

SHORT COMMUNICATION

ELECTROCHEMICAL FACETING OF POLYCRYSTALLINE PLATINUM IN HF SOLUTIONS

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Abstract—The electrochemical faceting of polycrystalline (pc) platinum yielding a (100)-preferred oriented electrode surface was accomplished in HF solutions by applying to the pc platinum electrode a square wave potential perturbation at 1 kHz in the 0.2 to 1.3 V range (*vs rhe*). SEM patterns of the resulting surfaces were also obtained. For HF concentrations up to 2 M no appreciable influence of the electrolyte concentration on the electrochemical faceting was noticed. Otherwise, the voltammetric response of the (100)-type preferred oriented platinum surface in the H-atom potential range when compared to previously reported data resulted remarkably sensitive to the electrolyte composition. The discussion of results was based on the non-equilibrium adsorption conditions for anions under the periodic perturbation.

The electrochemical faceting of polycrystalline platinum[1-3] involving different preferred crystallographic orientations was accomplished through the application of a relatively fast periodic potential perturbation of preset frequency, upper and lower potential limit values. Although the electrolyte composition apparently plays a minor influence in electrochemical faceting development, it may be significant in the stabilization stage of the faceted surfaces by potential cycling at low potential sweep rate[3, 4]. This note reports the conditions for the electrochemical faceting of pc platinum in HF and compares the voltammetric response at 0.1 V s^{-1} of (100)-type faceted platinum in different electrolytes.

The electrochemical faceting was made in HF solutions (0.1-2.5 M range) at 25°C by using an 80 ml capacity cell made of Teflon, working electrodes made from spectroscopic pc platinum wires (Johnson Matthey Co., 0.5 mm dia. and ca 1.6 cm² apparent area), a platinum counterelectrode of large area and a reversible hydrogen reference electrode (*rhe*). The working electrode was subjected to a symmetric repetitive square wave potential signal (RSWPS) at the frequency (f) ($0.5 \text{ kHz} \leq f \leq 5 \text{ kHz}$) between the upper (E_u) and the lower (E_l) potential limits ($1.0 \text{ V} \leq E_u \leq 1.6 \text{ V}$; $0.0 \text{ V} \leq E_l \leq 0.40 \text{ V}$), during a preset time (t). The optimal RSWPS characteristics for electrochemical faceting of platinum in 2 M HF in the direction of (100)-type-preferred orientation are $f = 1.0 \text{ kHz}$, $E_u = 1.30 \pm 0.05 \text{ V}$, $E_l = 0.3 \pm 0.1 \text{ V}$.

The development of faceting was voltammetrically followed at 0.1 V s^{-1} , in nitrogen saturated either 2 M HF or 1 M H₂SO₄ at 25°C covering either H-atom or both the H- and O-atom potential ranges. Solutions were prepared from a.r. chemicals (Merck) and triply distilled water.

Scanning electron microscopy (SEM) patterns of electrode surfaces resulting after 8 h electrochemical faceting were obtained.

The voltammograms of the starting pc platinum electrode run in 2 M HF and for the sake of comparison also in 1 M H₂SO₄, exhibit the two pairs of conjugated sharp current peaks usually assigned to weakly and strongly bound H-adatoms. These pairs of peaks in 2 M HF are broader and less symmetric than those observed in 1 M H₂SO₄ (Figs 1a and 1b).

The faceted platinum electrodes exhibit two stable voltammetric responses after repetitive triangular potential scanning in 2 M HF, at 0.1 V s^{-1} , depending whether the H-atom or the H- and O-atom potential ranges are covered (Figs 1c and 1f). These voltammograms are only qualitatively comparable to those obtained in 1 M H₂SO₄[4] as the single cathodic current peak related to the strongly bound H-atom in 1 M H₂SO₄ turns into two peaks in 2 M HF, one located at ca 0.22 V and another at ca 0.26 V, respectively (Fig. 1c).

The degree of development of (100)-type faceting in 2 M HF can be estimated through the strongly bound to the weakly bound H-atom electrodesorption peak height ratio (R) measured in 1 M H₂SO₄, as for the latter the greatest definition of peaks is observed. Thus, for $E_l = 0.04 \text{ V}$, $E_u = 1.30 \text{ V}$, and $t = 5 \text{ min}$, R exhibits a maximum in the $1.0 \text{ kHz} \leq f \leq 5 \text{ kHz}$ range, in agreement with results for other acids[4]. Otherwise, for $f = 1 \text{ kHz}$, $E_l = 0 \text{ V}$ and $E_u = 1.3 \text{ V}$, R attains a maximum for $t \approx 20 \text{ min}$. For longer t a slight decrease in R is noticed. Likewise, the value of R in 2 M HF decreases from 2.5 for a (100)-type faceted platinum electrode voltammetrically stabilized, at 0.1 V s^{-1} , in the H-atom potential range, to 1.8 for the electrode stabilized by potential scanning also at 0.1 V s^{-1} , but covering the O-atom potential range.

SEM patterns (Fig. 2) of faceted electrodes in 2 M HF solutions show a clear grain structure with crystallographic orientation in a particular direction, and net grain boundaries. Under the optimal conditions, (100)-type electrochemical faceting implies the

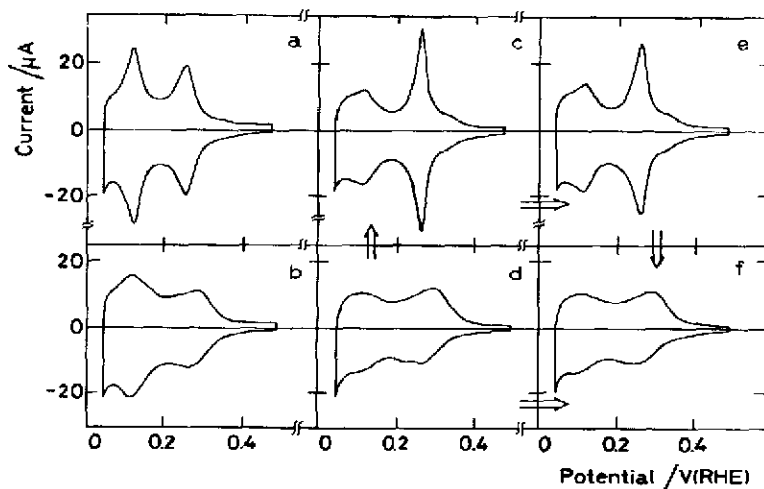


Fig. 1. Voltammograms run at 0.1 V s^{-1} ; 25°C . (a) and (b) correspond to the starting pc platinum in $1 \text{ M H}_2\text{SO}_4$ and 2 M HF , respectively. (c) (100)-type faceted platinum; 5 min faceting and voltammogram run in 2 M HF . The voltammogram corresponds to the 3rd cycle covering the H-atom potential range. Voltammetric response depicted in (c) turns into that shown in (d) by changing the electrolyte from 2 M HF into $1 \text{ M H}_2\text{SO}_4$. (e) (100)-type faceted platinum; voltammogram resulting from (d) after a few cycles in $1 \text{ M H}_2\text{SO}_4$ covering the O-atom potential range. (f) (100)-type faceted platinum; voltammogram resulting from (c) after a few cycles in 2 M HF covering the O-atom potential range. The same voltammogram results from (e) when the electrolyte is changed from $1 \text{ M H}_2\text{SO}_4$ into 2 M HF .

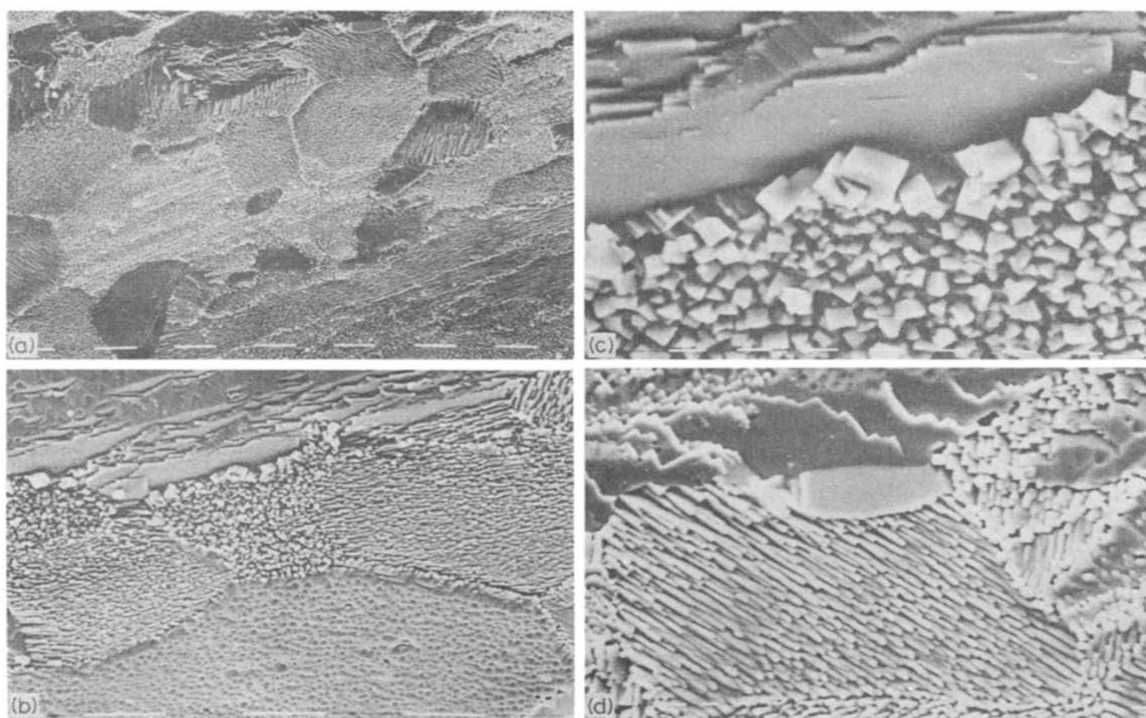


Fig. 2. Scanning electron microscopy patterns of (100)-type faceted platinum after 8 h faceting in 2 M HF at 25°C . (a) $\times 3200$ (scale $10 \mu\text{m}$); (b) $\times 6400$ (scale $10 \mu\text{m}$); (c) $\times 12600$ (scale $1 \mu\text{m}$); (d) $\times 12600$ (scale $1 \mu\text{m}$).

development of a grain structure which can be seen with a low magnification for t greater than 1 h. On increasing t the formation of stepped surfaces with a high density of kinks is observed. In addition, some patches of the surface comprises cubic-shaped twinned crystallographic structures.

Electrochemical faceting of platinum in acids involves an initial stage and a propagation stage[4, 5]. The initial stage provokes a weakening of metal-metal bonds through electroadsorption/electrodesorption reactions, principally at crystallographic defects in the lattice. The propagation stage implies a selective electrodisolution and electrodeposition of metal atoms during the potential cycling. For comparable electrochemical faceting treatments in different acids, the development of the (100)-type preferred oriented platinum surface is practically independent of the electrolyte composition[3]. This fact should be related to the slowness of the anion adsorption kinetics to follow the fast potential cycling developing electrochemical faceting.

In contrast there is a clear influence of the electrolyte composition on the voltammetric stabilization stage at 0.1 V s^{-1} . Thus, for a (100)-type preferred oriented platinum, this influence can be seen by changing an electrode prepared in 2 M HF exhibiting the voltammogram depicted in Fig. 1c, from 2 M HF into 1 M H_2SO_4 . Its voltammetric behaviour in 1 M H_2SO_4 (Fig. 1d) is similar to that of an electrode subjected to electrochemical faceting in 1 M H_2SO_4 [4] itself. Similarly, for an electrode faceted in 1 M H_2SO_4 and then stabilized by potential cycling in the same acid at 0.1 V s^{-1} covering the O-atom potential range (Fig. 1e), the change in electrolyte again from 1 M H_2SO_4 to 2 M HF, brings a voltammetric response similar to that for an electrode faceted in 2 M HF which has been cycled at 0.1 V s^{-1} in the O-atom potential range (Fig. 1f). After 4–8 h electrochemical faceting in 2 M HF, the splitting of the strongly bound H-atom electroadsorption current peak is also observed by changing the electrolyte to 1 M H_2SO_4 . For the latter the voltammetric splitting remains during cycling covering the H- and O-atom potential ranges. It should be noticed that these two cathodic current peaks were also seen during the first voltammetric scans in the H-atom potential range of

freshly prepared (100)-type faceted platinum both in 1 M H_2SO_4 and 0.5 M HClO_4 [6]. Therefore, the present results confirm that the voltammetric response of the preferred oriented platinum surfaces, as well as platinum single crystals[7–9] and polycrystalline platinum[10, 11], depends on both the proper surface structure and the electrolyte composition.

The voltammogram assigned to the stable electrode surface structure accomplished through potential cycling in the H-atom potential range is reached for only a few cycles in 1 M H_2SO_4 , it requires a longer potential cycling in 0.5 M HClO_4 , and it is practically not attained in 2 M HF. The time for the voltammetric stabilization at 0.1 V s^{-1} of (100)-type preferred oriented platinum in the different electrolytes correlates, in principle, with the decreasing adsorbability of anions in the order $\text{F}^- < \text{ClO}_4^- < \text{HSO}_4^-$ [7–11].

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