Potential dependence of the saturation CO coverage of Pt electrodes: The origin of the pre-peak in CO-stripping voltammograms. Part 1: Pt(1 1 1)

Ana López-Cudero, Angel Cuesta *, Claudio Gutiérrez

Instituto de Química Física Rocasolano, CSIC, C. Serrano, 119, E-28006 Madrid, Spain

Abstract

Combined CO-stripping cyclic voltammetry and FT-IR spectroscopy measurements have allowed us to monitor changes in the coverage and structure of CO adlayers on Pt(1 1 1) electrodes in 0.1 M H_2SO_4 as a function of potential. Our results show that in CO-free solutions the maximum coverage is $\theta_{CO} = 0.68$ and that higher coverages can only be achieved in the presence of CO in the solution. Saturation coverages can only be reached if the potential at which the electrode is held during CO adsorption (dosing potential, E_d) is more negative than 0.30 V vs. RHE. The lowest CO coverage at which hydrogen adsorption on the Pt(1 1 1) electrode is completely blocked is $\theta_{CO} = 0.63$, which corresponds to an $E_d = 0.50$ V vs. RHE. Our results suggest that the process at the pre-peak (and, hence, the oxidation at low overpotentials of bulk CO in CO-saturated solutions), corresponds to the oxidation of adsorbed CO by reaction with oxygenated species nucleating at steps, the main peak appearing when nucleation of oxygenated species at the terraces also occurs.
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1. Introduction

It has been shown [1,2] that, when CO is chemisorbed on a polycrystalline platinum electrode while holding the potential within the hydrogen adsorption region, bulk CO can be oxidised at a lower potential than that of the onset of platinum oxide formation, that is, in the presence of a compact CO overlayer. It has also been demonstrated that, under a wide variety of conditions, the oxidation of bulk CO on polycrystalline Pt at low overpotentials in CO-saturated solutions is always concomitant with the presence of a pre-peak in the corresponding CO-stripping voltammograms in CO-free solutions [3], indicating a close relationship between the two phenomena. A pre-peak preceding the main CO oxidation process has also been observed for platinized Pt [4], for Pt sponge [5] and for Pt(1 1 1), Pt(1 0 0) and Pt(1 1 0) [6,7].

Wieckowski et al. [7] and Kita et al. [8] postulated that the electrooxidation of dissolved CO in CO-saturated solutions at 0.6 V vs. RHE occurs only on the small fraction of Pt atoms liberated from CO in the aforementioned pre-peak. These CO-free islands were found to be the active sites for the electrooxidation in the lower potential range of H_2 on Pt/Vulcan in the presence of 250 ppm CO [9]. Akemann et al. [10] suggested that the process in the pre-peak in CO-stripping voltammograms on Pt(1 1 1) corresponds to the oxidation of CO adsorbed in the vicinity of steps.

The results provided here are part of a project in which, using Pt(poly), Pt(1 1 1), Pt(1 0 0), Pt(1 1 0) and stepped single-crystal electrodes, we are aiming to understand why, provided the dosing potential (E_d) lies within the hydrogen adsorption region, always a pre-wave precedes the main CO-oxidation peak in stripping CV's, and why, under the same conditions, bulk CO can be oxidised in the presence of a compact CO overlayer.

2. Experimental

The working electrodes were bead-type Pt single crystals (2 mm in diameter for cyclic voltammetry, 4 mm in diameter for FT-IR experiments) prepared according to the method developed by Clavilier et al. [11], oriented and polished parallel to the (1 1 1) plane (miscut < 3′). Before each experiment, the electrode was annealed in the flame of a Bunsen burner, cooled down to room temperature in a $H_2 + N_2$ atmosphere, and transferred either to the electrochemical or the spectroelectrochemical cell while protected by a droplet of ultrapure water saturated with the cooling gas mixture. Fig. 1 shows the cyclic voltammogram (CV) at 50 mV s^{-1} of a Pt(1 1 1) electrode, prepared according to this procedure, in 0.1 M H_2SO_4, illustrating the degree of surface order and the cleanliness of both the surface and the working solution.

A platinum wire was used as a counter electrode, and a reversible hydrogen electrode (RHE), to which all the potentials in the text are referred, was used as reference.

Saturated CO adlayers were formed potentiostatically at different dosing potentials (E_d), either by blowing pure CO into the hanging meniscus or by saturating the working solutions with CO. We measured the current flowing during the potentiostatic adsorption of CO and stopped the gas flow when it dropped to zero. The 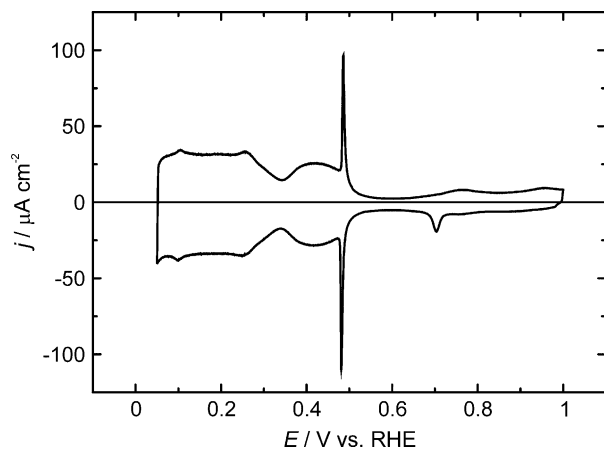solution was then purged with N_2 for 20 min, in or-der to remove traces of dissolved CO from the solution and the cell atmosphere, and a CO-stripping CV at 50 mV s^{-1} was recorded. Measurements in CO-saturated solutions were done after bubbling CO through the solution for at least 15 min, while keeping the electrode potential at the desired E_d.

Specular reflectance in situ FT-IR measurements were performed using a three-electrode spectroelectro-chemical cell with a 60° CaF$_2$ prismatic window attached to its bottom and placed in a Perkin–Elmer 1725X FT-IR spectrometer equipped with a narrow-band MCT detector, using p-polarized light. Each spectrum consisted of 100 interferograms, collected with a spectral resolution of 8 cm^{-1}. The differential spectra were calculated as $-\log(R_{sample}/R_{reference})$, where $R_{reference}$ and R_{sample} are the reference and sample spectra, respectively, collected either at different potentials or at different times. According to the equation above, positive absorption bands correspond to species present at the interface in the sample spectrum and absent in the reference spectrum, while negative absorption bands correspond to species present at the interface in the reference spectrum and absent in the sample spectrum. Bipolar bands would correspond to species present in both the sample and reference spectra, but whose frequency changed due to potential and/or coverage variations.

The working solution (0.1 M H_2SO_4) was prepared from concentrated H_2SO_4 (Merck Suprapure) and Milli-Q water (18 MΩ cm, 2–4 ppb TOC). Nitrogen (N50), hydrogen (N50) and carbon monoxide (N47, aluminium alloy cylinders) were supplied by Air Liquide.

3. Results

3.1. Cyclic voltammetry

Determination of surface coverages at the metal–electrolyte interface using the charge measured in stripping processes is far from straightforward, due to the necessity of a procedure to obtain the true double layer correction. In the case of CO adlayers, this is achieved with the CO-charge displacement technique, developed by the Alicante group [12,13]. We have recently shown [14] that this procedure is indeed based on a thermodynamic cycle and, hence, provides the true, exact thermodynamic double layer correction:

$$Q_{net}^{CO\ oxidation} = Q_{total}^{CO\ stripping} - \Delta Q$$
$$\Delta Q = Q_{ox}^{Pt} - Q_{initial}^{CO\ adsorption} \tag{1}$$

where ΔQ is the true value of the double layer correction, $Q_{net}^{CO\ oxidation}$ is the sought-after charge density corresponding exclusively to the faradaic oxidation of the CO adlayer, $Q_{total}^{CO\ stripping}$ is the charge density obtained by

Fig. 1. Cyclic voltammogram of the "defect-free", Clavilier-type Pt(1 1 1) electrode in 0.1 M H_2SO_4. Scan rate: 50 mV s^{-1}.