons R, Durand R, Lamy C, Leger J M: (1981), Formic Acid Oxidation on Single Crystal Platinum Electrodes. Comparison with Polycrystalline Platinum. J Electroanal Chem 124: 321-326.

[35] Clavilier J, Pineaux R: (1965), Comparison de la Dispersion de la Capacité Differentielle des Electrodes de Platine Lisse Monocristallin au Contact d'une Solution Electrolytique Aqueuse ou d'un Mélange de Sels Fondus. CR Acad Sci Paris Sér C 260. 891-894.

[36] Davies J A, Jackson D P, Matsunami N, Norton P R, Andersen J W: (1978), Temperature Dependence of Pt (111) Surface Relaxation. Surf Sci 78:274-294.

[37] Delahay P: Double Layer and Electrode Kinetics. Interscience, New York, 1965, p50.

[38] Dickertmann D, Koppitz F D, Schultze J W: (1976), A Method for Elimination of Side Effects on Electrochemical Measurements of Single Crystals. Electrochim Acta 21: 967-971.

[39] Dickertmann D, Schultze J W, Vetter K J: (1974), Electrochemical Formation and Reduction of Monomolecular Oxide Layers on (111) and (100) Planes of Gold Single Crystals. Electroanal Chem and Interface Electrochem 55:429-443.

[40] Ducros R, Merrill R: (1976), The Interaction of Oxygen With Pt (110), Surf Sci 55:227-245.

[41] Durand R, Faure R, Aberdam D, Traore S: (1989), LEEDS and AES Study of Emersed Platinum Electrodes. A Thermodynamic Interpretation. Electrochim Acta 34:1653-1657.

[42] El-Omar F, Durand R: (1984), Lead Deposition and Nitric Acid Reduction on Pt (100) and Pt (111) Electrodes in Perchloric Acid Solutions. J Electroanal Chem 178:343-350.

[43] Engel T, Ertl G, Eley D D, Pines H and Weisz PB: Advances In Catalysis Vol: 28, Academic Press, New York, 1979, p 1.

[44] Faure R: (1982), Realisation Characterization Physique et Compartemente Electrode Chimique de Faces Monocristalline de Platine D'orientation (100),(111) et (110), Thése de Doctorat, Institut National de Grenoble, Grenoble. (İh. D.)

[45] Faure R, Durand R, Aberdam D: (1989), Couplage Entre Electrochimie et Analyse de Surface: Structure et Composition d'electrodes Monocristallines de Platine Apres Traitements Electrochimiques. J de Chim Phys 86: 1223-1236.

[46] Fedak D G, Gjostein N A: (1966), Structure and Stability of the (100) Surface of Gold. Phys Rev Letters 16:171-175.

[47] Fedak D G, Gjostein N A: (1967), A Low Energy Electron Diffraction Study of the (100), (110) and (111) Surfaces of Gold. Acta Metallur 15: 827-840.

[48] Fedak D G, Gjostein N A: (1967), On the Anomalous Surface Stuctures of Gold. Surf Sci 8:77-97.

[49] Garwood G A, Hubbard A T: (1980), Superlattices Formed by Interaction of Hydrogen Iodide with Pt (111) and Pt (100) Studied by LEED, Auger and Thermal Desorption Mass Spectroscopy. Surf Sci 92:617-635.

[50] Gland J L, Somorjai G A: (1973), Low Energy Electron Diffraction and Work Function Studies of Benzene on Pt (111) and Pt (100) Single Crystal Surfaces. Surf Sci 389:157-186.

[51] Grand J J, Haas T W: (1969), The Structure of The Pt (100) Surface. Surf Sci 18: 457-461.

[52] Hamelin A, Clavilier J, Valette G: (1968), Influence de la Concentration de l'electrolyte Sur Les Courbes Capatice Différentielle-Potentiel des Electrodes d'or Monocristallines au Contacttude L'adsorption de solutions de Sulphate de Potassium. C R Acad Sci Paris Ser C 266:435-438.

[53] Hamelin A, Valette G: (1968), Étude de L'adsorption de La Pyridine Sur des Electrodes d'or Monocristallines D'orientations (111) et (110), C R Acad Sci Paris Sér C 267: 127-131.

[54] Hamelin A, Sotto M: (1970), Role de L'orientation Cristallographiques de L'electrode Sur la Formation et La Réduction de Composés Oxygénés a la Surface d'une Électrode d'or au Contact de Solutions Neutres de Sulfate de Potassium, en Régime Potendiodynamique. C R Acad Sci Paris Ser C 271:609-612.

[55] Hamelin A, Dechy P: (1971), Étude des Courbes Capacité Differéntielle-Potentiel D'electrodes D'or Monocristallines au Contact de Solutions Aqueuses de Bromure de Potassium. C R Acad Sci Paris Ser C 272:1450-1453.

[56] Hamelin A, Bellier J P: (1973), Role de L'orientation Cristallographique dans L'adsorption de L'ion Chlorure sur L'or I Zone $[1\bar{1}0]^*$. J Electroanal Chem 41:179-192.

[57] Heilman P, Heinz K, Müller K: (1979), The Superstructures of the Clean Pt (100) and Ir (100) Surfaces. Surf Sci 83:487-497.

[58] Hofman P, Bare S R, King D A: (1982), Surface Phase Transition in CO Chemisorption on Pt (110), Surf 117: 245-256.

[59] Hubbard A: (1980), Electrochemistry of Well Defined Surfaces: Accounts Chem Res 13:177-184.

[60] Hubbard A, Ishikawa R, Kutakaru J: (1978), Study of Platinum Electrodes by Means of Electrochemistry and Low Energy Diffraction. J Electroanal Chem 86:271-278.

[61] Jüttner K: (1984), Oxygen Reduction Electrocatalysis by Underpotential Deposited Metal Atoms at Different Single Crystal Faces of Gold and Silver. Electrochim Acta 29: 1579-1604.

[62] Jüttner K, Lorenz W: (1980), Underpotential Metal Deposition on Single Crystal Surfaces. Z Phys Chem 122:163-185.

[63] Kaischew R, Mutaftschiew B: (1955), Electrolytische Keimbildung auf Kugelförmigen Pt-Ein Kristallelektroden. Z Phy Chem 204:334-347.

[64] Katekaru J, Garwood G, Hershberger G, Hubbard A: (1982), Structure and Composition of Adsorbed Layers Formed by Sequential Exposure of Pt (100) and Pt (111) to Pairs of Compounds: Solvents and Electrolytic Substances. Surf Sci 121:396-410.

[65] Kokkininidis G, Leger J M, Lamy C: (1988), Structural Effects in Electrocatalysis. Oxidation of D-glucose on Pt(100), Pt(110), Pt(111) Single Crystal Electrodes and the Effect of UPD Adlayers of Pb, TI and Bi, J Electroanal Chem 242: 221-242.

[66] Lang B, Joyner R, Somorjai G: (1972), Low Energy Electron Diffraction Studies in High Index Crystal Surfaces of Platinum. Surf Sci 30:440-453.

[67] Lamy C, Leger J M, Clavilier J, Parsons R: (1988), Structural Effects in Electrocatalysis. A Comparative Study of the Oxidation of Carbon Monoxide, Formic Acid and Methanol on Single Crystal Platinum Electrodes. J Electroanal Chem 150:71-77.

[68] Leger J M, Beden B, Lamy C, Bilmes S: (1984), Carbon Monoxide Electrosorption on Low Index Platinum Single Crystal Electrodes. J Electroanal Chem 170:305-317.

[69] Love B, Seto K, Lipkowski J: (1986), Adsorption of Hydrogen on Stepped Pt Single Crystal Surfaces. J Electroanal Chem 199:219-228.

[70] Lyon L B; Somorjai F A: (1967), LEED Study of Clean (100),(111) and (110) Faces on Platinum. J Chem Phys 46:2539-2550.

[71] Mattera A M, Goodman R M, Somorjai G A: (1967), Leed of the (100) Face of Au, Ag and Pd. Surf Sci 7:26-40.

[72] Morgan A E, Somorjai G A: (1968), Low Energy Electron Diffraction Studies of Gas Adsorption on the Platinum (100) Single Crystal Surface. Surf Sci 12:405-425.

[73] Margon A E, Somorjai G A: (1969), Low Energy Electron Diffraction Studies in the Adsorption of Unsaturated Hydrocarbons and Carbon Monoxide on the Platinum (111) and (100) Single Crystal Surfaces. J Chem Phys 51:3309-3320.

[74] Motoo S, Furuya N: Electrochemistry of Platinum Single Crystal Surfaces. Part I. Stuructural Change of the Pt (111) Surface Followed by an Electrohemical Method. J Electroanal Chem 172:339-359 (1984).

[75] Motoo S, Furuya N: (1984), Electrochemistry of Platinum Single Crystal Surfaces. Part II. Structural Effect on Formic Acid Oxidation and Poison Formation on Pt (111(100) and (110), J Electroanal Chem 184:303-316.

[76] Mundschau M, Vanselow R: (1985), Difficulties in the Detection of Surface Impurities on Platinum Using Auger Electron Spectroscopy. Surf Sci 157:87-98.

[77] Norton P R, Davies J A, Jackson D P, Matsunami N: (1979), A Study of Phase Transition and Relaxation of a Pt (100) Surface by MeV Ion Backscattering Channeling. Surf Sci 85:269-275.

[78] Norton P R, Richards P J: (1974), The Heat of Adsorption of Hydrogen on Platinum Surf Sci 44:129-140.

[79] Palmberg P W, Rhodin T N: (1967), Surface Structure of Clean Au (100) and Ag (100) Surfaces. Phys Rev 161: 586-588.

[80] Palmberg P W, Rhodin K H: (1968), Atomic Arrangement of Au (100) and Related Metal Overlayer Surface Structures. J Chem Phys 49: 134-146.

[81] Palmberg P W, Rhodin T N: (1968), Auger Electron Spectroscopy of fcc Metal Surfaces. J Apply Phys 39:2425-2432.

[82] Pletner D: (1984), Electrocatalysis Present ad Future. J Apply Electrohem 14:403-415.

[83] Raub C J, Bockris J'OM, Conway B E, Yeager E, White R E: (1981), Comprehensive Treatise of Electrochemistry, Vol: 2 Plenum Press, New York.

[84] Ray N K, Anderson A B: (1982), Molecular Orbital Study of Carbon Monoxide Chemisorption and Oxidation on a Platinum (111) Surface. Surf Sci 119:35-45.

[85] Ross P: (1979), Structure Sensitivity in the Electrocatalytic Properties of Pt. Hydrogen Adsorption on Low Index Single Crystals and the Role of Steps. J Electrochem Soc 126:67-77.

[86] Ross P: (1981), Hydrogen Chemisorption on Pt Single Crystal Surfaces in Acidic Solutions. Surf Sci 102:463-485.

[87] Ross P N, Wagner F T: (1984), Advances in Electrochemistry and Electrochemical Engineering Berkeley, Lawrence, p 70.

[88] Salmeron M, Somorjai G: (1980), LEED-AES Study of the Reconstructed Pt (110) Surface. Surf Sci 91:373-384.

[89] Santos E, Leiva E P M, Vielstich W, Linke U: (1987), Comparative Study of CO Adsorbates For Different Structures of Platinum Surfaces. J Electroanal Chem 227: 199-211.

[90] Sanz J G, Armand G: (1982), Soft Surface Phonons and Reconstruction Platinum and Copper (100) Faces. Surf Sci 118:291-302.

[91] Sayed S M, Jüttner K: (1983), Electrocatalysis of Oxygen and Hydrogen Peroxide Reduction by UPD of Bismuth on Poly-and Monocrystalline Gold Electrodes in Acid Solutions: Electrochim Acta 28:1635-1641.

[92] Scherson D A, Kolb D M: (1984), Voltammetric Curves for Au (111) in Acid Media. J Electroanal Chem 176:353-357.

[93] Scortichini C L, Woodward F E, Reilley C N: (1982), Surface Characterization of Platinum Electrodes Using Underpotential Deposition of Hydrogen and Copper, Part III. Surface Improvement of the Flame-Annealed Platinum (100) and (111) Electrodes Via Potential Cycling. J Electroanal Chem 139:265-274.

[94] Sheppard N, Nguyen T T, Clark R J H and Hester R E: (1978), Advances in Infrared and Raman Spectroscopy, Heyden, London, p 67.

[95] Somorjai G A, Szalkowski F T: (1971), Auger Electron Spectroscopy on Surfaces. Advan High Temp Chem 41:137-160.

[96] Somorjai G A, Farrell H H: (1971), Low Energy Electron Diffraction. Advan Chem Phys 20:215-239.

[97] Sotto M, Hamelin A, Valette G. (1972), Modifications Microgéométriques des Surfaces Monocristallines d'or et D'argent au Contact de Solutions aqueuses. C R Acad Sci Paris Sér C 274:1138-1141.

[98] Sotto M: (1976), Oxydation Anodique de L'or: Partie I. Conditions Expérimentales Prétraitiment Anodique. Évolution de la Surface Activée. J Electroanal Chem. 69:229-237.

[99] Sotto M: Oxydation Anodique d L'or: (1976), Partie II. Étude de la Réduction du Film D'oxyde Formé Anodiquement par la methode de Chronoampérometrie a Variation Linéaire de Potentiel. J Electroanal Chem 70: 291-315.

[100] Sotto M: Oxydation Anodique de L'or: (1976), Partie III. Étude de la Formation du Film D'oxyde par la Méthode de Chronoampérométrie a Variation Linéaire de Potential J Electroanal Chem 72:287-306.

[101] Spencer N D, Lambert R M: (1981), Chlorine Chemisorption and Surface Chloride Formation on Au (111), Surf Sci 107:237-248.

[102] Wagner F T, Yeager E: (1981), Recent Advances in the Sciences, J Electrochem Soc 128:160 C-171 C.

[103] Wagner F T, Ross N Jr: (1983), LEED Analysis of Electrode Surfaces. Stuructural Effects of Potentiodynamic Cycling on Platinum Single Crystals. J Electroanal Chem 150:141-164.

[104] Will F G: (1965), Hydrogen Adsorption on Platinum Single Crystal Electrodes. I . Isotherms and Heats of Adsorption. J Electrochem Soc 112:451-455.

[105] Woodward F E, Scortichini C L, Reilley C N: (1983), Hydrogen Chemisorption and Related Anion Effects on Platinum (110) Electrodes. J Electroanal Chem 151:109-131.

[106] Yeager E, O'Grady W E, Woo MYC, Hagans P: (1978), Hydrogen Adsorption on Single Crystal Platinum. J Electrochem Soc 125: 348-349.