

This paper is in a collection of

**“Historic Publications in Electrochemistry”**

which is part of

**Electrochemical Science and Technology Information  
Resource (ESTIR)**

(<http://electrochem.cwru.edu/estir/>)

JOURNAL  
*of*  
ELECTROANALYTICAL CHEMISTRY  
*and*  
INTERFACIAL ELECTROCHEMISTRY

AN INTERNATIONAL JOURNAL DEVOTED TO ALL  
ASPECTS OF ELECTRODE KINETICS, INTERFACIAL  
STRUCTURE, PROPERTIES OF ELECTROLYTES,  
COLLOID AND BIOLOGICAL ELECTROCHEMISTRY

EDITOR R. PARSONS  
U.S. REGIONAL EDITOR R. DE LEVIE

EDITORIAL BOARD

F. ANSON ( <i>Pasadena, CA</i> )	J. LYKLEMA ( <i>Wageningen</i> )
G.C. BARKER ( <i>Bristol</i> )	H.W. NÜRNBERG ( <i>Jülich</i> )
J.O'M. BOCKRIS ( <i>College Station, TX</i> )	C.N. REILLEY ( <i>Chapel Hill, NC</i> )
B.E. CONWAY ( <i>Ottawa</i> )	J.M. SAVÉANT ( <i>Paris</i> )
I. EPELBOIN ( <i>Paris</i> )	D.E. SMITH ( <i>Evanston, IL</i> )
H. GERISCHER ( <i>Berlin</i> )	R. TAMAMUSHI ( <i>Saitama</i> )
L. GIERST ( <i>Brussels</i> )	S. TRASATTI ( <i>Milan</i> )
W. KEMULA ( <i>Warsaw</i> )	P. ZUMAN ( <i>Potsdam, NY</i> )
J. KORYTA ( <i>Prague</i> )	

VOL. 107

1980



ELSEVIER SEQUOIA S.A.  
LAUSANNE

## Preliminary note

---

# PREPARATION OF MONOCRYSTALLINE Pt MICROELECTRODES AND ELECTROCHEMICAL STUDY OF THE PLANE SURFACES CUT IN THE DIRECTION OF THE {111} AND {110} PLANES

J. CLAVILIER

*Laboratoire d'Electrochimie Interfaciale du C.N.R.S., 1, Place A. Briand, 92190 Meudon-Bellevue (France)*

R. FAURE, G. GUINET and R. DURAND

*Laboratoire d'Energétique Electrochimique L.A. C.N.R.S., 265 E.N.S.E.E.G., 38401 St.-Martin d'Hères (France)*

(Received 23rd November 1979)

## INTRODUCTION

The present paper briefly describes a technique to obtain monocrystalline platinum microelectrodes and gives some preliminary results on the interfacial behaviour of plane surfaces cut parallel to the {111} and {110} direction of planes in contact with 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solutions.

The preparation and physical measurement of samples were done in the "Laboratoire d'Energétique Electrochimique" while the surface pretreatments and electrochemical study were done in the "Laboratoire d'Electrochimie Interfaciale".

### (I) SAMPLE PREPARATION

It has been recognized that spherical Pt single crystals could be obtained by melting the extremity of Pt wires [1]. Such monocrystals may be obtained easily in a gas–oxygen flame [2, 3] using a very small quantity of metal; the method probably acts at the same time to purify the sample from many metallic impurities and also from S and C [4]. The previous technique [3] has been slightly modified, replacing the gas–oxygen flame by hydrogen–oxygen and blowing in the vertical direction in order to increase the size of the monocrystal to the detriment of the sphericity (which is unimportant with respect to the aim of this work).

The 5 N Pt (Johnson Matthey) was supplied as wires of 1 mm diameter; the surface of the wire was etched in *aqua regia* before melting to eliminate surface impurities. The monocrystalline beads of platinum obtained after melting were about 3 mm in diameter. The direction in which the crystal should be cut was roughly determined after etching the bead in *aqua regia* which revealed clearly its monocrystalline structure.

At the point opposite to the plane of cutting a second wire was fused to hold the electrode firmly during further cutting and polishing operations. After fusing

the second wire to the bead the first one was cut as short as possible and the bead was partially melted, when the melting zone reached the remaining part of the wire the drop was slowly recrystallized using the unmelted part of the bead to keep the orientation of the single crystal constant.

The monocrystal was then cut, polished and annealed in the hydrogen—oxygen flame near  $1100^{\circ}\text{C}$  for about ten minutes. This annealing procedure is sufficient to restore a good Laue diagram with very sharp spots after the mechanical polishing and it gives better results than the electropolishing treatment also tried.

As regards the single crystals used in this work which were cut following the  $\{111\}$  and  $\{110\}$  orientations, the X-ray diagrams obtained by Bragg's method indicated an orientation better than  $1^{\circ}$ .

Preliminary LEED study of the surface of the  $\{111\}$  sample indicated that the  $\{111\}$  structure was maintained to the very first atomic layers.

## (II) SURFACE PRETREATMENTS AND ELECTROCHEMICAL RESULTS

The electrochemical studies were done in  $0.5\text{ M H}_2\text{SO}_4$  solutions using ultra-pure water (Millipore Super Q system) and Merck "suprapur" sulphuric acid with no further purification. It has been recognized all along this work that the main source of solution contaminants was from the acid, nevertheless the level of contamination was extremely low.

No kind of holder or resin was used to delimit the surface of contact of the electrode with the electrolyte, so the electrodes after surface pretreatment — essentially high-temperature treatment — were quickly brought in contact with the solution using the dipping technique [5].

Various surface treatments always leading to the same electrochemical results have been used, annealing in argon atmosphere at  $1000^{\circ}\text{C}$ , annealing in a gas—oxygen flame with slow or fast cooling. After treatment the electrode surface was protected by a droplet of ultra-pure water during transfer to the solution. To understand the role of these pretreatments it is interesting to note that it is always the  $\{111\}$  planes which are spontaneously formed during crystallization of Pt droplets in a gas—oxygen flame.

Although at present no direct knowledge of the surface structures studied is available from LEED experiments, it can be assumed that voltammetry gives information of this type, being sensitive to such surface structures and their changes.

Typical voltammograms for the  $\{111\}$  and  $\{110\}$  directions of planes are given on Figs. 1 and 2. The potential range chosen here avoids the electrochemical adsorption—desorption of oxygen and the shape which is achieved at the first hydrogen desorption did not change for tens of cycles, the change depending essentially on the purity of the solution. The total quantity of electricity measured during H desorption was respectively  $255\ \mu\text{C cm}^{-2}$  and  $220\ \mu\text{C cm}^{-2}$  for the  $\{111\}$  and  $\{110\}$  directions (no double-layer correction but this is probably small). The first value fits well with a coverage of one H atom per Pt surface atom of an ideal  $\{111\}$  plane the second is significantly higher than for an ideal  $\{110\}$  plane ( $243\ \mu\text{C cm}^{-2}$  and  $147\ \mu\text{C cm}^{-2}$  respectively).

While the shape of the voltammogram for the sample oriented in the  $\{111\}$  directions is completely different from other previous work [6–10] there is

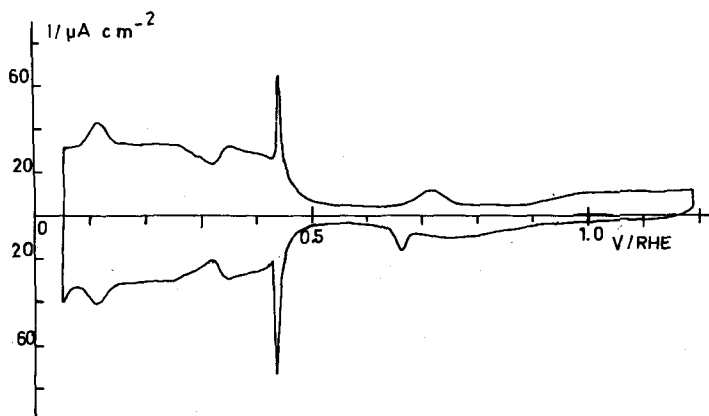


Fig. 1. Voltammogram for the  $\{111\}$  direction after annealing. Sweep rate  $50 \text{ mV s}^{-1}$ ,  $0.5 \text{ M H}_2\text{SO}_4$ .

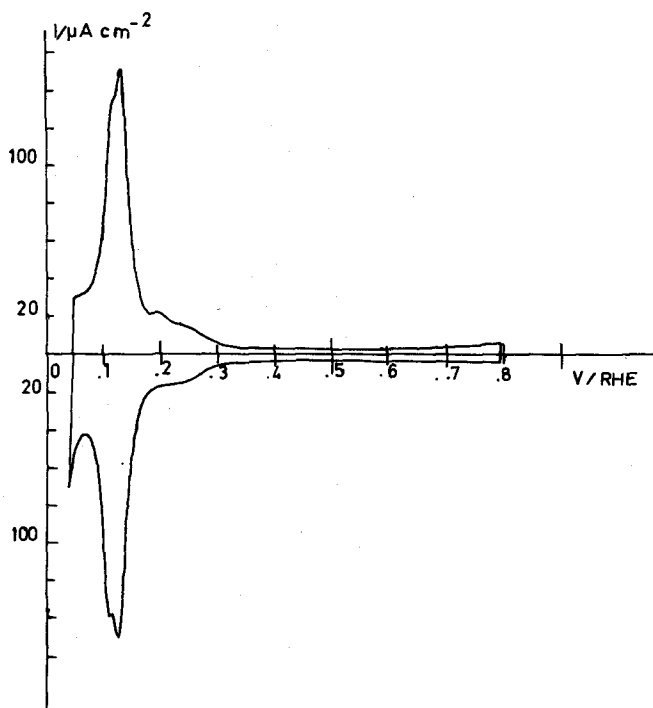


Fig. 2. Voltammogram for the  $\{110\}$  direction after annealing. Sweep rate  $50 \text{ mV s}^{-1}$ ,  $0.5 \text{ M H}_2\text{SO}_4$ .

practically no difference between the voltammogram of Fig. 2 and the curve published in reference [10]. It is interesting to note on Fig. 2 the fine structure which appears in the main peak.

After recording voltammograms of the samples, with surfaces "as received", in the hydrogen and double-layer region and without any used of the so-called

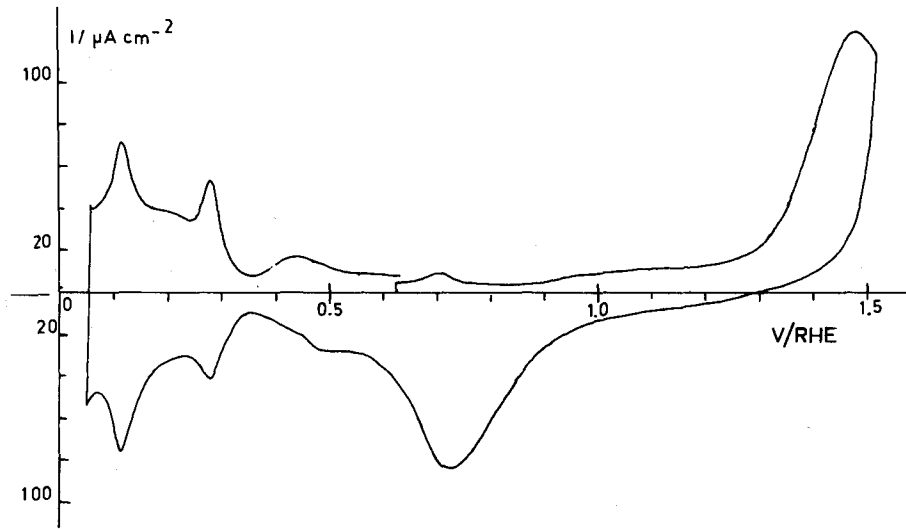


Fig. 3. Voltammogram for the first adsorption-desorption of oxygen and the subsequent adsorption-desorption of hydrogen for the {111} direction. Sweep rate  $50 \text{ mV s}^{-1}$ ,  $0.5 \text{ M H}_2\text{SO}_4$ .

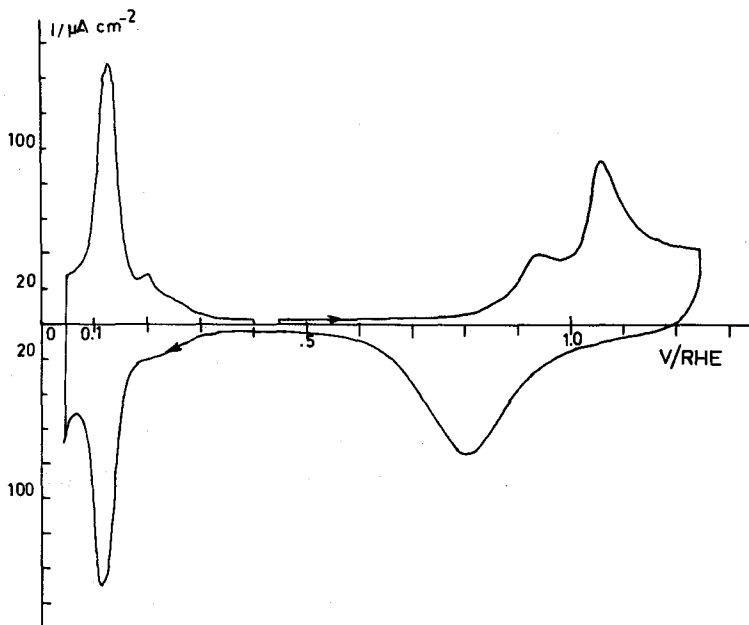


Fig. 4. Voltammogram for the first adsorption-desorption of oxygen and the subsequent adsorption-desorption of hydrogen for the {110} direction. Sweep rate  $50 \text{ mV s}^{-1}$ ,  $0.5 \text{ M H}_2\text{SO}_4$ .

“electrochemical cleaning treatment” the electrode was subjected to one run of adsorption—desorption of oxygen. Figures 3 and 4 give voltammograms respectively for the {111} and {110} directions of planes showing the first adsorption desorption of oxygen and the subsequent adsorption—desorption of hydrogen. The latter process is completely modified with the {111} direction of plane whereas there is no significant change with the {110} direction. The balance of charge for the adsorption ( $Q_{ad}$ ) and desorption ( $Q_{des}$ ) of oxygen gives  $Q_{ad}/Q_{des} = 1.01 \pm 0.01$  for the {111} direction, the total charge evolved being  $550 \mu\text{C cm}^{-2}$ , at the same time a delay in the beginning of adsorption of oxygen is observed. For the {110} direction the balance gives a ratio of 1.08 which falls to 1.01 at the second adsorption—desorption oxygen process for a total charge equal to  $380 \mu\text{C cm}^{-2}$  (value depending on the arbitrary choice of reversing potential). This slight deviation from unity is related to a slight residual surface contamination before the first oxidation of the {110} plane. The peaks of oxygen adsorption are characteristic for this direction.

The unity value of the ratio  $Q_{ad}/Q_{des}$  obtained with the {111} direction is evidence for a good initial cleanliness of surfaces giving voltammograms like those of Fig. 1 (absence of side reactions). The change in the character of the adsorption—desorption process of hydrogen may then be attributed to a change in the surface structure which is practically achieved after the adsorption—desorption of one monolayer of oxygen, giving evidence for the fact that reconstruction process by dissolution and redeposition cannot be considered at such sweep rates. Furthermore this results proves that reconstruction is a faster process than decontamination which generally needs tens of cycles in the same range of potential.

The present results concerning the {111} plane reveal that hydrogen may appear with high bonding energy with some Pt surface structures up to 0.5 V/RHE, and that with this orientation at least two surface structures may exist in contact with a solution as well as the intermediate reconstructed states.

## REFERENCES

- 1 R. Kaischew and B. Mutaftschiew, *Z. Phys. Chem.*, **204** (1955) 334.
- 2 J. Clavilier and R. Pineaux, *C.R. Acad. Sci: Paris*, **260** (1965) 891.
- 3 J. Clavilier, Thèse, Paris, 1968.
- 4 J. Clavilier, J.P. Chauvineau, *J. Electroanal. Chem.*, **100** (1978) 461.
- 5 D. Dickertmann, F.D. Koppitz and J.W. Schultze, *Electrochim. Acta*, **21** (1976) 967.
- 6 F.G. Will, *J. Electrochem. Soc.*, **112** (1965) 451.
- 7 E. Yeager, W.E. O'Grady, M.Y.C. Woo and P. Hagans, *J. Electrochem. Soc.*, **125** (1978) 348.
- 8 A.T. Hubbard, R.P. Ishikawa and J. Katekaru, *J. Electroanal. Chem.*, **86** (1978) 271.
- 9 P.N. Ross, *J. Electrochem. Soc.*, **126** (1979) 67.
- 10 K. Yamamoto, D.M. Kolb, R. Kotz and G. Lehmpfuhl, *J. Electroanal. Chem.*, **96** (1979) 233.