

Research Article

The Electrochemical Development of Pt(111)Stepped Surfaces and Its Influence on Methanol Electrooxidation

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The progress in the preparation of new electrode surfaces by electrochemical treatments exhibiting high faradaic efficiencies towards industrial electrocatalytic processes has gained more attention in today's scientific community. Most of the papers report new catalysts dispersed on different substrates, but some fundamental studies required for electrochemical and physical characterizations are sometimes forgotten. In this paper, we make a full staging of two electrochemical treatments that can be conducted to enhance the electrocatalytic activity of platinum surfaces, such as, electrofacetting through square wave potential programs and constant cathodic polarizations in the net hydrogen evolution region. The cathodic treatment applied at -2 V clearly develops (111) stepped planes similarly to the electrofacetting performed after applying the square wave program between 1.40 V and 0.70 V at 2.5 kHz. The X-ray diffraction patterns of both surfaces as well as on other electrofaceted platinum electrodes are obtained for comparison purposes. Moreover, the electrocatalytic activity towards methanol electrooxidation also exhibits equivalent coulombic efficiencies and 200% higher than on polycrystalline platinum as demonstrated by linear sweep voltammetry and potentiostatic current decays.

1. Introduction

A solid surface is a physical region that confines the crystal growth and the emergence of new physical properties different to those of the bulk. In the case of a solid/(liquid or gas) interface, the heterogeneous catalyst can lead to significant changes depending on the presence or the absence of an electric field. Moreover, a single-crystal (sc) solid/liquid interface is of special interest since it restricts the freedom degrees of surface mobility. Thus, surface atoms can take positions different from those expected depending on the characteristics of the applied electrode potential. This surface phenomenon is called reconstruction and is usually studied in physics with the help of ultrahigh vacuum (UHV) techniques [1]. However, this process strongly depends on the nature of the metal. Thus, platinum type metals are considered one of the most important catalysts as anodes

and cathodes in polymer electrolyte fuel cells. This is mainly due to the large values of exchange current densities of the electrochemical reactions and the surface stability in the case of electrodisolution and/or electrodeposition [2, 3]. Surface reconstruction at platinum/solution interface is usually the result of an electronic redistribution occurring as a consequence of either ion adsorption or oxygen-containing species formation, finally leading to surface facets. In the case of polycrystalline (pc) surfaces, the formation of facets of a fixed crystal orientation is of particular interest for industrial applications such as electrosynthesis, fuel cell technology, and electrolysis [4, 5] due to the large stability even at potentials as high as 1.6 V.

The surface structure of a sc can be checked by a number of selected techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) [6]; however, in the case of electrofaceted surfaces the atomic

resolution is difficult to achieve due to the large number of defects. Moreover, other techniques are currently used to obtain the fingerprint of the electrode surface such as cyclic voltammetry (CV), which offers current versus potential data for sc and also for pc surfaces. CVs give important information about the adsorption/desorption states, phase formation of transitions, and so forth at the electrode surface as a function of potential. From the CV of platinum recorded between the potentials of solvent stability, one can distinguish the potential regions corresponding to the double-layer charging, hydroxide/oxide layer formation/reduction, and hydrogen adsorption/desorption [7].

In the case of noble metal interfaces, some CV current peaks can be assigned to defined X-ray diffraction (XRD) patterns [8, 9]. It was commonly accepted that a voltammetric peak is directly connected to a single X-ray excitation. However, it has been found that current intensities can also change between subsequent cycles because of surface restructuring induced by the electrode potential cycling [10, 11]. In the case of platinum, the effects of such cycles have been interpreted [12] as the progressive development of (110) or higher atomic stepped equivalent facets because of platinum oxide phase formation and reduction.

The morphology and structure of a catalyst surface has a strong weight on its electrochemical reactivity [3]. Thermo- or potential-induced surface reconstruction has been observed on clean metal surfaces with different crystallographies depending on type of atmosphere where the process is developed. If the rearrangement of surface atoms goes much further than atomic spacing, macroscopic changes, which are called surface reshaping, could happen to the surface morphology [13]. In particular, when pc metals are treated by periodic perturbing potentials, they are susceptible to remarkable changes in surface roughness and in the distribution of crystallographic faces, which is denoted as preferred crystallographic orientations via electrochemical faceting, [6, 8]. Tian et al. [14] reported the synthesis of platinum nanocrystals using repetitive square wave routines, and the obtained nanocrystals display high-index facets with a 400% more reactive activity than existing commercial platinum catalysts. Thus, surface restructuring in electrochemistry produces changes in the kinetics or even in the mechanism of various processes because of their strong sensitivity towards the metal surface structure [12, 15]. It has to be said that pc surfaces also exhibit surface restructuring, and in the case of the application of periodic potentials, they lead to the electroformation of microfacets [12]. It is well known that the application of fast potential periodic programs on platinum, rhodium, iridium, gold, or palladium produces permanent morphological changes with defined orientations, which depend on the potential limits and frequency of the routine by a microfacetting process [16–18]. The electrochemical responses of these stepped surfaces are similar to those of stepped crystalline surfaces [19, 20].

It has been shown in a previous paper [21] that besides the main forces that drive the surface restructuring and microfacetting (oxygen and hydrogen electroadsorption) the frequency of the square wave potential itself leads to a

single propagation mode. This is the one responsible of the crystal lattice surface rearrangement, with new equilibrium positions that can be calculated with the potential periodic perturbations as parameters.

The voltammetry for the oxidation of methanol on sc platinum shows a clear hysteresis between the positive and negative going scans due to the accumulation of the poisoning intermediate at low potentials and its oxidation above 0.7 V versus RHE [22]. Additionally, the reaction is also very sensitive to the surface structure. The Pt(111) electrode has the lowest catalytic activity and the smallest hysteresis in a single voltammetric scan whereas Pt(100) electrode displays a much higher catalytic activity and a fast poisoning reaction. On the other hand, Pt(110) electrode depends on the pretreatment of the surface [23].

Besides the studies with the three basal planes, methanol electrooxidation was also performed on stepped platinum surfaces in order to clarify how exactly the step density influences this reaction. Shin and Korzenicwski [24] suggested that an increase of the step density catalyzes methanol decomposition whereas Tripković and Popvić [25] showed that the increase in the step density leads to a decrease in the surface activity towards methanol electrooxidation, both authors using Pt[$n(111) \times (100)$]. Housmans and Koper [26] studied methanol oxidation on Pt[$n(111) \times (110)$] stepped surfaces, and reported an increase in the activity with the step density, suggesting that the presence of steps with a (110) orientation catalyzes methanol decomposition, carbon monoxide oxidation, and also the direct methanol oxidation. These kinds of studies are relevant not only from a fundamental point of view, but also for technical purposes, that is, once the proper crystallographic orientation is found, the technical electrode can be designed. Surfaces nanoparticles should be deposited in the carbon supported with the corresponding crystallographic orientation that resulted with the best electrocatalytic performance.

2. Experimental

Electrochemical runs were performed using a three-electrode compartment cell with a pc platinum wire of 0.5 mm diameter as a working electrode (99.999% purity, from Goodfellow Cambridge). A large area smooth platinum counter electrode and a reversible hydrogen reference electrode with a Luggin-Haber capillary tip completed the electrochemical system. Potential values in the text are given on the hydrogen reference electrode (RHE) scale. We employed 1 M sulphuric acid (96–98% analytical reactive from Baker) as supporting electrolyte, which was prepared using ultrapure water from Millipore-MilliQ plus (18.2 M Ω cm of resistivity). We performed the electrochemical experiments using a PGZ 301 Voltalab potentiostat-galvanostat with the Voltmaster 4 software.

To obtain the electrofaceted platinum surfaces (PtF), the electrodes were subjected to different potential techniques. However, the most attractive of all was the repetitive square wave potential scanning (RSWPS) in the symmetric form to avoid large surface roughness. To optimize the square wave potential parameters, we changed the lower E_d and

upper E_u potentials together with the applied frequency, f , only in the symmetric mode during a certain time t . In all cases, the process was followed by registering the CV profile of the interface between 0.05 and 1.45 V at 0.10 Vs^{-1} , always comparing with the nonperturbed electrode. The preferential oriented surface (faceted surface) with symmetries equivalent to (111) and (100) are obtained by widely changing the parameters shown above. The electrochemical experiments comprised the following stages: (i) electrode pretreatment involving repetitive triangular potential cycling at 0.1 Vs^{-1} between 0.05 and 1.50 V until a stabilized voltammogram was attained; (ii) the pretreated electrode was subsequently subjected to an *RSWPS* between E_d and E_u at f , during a certain time t or a cathodic treatment at $E = -2 \text{ V}$ during 30 min; (iii) the CV of the treated electrode was recorded again under the same conditions indicated in (i); (iv) XRD of the treated electrode were then obtained systematically.

We used the following criteria to estimate the development of preferred crystallographic orientation [6, 16]. The main voltammetric peak at low potentials of weakly bound hydrogen electrosorption at the platinum/acid interface (h_1), originally assigned to the H-adatom-Pt(111) site interaction, corresponds to H-electrosorption on disturbed Pt(111) surfaces with a larger number of Pt(110) sites whereas the main voltammetric peak at higher potentials (h_2 ; strongly bound H-adatoms) represents the H-adatom-Pt(100) site interaction. Accordingly, the height ratio between these two peaks, h_2/h_1 , can be taken arbitrarily to follow the degree of preferred crystallographic orientation achieved throughout the treatment described in (ii). Thus, for the untreated platinum surfaces electrode, the average h_2/h_1 ratio was ca. 0.84.

The most representative and relevant results involved a repetitive 5 KHz wave between $E_u = 1.50 \text{ V}$ and $E_d = 0 \text{ V}$ for faceted Pt(100) surfaces and the application of a 2.5 KHz between $E_u = 1.40 \text{ V}$ and $E_d = 0.70 \text{ V}$ for faceted Pt(111) surfaces. The current transients were recorded during the process and a potentiostatic holding at 0.05 V for 10 min was applied to eliminate dissolved molecular hydrogen under continuous nitrogen bubbling. Immediately after and under a continuous potential control, the CVs were run from 0.05 to 0.70 V at 0.10 Vs^{-1} . All runs were achieved at $20 \pm 2^\circ \text{C}$, under free oxygen conditions using nitrogen (99.998% purity) from Linde-Gas.

In order to study the electrocatalytic performance of the new surfaces produced by the electrofaceted and cathodic pretreatments two methodologies were carried out in oxygen-free 0.1 M methanol + 1 M sulphuric media, namely, linear sweep voltammetry and potentiostatic chronoamperometric curves. Linear sweep voltammetry was conducted on each surface starting from 0.10 V and scanning towards positive values at 0.010 Vs^{-1} . Chronoamperometric curves were performed until 10 minutes at 0.60 V and 0.70 V for the nonperturbed and the treated surfaces. The charge density values under the chronoamperometric plots were calculated until that time only for comparison purposes.

X-ray powder diffraction data were collected using a Rigaku ULTIMA IV, 285 mm radius, Powder Diffractometer

operating in Bragg-Brentano geometry. $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) monochromatized with a diffracted beam bent germanium crystal was used to collect data over the 39 to 90 degree 2θ range in steps of 0.02° and 0.01° deg using a scintillation detector. Peak positions were extracted from the diffractograms using the program POWDERX [27]. Multiple datasets were collected for each sample in order to obtain representative values.

3. Results

3.1. Electrochemical Characterization. Figure 1(a) depicts the electrochemical profile of platinum after annealing. For these surfaces the current intensities ratio between h_2 and h_1 is 0.84. This is the original surface, which is taken as the blank of all the applied pretreatments. Figure 1(b) shows in this case a clear trend to develop the (111) terraces with a ratio $h_2/h_1 = 0.52$. The *RSWPS* treatment under the conditions described in Figure 1(c) produces remarkable changes in the voltammetric response of the treated surfaces as well as in the corresponding surface morphologies comparing to the blank. Likewise, the relative distribution of voltammetric peaks is modified, that is, the Pt F100 develops the $h_2/h_1 = 1.80$ ratio. On the other hand, the cyclic voltammetric profile as a result of the cathodic treatment is shown in Figure 1(d). The relative distribution of peaks is between the blank and the profile of Pt F(111), that is the h_2/h_1 ratio is 0.75. Due to the appearance of more electrochemical contributions, the voltammetric contours are slightly wider. It is likely that a stepped surface arises with global (111) planes between that we consider the blank and the Pt F111.

3.2. Structural Characterization by X-Ray Powder Diffraction (XRPD). All the samples shown above in Figure 2 exhibit peak positions strictly corresponding to Pt^0 , which indicates no further oxidation at the catalyst occurring after applying the *RSWPS*. It is important to mention that all the samples present good stability, since they were also measured after periods of one month and presented no difference in the diffractograms.

When comparing the diffractograms of the treated samples, important changes can be seen in the relative intensity of the Bragg's peaks. This fact reflects the preferential orientation obtained by the *RSWPS* and the stepped planes developed after the CT, see Table 1 for details.

In the first case, the starting sample corresponds to the pc platinum wire with the intensity of (220) and (311) reflections considerable higher than the others. Since it is difficult to establish a direct comparison between the occurrences of lattice planes with the corresponding reflection intensities, we defined a "weighted intensities" using relative currents. The weights are cleared in terms of the intensities of the bulk platinum reflections. For example, platinum bulk has $I(111) = 100$ and $I(200) = 53$. They have equal occurrence in pc samples, so the direct ratio between unnormalized intensities leads to $I(111)/I(200) = 0.53$. If we define the weighted ratio as $I_w(111)/I_w(200) = I(111)/I(200) * (I_{\text{bulk}}(200)/I_{\text{bulk}}(111)) = 1$, the number

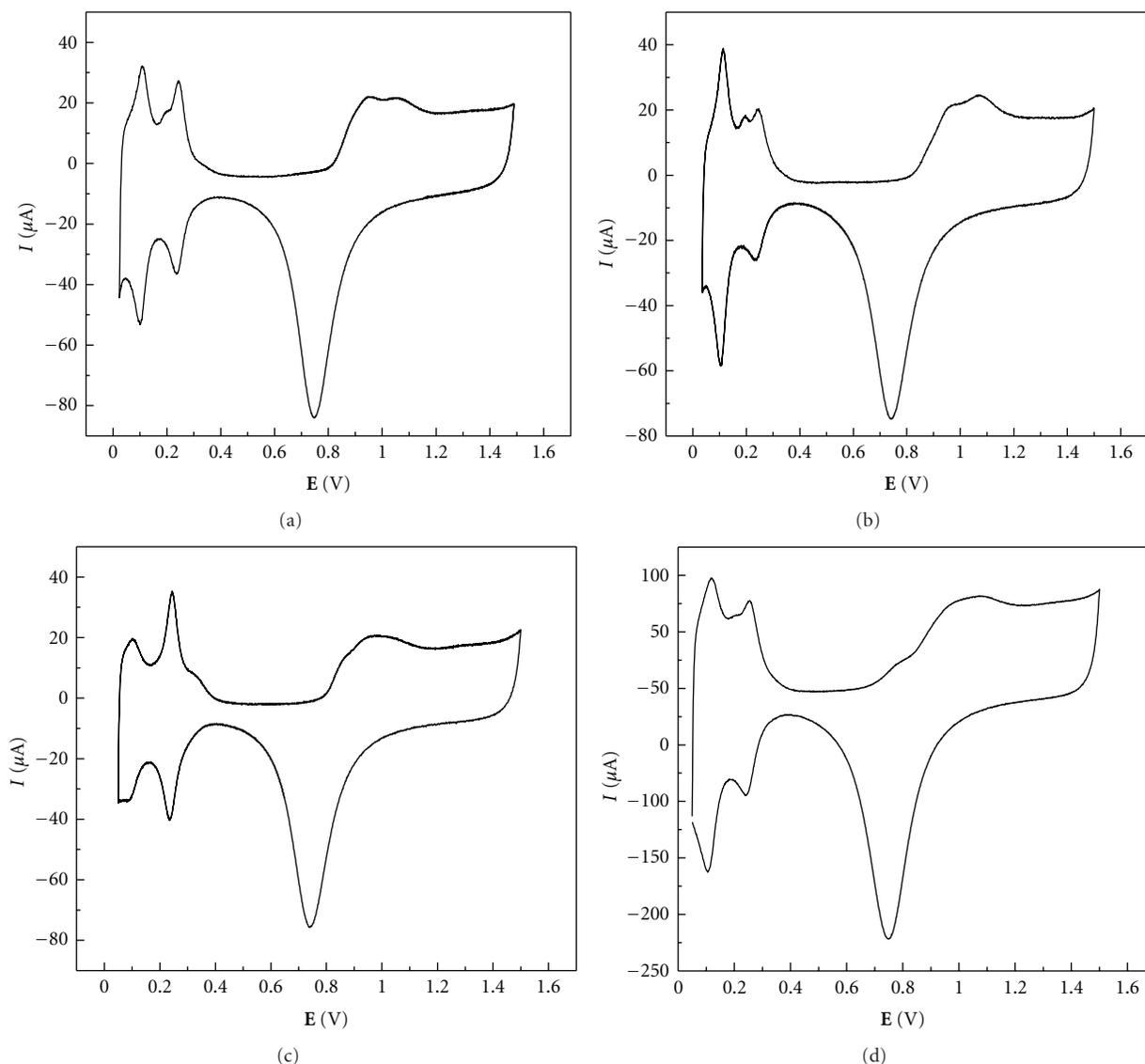


FIGURE 1: Cyclic voltammetry in 1 M sulphuric acid between 0.05 V and 1.50 V run at 0.10 V s^{-1} for (a) Pt pc annealing $h_2/h_1 = 0.84$; (b) Pt F(111) after a RSWPS $E_d = 0.70 \text{ V}$, $E_u = 1.40 \text{ V}$, $f = 2.5 \text{ kHz}$, $t = 10 \text{ minutes}$, $h_2/h_1 = 0.52$; (c) Pt F(100) after an RSWPS $E_d = 0.00 \text{ V}$, $E_u = 1.50 \text{ V}$, $f = 5.0 \text{ kHz}$, $t = 10 \text{ minutes}$, $h_2/h_1 = 1.80$; (d) CT Pt after $E = -2 \text{ V}$, $t = 30 \text{ minutes}$. $h_2/h_1 = 0.75$.

give us a direct estimation of the proportion between lattice planes.

Table 2 presents the weighted ratio for all the studied samples. According with this data pc platinum has an important contribution from (100) reflection in comparison with (111), that is, $I_w(100)/I_w(111) = 3.34$. This behavior is similar to the sample with CT, followed by the sample with faceting treatment to (100) direction (F100). The same trend is observed for (311) reflection in the three cases. The main difference between pc and CT platinum is in the (220) reflection, which is considerably high for the first sample. The XRPD is not grazing incidence experiments, so the conclusions cannot be only attributed to surface phenomena, but they can be attributed to both surface and bulk material. In this sense, the pc orient planes (220) and (311) and (200) can be easily interpreted in terms of (111) and (100) surface stepping like $(111) \times (111) \rightarrow (220)$ and $(111) \times (100) \rightarrow$

(311). This feature is slightly modified after the CT, since the intensity of the (220) reflection is reduced by a factor of ca. 3.8. This fact is interpreted as a reduction in the $(111) \times (111)$ stepping, when a restitution of the (111) reflection occurs characterized by the weighted ratio $I_w(111)/I_w(222) = 1.09$. According to this, the CT favors the (111) and (100) stepping as presented in Figure 2 and Table 2.

Regarding the Pt F100 sample, the faceting process does not establish a clear change in the proportion of the (200) lattice planes, since the weighted ratio shows the lowest value after comparing Pt F100 with pc platinum and CT platinum. Another feature is the intensity of the (220) reflection, which shows an intermediate contribution with an intensity positioned between those of pc and CT platinum.

Finally, the Pt F111 sample is the one with greatest differences, with a nearly net contribution arises from the (111) lattice planes referred with the (222) lattice planes.

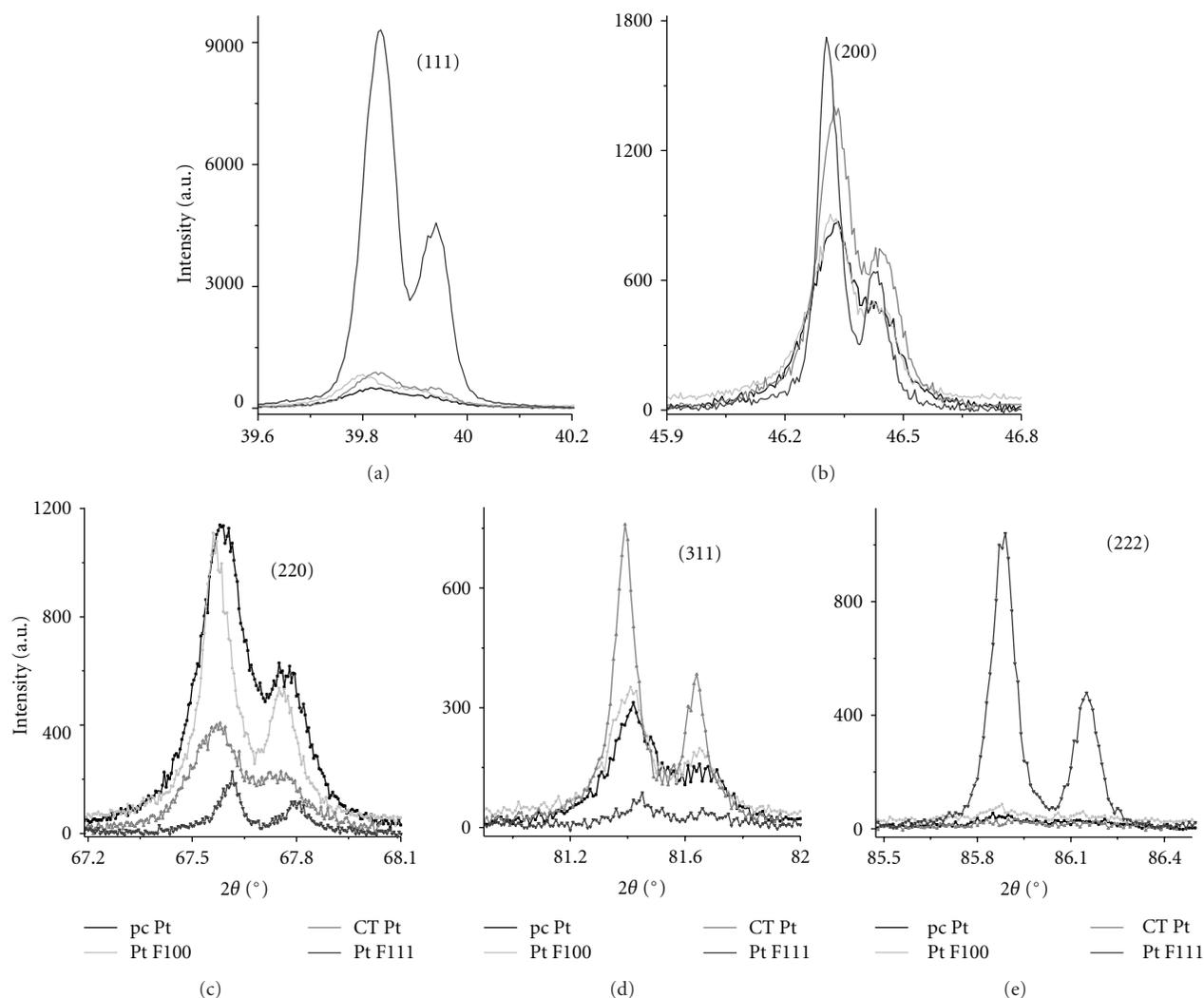


FIGURE 2: *Ex situ* X-ray powder diffraction pattern peaks (111), (200), (220), (311), and (222) for pc Pt (black lines), Pt F100 (light grey lines), CT Pt (grey lines), and Pt F111 (dark grey lines).

TABLE 1: Integrated intensities for pc Pt, CT Pt, Pt F100, and Pt F111 electrodes. The intensities are expressed as intensity $\times \Delta(2\theta)$ = counts \times degree.

Reflection	Pt bulk	pc	CT	F100	F111
(111)	100	108	155	129	1118
(200)	53	190	257	167	191
(220)	31	321	118	208	36
(311)	33	101	151	94	23
(222)	12	23	17	18	178

Note: in the case of Pt bulk, reflection (111) is referred as the intensity 100%.

Additionally, the contribution of (220) and (311) reflections is considerably lower than on the other samples. This is a confirmation that the faceting process is a process after which there is a strong decrease in the proportion of surface stepping, as observed in pc and CT platinum.

3.3. Electrocatalytic Activity Towards Methanol Oxidation.

TABLE 2: Weighted ratio for the reflections in pc Pt, CT Pt, Pt F100, and Pt F111 electrodes.

	Pt bulk	pc	CT	F100	F111
$I_w(200)/I_w(111)$	1.00	3.34	3.12	2.44	0.32
$I_w(311)/I_w(111)$	1.00	2.84	2.94	2.21	0.06
$I_w(220)/I_w(111)$	1.00	9.61	2.46	5.19	0.10
$I_w(111)/I_w(222)$	1.00	0.57	1.09	0.87	0.75

Note: we consider reflection (200) as a representative of reflection (100).

3.3.1. Linear Sweep Voltammetry in Methanol Acid Media. The first positive-going potential scan starting from 0.10 V up to 1.20 V for methanol electrooxidation on annealing Pt pc and electrofaceted platinum surfaces in 0.1 M methanol + 1 M sulfuric acid media are shown in Figure 3. A maximum current density is observed at ca. 0.85 V, above which the rate of methanol oxidation decreases due to platinum oxide formation (which also deactivates the surface). After the

TABLE 3: Integrated charge densities found under the current transients for methanol electrooxidation after 10 min. in oxygen-free 0.1 M methanol + 1 M sulphuric media on the studied platinum surfaces.

	Charge density ($\text{mC}\cdot\text{cm}^{-2}$)	
	0.60 V	0.70 V
Pt F100	<3	99.6
Pt F111	61.5	180.6
CT Pt	6.9	197.4
pc Pt	<3	97.7

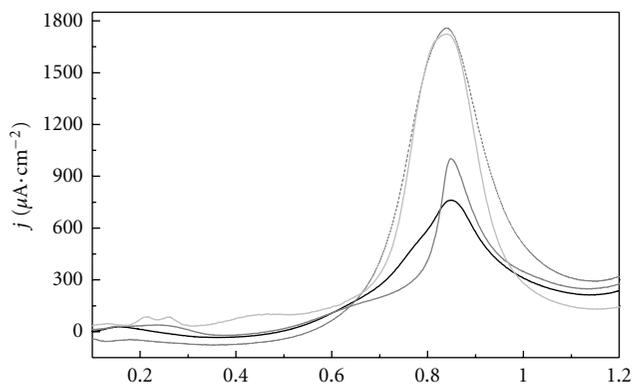


FIGURE 3: First positive-going potential scan for methanol oxidation run at 0.10 V s^{-1} between 0.10 and 1.20 V in oxygen-free 0.1 M methanol + 1 M sulphuric media on Pt F(111) (dotted gray lines); CT Pt (gray lines); Pt F(100) (dark gray lines) and annealed Pt (black lines).

pretreated procedure was applied in acid solution, the peak current density for Pt F111 depicts the greatest value, very similar to CT Pt. These values were more than 200% greater than that obtained on the untreated electrode. The electrocatalytic activity of pretreated surfaces was enhanced even after several cycles; contrary to the expected results on carbon monoxide poisoning induced on platinum surfaces.

3.3.2. Chronoamperometric Plots in Methanol Acid Media. Chronoamperometric curves were run for methanol oxidation on all platinum surfaces under two different constant potentials 0.60 V (not shown) and 0.70 V (Figure 4). All surfaces usually illustrate a typical diffusion-controlled current decay, but at 0.70 V, pc surfaces exhibit a first current increase at very short times. This fact is the result of a competitive process between adsorbed carbon monoxide and methanol oxidations with opposite contributions in the parallel oxidation mechanism, that is, the competition between the series and direct methanol oxidations. The pc platinum surface seems to be poisoned by a greater extent of carbon monoxide adsorbates. This effect is not observed at potentials lower than 0.70 V. The charge density at a fixed potential found under the current transients evidenced the real electrocatalytic activity of the surface. Table 3 represents the integration of the charge until 10 min (as comparison) for treated and untreated electrodes as a function of the

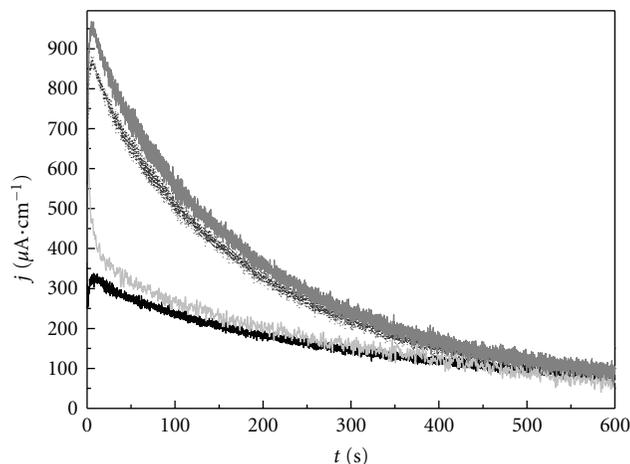


FIGURE 4: Chronoamperometric plots for methanol oxidation in oxygen-free 0.1 M methanol + 1 M sulphuric media at 700 mV on: pc Pt (black lines), Pt F100 (light grey lines), CT Pt (grey lines), and Pt F111 (dark grey lines).

potential. At 0.60 V, methanol oxidation did show a current contribution on the cathodic treated surface as well as on the Pt F111, not distinguished on the others surfaces. However, for 0.70 V, the charge densities found on the CT and Pt F111 surfaces are always higher than those of untreated platinum and other electrofaceted surfaces.

4. Discussion

The electrode composition plays an important role in the course of an electrocatalytic reaction, especially in the poison species removal. However, the surface morphology of technical electrodes is also important since it controls other factors associated with the formation and conversion of adsorbates. The relationship between the particle shape and the surface structure is of real importance in Electrocatalysis since its optimization is one of the best ways to enhance the selectivity and efficiency in the search of an adequate surface distribution for coadsorbate reactions.

Platinum crystallizes as a face centered cubic system with a cell parameter of 3.92 \AA . This system presents three base planes normal to the (111), (110), and (100) vectors in its three-dimensional crystal lattice. In fact the (110) plane is really $(110) = (111) \times (111)$, and not a true basal plane, so it is the first clue of an intrinsic atomic reconstruction. These three main vectors are the origin of the lowest Miller indices surfaces with a single type of symmetry. When the Miller indices increase, also does the complexity of the surface. For simplicity, these high Miller indices surfaces are considered as a combination of the different base planes in different proportions yielding terraces, monoatomic step and also *kinks*. The stepped surfaces present atomic terraces with a define orientation corresponding to a single base plane, separated by monoatomic steps of a certain symmetry. Lang et al. [28] proposed that the stepped surfaces have to be named taking the Miller indices of each terrace and step, with also the number of atomic files at the terrace. The

nomenclature for a stepped surface is $\mathbf{M}(s)[n(hkl) \times (h'k'l')]$ being \mathbf{M} the chemical symbol of the metal, n the number of atomic files at the terrace, the letter s between parenthesis indicates that it is a stepped surface and (hkl) and $(h'k'l')$ the Miller indices of the base planes that define the terraces and steps, respectively.

Methanol electrooxidation on platinum stepped or disordered surfaces is driven by two important factors; the total surface charge and the presence of water adjacent molecules in the aqueous phase. At the Pt(111) single crystal surface, the methanol molecule is located at a reactive position due to the formation of hydrogen bonds with a preadsorb water molecule [29]. It has been observed that the hydrogen bond strength of the methanol-water interaction at the (211) surfaces is larger than on (111), leading to a more exothermic adsorption for methanol [30]. However, the importance of the presence of preadsorbed water is demonstrated from the fact of the lower total exothermic condition for the cascade dehydrogenation (0.7 eV) at the Pt(111)/water interphase than at the Pt(111)/vacuum interphase [31, 32]. This fact is explained by the stabilization of the hydrogen bond in the complex and the weakened of the water/platinum interaction. Thus, adsorbed water molecules on platinum in acid media vibrates from 3500 to 3000–3100 cm^{-1} , but in the presence of adsorbate neighbours changes to a new vibration range due to the asymmetric stretching of the O-H bond at 3658 cm^{-1} [33]. Using *in situ* ATR-SEIRAS techniques it is demonstrated that water coexists with adsorbed carbon monoxide derived from methanol partial oxidation. Water is consumed during oxidation according to the adsorbed water and on-top carbon monoxide intensities. This is a strong confirmation that both water and carbon monoxide molecules coexists at the surface and that each species directly react from the surface promoting the further oxidation of other methanol molecules [34].

On the other hand, the change in the structure of the interfacial water structure caused by methanol adsorption is responsible of the difference between the experimental potential of zero charge (*pzc*) determined for the Pt(111-) CO interaction, 1.10 V, and the *pzc* estimated for the Pt(111-) water, 0.23 V [35]. Using these values it is possible to calculate mean angle between the water dipolar moment and the platinum surface. At room temperature *pzc*, diminishes from 7.85° for Pt(111-) water to 1.46° for Pt(111)-CO [35]. Chang and Weaver [36] have found that the water coadsorption at low coverages favours on Pt(111) the formation of bridge CO_{ads} . The vibration frequencies for linear and bridge geometries at high surface coverages by carbon monoxide are at least 20–30 cm^{-1} lower in the electrochemical environments than in UHV conditions. These environmental effects observed for the CO_{ads} bond suggests that the double layer effects are much more important than expected in the early stages of the anodic electrocatalytic reactions. Besides, the same important interaction between water and CO_{ads} has been also observed using *in situ* IRAS and STM techniques [37]. Adsorbed carbon monoxide on Pt(111) at 0.40 V shows a strong interaction with water molecules at the external layer retarding methanol oxidation to carbon dioxide, while its adsorption at 0.050 V reports lower values of oxidation

onset potentials. Moreover, it has been also reported that [29] methanol oxidation starts with the formation of a strong interaction leading to a hydrogen bond between the hydroxyl group of methanol with the water molecule. The first step of the reaction is the anchorage of a carbon-hydrogen bond focused towards the platinum surface. In this sense, our results clearly shows a larger activity in the case of the cathodic treated and the (111-) faceted platinum surfaces where the presence of stepped (111) planes are able to produce this strong interaction between partially dissociated water on (111) steps and adsorbed carbon monoxide from methanol partial oxidation on (100) terraces. The perfect combination of both effects of a proper crystal orientation at the steps and a distinct but adequate in the terraces are the theoretical concept in the catalysts design for the electrocatalytic oxidation reaction. The Pt F111 surface exhibit a good catalytic activity at lower potentials than CT Pt, but the latter exhibits larger charge densities at 0.70 V. This fact is the result of adsorbed hydroxyl species are produced on Pt F111 at lower potentials increasing then the catalytic activity at 0.60 V. However, since methanol posses a larger affinity towards the (100) oriented surfaces (as a consequence of its structural spatial conformation), at 0.70 V the stepped (111) \times (100) produced from the cathodic polarization method will exhibit a higher activity towards methanol oxidation. The relation between crystallographic orientation and oxidation catalytic activities are confirmed in the case of comparing Pt F100 and pc platinum surfaces.

5. Conclusions

(a) The electrochemical perturbation of platinum surfaces through *RSWPS* changes the surface relative distribution of crystallographic planes. This effect reaches the bulk of the metal up to the first layers of platinum, making possible the X-ray diffraction analysis.

(b) A net and practically single (111) plane contribution is obtained after obtaining a Pt F111 surface, however, for Pt F100, a stepped surface with a (220) plane main contribution is developed. The latter seems to be more an intermediate surface between pc and CT platinum. Moreover, the rearrangement produced at the CT platinum surface, yields facets with stepped planes equivalent to $[n(111) \times (100)]$.

(c) The electrocatalytic studies towards methanol oxidation conclude that both Pt F111 and CT Pt exhibit similar results and better than pc platinum with also a better tolerance upon surface poisoning. According to our knowledge water species are activated on (111) terraces at lower potentials than on (100) planes leading to adsorbed OH species with larger adsorption energies. Consequently, methanol adsorbates are not able to displace these ordered water species only enabling its surface diffusion from (111) terraces to (100) steps to finally adsorb there.

(d) The simple application of a constant cathodic current in the true hydrogen evolution region on pc platinum enhances the catalytic activity towards methanol

electrooxidation, since the stepped Pt[$n(111) \times (100)$] are morphologically more adequate to catalyse the reaction.

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