



# Study of the electrochemical oxidation of ammonia on platinum in alkaline solution: Effect of electrodeposition potential on the activity of platinum

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## ABSTRACT

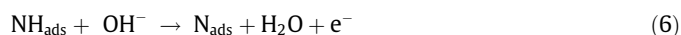
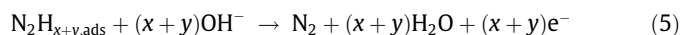
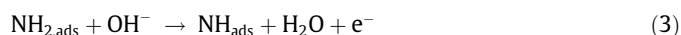
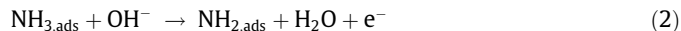
The electrochemical activity for the oxidation of ammonia of Pt electrodes, prepared by pulse potentiostatic electrodeposition on glassy carbon, was investigated by cyclic voltammetry and chronoamperometry. The morphology of the platinum deposits was observed by scanning electron microscopy. It was demonstrated that the crystallographic structure of the Pt electrodes probed by electrochemistry, instead of their morphology, has an important impact on the activity of platinum for the oxidation of ammonia in alkaline media. A deposition sequence, where a very negative reducing potential in the hydrogen evolution region and an oxidative potential in the H-desorption region are applied, leads to the formation of preferentially oriented Pt (100) electrodes. The presence of large (100) terraces enhances the Pt electrode activity for the oxidation of ammonia but has no impact on its poisoning by reaction intermediates. The stability of these electrodes was investigated by applying a repeated oxidation/reduction cycling procedure. It was found that when the upper potential is less positive than 0.6 V (beginning of the formation of Pt oxides) the preferential orientation of platinum is not affected by the oxidation/reduction cycling whereas for more positive upper potential limit, long range order of Pt is perturbed. As a consequence, the electrochemical activity of the resulting electrodes for the oxidation of ammonia significantly decreased in the latter case.

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## 1. Introduction

Energy and environmental issues are among the most important challenges in the field of electrochemistry. During the past decades, electrocatalytic oxidation of ammonia attracted a lot of interest because of the viewpoint of wastewater treatment [1–8], its possible application in direct ammonia fuel cell (DAFC) [9–12] and as a source for ultra-pure hydrogen which could be used in proton exchange membrane fuel cell (PEMFC) [13–18] and even in solid oxide fuel cell (SOFC) [19–22].

The electrochemical oxidation of ammonia in alkaline media has been extensively studied on several electrodes including platinum which has been shown to be one of the most active [14,23–37]. The mechanism for the direct electrochemical oxidation in alkaline media at a Pt electrode can be described by Eqs. (1)–(6) [26]. It is a very complex process involving a multi-step dehydrogenation of the N-species leading to formation of several adsorbed  $\text{NH}_x$  ( $x = 0, 1$  or  $2$ ) intermediates. Two intermediates ( $\text{NH}_x$  and  $\text{NH}_y$ , with  $x = 1$  or  $2$  and  $y = 1$  or  $2$ ) recombine together by chemical reaction and, once the new compound  $\text{N}_2\text{H}_{(x+y)}$  is formed, it is further electrochemically oxidized into molecular nitrogen.



(with  $x = 1$  or  $2$  and  $y = 1$  or  $2$ )

Unfortunately, some reaction intermediates and adsorbed species also lead to the deactivation of platinum during the oxidation of ammonia. The formation of  $\text{N}_{\text{ads}}$  causes the poisoning of the Pt surface because the adsorption energy of  $\text{N}_{\text{ads}}$  on Pt is too high to permit the recombination of two N adatoms and thus  $\text{N}_2$  cannot be formed [26].

Studies dealing with the electrochemical oxidation of ammonia on platinum revealed that the  $\text{NH}_3$  oxidation reaction is a very structure sensitive process that takes place almost exclusively on Pt (100) sites [27,31–34,38–40]. This  $\text{NH}_3$  oxidation reaction is also influenced by the neighborhood and the size of the Pt sites

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with Pt (100) large terraces being the most active [38]. It was also shown that the activity of the shorter Pt (100) terraces is directly related to the nature of the stepped surface. More specifically, the (100) × (111) junction (where (100) and (111) represent the orientation of the terraces and the steps, respectively) is more efficient than the (100) × (110) junction for the oxidation of ammonia. Subsequently, it has been shown that  $\text{NH}_{2,\text{ads}}$  is the stable intermediate on Pt (100) domains and that two  $\text{NH}_{2,\text{ads}}$  species recombined to form hydrazine which is readily oxidized to nitrogen [31]. On the other hand, on Pt (111) the only stable intermediates are  $\text{NH}_{\text{ads}}$  and  $\text{N}_{\text{ads}}$ , which are both inactive for the formation of nitrogen. The role of  $\text{OH}^-$  species during the oxidation of ammonia has been also investigated and it was found that they do not need to be adsorbed at the platinum surface during ammonia oxidation since this latter reaction starts at more negative potentials [29,31].

Most of the early studies on the oxidation of ammonia on platinum have been performed using single crystal electrodes [32–34,38,39]. More recently, polycrystalline Pt electrodes have been investigated [27,41,42]. By changing electrodeposition parameters such as the current density, platinum with different morphologies and electroactive surface areas were obtained and it was concluded that the enhanced activity of the platinum deposits is due to the increase of the electroactive surface area [41,42].

In this work, the cyclic voltammetry behavior of Pt electrodeposited onto glassy carbon electrodes by an innovative pulse potentiostatic method and their activity for the electrochemical oxidation of  $\text{NH}_3$  was investigated. The purpose of this work is to study: (i) the role of deposition parameters (potential and time) on the Pt electrode structure which can be established by its cyclic voltammetry behavior in 0.5 M  $\text{H}_2\text{SO}_4$ ; (ii) the role of the Pt electrode structure on its electrocatalytic activity for the oxidation of  $\text{NH}_3$ ; (iii) the poisoning of Pt electrode during short potentiostatic electrolysis of  $\text{NH}_3$ ; and (iv) the stability of the preferential orientation under repeated oxidation/reduction cycling procedure.

## 2. Experimental

### 2.1. Electrode preparation

Glassy carbon (diam. = 3 mm) electrodes (BASi) and plates ( $1.4\text{cm}^2$ ) were used as substrates for the preparation of supported Pt electrodes. Pt electrocatalysts were prepared by electrodeposition from a 5 mM  $\text{H}_2\text{PtCl}_6$  (Aldrich, >99.9%) in 0.5 M  $\text{H}_2\text{SO}_4$  (Fisher, >95%) solution. Carbon substrates were carefully polished and cleaned by an ultrasonic treatment in water before each deposition. A pulse potentiostatic method was used for the electrochemical deposition of catalysts. In this section, all potentials are quoted with respect to the Ag/AgCl ( $\text{KCl}_{\text{sat}}$ ) reference electrode. Glassy carbon electrodes were immersed in the plating bath at a potential ranging from 0.5 to 0.65 V which corresponds to the open circuit potential (OCP) of the glassy carbon electrode in the solution, in conditions where no platinum should be spontaneously deposited [43]. The depositions were performed at potentials ranging between  $-0.24$  and  $-0.35$  V in the hydrogen evolution region because a high concentration of hydrogen during the deposition process can favor a preferential orientation (100) of the Pt deposits [44]. By varying deposition conditions it is expected that different structures and morphologies would be obtained and this would allow the determination of their influence on the oxidation of  $\text{NH}_3$ . The pulse method developed in this study consists to apply a cathodic potential (between  $-0.24$  and  $-0.35$  V) for a given time and then to apply an oxidative potential (between 0 and  $-0.2$  V) for a period of time three times longer. This sequence differs from a classical pulse method for which, after application of the cathodic

potential, the electrode potential is left at the OCP [29,45]. The method was optimized by repeating the sequence with reduction and oxidation times ranging from 0.001 to 1 s and 0.003 to 3 s, respectively, as many times as necessary in order to obtain total deposition time of 5, 60 and 600 s. The results of the optimization are presented as Supporting Information (Fig. S1).

### 2.2. Electrochemical measurements

Electrochemical characterizations were carried out at room temperature in a typical one-compartment cell using a three-electrode configuration with a potentiostat/galvanostat VMP3 (BioLogic Science Instrument). An Ag/AgCl reference electrode ( $E^0 = 0.199$  V vs. NHE) and a platinum gauze counter electrode were used for all experiments performed in acid media. In alkaline media, a Hg/HgO (1 M KOH) was used as reference electrode. All solutions were degassed by bubbling with nitrogen (grade 4.8) for at least 30 min. Prior to each experiment, the specific area of the Pt deposit was estimated from cyclic voltammetry in 0.5 M  $\text{H}_2\text{SO}_4$  ( $50\text{mV s}^{-1}$ ) by using the H-adsorption peaks (between 0.2 and  $-0.2$  V) [46]. Crystallographic structures of the platinum were determined by the voltammetric features of the H-desorption peaks [44,47–51]. Based on literature, peaks  $h_1$ ,  $h_2$  and  $h_3$  at  $-0.1$ , 0.04 and 0.1 V (Fig. 1) vs. Ag/AgCl are related to the H-desorption on (110) steps, (100) steps and (100) terraces, respectively, and the peak  $h_4$ , at 0.3 V (Fig. 1), corresponds to anion ( $\text{SO}_4^{2-}$ ) adsorption on (111) terraces. The behavior of the electrodeposited Pt electrodes, when an oxidation/reduction cycling procedure is applied, was investigated. Up to 50 cycles between  $-0.2$  and 0.6 or 1.2 V with a scan rate of  $50\text{mV s}^{-1}$  were performed in  $\text{H}_2\text{SO}_4$  solution and the evolution of the voltammetric profiles was analyzed. The electrocatalytic activity of the Pt electrodes for  $\text{NH}_3$  (obtained from  $\text{NH}_4\text{OH}$ ) oxidation was investigated by cyclic voltammetry and short potentiostatic experiments (5 min). A significant decrease of the anodic peak current is seen between the first and the second cycle and this decrease becomes less important on subsequent scans. All the cyclic voltammograms reported in this work are for the second cycle.

### 2.3. Sample characterization

Morphologies of Pt deposits on glassy carbon were observed by field emission scanning electron microscopy (FE-SEM) using a JEOL JSM – 7600 TFE microscope at an accelerating voltage of 5 kV.

## 3. Results and discussion

### 3.1. Effect of deposition potential on the behavior of Pt electrode and consequences for the oxidation of ammonia

The cyclic voltammetry behavior of several electrodeposited Pt electrodes in 0.5 M  $\text{H}_2\text{SO}_4$  is compared in Fig. 1 and characterized by the so-called hydrogen adsorption/desorption (between  $-0.2$  and 0.2 V) and double layer (between 0.2 and 0.6 V) regions [44,46–52]. The former has been extensively studied and corresponds to H-adsorption/desorption on different ordered domains of platinum [44,50]. During the positive scan, up to four peaks can be observed at  $-0.12$  ( $h_1$ ), 0 ( $h_2$ ), 0.07 ( $h_3$ ) and 0.3 V ( $h_4$ ). It is now widely accepted that the  $h_1$  peak corresponds to desorption of weakly bonded hydrogen, and peak  $h_2$  is attributed to desorption of the strongly bonded hydrogen [44]. Based on literature, the peaks  $h_1$ ,  $h_2$  and  $h_3$  at  $-0.12$ , 0 and 0.07 V are related to the H-desorption on (110) steps, (100) steps, (100) terraces, respectively, and the peak  $h_4$  at 0.3 V corresponds to  $\text{SO}_4^{2-}$  anions adsorption on (111) terraces [47,50]. The cyclic voltammetric profiles of

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