Preliminary note

CHANGES IN THE ELECTROCHEMICAL RESPONSE OF POLYCRYSTALLINE PLATINUM ELECTRODES PROMOTED BY FAST REPETITIVE SQUARE WAVE POTENTIAL SIGNALS

J.C. CANULLO, W.E. TRIACA and A.J. ARVÍA

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Casilla de Correo 16, Sucursal 4, 1900 La Plata (Argentina)

(Received 19th March 1984; in final form 11th June 1984)

There is a great interest in modifying the properties of solid electrodes to achieve their best performance under definite operating conditions. In this sense, at present the preparation, stabilization and reproducibility in the electrochemical response of solid electrode surfaces are subjects of special attention [1–4]. A recent contribution in this respect that polycrystalline platinum electrodes immersed in acid electrolytes after being subjected to a fast repetitive triangular potential scanning under carefully selected potential perturbation conditions show remarkable changes in the potentiodynamic \( I/E \) profiles at \( v = 0.1 \) V s\(^{-1}\) corresponding to the H- and O-adatom electroadsorption/electrodesorption potential region with respect to those of the initial polycrystalline material [5]. These results suggested that the same changes in the electrochemical response of platinum electrodes could be achieved by means of a fast repetitive square wave potential signal covering the potential range of the H- and O-adatom electroadsorption/electrodesorption.

When a polycrystalline platinum electrode immersed in 1 M \( \text{H}_2\text{SO}_4 \) at 25°C, which has been previously electropolished with ac (50 Hz; 10–20 V) in a slightly acid (HCl) saturated \( \text{CaCl}_2 \) solution, is subjected to a repetitive square wave potential signal (RSWPS) between 0.70 and 1.40 V (vs. RHE) at 0.5 kHz during 3 min, the voltammogram run immediately afterwards by applying a symmetrical triangular potential scan (RTPS) at 0.1 V s\(^{-1}\), in the 0.04–1.50 V range (Fig. 1), approaches closely the characteristics of a Pt (111) single crystal surface after it has been cycled at a low potential sweep rate a few times through the anodic oxide region (Type-I electrode) [6–12]. Thus, the corresponding voltammogram shows the reversible conjugated current peaks of H-adatom electroadsorption/electrodesorption at ca. 0.11 V, a relative increase in height of the second broad anodic current peak associated with the O-electroadsorption and a shift of the potential of the O-electrodesorption current peak towards more negative values than those found in comparable voltammograms for polycrystalline platinum. An appreciable increase in the electrode active area, as measured through either the H-adatom monolayer charge or the O-monolayer electrodeposition charge, is also observed.
Fig. 1. Stabilized voltammograms (third cycle) run at 0.1 V s\(^{-1}\) in 1 M H\(_2\)SO\(_4\) at 25° C.
(— — —) Electropolished polycrystalline platinum electrode; (——) after 3 min RSWPS at 0.5 kHz between 0.70 and 1.40 V.

On the other hand, when the pretreated polycrystalline platinum electrode is subjected to a RSWPS of larger amplitude, e.g., 0.8 V, between 0.20 and 1.00 V at 0.5 kHz during 20 min, the following voltammogram run at 0.1 V s\(^{-1}\) between 0.04 and 1.50 V (Fig. 2) approaches closely that depicted in the literature as the electrochemical response of the Pt (100) single crystal surface (Type-II electrode) [7,8,10–13]. Thus, the voltammogram exhibits the conjugated current peaks of the H-adatom electroadsorption/electrodesorption at ca. 0.25 V, which render the greatest current contribution in the H-adatom potential range, a relative increase of the first broad anodic current peak related to the O-electroadsorption, and a shift of the potential of the O-electrodesorption current peak towards a potential value slightly more positive than that observed in the conventional voltammogram for polycrystalline platinum. In this case, when the starting surface is polycrystalline platinum, no appreciable change in the electrode active area is noticed. The electrochemical characteristics of the resulting platinum surface remain practically unchanged, except for an apparent minor surface reconstruction after 2 h RTPS between 0.04 and 1.50 V at 0.1 V s\(^{-1}\).
The polycrystalline platinum electrochemical response can be recovered by etching both Type-I and Type-II electrodes in aqua regia followed by a slight electropolishing.

By properly adjusting the potential preturbation parameters the RSWPS technique also provides a direct interconversion from a Type-I electrode into a Type-II electrode and vice versa. Thus, when a Type-I electrode is subjected to RSWPS between 0.40 and 1.20 V at 0.5 kHz during 30 min, the conversion to a Type-II electrode is accomplished (Fig. 3). In this case, there is an appreciable reduction in the electrode active area. Correspondingly, the H-adatom monolayer charge ratio resulting from the RTPS voltammograms is ca. 1.4. This figure is close to the value of 1.2 which has been reported for the H-adatom monolayer charge ratio between the (111) and (100) platinum single crystals \cite{14} ($Q_H^{(111)} = 0.243 \text{ mC/cm}^2$ and $Q_H^{(100)} = 0.208 \text{ mC/cm}^2$).

![Fig. 3. Stabilized voltammograms (third cycle) run at 0.1 V s$^{-1}$ in 1 M H$_2$SO$_4$ at 25°C (---) after applying to a polycrystalline platinum electrode 5 min RSWPS at 0.5 kHz between 0.7 and 1.4 V; (---) after applying to a Type-I electrode 30 min RSWPS at 0.5 kHz between 0.40 V and 1.20 V.](image)

The preparation of both Type-I and Type-II platinum electrodes was carried out in a low resistance designed electrochemical cell consisting of a polycrystalline platinum wire working electrode (ca. 0.17 cm$^2$ geometric area) concentrically surrounded by a large area platinum counter electrode (ca. 50 cm$^2$). The potential of the working electrode was measured against a hydrogen reference electrode in the same acid electrolyte solution.

The transient current measured during the application of each half-cycle of the RSWPS reveals a considerable capacitive current component which is apparently related to the modification in the electrochemical response of the platinum surface at low potential sweep rates. Furthermore, the type of the electrode pretreatment required for the efficient application of the RSWPS technique suggests that a sort of “softening” of the polycrystalline surface assists the modification of its electrochemical response promoted by the RSWPS.

The discovery reported in this preliminary communication may be relevant for the development of metallic surfaces of potential interest in electrocatalysis. Both Type-I and Type-II platinum electrodes exhibit sharply different
voltammetric response to the electrooxidation either in acid or base electrolyte of carbon monoxide, reduced carbon dioxide, formic acid, methanol, ethylene glycol and to the upd of metals. The corresponding results will be presented in the near future.

ACKNOWLEDGEMENTS

INIFTA is sponsored by the Universidad Nacional de La Plata, the Consejo Nacional de Investigaciones Científicas y Técnicas and the Comisión de Investigaciones Científicas (Provincia de Buenos Aires).

REFERENCES

1 J.P. Ganon, N.V. Huong and J. Clavilier, Surf. Sci., 79 (1979) 245.
2 A.T. Hubbard, Acc. Chem. Res., 13 (1980) 177.
3 A. Hamelin, Soviet Electrochem., 18 (1982) 1259.
4 P.N. Ross, Jr., J. Electrochem. Soc., 126 (1979) 67.
5 R.M. Cerviño, W.E. Triaca and A.J. Arvia, J. Electroanal. Chem., submitted.
6 P.N. Ross, Jr., J. Electroanal. Chem., 76 (1977) 139.
7 A.T. Hubbard, R.M. Ishikawa and J. Katekaru, J. Electroanal. Chem., 86 (1978) 289.
8 K. Yamamoto, D.M. Kolb, R. Kotz and G. Lehmpfuhl, J. Electroanal. Chem., 96 (1979) 233.
9 J. Clavilier, R. Faure, G. Guinet and R. Durand, J. Electroanal. Chem., 107 (1980) 205.
10 P.N. Ross, Jr., Surf. Sci., 102 (1981) 463.
11 F.E. Woodard, C.L. Scortichini and C.N. Reilley, J. Electroanal. Chem., 151 (1983) 109.
12 F.T. Wagner and P.N. Ross, Jr., J. Electroanal. Chem., 150 (1983) 141.
13 E. Yeager, W.E. O’Grady, M.Y.C. Woo and P. Hagans, J. Electrochem. Soc., 125 (1978) 348.
14 J.-M. Léger, Ph.D. Thesis, University of Poitiers, France (1982).