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On the voltammetric behavior of a platinized titanium surface with respect to the specific hydrogen and anion adsorption and charge transfer processes

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The procedure for obtaining platinized titanium (Pt/Ti) electrodes has been optimised in order to avoid the contamination produced by the presence of chloride anions and other impurities and the formation of titanium oxide on the titanium surface. It has been demonstrated that the surface preparation of the titanium substrate and the washing procedure are crucial steps for obtaining Pt/Ti electrodes with hydrogen adsorption–desorption behaviour similar to that of polycrystalline platinum electrodes. The plating bath is a solution of H_2PtCl_6 ($1.79\ \mathrm{g\ dm^{-3}}$ of platinum at pH lower than 1). The deposition process is carried out at a constant current density of $5\ \mathrm{mA\ cm^{-2}}$ for 100 min and at a temperature of 90–95 °C. Under these conditions, deposits with a thickness of 5–10 μm are obtained. The roughness factor of the Pt/Ti electrode is approximately 125.

Introduction

Platinum is normally employed as the electrode in electrochemical processes due to its high catalytic activity and stability, even in aggressive media, and for a wide range of current densities.[1–3] Because the use of massive Pt electrodes is obviously out of the question due to the high cost, Pt/Ti electrodes are normally substituted for Pt electrodes for industrial purposes. Titanium metal is passivated and covered by a hard oxide film with a high resistance when exposed to air or other oxidising environments. Thus, for the development of a lasting Pt/Ti electrode it is very important to avoid titanium passivation during surface preparation and metallic deposition, otherwise, the high ohmic drop in the oxide film makes the electrode useless. At the same time, the surface treatment must improve the adherence of the platinum coating to the substrate.

Pt/Ti electrodes described in ref. 4 do not clearly show the typical voltammetric adsorption–desorption profile, at the potential interval between -0.24 and $+0.2$ V *vs.* saturated calomel electrode (SCE), of either a polycrystalline Pt electrode or a platinized Pt electrode. Hence, from this fact, it can be inferred that these Pt/Ti electrodes do not have their adsorption capabilities developed to the maximum. All these facts clearly show that during its preparation, the electrode has a strongly contaminated surface and that this contamination is not eliminated during the washing process.

The typical platinum bath for obtaining Pt/Ti electrodes is a hexachloroplatinic acid solution and, if the washing step is not carried out very carefully, chloride anions and other impurities can remain on the surface. It is very well known that adsorbed impurities cause an important adsorption decrease, while chloride anions strongly modify the voltammetric profile in the so-called hydrogen adsorption–desorption zone. This contamination diminishes the utility of Pt/Ti electrodes for industrial applications, especially in sensor devices.

As with all coatings on titanium, including metallic oxides, a very critical parameter determining the stability of the electrode is the preparation of the titanium surface prior to coating. Several publications have reviewed the different processes for manufacturing dimensionally stable anodes, DSAs and conclude that their successful production of these stable anodes depends on the surface preparation for avoiding, among other things, titanium passivation.[5–7]

The typical surface treatment of titanium involves cleaning the surface followed by activation of the same. Several authors[8–10] have studied the question of how to eliminate the oxide insulating film and activate the surface. However, there still remain some discrepancies and contradictions between the different procedures normally used to manufacture coated titanium electrodes.

The composition of the bath for platinum electroplating—not only for obtaining Pt/Ti electrodes but also for thick electroplated Pt—has been thoroughly studied but, nevertheless, papers related to its optimisation have recently appeared. Baumgärtner and Raub[11] have extensively reviewed the more common electroplating baths for platinum deposition and it is clear that some problems relating to the performance of many of the baths remain obscure. Skinner[12] describes a new bath for electroplating that offers excellent characteristics and may be appropriate for obtaining thick films of platinum. Most recently, Pletcher *et al.*[13–22] have proposed a new modified bath for electroplating platinum on copper, platinum and Ebonex® ceramic (Ti_nO_{an-1} where n is a number between 4 and 10) substrates (tetraammineplatinum(II) in phosphate buffer solution, pH 10.4). These authors have focused on several aspects of the influence of pre-treatment, pH, temperature, concentration of platinum, current densities and stability of the platinum complex on the efficiency of the bath.

The aim of this work is to develop an optimised method to manufacture Pt/Ti electrodes in which most of the hydrogen adsorption capabilities can be obtained.

Different test solutions and processes were used to compare the behaviour and the surface state of a Pt/Ti electrode with those of a polycrystalline platinum electrode. The redox couples studied were Fe(III)/Fe(II), $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and Ce(IV)/Ce(III).

Experimental

Apparatus and solutions

Voltammetric experiments were performed at room temperature using an undivided Pyrex glass cell with three electrodes. Pt/Ti, polycrystalline Pt and platinized Pt were employed as working electrodes. The polycrystalline platinum electrode was a platinum bead of $8.04\ \mathrm{mm^2}$ geometric area obtained by fusion of a Pt wire of 99.995% purity obtained from Sociedad Española de Metales Preciosos. Before each experiment, the electrode was thermally treated as usual and cooled in air protected by a droplet of water, following Clavilier's approach.[23] Titanium wire from Goodfellow (0.5 mm diameter and 99.6% purity) was used as the substrate for Pt/Ti electrodes. The counter electrode was a platinum wire (Sociedad Española de Metales Preciosos) 0.5 mm in diameter and 10 cm long shaped as a spiral. The background electrolytes used for the voltammetric experiments were 0.5 M H_2SO_4 or 0.5 M K_2SO_4 solutions prepared from Merck a.r. products. $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, $K_3Fe(CN)_6$ and Ce_2SO_4 were of the purest grade available (Merck a.r. grade). Ce(III) solutions were prepared *via* reduction of Ce(IV) in sulfuric acid solution with hydrogen peroxide. Water was purified by means of a Millipore MilliQ system. Hexachloroplatinic acid was prepared by dissolving platinum in a 2/1 (v/v) HCl/HNO_3 solution. Solutions were deoxygenated by bubbling nitrogen N50 through them. Voltammetric experiments were performed with an EG&G PARC model 175 generator, an AMEL model 553 potentiostat and a Philips PM 8133 X-Y recorder. Platinum deposition was carried out at constant current using a home-made galvanostat. All potentials refer to the saturated calomel electrode (SCE). Scanning electron microscopy was carried out using a JSM 840A JEOL microscope. The surface composition of the electrode was analysed with a Link QX 200 EDX system. The Pt content of the Pt/Ti electrodes was measured by dissolving the deposit and analysing the platinum content by atomic absorption spectroscopy using a Perkin Elmer OPTIMA spectrometer. The sonication of the Pt/Ti electrodes was carried out with a Selecta ultrasonic cleaning bath operating at 30 kHz and 100 W.

Titanium surface treatment

The treatment of the titanium surface developed by us consists of several steps. First, the surface is physically eroded by sandblasting followed by etching in boiling 15% oxalic acid for 60 min. After this, the titanium surface is immersed in concentrated sulfuric acid (96%) for 2 s and washed thoroughly with deionized water.

Preparation of the platinized titanium electrode

The electroplating experiments were carried out in an open beaker at 90–95 °C. The composition of the hexachloroplatinic acid bath solution was 1.79 g dm^{-3} of platinum at pH lower than 1 (HCl). Electrodeposition was carried out at a constant current of 5 mA cm^{-2} for 100 min in a stirred solution (magnetic stirring). To obtain a good electric field distribution, the titanium electrode was surrounded with a platinum spiral. The pH of the bath was maintained by periodic additions of hydrochloric acid. The value of the pH must be kept constant within a narrow range in order to avoid hydrolysis of the platinum salt that, in this bath, starts between pH 2.0 to 2.2. Calculated amounts of platinum were added to maintain a constant concentration during the electrolysis. Once the electrode was obtained, it was immersed in 250 mL of stirred hot water for at least 6 h until the water temperature reached room temperature. This procedure allows not only the removal of chloride anions from the deposit, but also avoids stressing the deposit. After this, the electrode was electrochemically cleaned by applying a fast scan rate (1 V s^{-1}) for one minute between the potential limits corresponding to oxygen and hydrogen evolution. This procedure was shown to be crucial for obtaining good and reproducible voltammograms that show well-developed peaks in the so-called hydrogen adsorption–desorption zone (-0.24 to $+0.2$ V *vs.* SCE) which clearly show that the platinum surface has very little or no contamination. The roughness factor of this electrode was approximately 125 calculated from the relation between the voltammetric electric charge densities (μC cm^{-2}) measured between -0.24 and $+0.2$ V for the Pt/Ti and the polycrystalline Pt electrodes.

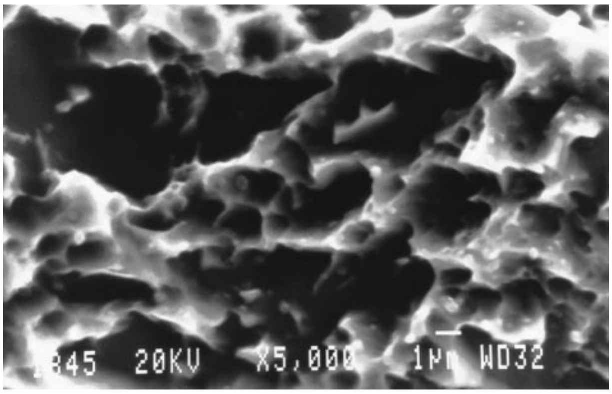

Fig. 1 Photomicrograph of a titanium surface treated by sandblasting followed by etching in boiling 15% oxalic acid.

Preparation of platinized platinum surface

The platinum surface was initially treated with aqua regia for 5 min, then rinsed with water and finally cathodically polarised in 0.5 M H_2SO_4 for 2 min using a current density of 300 mA cm^{-2}. After electrodeposition of Pt, using the same conditions employed to obtain the Pt/Ti electrode, the platinized/Pt electrode was cathodically polarised to eliminate any chloride anions adsorbed or present on the electrode surface. The roughness factor of this electrode was approximately 45.

Results

(a) Morphology of the deposits

Fig. 1 shows an SEM photograph of the titanium surface after the sandblasting step and after the chemical treatment. The sandblasting produces a micro-rough surface with many small deep pores that favour the adherence of platinum to the surface.

All deposits were matt and not or poorly reflecting. The adhesion was good. The SEM photograph of a Pt/Ti electrode is given in Fig. 2 and shows that no cracks exist on the surface and that the platinum deposit is uniform and formed by small crystallites. The average thickness and the platinum dropping were calculated by measuring the concentration of platinum when the deposits were dissolved. The deposits were 5–10 μm thick. An EDX analysis was carried out to investigate the presence of contaminants on the surface. Neither Cl nor S were detected.

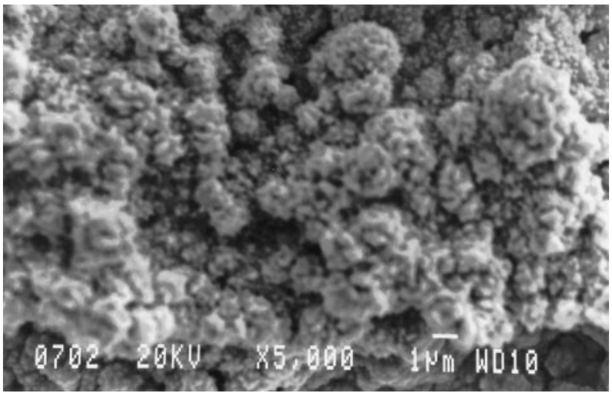

Fig. 2 Photomicrograph of a platinized titanium surface.

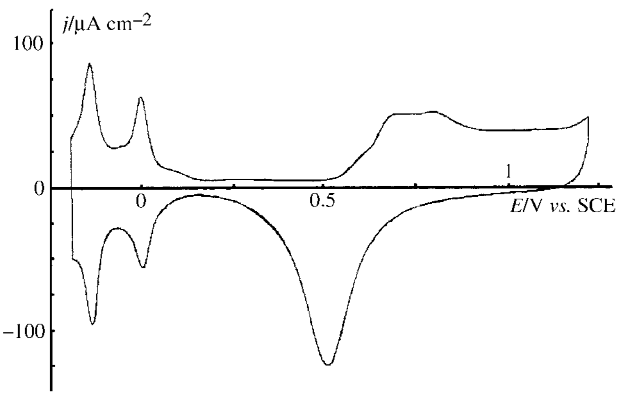

Fig. 3 Voltammetric curve in 0.5 M H_2SO_4 using a polycrystalline platinum electrode. Second cycle, $v = 50$ mV s^{-1}.

(b) Cyclic voltammetry

(b1) Acid media. Figs. 3 and 4 show the voltammetric profiles obtained for polycrystalline Pt and Pt/Ti electrodes immersed in 0.5 M H_2SO_4. The adsorption processes at the interval of potentials between −0.24 and +0.2 V, the so-called adsorption–desorption hydrogen zone, are very similar for both electrodes. The two characteristic peaks for the adsorption–desorption processes of hydrogen and anions on the [110] and [100] basal planes appear very well defined[24] but, for the Pt/Ti electrode, the anodic (cathodic) peaks are shifted to more positive (negative) potentials than those for the smooth polycrystalline platinum electrode.

The difference between anodic and cathodic peaks for the Pt/Ti electrode is 15 mV for the more positive couple peaks (basal plane [100]), and 25 mV for the more negative pair (basal plane [110]). The smooth polycrystalline Pt electrode does not show any difference. To investigate the cause of this shift between cathodic and anodic peaks, a study of the influence of the potential scan rate on the shift separation was carried out. The shift decreases with the scan rate, as shown in Table 1. The shift is 25 and 15 mV respectively, for a scan rate of 50 mV s^{-1}. Horányi *et al.*[25–28] have also recently looked into the relationship between voltammetric behaviour and electrocatalytic activity for the reduction of perchlorate and nitrate anions at platinized platinum electrodes with a roughness factor of 100. Their voltammetric curves show similar shifts for both [100] and [110] peaks—44 and 32 mV respectively—as those given in Fig. 4 and Table 1.

The difference in the peak potentials for a platinum electrode, and a Pt/Ti electrode and the shifts between peak potentials, could be caused by the existence of an ohmic drop between the platinum layer and the titanium surface due to the passivation of the titanium support. To verify this hypothesis, a study of the voltammetric behaviour of a platinized platinum electrode, in which there is no contact resistance between the layer of platinum deposit and the platinum support, was carried out. Similar shifts between anodic and cathodic peaks were obtained, in agreement with the results of Clavilier.[29]

A plausible explanation for the existence of this shift could be that inside the pore and during, for example, the reductive electroadsorption of H^+ to yield Pt–H, an increase in pH is produced. This increase would cause a shift in the equilibrium potential of the reductive electrosorption to more negative values than that corresponding to the pH of the bulk solution. Conversely, during the oxidation of the adsorbed hydrogen, a decrease in pH is produced that shifts the equilibrium potential to more positive values. This shift of the equilibrium potentials also shifts the cathodic and anodic peak potentials in the same sense. The magnitude of the shift depends on the dimensions and types of the pores and on the buffer capacity of the solution.

Table 1 Experimental values for the difference between anodic–cathodic couple peaks corresponding to the so-called hydrogen adsorption–desorption zone for a Pt/Ti electrode. Influence of the sweep rate. Supporting electrolyte 0.5 M H_2SO_4

Scan rate/mV s^{-1}	$\Delta E_{\mathrm{peak}\ 100}$/mV	$\Delta E_{\mathrm{peak}\ 110}$/mV
50	15	25
20	10	12
10	2.5	7
5	2.5	10

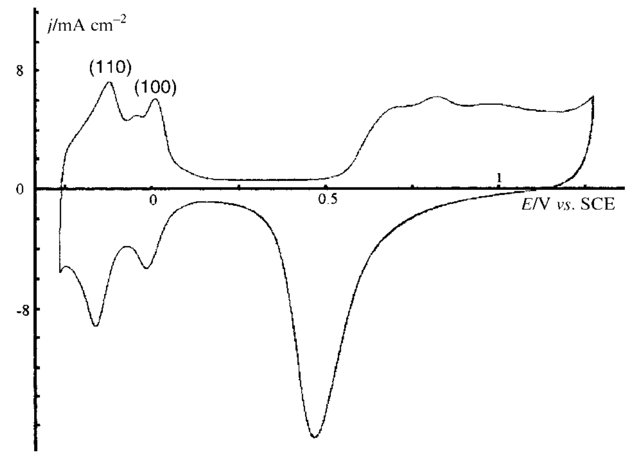

Fig. 4 Voltammetric curve in 0.5 M H_2SO_4 using a platinized titanium electrode. Second cycle, $v = 50$ mV s^{-1}.

We have also studied the Fe^{3+}/Fe^{2+} redox process on Pt/Ti and polycrystalline Pt electrodes in acidic media. The reduction of Fe(III) follows an outer sphere mechanism and it is well known[30,31] that in sulfuric acid solutions the process is slow and catalysed by the presence of chloride anions through a chloride bridge mechanism. Fig. 5 shows the voltammograms obtained in sulfuric acid. The anodic peak potentials are 0.48 and 0.51 V for the polycrystalline platinum and Pt/Ti electrodes, respectively. The anodic–cathodic peak potential separation is 110 mV for Pt/Ti and 130 mV for polycrystalline

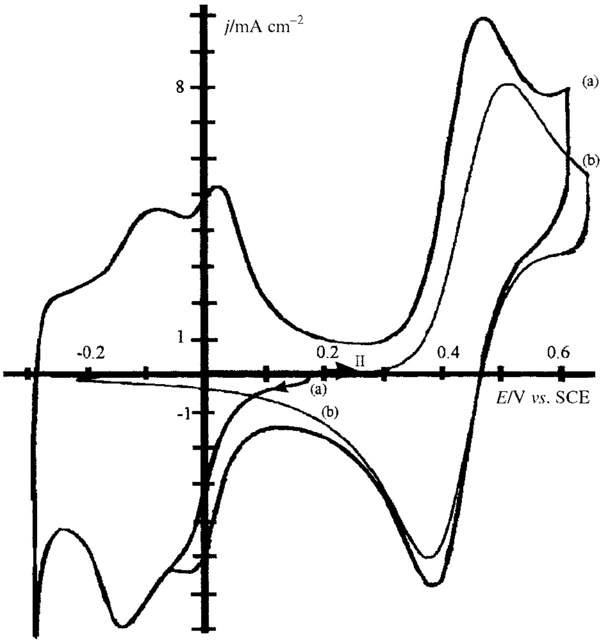

Fig. 5 Voltammetric curve in 0.5 M H_2SO_4 + 0.1 M $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ for a platinized titanium electrode [curve (a)] and for a polycrystalline platinum electrode [curve (b)]. First cycle, $v = 50$ mV s^{-1}.

Table 2 Experimental values for the difference between anodic–cathodic peaks of a Fe(III)/Fe(II) couple for polycrystalline Pt and Pt/Ti electrodes for different sweep rates

Scan rate/mV s^{-1}	ΔE_{peak}/mV Pt electrode^a	ΔE_{peak}/mV Pt/Ti electrode^a	ΔE_{peak}/mV Pt electrode^b	ΔE_{peak}/mV Pt/Ti electrode^b
50	130	110	100	90
20	110	95	—	82
10	100	90	—	77
5	95	—	87	—

^{a}Without chloride in the solution. ^{b}Chloride concentration 8×10^{-4} M. Supporting electrolyte 0.5 M H_2SO_4.

Pt. Both values are very different to the theoretical separation expected for a reversible single-electron process (59 mV) and clearly show the irreversibility of the process in sulfuric acid solutions. Likewise, for both electrodes, the large differences between current densities (calculated in relation to the geometric area of the electrode) corresponding to the surface process (adsorption–desorption zone) should be noted, whereas the current densities corresponding to the redox process are very similar. This can easily be explained because the different roughness factors of both electrodes (125 for the Pt/Ti electrode and approximately 1 for the polycrystalline one) make the surface area for the adsorption–desorption process much bigger for the Pt/Ti electrode than for the polycrystalline platinum electrode. However, if the electrode surface roughness is much smaller than the Nernst diffusion layer thickness, the peak diffusion current is determined by the geometric area of the electrode. This area is approximately the same for both electrodes and so both redox processes have approximately the same current density.

Table 2 shows that the peak separation is less for the Pt/Ti electrode. It is well known that some outer sphere mechanisms, such as the Fe^{3+}/Fe^{2+} process, are catalysed by the presence of adsorbed chloride anions.[31] Thus, a minute amount of adsorbed chloride anions on the Pt/Ti surface could be the cause of the decrease in the peak separation for this electrode. For this reason, a study was carried out in order to determine the influence of chloride anion concentration on the separation of the peaks. Table 2 shows that this separation is lower when chloride anions are present. Thus, in order to eliminate the possible contamination produced by chloride anions, the Pt/Ti electrode was sonicated and at the same time cathodically polarised in 0.5 M H_2SO_4 at a constant current density of 100 mA cm^{-2} for 10 min. Under sonication, some of the platinum deposit is lost and the roughness factor decreases to about three times lower than the initial value. Table 3 shows that the peak separations decrease when the chloride concentration increases. This clearly demonstrates that the difference in peak separation between both electrodes in sulfuric acid solutions is almost certainly caused by a very small chloride contamination of the Pt/Ti surface. Due to the porous character of this surface, some chloride anions are retained in the pores, but in such a small amount that the voltammetric profile in the background electrolyte looks very similar to that of a polycrystalline platinum surface in sulfuric acid. The presence of Cl^- was only detected by their electrocatalytic activity on the Fe^{3+}/Fe^{2+} process.

(b2) Neutral media. Fig. 6 shows the voltammetric profiles corresponding to the reduction of $K_3Fe(CN)_6$ on polycrystalline Pt and on Pt/Ti electrodes. The peak potentials for the anodic process are the same for both electrodes (0.29 V), as are the peak current densities. In agreement with the results obtained in acidic media both electrodes behave similarly for the redox process. However, the current density (calculated using the geometric area) corresponding to the surface processes (*i.e.* the so-called hydrogen adsorption–desorption zone, the surface oxidation and the capacitative current) demonstrates the big difference in the amount of active surface that exists between the rough Pt/Ti surface and the smooth polycrystalline platinum surface. Due to the micro-roughness of the Pt/Ti electrode, this difference in active area does not exist for processes for which diffusion totally or partially controls the current. In this case, the real surface area and the geometric area are very similar. From the measured value for the diffusion coefficient of Fe^{3+} (2.63×10^{-10} m^2 s^{-1}), using a polycrystalline electrode, the calculated geometric area of the Pt/Ti electrode is 4.8 mm^2, very similar to the measured geometric area, 5.1 mm^2.

(b3) Ce^{4+}/Ce^{3+} process. Ce^{4+} is a strong oxidant that, for its stability and solubility in acidic media, and excellent selectivity, is particularly appropriate for the synthesis of aromatic aldehydes and ketones from anyl aromatic compounds.[32,33] Ce^{4+} can be electrochemically regenerated from spent Ce^{3+} solutions using Pt/Ti electrodes.[34] Fig. 7 shows the voltammograms for the oxidation of Ce^{3+} on Pt/Ti and polycrystalline Pt electrodes. Once again, the voltammogram corresponding to the Pt/Ti electrode shows the presence of both surface and diffusion controlled Ce^{4+}/Ce^{3+} processes while on

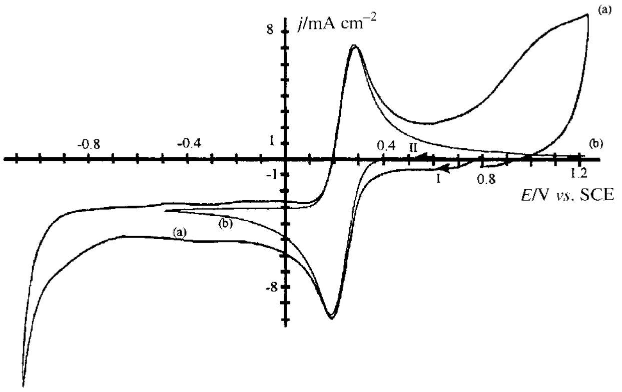

Fig. 6 Voltammetric curve in 0.5 M K_2SO_4 + 0.1 M $K_3Fe(CN)_6$ for a platinized titanium electrode [curve (a)] and for a polycrystalline platinum electrode [curve (b)]. First cycle, $v = 50$ mV s^{-1}.

Table 3 Experimental values for the difference between anodic–cathodic peaks of a Fe(III)/Fe(II) couple for polycrystalline Pt and Pt/Ti (after electrochemical and ultrasonic treatment) electrodes for different chloride concentrations. Scan rate 50 mV s^{-1}. Supporting electrolyte 0.5 M H_2SO_4

Chloride concentration/ $\times 10^{-5}$ M	ΔE_{peak}/mV Polycrystalline Pt	ΔE_{peak}/mV Pt/Ti
0	130	135
0.27	125	130
2.2	118	125
2.9	110	120
4.5	105	115

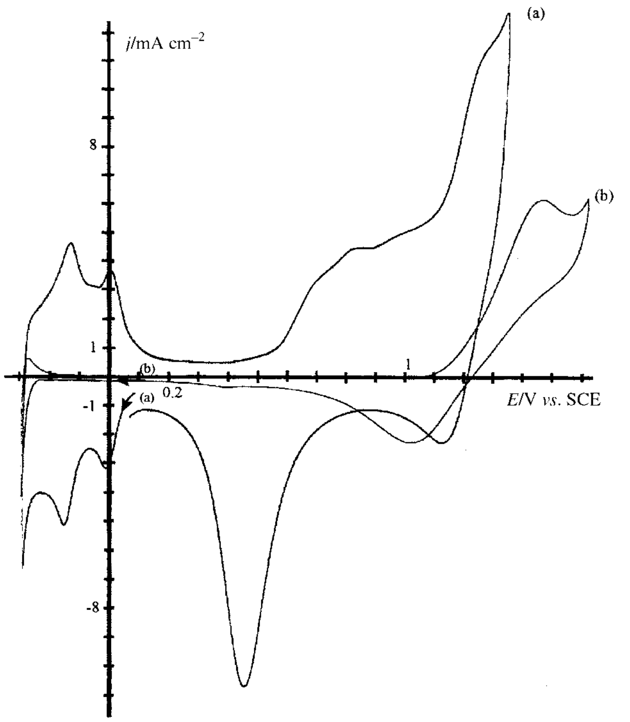

Fig. 7 Voltammetric curve in 0.5 M H_2SO_4+0.1 M Ce(III) for (a) a platinized titanium electrode and (b) a polyoriented platinum electrode. First cycle; v = 50 mV s^{-1}.

Pt electrodes, only the diffusion controlled process, at the same scale of current density, is seen. The redox reaction takes place within the potential range of platinum surface oxidation, which makes a comparison between the behaviour of the redox process on both electrodes difficult.

Conclusion

The sandblasting treatment of the titanium surface produces a micro-rough surface with many small deep pores that favour the adherence of the platinum coating. The ohmic drop at the interface, if any, is very low showing that the treatment used avoids the passivation of the titanium surface. The process for obtaining a Pt/Ti electrode has been improved and it has been demonstrated that washing and electrochemical cleaning are crucial steps in order to minimise or avoid chloride contamination. The Pt/Ti electrode fabricated following our procedure and the polycrystalline platinum electrode behave similarly, showing from the outset well-developed peaks at the so-called hydrogen adsorption–desorption zone. The surface of the Pt/Ti electrode behaves in different ways for adsorption controlled processes or for diffusion controlled processes. In the case of the former, the active surface area of the Pt/Ti electrode is 125 times larger than that of a polycrystalline platinum electrode of similar geometric area. However, for diffusion controlled processes both electrodes behave as if they had very similar active areas.

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