



## Review

# Electrochemical CO stripping on nanosized Pt surfaces in acid media: A review on the issue of peak multiplicity

Eduardo G. Ciapina<sup>a,c,\*</sup>, Sydney F. Santos<sup>b</sup>, Ernesto R. Gonzalez<sup>c</sup>

<sup>a</sup> São Paulo State University (Unesp), School of Engineering, Guaratinguetá, Av. Ariberto Pereira da Cunha, 333, 12.516-410, Guaratinguetá, SP, Brazil

<sup>b</sup> Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, – UFABC, Av. dos Estados 5001, 09210-580, Santo André, SP, Brazil

<sup>c</sup> Instituto de Química de São Carlos, – USP, C.P. 780, 13560-970, São Carlos, SP, Brazil



## ARTICLE INFO

## Keywords:

CO stripping  
Platinum  
Electrocatalysts  
Peak multiplicity  
Electrocatalysis  
CO oxidation  
Particle size  
Nanoparticle

## ABSTRACT

This manuscript reviews the complex behavior of the electrochemical oxidation of adsorbed CO (CO stripping) on Pt nanoparticles in acid media. While on low-index Pt single crystals the so-called CO stripping generally exhibits a single, narrow, and well-defined oxidation peak, its oxidation on Pt nanoparticles may produce multiple peaks instead, whose origin is still not fully understood. The issue of peak multiplicity is reviewed based on published articles in the field of electrocatalysis and also on new experimental results. The aim of the present contribution is to highlight the extreme sensitivity of this reaction with respect to the state of the surface, microstructure and discuss some other important related features, including the role played by the experimental protocol itself. The influence of the index of crystallographic planes exposed to the electrolyte, particle size, particle agglomeration, CO surface diffusion, adsorbed anions, catalyst support, among other factors on the CO electro-oxidation are presented and discussed. In turn, the ideas presented herein would help scientists to avoid misinterpretation of the experimental results, better design experimental procedures and thus advance in the required knowledge for tuning the Pt nanoparticles to fulfill the requirements for specific applications, such as fuel cell catalysts resistant to CO poisoning.

## 1. Introduction

The electrochemical oxidation of carbon monoxide (CO) pre-adsorbed on Pt electrodes, the so-called “CO stripping”, is one of the most studied electrochemical reactions. Despite the importance of this reaction for gas sensors and surface science studies, the oxidation of CO is of paramount importance for the development of low-temperature Fuel Cells [1–4]. In these systems, such as H<sub>2</sub>-fed Polymer Electrolyte Membrane Fuel Cells (PEMFC), even trace amounts of CO as low as 10 ppm may drastically reduce the ability of the Pt-based electrocatalyst to efficiently oxidize H<sub>2</sub>. Due to the intrinsic mechanism of the reaction and the rather high enthalpy of adsorption on Pt (values up to 140 kJ mol<sup>-1</sup> at low coverages were measured on Pt (111) single crystals [5]), in Pt electrodes the oxidation of CO to CO<sub>2</sub> only starts at a significant rate at rather high potentials (above ≈ 0.6 V vs. reversible hydrogen electrode), making CO a catalytic poison for hydrogen/oxygen PEMFCs. Thus, the long-term operation of such Fuel Cells depends critically on the understanding of the fundamental parameters that control the oxidation of CO in real Pt-based electrocatalysts. Other types of low temperature Fuel Cells based on the oxidation of organic

fuels such as formic acid, methanol, ethanol also depend on the kinetics of CO oxidation, since it has been found as an adsorbed intermediate of such reactions [6,7].

As it will become clear in this manuscript, in contrast to the narrow single peak usually found using low Miller index well-defined Pt single crystals electrodes, such as Pt (111), Pt (110), and Pt (100), CO stripping on Pt nanoparticles usually shows multiple peaks in addition to the well-known pre-ignition peak also present on single crystal and smooth Pt electrodes. In such materials, especially carbon-supported Pt nanoparticles (the actual electrocatalysts used in Fuel Cells), the origin of such peak multiplicity is still an open question.

A survey of the published works in the literature revealed several explanations for the occurrence of multiple peaks in the CO stripping voltammetry, such as the effect of crystallography of surface planes [8], surface defects (edges and terraces) which are particle size dependent [9], particle size distribution [10], particle agglomeration [11], [12–14], and CO surface diffusion on the facets of a nanoparticle [15,16], among others.

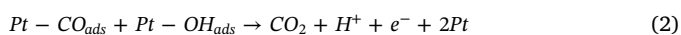
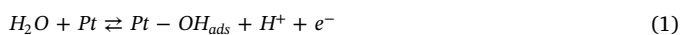
The aim of the present paper is to provide an overview of the major ideas regarding the origin of the peak multiplicity on Pt nanoparticles

\* Corresponding author at: São Paulo State University (Unesp), School of Engineering, Guaratinguetá, Av. Ariberto Pereira da Cunha, 333, 12.516-410, Guaratinguetá, - SP, Brazil.  
E-mail address: [eduardociapina@feg.unesp.br](mailto:eduardociapina@feg.unesp.br) (E.G. Ciapina).

(both supported and unsupported) in acidic media and discusses some important related features, including the role played by the experimental protocol itself. We believe this manuscript might be helpful to support scientists to conduct more in-depth interpretation on their results concerning this complex reaction and highlight its extreme surface-sensitivity. It is clear that a comprehensive knowledge of the reaction is needed for the design of new electrocatalytic materials for Fuel Cells applications. However, only by understanding the fundamental aspects of the CO oxidation on real electrocatalysts, it will be possible to improve the performance (particularly, the CO tolerance) of these nanomaterials and contribute to scale-up the use of Fuel Cells.

### 1.1. Fundamental background

From the mechanistic point-of-view, the electrochemical oxidation of CO is believed to occur by adsorbed CO and oxygen-containing molecules (generally ascribed to be OH). A simplified version of the mechanism of the reaction is given according to the reactions below:



In the first step (1) oxygen-containing species (denoted here as  $OH_{ads}$ ) are formed through the oxidation of water on free Pt sites; the conversion of CO to  $CO_2$  is accomplished as described by Reaction (2): adsorbed CO molecules interact with adsorbed  $OH_{ads}$  molecules yielding  $CO_2$ ,  $H^+$ , electron, and two free Pt sites. The overall process involves 2 Faradays per mol of reaction. Since Reaction (2) is a surface reaction between two adsorbed molecules, it belongs to the so-called Langmuir-Hinshelwood type of reaction. Therefore, the mobility of the adsorbed species at the surface as well as the active sites for the reaction are of extreme importance for the overall understanding of the process [10,13,15] as it will be later discussed in the text. As we shall see, these features determine the strong dependence of the reaction with structural characteristics of the electrode. Although Reactions (1) and (2) provide a good overview of the mechanism for CO oxidation, a more complex mechanism (i.e., involving an adsorbed intermediate such as  $COOH_{ad}$ ) has also been proposed, as reviewed in ref. [1].

Fundamental electrochemical studies regarding the oxidation of CO can be carried out under three distinct situations: i) oxidation of a monolayer of CO adsorbed on the electrode (CO stripping) and, ii) continuous (bulk) CO oxidation and iii) CO-contaminated  $H_2$  gas. Only the first situation (CO stripping) will be considered here since our main focus is to discuss the issue of the peak multiplicity observed in the oxidation of a pure adsorbed CO layer in a CO-free solution. In a typical electrochemical experiment of CO stripping in aqueous solution, CO is introduced in the electrochemical cell and allowed to adsorb on Pt electrode surface at a controlled potential where no oxidation occurs, i.e., close to the thermodynamic potential. Next, dissolved CO molecules are removed from the solution by purging the system with the aid of some inert gas, usually nitrogen or argon. Then, a potential sweep (or a potential step for chronoamperometric experiments) is initiated and the behavior of the current as function of potential (or the current as function of time) is recorded. Fig. 1 illustrates a typical CO stripping experiment on a carbon supported Pt electrocatalysts (Pt/C) recorded with cyclic voltammetry (Fig. 1a) and, on a separate experiment, with chronoamperometry at a constant potential (Fig. 1b).

As depicted in Fig. 1a, CO oxidation currents above the base voltammogram (the subsequent scan after the CO stripping) are observed only above 0.6 V, defining a single peak centered at 0.79 V (RHE, reversible hydrogen electrode in the same solution). If CO stripping is carried out at a constant potential (Fig. 1b) it is observed a current decay at short times followed by a broad peak centered at about 12 s, with levels off at about 50 s indicating the end of the reaction. Peak-shaped transients are generally expected in process involving nucleation and growth of reacting centers. For the specific case of the

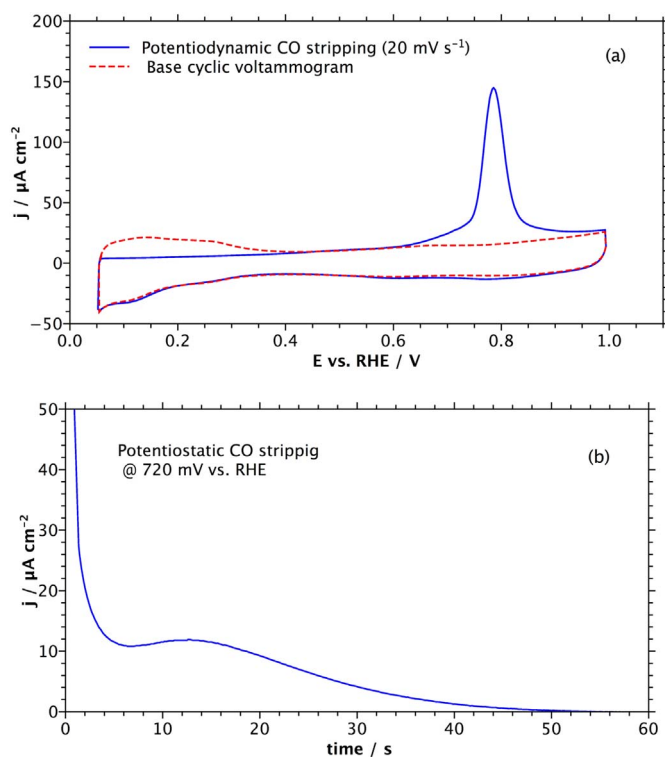


Fig. 1. Electrochemical CO stripping obtained for a carbon-supported Pt nanoparticles (Pt/C, average particle size of 2.8 nm determined by Transmission Electron Microscopy, see ref. [37]) in  $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ ;  $T = 25^\circ \text{C}$ . a) Potentiodynamic CO oxidation at  $20 \text{ mV s}^{-1}$  (line) and subsequent cycle (dashed); b) Potentiostatic CO stripping at  $0.72 \text{ V}$  (RHE).

oxidation of adsorbed CO, this is a consequence of the Langmuir-Hinshelwood mechanism, where the reaction rate (and therefore, the current) is expected to be proportional to the product of the surface coverage of  $CO_{ads}$  and  $OH_{ads}$ . The reader is referred to ref. [1] for further details on the mechanism of the reaction. However, in contrast to the behavior shown in Fig. 1, where a well-defined single peak develops in the positive-going sweep, CO stripping on Pt-based electrocatalysts can also depict multiple peaks in both potentiodynamic and potentiostatic experiments [10,11,17].

Herein, we focus on the origin of the peak multiplicity generally observed on carbon-supported Pt electrodes and other high-surface area electrocatalysts, such as Pt blacks and platinum electrodeposits. Although the discussion concerning the several effects that can lead to peak multiplicity will be made separately, it has to be clearly stated that all of them may be somehow interconnected and thus a careful analysis is required to understand the factors governing the peak multiplicity for each particular case.

## 2. The effect of the surface crystallographic planes and surface defects

Innumerable published papers have shown that CO electro-oxidation belongs to the family of the so-called structure-sensitive reactions (see, for instance refs [5,18] for a detailed review). Fig. 2 best illustrates this behavior, where the CO stripping voltammetry was carried out at two Pt single crystals electrodes presenting distinct crystallographic planes, namely Pt (111) and Pt (100) [19].

As it can be clearly observed in Fig. 2, two important features are highlighted: i) only a single CO stripping peak develops on the low index Pt( $hkl$ ) surfaces, and ii) the potential at which the peak appears depends on the surface crystallographic plane. It is well known that the chemical activity of a metallic surface is strongly dependent to the surface crystallography. For instance, the (100) surface crystalline

Download English Version:

<https://daneshyari.com/en/article/6661911>

Download Persian Version:

<https://daneshyari.com/article/6661911>

[Daneshyari.com](https://daneshyari.com)