

**Short communication**

**CHANGES IN THE MORPHOLOGY OF PLATINUM ELECTRODEPOSITION INDUCED BY FAST SQUARE WAVE POTENTIAL MODULATION**

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Faceting of platinum with preferred orientation can easily be produced by applying, during a certain time, a potential, cycling at a frequency greater than 0.5 kHz, to a polycrystalline electrode in acid solution within the potential range of the underpotential decomposition of water [1,2]. By adequately changing the potential limits, the frequency and the duration of the periodic perturbation applied to the electrode, different platinum surfaces are produced whose voltammetric behaviour approaches that reported from initially single crystal platinum surfaces under definite perturbation conditions [3]. Each type of faceted surface with preferred orientation exhibits well-defined forms in SEM microphotographs [4].

These early results suggest that faceted platinum surfaces with preferred orientation can also be produced by square wave potential-modulated dc electrodeposition. The application of ac signals superimposed on a stationary dc potential was already studied to increase the yield and modify the characteristics of metal electrodeposits through relaxation of the diffusional boundary layer associated with the electrochemical reactions [5,6].

Runs were made with polycrystalline platinum wires (Johnson Matthey Chem. Co) of 0.5 mm diameter and with an apparent area between 0.12 and 1 cm<sup>2</sup>, polished mechanically beforehand with a suspension in water of fine grade alumina powder (0.5 μm). The polished polycrystalline electrodes were platinum electroplated in an aqueous solution containing 2% H<sub>2</sub>PtCl<sub>6</sub> and 4% HCl, prepared from AR chemicals and triply distilled water. The platinum was electrodeposited by applying a square wave signal reaching from the lower ( $E_l$ ) to the upper ( $E_u$ ) potential limits at a frequency  $f$  during a time  $t$ . The average potential,  $(E_l + E_u)/2$ , was negative with respect to the potential of the Pt/Pt(IV) redox couple ( $E^\circ_{\text{Pt/Pt(IV)}} = 0.760$  V (vs. SHE)). The different perturbation parameters were selected within a certain range, yielding optimum faceting characteristics of the electrodeposits. The degree of preferred-orientation platinum electrodeposition was followed voltammetrically through the response of the electroadsorption/electrodesorption of H adatoms in H<sub>2</sub>SO<sub>4</sub> solutions of different concentration at 25°C. The electrode potentials are given with respect to the standard hydrogen electrode.

For  $E_u = 1.30$  V,  $E_l = -0.20$  V,  $f = 2.5$  kHz and  $t = 20$  min, the SEM micropho-

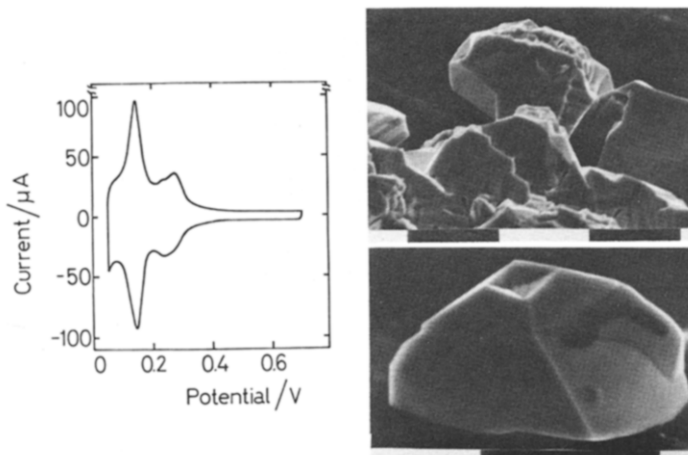


Fig. 1. Voltammogram run in 1 M  $\text{H}_2\text{SO}_4$  at 0.2 V/s and SEM microphotographs of platinum electrodeposits made at  $E_u = 1.30$  V,  $E_l = -0.20$  V,  $f = 2.5$  kHz and  $t = 20$  min, 25°C. The bars represent 10  $\mu\text{m}$ . Apparent electrode area:  $8 \times 10^{-2}$   $\text{cm}^2$ .

tographs of platinum electrodeposits correspond to well-defined isolated crystallites on the polycrystalline platinum substrate (Fig. 1). Under these conditions, no alterations are apparent in the substrate. The voltammogram of the test reaction (Fig. 1) in 1 M  $\text{H}_2\text{SO}_4$  at 0.2 V/s is clearly different from that of the original polycrystalline electrode, as the new electrode surface exhibits a considerable increase in the reversible weak H electroadsorption/electrodesorption processes occurring at ca. 0.165 V. The electrochemical spectrum depicted in Fig. 1 approaches that reported in the literature for a Pt (111) single crystal electrode with an induced surface disorder resulting from a few potential cyclings covering the potential range of H and O adatom electroadsorption/electrodesorption [7–9]. In this case, by taking a monolayer charge for H adatoms in the Pt (111) single crystal equal to 235  $\mu\text{C}/\text{cm}^2$ , a roughness factor of 5.0 is obtained.

A similar voltammetric response results when  $E_u = 1.25$  V,  $E_l = -0.15$  V,  $f = 1$  kHz and  $t = 10$  min. In this case, SEM pictures show that the surface of the electrode is covered with a large number of faceted crystallites (Fig. 2). The corresponding voltammogram run in 0.5 M  $\text{H}_2\text{SO}_4$  (Fig. 2) shows current peaks steeper than those seen in Fig. 1. On the other hand, the electrochemical spectrum depends remarkably on the electrolyte concentration (Fig. 2). In this case the estimated roughness factor is 6.3. Thus, in 0.005 M  $\text{H}_2\text{SO}_4$  there is a net splitting of the voltammogram on the positive sweep into at least four current peaks, as well as a splitting of the voltammogram on the negative sweep into at least three current peaks. These results indicate the influence of anion concentration on  $\text{HSO}_4^-$  adsorption and the competition between the adsorbed anions and adsorbed hydrogen atoms, as already reported for various single crystal noble metal electrodes [10–13].

The substrate becomes completely covered with electrodeposited platinum when

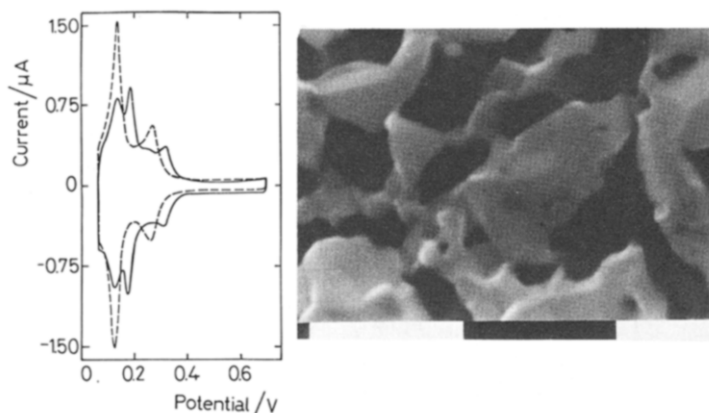


Fig. 2. Voltammogram run at 0.05 V/s ((---) 0.5 M H<sub>2</sub>SO<sub>4</sub>; (—) 0.005 M H<sub>2</sub>SO<sub>4</sub>) and SEM microphotograph of a platinum electrodeposit made at  $E_u = 1.30$  V,  $E_1 = -0.15$  V,  $f = 1$  kHz and  $t = 10$  min, 25°C. The bar represents 1  $\mu\text{m}$ . Apparent electrode area:  $1.96 \times 10^{-3}$  cm<sup>2</sup>.

$E_u = 1.15$  V;  $E_1 = -0.15$  V,  $f = 1.0$  kHz and  $t = 10$  min (Fig. 3). In this case, the electrodeposit exhibits a clear faceting, but the electrochemical response of the test reaction is different from those described before (Fig. 3). Thus, the voltammogram run in 0.5 M H<sub>2</sub>SO<sub>4</sub> shows that the relative contribution of H adatom electroadsorption/electrodesorption current peaks at ca. 0.35 V, usually assigned to strongly adsorbed H adatoms, becomes greater than in the runs described previously. These current peaks are seen clearly with Pt (100) single crystal electrodes in acid solutions [7–9]. Both the relative distribution of current peaks and their peak potential values are, in these cases, very sensitive to the composition of the electrolyte. Considering

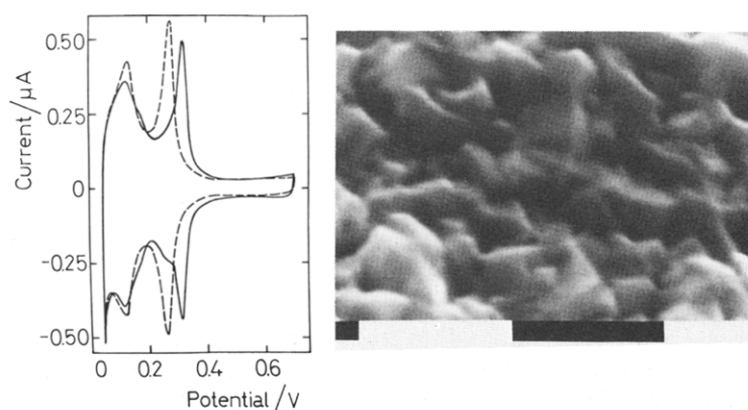


Fig. 3. Voltammogram run at 0.05 V/s ((---) 0.5 M H<sub>2</sub>SO<sub>4</sub>; (—) 0.005 M H<sub>2</sub>SO<sub>4</sub>) and SEM microphotograph of a platinum electrodeposit made at  $E_u = 1.15$  V,  $E_1 = -0.15$  V,  $f = 1$  kHz and  $t = 10$  min, 25°C. The bar represents 1  $\mu\text{m}$ . Apparent electrode area:  $1.96 \times 10^{-3}$  cm<sup>2</sup>.

that the H adatom monolayer charger of the Pt (100) single crystal is  $208 \mu\text{C}/\text{cm}^2$ , the roughness factor resulting for the electrodeposited platinum electrode is 3.8.

In any case, for  $E_1 = -0.15 \text{ V}$  and  $f = 1 \text{ kHz}$ , preferred-orientation platinum faceting is accomplished, provided that  $E_u$  is greater than 1.25 V and that  $(E_1 + E_u)/2$  is comprised within the potential range of the underpotential oxidation of water, yielding adsorbed OH species [14]. Otherwise, when  $E_u$  is lower than 1.25 V, the electrochemical behaviour of the electroplated platinum surface is similar to that of a galvanostatically formed platinized platinum electrode [15].

The electrochemical responses of the faceted platinum surfaces are probably determined by the relative densities of the (100) and (111) surface planes at the stepped surfaces resulting from the square wave modulated electrodeposition of platinum. The voltammetric response of the stepped surface depends on the distribution and relative densities of the different planes [16].

The present results suggest it is worthwhile to consider the square wave modulated electrodeposition of metals as a promising technique for combining the growth of electrodeposits with preferred surface orientation (faceting) and the increase in the active area of noble metal electrocatalysts.

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#### REFERENCES

- 1 R.M. Cerviño, W.E. Triaca and A.J. Arvia, *J. Electrochem. Soc.*, 132 (1985) 267.
- 2 J.C. Canullo, W.E. Triaca and A.J. Arvia, *J. Electroanal. Chem.*, 175 (1984) 337.
- 3 R.M. Cerviño, W.E. Triaca and A.J. Arvia, *J. Electroanal. Chem.*, 182 (1985) 51.
- 4 R.M. Cerviño, A.J. Arvia and W. Vielstich, *Surf. Sci.*, 154 (1985) 623.
- 5 J. Amblard, M. Froment and G. Maurin, 35th ISE Meeting, 1984, Abstr. B3-16.
- 6 A.R. Despic and K.J. Popov in B.E. Conway and J.O'M. Bockris (Eds.), *Modern Aspects of Electrochemistry*, Vol. 7, Plenum Press, 1972, Ch. 4, p. 199.
- 7 P.N. Ross, Jr., *J. Electroanal. Chem.*, 76 (1977) 139.
- 8 A.T. Hubbard and R.M. Ishikawa, *J. Electroanal. Chem.*, 86 (1978) 271.
- 9 D. Aberdan, C. Corotte, D. Dufayard, R. Durand, R. Faure and G. Guinet in A.A. Degras and M. Costa (Eds.), *Proc. Fourth International Conference on Solid Surfaces*, Cannes, Vol. 1, p. 622, Supplement of *Le Vide, les Couches Minces*, N 201 (1980).
- 10 R.M. Ishikawa and A.J. Hubbard, *J. Electroanal. Chem.*, 69 (1976) 317.
- 11 F.E. Woodard, C.L. Scottichini and C.N. Reilley, *J. Electroanal. Chem.*, 151 (1983) 109.
- 12 D. Dickertmann, S.W. Schultze and K.J. Vetter, *J. Electroanal. Chem.*, 55 (1974) 429.
- 13 A. Hamelin, *J. Electroanal. Chem.*, 142 (1982) 299.

- 14 B.E. Conway, H. Angerstein-Kozłowska, F.C. Ho, J. Klinger, B. MacDougall and S. Gottesfeld, *Faraday Discuss. Chem. Soc.*, 56 (1973) 210.
- 15 A.C. Chialvo, W.E. Triaca and A.J. Arvia, *An. Asoc. Quím. Arg.*, 73 (1985) 23.
- 16 E.R. Custidiano, A.C. Chialvo and A.J. Arvia, in preparation.