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Evolution of adsorbed CO on Pt and Pt/Au surface

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ABSTRACT

In this work, we studied in detail one of the possible limiting-steps during CO oxidation at Pt and Pt/Au electrodes, namely CO adsorption and diffusion at the electrode's surface. With this aim, we used an electroless method for Pt surface modification, which entails the spontaneous deposition of gold at Pt electrodes. We also use a home-made fast-response (four electrodes) flow cell that allows an accurate control of the electrode exposition time to CO (t_{ad}) and of the time interval (t_w) before stripping of the adsorbed CO (CO_{ad}). Thus two key experimental parameters of the electro-oxidation process can be independently modified and the results evaluated. Our results are consistent with a mechanism in which CO is initially adsorbed onto active sites and then moves away by surface diffusion. As a result, the subsequent oxidative stripping elimination of CO starts with CO_{ad} far away from the most active sites. The experiments carried out for Pt/Au electrodes with different fraction of electrode area covered by CO (θ_{CO}) demonstrate that Au acts as a barrier, hindering the surface diffusion of CO from/to the active sites, giving raise to the multiple pecks observed when t_w is low.

1. Introduction

In the search for new and more efficient portable power sources, a broad diversity of fuel cells devices has been explored [1]. For low power generation, (from a few mW up to 100 W) the most promising fuel cells are those designed to be fed by liquid fuels, like methanol or formic acid [2,3]. When compared with methanol, the use of direct formic acid fuel cells (DFAFCs) has two important advantages, the first is the lower fuel crossover through the polymer electrolyte membrane (PEM), and the second one is the higher operative power output. However, the oxidation of formic acid on pure Pt and Pd surfaces leads to surface poisoning by adsorbed CO (CO_{ad}) [4,5]. In an attempt to overcome these limitations, catalysts composed of different metal combinations have been recently tested [6]. Naturally in the design of these materials the main effort focuses in the pursuit of lower poisoning rates and improved stability, principally for the most active Pt and Pd based catalysts.

Nowadays, one of the most interesting catalytic surfaces is that formed by a combination of Pt (active) and Au (supposed inactive). The addition of an allegedly "inactive" patch of gold onto Pt results in a synergic effect, where the resultant catalytic activity is clearly better than that expected "*a priori*", considering the catalytic properties of each individual surface [7]. As has been clearly demonstrated in the literature, the performance improvement in Pt/Au catalysts is due to a change in the reaction mechanism [7,8]. It has also been proposed that CO adsorption cannot take place in Pt/Au surfaces thus leaving the active sites available for electro-oxidation of formic acid to CO_2 through the so-called direct path (see path (I) in Scheme 1) [9]. CO is generated by the spontaneous dehydration of formic acid (a chemical reaction without net electron transfer to the surface) and promoted by the formation of strong CO-Pt interaction at low potential (from 0 to 0.4 V_{HRE}) [10]. This second pathway is known as the indirect oxidation path (see path (II) in Scheme 1 for details).

In a previous paper we reported, for the first time, a strong time-dependent behavior for the oxidation of formic acid on Pt/Au surface and demonstrated that, in the presence of formic acid, at sufficiently long equilibration periods the surface is covered with adsorbed species yielding both, the mixed-metal and the neat Pt surfaces, equally inactive [11]. On the other hand, in the neat Pt surface the poisoning rate is so high that only the indirect pathway

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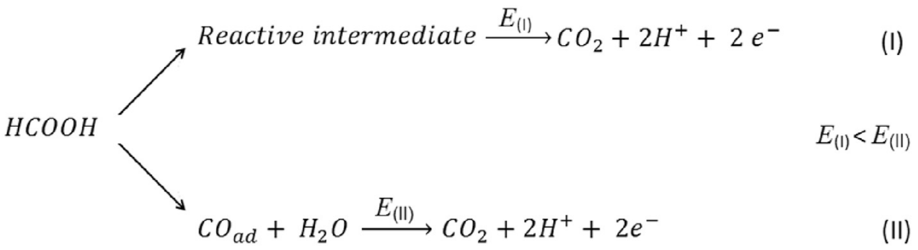

Scheme 1. Currently accepted path for formic acid oxidation.

is observed. When Au is present, the poisoning rate decreases on the remaining (uncovered) Pt surface. In our previous work this hindering of the dehydration pathway in the presence of Au was tentatively discussed in terms of the "active site model" however, to date, this hypothesis has not been conclusively proven.

The concept of the active site and its role in electrocatalysis is not new [12,13]. In general, it is accepted that O_2, CO, OH, and other species react preferentially at defects (steps, kinks, borders, etc.) in the catalyst's surface. In parallel, the active site concept also implies that, under certain conditions, the adsorbed species (e.g. CO_{ad}) are able to move away from active sites to cover the whole metal surface [14]. Interestingly, for the oxidation to CO_2, CO_{ad} must react with a contiguously adsorbed OH (OH_{ad}). In most cases this requires diffusion of one or both species [15,16]. Therefore, surface diffusion is a key factor for the CO electro-oxidation process, especially in situations where the mobility of the reactive species is suspected to be limited by a potential barrier, as was recently demonstrated [13,16].

In this work, we studied in detail one of the possible limiting-steps during CO oxidation at Pt and Pt/Au electrodes, namely CO adsorption and diffusion at the electrode's surface. To this end, we used a previously reported electroless method for Pt surface modification, that entails the spontaneous deposition of gold at Pt electrodes [11]. Our group developed this process as a clean way to obtain Au modified Pt electrodes by repetitive immersion of Pt electrodes in $HAuCl_4$ solution. The method allows to accurately control the Au surface coverage on Pt electrodes. In this work, we also take advantage of a relatively recent surface characterization technique developed by Ambrozik et al. [17].

2. Experimental

2.1. Materials

Perchloric acid (70% w/w) and sulphuric acid (98% w/w), were purchased from Cicarelli. Tetrachloroauric acid (trihydrate; 99.5%) was purchased from Sigma Aldrich, CO (99.5%) and Ar (99.9) were purchase from Linde Gas. All reactants were used as received. Solutions were prepared from ultra-pure water (18.2 MΩ cm, from Milli-Q Water Purification System).

2.2. Preparation of Au-modified platinum electrodes

Au-modified Pt electrodes were prepared using the spontaneous deposition (electroless) technique [11]. Briefly, neat Pt electrodes were soaked in a 1 mM $AuHCl_4$/0.5 M $HClO_4$ solution for 15 min and then washed copiously with ultra-pure water. Afterwards, electrodes were first cycled between 0.05 and 0.85 V (*vs.* reversible hydrogen electrode (RHE)) in 0.5 M $HClO_4$ solution (5 cycles), and then between 0.05 and 1.5 V (*vs.* RHE) at 50 mVs^{-1} (0.5 M H_2SO_4 solution) to achieve a reproducible cyclic voltammogram (CV). The percentage of Pt electrode area covered by Au (θ_{Au}) was calculated by the decrease of the measured charge in the Pt hydrogen (or CO) adsorption/desorption region (assuming 210 mC cm^{-2} and 420 μC cm^{-2} for a monolayer of adsorbed hydrogen and CO, respectively). Typically, θ_{Au} of 20–30% were obtained upon single exposition to $HAuCl_4$ solution. Higher θ_{Au} were achieved by successive $HAuCl_4$ expositions. The process described above for electrode modification is highly reproducible (in terms of θ_{Au}, ~2% discrepancy between experiments).

2.3. Electrochemical experiments

A home-made electrochemical flow cell with a four-electrode configuration was used for all electrochemical experiments (see Fig. 1 S.I. for details). The cell was designed to allow fast solution exchange while maintaining potential control of the working electrodes (WE). Polycrystalline platinum wire (0.5 mm diameter) was used, with or without Au modification (*vide supra*), for both working electrodes, WE1 (upstream) and WE2 (downstream). WE1 was set as a conventional working electrode, while WE2 was used as secondary electrode (E_{WE2} set at 1 V_{RHE}) for accurate measurement of the exposition time of WE1 to CO. RHE and platinum wire were used as reference and counter electrodes, respectively. All potentials in this work are given against the RHE (V_{RHE}). Deoxygenated solutions were prepared by argon purging for 30 min. Solutions containing different oxygen concentrations were prepared by successive dilution of an O_2 saturated solution with deoxygenated 0.5 M H_2SO_4. A Pine Research AFCRDE5 analog bipotentiostat with a homemade A/D converter and data recorder was used to carry out the electrochemical measures. All the experiments were conducted at 25 °C. CO_{ad} stripping experiments were performed at the W1 electrode after exposure to a CO saturated solution for a given time, while keeping the applied potential at 0.2 V. The subsequent CO_{ad} stripping voltammograms were recorded by scanning the W1 electrode potential positively up to 1.55 V.

3. Results and discussion

Fig. 1A and B (grey line) show cyclic voltammograms of bare Pt and Pt/Au electrodes, respectively. The effect of Au modification on the electrode's electrochemical response is clearly seen in Fig. 1 and has been previously reported elsewhere [7,11]. The Pt/Au electrode shows a substantial current decrease, as compared to the neat Pt electrode, due to the lower available Pt surface in the former. Additionally, a cathodic peak at 1.17 V is observed during the negative scan for the Pt/Au electrode, and can be assigned to the reduction of gold oxide produced during the previous positive-going scan.

Fig. 1 (black lines) shows the stripping voltammograms (after 900 s of CO exposition and subsequent fast electrolyte exchange) observed for both electrodes. A single CO stripping peak (at 0.90 V) is observed for the neat Pt electrode, whereas two peaks (at 0.84 V and ~1 V) are easily observable for the Pt/Au electrode. For Pt/Au