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Oxidation of carbon monoxide on poly-oriented and single-crystalline platinum electrodes over a wide range of pH

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ABSTRACT

The oxidative stripping of pre-adsorbed carbon monoxide has been studied on poly-oriented platinum, and on Pt(1 1 1), Pt(1 0 0) and Pt(1 1 0) single-crystal electrodes in phosphate buffer solutions as a function of pH, both stripping voltammetry and chronoamperometry. It was found that the stripping peak potential has a tendency to decrease as a function of pH until a pH of ca. 10–11, which is ascribed to a weaker adsorption of phosphate on platinum with increasing pH. Above a pH of ca. 11, the stripping peak appears to stay constant or increase, depending on the surface structure. We hypothesize that this may be due to the fact that above a pH of ca. 10–11, the main product of carbon monoxide oxidation is carbonate, which may be block active sites on the surface. By comparison with the stripping on the single-crystalline Pt, the stripping voltammetry on the poly-oriented Pt electrode appears as a convolution of the oxidation on the different facets. A similar conclusion is drawn for the chronoamperometry experiments, and it is suggested that this may be the main reason for the asymmetrical transients observed on the poly-oriented Pt electrodes, as well as on other strongly heterogeneous Pt electrodes that have been studied in the literature.

1. Introduction

The electrochemical adsorption and oxidation of carbon monoxide on platinum electrodes are among the most studied reactions in the electrocatalysis field during the last decades [1–13]. One of the principal reasons for the interest in this reaction is that CO results from the incomplete oxidation of small organic molecules (methanol, ethanol, etc.) in low temperature fuel cells. The CO produced is adsorbed strongly, poisoning the platinum surface and thereby severely limiting the catalytic oxidation activity [14,15]. Also, CO is present as an impurity in hydrogen fuel produced from hydrocarbons through the reformate process. Although the CO percentage in the reformate gas is very low, the platinum based catalyst still becomes poisoned and consequently the performance of the fuel cell is compromised [14,15]. For these reasons, one of the major objectives in fuel cell catalysis is to develop catalysts with higher catalytic activity towards CO oxidation or with a higher specificity towards a fuel oxidation path in which the formation of poisoning species is avoided [14–19].

Besides the practical interest, the oxidation of carbon monoxide on a platinum electrode is also an important model reaction [20]. It is well known that the kinetics of CO oxidation on platinum does not only depend on the structure of the platinum surface [2–7,21–23], but also depend on the properties of the electrolyte solution [4–7,24–27]. In fact, there is consensus in the literature about the higher relative catalytic activity for CO oxidation on platinum in alkaline solution compared to acidic solution, but there is little molecular-level understanding as to why this is. In acidic media, it is now well-established that step and defect sites possess a unique activity for CO oxidation, even to the extent that on a series of stepped Pt electrodes, it has been concluded that all CO, both those initially adsorbed at or near the step and those initially adsorbed on the terrace, react to CO_2 at the step sites [3,23]. CO oxidation on the Pt(1 1 1) terrace is essentially negligible, and all CO will diffuse rapidly to the step or defect sites and be oxidized there. On the other hand, more recently, we have studied CO oxidation on Pt[n(1 1 1) × (1 1 0)] stepped electrodes in alkaline solution, and indeed observed that the CO oxidation potential is lower than in perchloric acid solution. Surprisingly, four different active oxidation sites on the surface, i.e. sites with (1 1 1), (1 1 0) and (1 0 0) orientation, and kink sites can be observed during CO stripping voltammetry [4]. It was found that the catalytic activity towards the CO oxidation increases in the following way: kink > step > terrace sites [4]. Moreover, from Fourier transform infrared spectroscopy

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and potential-step experiments, we concluded that there is a high mobility of CO on the (1 1 1) terrace in alkaline media and that the CO oxidation takes place first on defect sites, producing carbonate which adsorbs close to or on the defect site [6,7]. This blocking effect would explain the multiple CO oxidation peaks observed during the CO stripping voltammetry. In addition, by a combination of chronoamperometry with voltammetry on a Pt(15 15 14) electrode in alkaline media, we have shown that there is a dual role of the step site towards the CO oxidation. CO adsorbed on one side of the step site is very reactive, while the CO located on other side (presumably adsorbed on top of the step) is less active and reacts with OH from the terrace [5].

Considering the amount of work done in acidic and alkaline media, and the different behaviors observed in the two media, it is of interest to investigate the CO oxidation reaction over a wide range of pH, not only in very acidic or very alkaline media, to include the effect of the pH dependence on the final product of the reaction. However, such a study is not without caveats. A detailed experimental analysis of the pH effect requires working with buffer solutions, implying that the buffer anions may adsorb specifically onto the platinum surface and may consequently obscure the proper pH dependence of the CO oxidation reaction. Therefore, we recently studied the adsorption of phosphate anions from phosphate solutions at poly-oriented and single crystal platinum electrodes over a wide range of pH by cyclic voltammetry [28]. In that work, we proposed that the phosphate adsorption strength decreases with increasing alkalinity of the solution, and that the main features observed at the poly-oriented Pt electrode in phosphate solution are related to the different crystalline facets, the (1 1 1) orientation presenting the most easily recognizable behavior in terms of phosphate adsorption.

Following these earlier studies, the aim of this paper is to study the CO oxidation reaction on poly-oriented and single crystal Pt electrodes in phosphate buffer solutions over a wide range of pH, in order to obtain more insight into the origin of the enhanced catalytic effect reported for alkaline media. The influence of different pH, anion co-adsorption and platinum structure surface on the CO adsorption and oxidation will be examined and discussed.

2. Experimental

Bead-type single crystals of Pt(1 1 1), Pt(1 0 0), Pt(1 1 0) orientation, and poly-oriented Pt bead-type electrodes (electro-active area = 0.165 cm^2) were prepared according to the Clavilier method [29]. Before each experiment the electrode was flame annealed and cooled down to room temperature in a H_2 + Ar atmosphere, after which it was transferred to the cell under the protection of a droplet of ultra-pure water saturated with the cooling gases.

A platinum wire was used as a counter electrode and a reversible hydrogen electrode (RHE) in the supporting electrolyte was employed as reference electrode. All potentials in the text are referred to this electrode, unless otherwise indicated. Electrochemical measurements were performed with a computer-controlled Autolab PGSTAT12 potentiostat–galvanostat. All experiments were carried out at room temperature (22 °C) in an electrochemical flow cell using a three-electrode configuration. The cell and all glassware were first cleaned by boiling in a mixture of 1:1 concentrated nitric and sulfuric acid, followed by washing with ultra-pure water. Next, glassware was cleaned by permanganate in alkaline media, followed by peroxide in acidic media, and finally thoroughly washed with ultra-pure water.

Experiments were carried out in aqueous phosphate buffered solutions prepared from high purity reagents (H_3PO_4, NaH_2PO_4, Na_2HPO_4 and NaOH from Merck Suprapur and Na_3PO_4 from Aldrich Ultrapure) and ultra-pure water (Millipore MilliQ gradient A10 system, 18.2 MΩ cm, 2 ppb total organic carbon). All buffer solutions had a constant ionic strength of 0.1 mol dm^{-3} and their pH was checked after preparation. Argon (N66) was used to deoxygenate all solutions and CO (N47) to dose CO. CO stripping experiments were obtained after bubbling CO through the cell for 4 min while keeping the Pt electrode at 0.10 V, followed by argon purging and electrolyte exchange to remove the excess CO. CO stripping voltammograms were recorded, by first scanning negatively until 0.05 V so that entire hydrogen region was probed, and then scanning positively up to 0.85 V. Chronoamperometric CO stripping transients were obtained by stepping the potential from 0.10 V to the final oxidation potential.

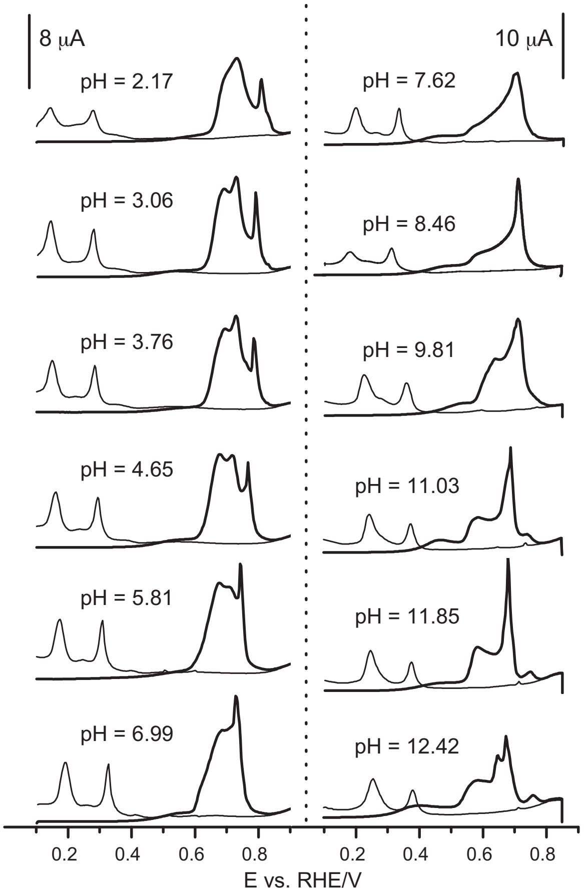

Fig. 1. CO stripping voltammograms recorded at the Pt poly-oriented electrode in phosphate solutions. E_{ad} = 0.1 V, sweep rate = 20 mV s^{-1}.

3. Results

3.1. CO stripping

Fig. 1 shows the CO stripping voltammogram (bold curve) and the subsequent cyclic voltammogram (thin curve) for a poly-oriented Pt electrode in a phosphate buffer solution in a broad pH range obtained at a scan rate of 20 mV s^{-1}. The blank voltammetric profiles obtained after CO stripping agree well with previous results [28], in which all the features were characterized in detail and related to the adsorption of phosphate species, specifically to sites of different crystallographic orientation, in particular of (1 1 1) symmetry. One clear observation is that the CO stripping voltammogram exhibits a different number of peaks and that the corresponding peak potentials shift with pH. Also, it is notable that the onset for the CO oxidation reaction (from ca. 0.3–0.5 V) increases in intensity and shifts to lower potentials as the pH