Preliminary note

ELECTROCHEMICAL FACETING OF SINGLE CRYSTAL PLATINUM ELECTRODES

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

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

The surface of a single crystal metallic sphere presents, in principle, all possible crystallographic planes. When such a surface structure is modified by one of the procedures described for the development of preferred orientation [1,2], one can develop a well defined atomic arrangement involving a certain particular crystallographic plane, depending on the set of parameters defining the fast potential perturbation. Due to the spherical geometry, the changes operating in the surface should require a very symmetrical stereospatial reconstruction, which results in the development of poles of the particular enhanced crystallographic plane and the disappearance of others. The simplest surface arrangement (111), (110) and (100), resulting from the reconstruction of an fcc single crystal sphere, are depicted as schemes in Fig. 1, where the different crystallographic poles are identified in Fig. 1a.

The changes described above can be clearly seen by using as a working electrode a polycrystalline platinum wire, one of its extremes ending in a single crystal sphere prepared according to Clavilier's method [3]. The initial sphere surface obtained in this way has a smooth surface on the scale of SEM magnification ($\times$ 300 to $\times$ 15000), involving flattened [111] poles whereas the REM image shows wide terraces with a few atomic steps [4]. The voltammetric response of this spherical platinum electrode without cutting and polishing in 1 M H_2SO_4 is similar to that already known for any polycrystalline platinum electrode [5]. Otherwise, when this sphere is cut in a proper direction and the new surface is put in contact with the electrolyte according to the dipping method [6], the corresponding single crystal voltammogram is obtained. This procedure was used by different authors contributing to single crystal electrode study [3,7—10].

On the other hand, when a single crystal platinum sphere is subjected to electrochemical faceting in 1 M H_2SO_4 at 25°C, with a symmetric periodic perturbation at 3.5 kHz, upper potential 1.23 V (vs. RHE), lower potential 0.23 V, for 15 h, the resulting surface exhibits a voltammogram in the H-adatom electroadsorption/electrodesorption potential range, at 0.1 V/s, like that found with the (100) plane [8,11—14]. Likewise, the platinum surface sphere exhibits a

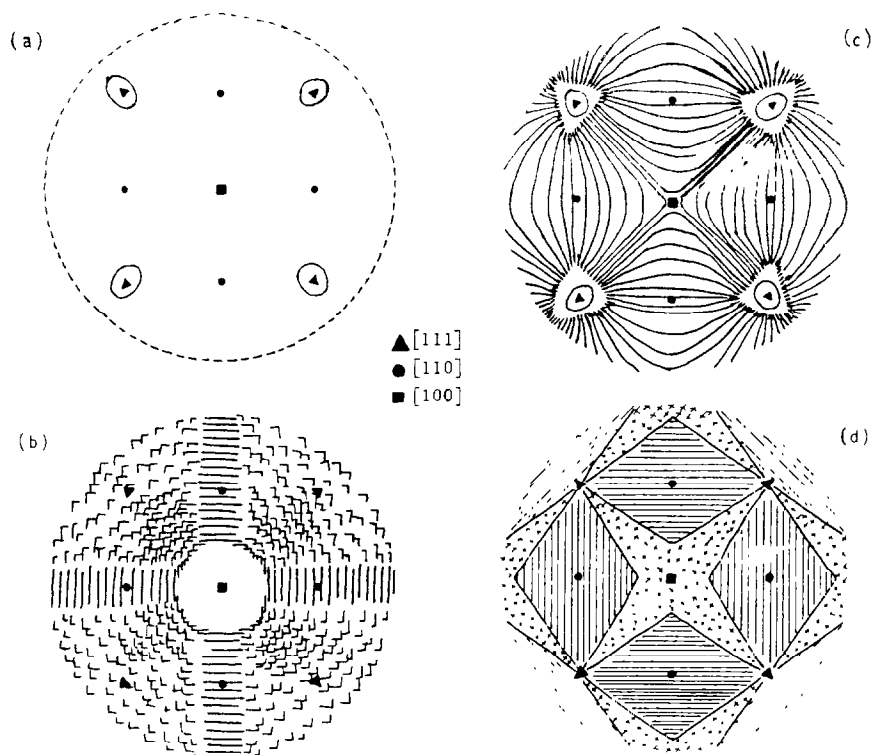* Facultad de Ciencias Exactas, Universidad Nacional de La Plata.

Fig. 1. Scheme of expected SEM patterns from a single crystal sphere. (a) Untreated single crystal sphere, (b) (100)-type faceting, (c) (111)-type faceting, (d) (110)-type faceting.

dramatic change in the SEM pattern. This pattern (Fig. 2) exhibits the trend that each [100] pole becomes the origin of four symmetrical and perpendicular bands of steps which develop in the [110] direction to reach the crystallographically equivalent next neighbouring [100] pole, as shown ideally in Fig. 1b. On moving from the [100] pole in the direction of the [111] pole, the surface acquires a faceted kink structure maintaining the cubic geometry while the [111] pole practically disappears.

Voltammetric behaviour like that shown by the (111) plane [8,13,15] results when the single crystal platinum sphere is perturbed with an asymmetric square wave periodic potential at 3.5 kHz between 0.70 V (vs. RHE) and 1.40 V for 15 h. The upper-to-lower potential holding time ratio was about 0.26. The SEM pattern obtained after the treatment reveals the absence of a cubic geometry (Fig. 3). Now each [111] pole becomes the origin of three symmetric grooved bands. Neighbouring [111] poles are connected by a straight-line groove going through the [110] pole. Furthermore, the [111] poles develop a triangular smooth surface which is larger than the original circular flat surface. The ideal situation is depicted in Fig. 1c.

Finally, when the single crystal platinum sphere is subjected to a symmetric square wave potential perturbation at 3.5 kHz, from 0.5 V (vs. RHE) to 1.35 V, for 3.5 h, the resulting voltammogram at 0.1 V/s in 1 M H_2SO_4 exhibits the characteristics of that of the (110) plane (or the reconstructed (110) plane)
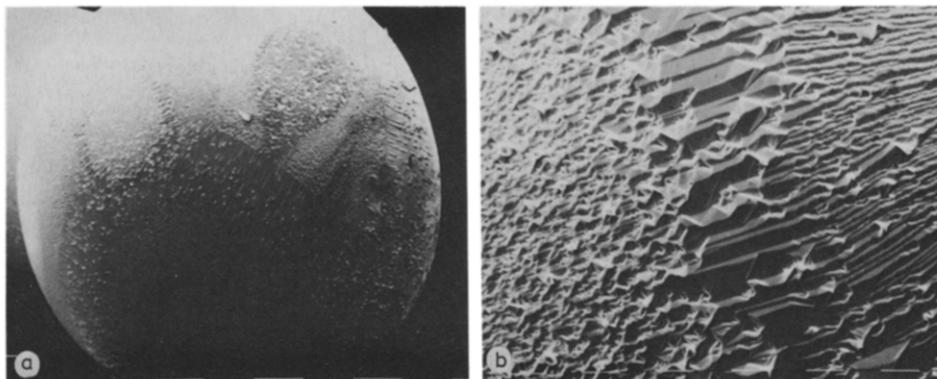
Fig. 2. SEM pattern of a platinum single crystal sphere after 15 h RSWPS treatment (E_l = 0.23 V, E_u = 1.23 V, f = 3.5 kHz) in 1 M H_2SO_4 at 25°C. Scale: (a) 100 μm, (b) 10 μm.
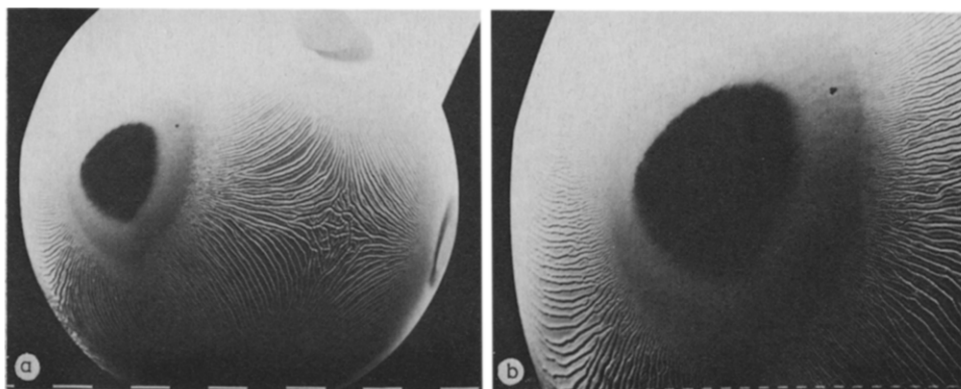

Fig. 3. SEM pattern of a platinum single crystal sphere after 15 h RSWPS treatment (E_l = 0.70 V, E_u = 1.40 V, f = 3.5 kHz, upper/lower half-cycle ratio = 0.26). Scale: (a) 100 μm, (b) 10 μm.

[8,9,11,16]. The corresponding SEM pattern (Fig. 4) approaches rhombo-hedral planes involving the [110] pole at the center of the plane, and the op-posed edges converging at the [111] poles. The plane shows steps with edges parallel to the zone which joins the [111] and [110] poles. The other edges of the plane move according to the electrochemical faceting time in the direction of the [100] poles. The rest of the surface displays a four-pointed star-like figure centered at the [100] poles, each point of the star being located at a [111] pole. The ideal picture is shown in Fig. 1d. The microstructure of this area cor-responds to a faceting in the form of small four-faced pyramids (Fig. 4) whose angular inclination appears similar to that exhibited by the (110) planes.
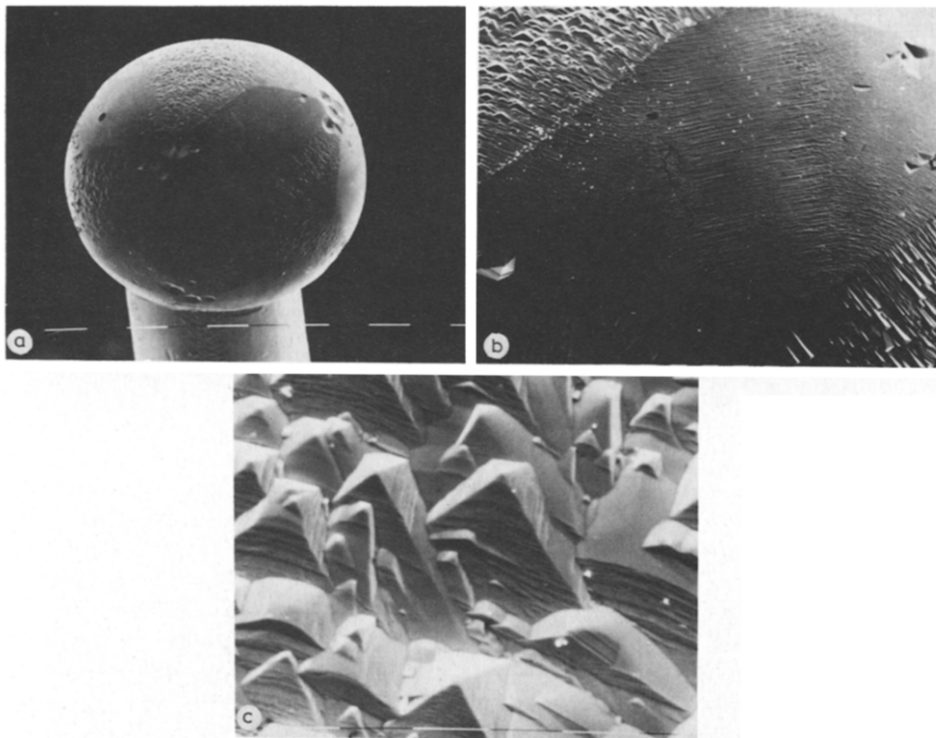
ACKNOWLEDGEMENT

Fig. 4. SEM pattern of a platinum single crystal sphere after 3.5 h RSWPS treatment (E_l = 0.50 V, E_u = 1.35 V, f = 3.5 kHz). Scale: (a) 100 μm, (b) 10 μm, (c) 1 μm.

REFERENCES

1   R. Cerviño, W.E. Triaca and A.J. Arvia, J. Electrochem. Soc., 132 (1985) 266.
2   J.C. Canullo, W.E. Triaca and A.J. Arvia, J. Electroanal. Chem., 175 (1984) 337.
3   J. Clavilier, R. Faure, G. Guinet and R. Durand, J. Electroanal. Chem., 107 (1980) 205.
4   Y. Uchida, G. Lehmpfuhl and J. Jager, Ultramicroscopy, 15 (1984) 119.
5   B.E. Conway, H. Angerstein-Kozlowska, F.C. Ho, J. Klinger, B. MacDougall and S. Gottesfeld, Faraday Discuss. Chem. Soc., 56 (1973) 210.
6   D. Dickertmann, F.D. Koppitz and J.W. Schultze, Electrochim. Acta, 21 (1976) 967.
7   J. Clavilier, R. Durand, G. Guinet and R. Faure, J. Electroanal. Chem., 127 (1981) 281.
8   C.L. Scortichini and C.N. Reilley, J. Electroanal. Chem., 139 (1982) 233.
9   F.E. Woodward, C.L. Scortichini and C.N. Reilley, J. Electroanal. Chem., 151 (1983) 109.
10 S. Motoo and N. Furuya, J. Electroanal. Chem., 172 (1984) 339.
11 K. Yamamoto, D.M. Kolb, R. Kotz and G. Lehmpfuhl, J. Electroanal. Chem., 96 (1979) 233.
12 P.N. Ross, J. Electrochem. Soc., 126 (1979) 67.
13 F.T. Wagner and P.N. Ross, J. Electroanal. Chem., 150 (1983) 141.
14 E. Yeager, W.E. O'Grady, M.Y.C. Woo and P. Hagans, J. Electrochem. Soc., 125 (1978) 348.
15 A.T. Hubbard, R.M. Ishikawa and J. Katekaru, J. Electroanal. Chem., 86 (1973) 271.
16 D. Aberdam, C. Corotte, D. Dufayard, R. Durand, R. Faure and G. Guinet in P.A. Degras and M. Costa (Eds.), Proc. 4th Int. Conf. on Solid Surfaces, Cannes, Vol. 1, p. 622, Suppl. Vide Couches Minces, 201 (1980).