Influence of spontaneous decomposition on the electrochemical formic acid oxidation on a nanostructured palladium electrode

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ABSTRACT

The formic acid electrooxidation reaction was studied in a flow cell in 1 M HCOOH–0.5 M H_2SO_4 solution on a palladium film electrode. The evaluation of the open circuit potential (OCP) decay demonstrated that the spontaneous dehydrogenation of formic acid is quickly verified, leading to hydrogen adsorption and absorption. Moreover, the absence of carbon containing adsorbed species was verified by the application of voltammetric stripping after OCP and chronoamperometry. The results obtained demonstrate that the electrocatalytic oxidation of formic acid on Pd takes place through the spontaneous HCOOH dissociative adsorption with CO_2 evolution and the adsorbed hydrogen electrooxidation.

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1. Introduction

The study of formic acid electrooxidation reaction is not only important for the development of the direct formic acid fuel cell (DFAFC) [1,2, 4,5], but also because the intermediate species involved in this reaction participate in the more complex kinetic mechanisms of the respective electrooxidation reactions of other organic molecules involved in low temperature fuel cells [6–8]. Thus, there are many works that studied the reaction on different electrocatalytic materials, being widely accepted that it is verified basically through two routes, direct and indirect. Briefly, starting from the common electroadsorption step [2],

$$HCOOH \rightarrow HCOO_{ad} + H^+ + e^- \qquad (1)$$
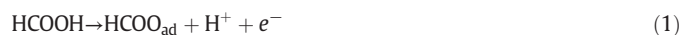
the direct route is completed by,

$$HCOO_{ad} \rightarrow CO_2 + H^+ + e^- \qquad (2)$$

In the indirect route, step (1) is followed up by [5,9],

$$HCOO_{ad} + e^- + H^+ \rightarrow CO_{ad} + H_2O \qquad (3a)$$

$$CO_{ad} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \qquad (3b)$$

where at least two adsorbed species are involved, plus OH_{ad} from water electroadsorption [5,9]. More details about the kinetic mechanism on noble metals can be found elsewhere [10,11].

Moreover, it is well known that in liquid solution formic acid can also be decomposed by solid catalysts, mainly the same metals used in the electrocatalytic oxidation. This reaction takes place through two possible chemical processes, dehydrogenation and dehydration respectively [12–17],

$$HCOOH \rightarrow CO_2 + H_2 \qquad (4)$$

$$HCOOH \rightarrow CO + H_2O \qquad (5)$$

The reaction Gibbs free energies of both are negative, being therefore thermodynamically favoured [12]. Thus, the decomposition of formic acid in aqueous solutions on metal catalysts takes place spontaneously [12–17]. In this context, it should be important to analyze the relationship between this spontaneous process and the electrooxidation reaction.

Among the different metals that are employed in both, catalytic and electrocatalytic reactions, one of the most active is palladium, which has the characteristic of being a hydrogen absorbing metal. Moreover, it is accepted that HCOOH decomposition on palladium in aqueous solution is verified through the dehydrogenation route, involving the adsorbed hydrogen (H_{ad}) intermediate [13,16,17]. It is straightforward that in this case H_{ad} will be absorbed within the metal matrix (H_{ab}). The presence of this species can be easily detected on a Pd thin film electrode by open circuit potential decay, where it is defined the transition between α-Pd/H and β-Pd/H at about 0.05 V vs. RHE [18, 19]. Therefore, the formic acid electrooxidation reaction on Pd should also involve adsorbed hydrogen, as well as a current contribution due to its oxidation.

In this context, the present work studies and discusses the role played by the catalytic spontaneous decomposition on the formic acid electrooxidation on palladium.

2. Materials and methods

2.1. Electrode preparation and characterization

Working electrodes were prepared via sputtering on a glassy carbon (SPI-Glas™ 25) substrate from a palladium target (Goodfellow Corp.) in Ar atmosphere (0.1 mbar), using a sputter coater Emitech K500X, operated at 30 mA during 240 s. Previously to Pd deposition, the substrate was mirror polished and subjected to ultrasonic cleaning in ultrapure water and then was voltammetrically characterized to ensure a clean and reproducible deposition surface.

The surface morphology of the Pd electrodes was characterized by AFM. Images were obtained using a multi-technique Agilent microscope model 5400, operated in tapping mode and processed with software WSxM 6.2. The electrode was also characterized electrochemically by cyclic voltammetry.

2.2. Electrochemical measurements

Electrochemical measurements were carried out in a three electrodes flow cell with a small volume of about 2 cm^3, fed from two vessels. One of them contains a solution of 1 M HCOOH–0.5 M H$_2$SO$_4$ saturated with N$_2$. The other contains 0.5 M H$_2$SO$_4$ solution saturated with H$_2$ or N$_2$. Solutions were prepared with ultra-pure water (PureLab, Elga LabWater). The flow cell has inlet valves from the vessels and a hydraulic seal valve for the outlet, which allows a quick renewal of the electrolyte in conditions of electric closed circuit. A hydrogen electrode in the same solution (RHE) was used as the reference electrode and a large area palladium wire acted as the counter electrode. Experiments were carried out at room temperature (~22 °C).

2.3. Open circuit potential (OCP) determinations

The OCP determinations consisted in a sequence of steps. At first, a potentiodynamic profile was recorded in the N$_2$ saturated 0.5 M H$_2$SO$_4$ solution. It was followed by holding the electrode for 60 s at 1.0 V in the same solution in order to ensure a reproducible initial condition, with the surface free from adsorbed species derived from HCOOH. Then the electrolyte solution was changed to N$_2$ saturated 1 M HCOOH–0.5 M H$_2$SO$_4$ solution, holding the electric circuit closed at 1 V for another 60 s. After that, the circuit was opened and OCP was recorded up to 2400 s. Immediately after, a voltammetric stripping was carried out as is described in the next section. The same sequence was followed for the OCP determinations in the H$_2$ saturated 0.5 M H$_2$SO$_4$ solution, as well as in the blank solution (N$_2$ saturated 0.5 M H$_2$SO$_4$ solution).

2.4. Voltammetric stripping

Two types of voltammetric stripping were applied to the Pd electrode in order to evaluate the presence of adsorbed species involved in the HCOOH oxidation. The first type was carried out after OCP measurements in N$_2$ saturated 1 M HCOOH–0.5 M H$_2$SO$_4$ solution and H$_2$ saturated 0.5 M H$_2$SO$_4$ solution. It started with the polarization at the potential reached at OCP (E$_{oc}$), followed by the solution renewal to N$_2$ saturated 0.5 M H$_2$SO$_4$ solution. Then the voltammetric stripping was applied at 0.01 V s^{-1} from E$_{oc}$ to 1.1 V, followed by a second voltammetric cycle.

The second type consisted of holding the potential at 1 V for 60 s in N$_2$ saturated 1 M HCOOH–0.5 M H$_2$SO$_4$ solution and then applying a step to a given potential (E$_s$) corresponding to the region where HCOOH oxidation takes place ($0.10 \leq E_s/V \leq 0.50$) and holding it for 2400 s. The solution was replaced by N$_2$ saturated 0.5 M H$_2$SO$_4$ while the electric circuit was held at E$_s$ and then the voltammetric stripping was applied at 0.01 V s^{-1} from E$_s$ to 1.1 V, followed by a voltammetric cycle between 0.02 V and 1.1 V.

3. Results and discussion

Fig. 1a shows the voltammogram of the Pd electrode in N$_2$ saturated 0.5 M H$_2$SO$_4$ solution. It can be observed that the hydrogen absorption process, confined to a thin metal film, enables the voltammetric peaks corresponding to the adsorption/desorption of the underpotentially deposited hydrogen (H$_{UPD}$) to be distinguished. This profile is similar to those already obtained in similar conditions [17,18]. Moreover, Fig. 1b shows the surface morphology of the working electrode.

Fig. 2A shows the potential transients resulting from the OCP measurements. The behaviour of Pd in the presence of formic acid (N$_2$ saturated 1 M HCOOH–0.5 M H$_2$SO$_4$ solution) exhibits an extremely fast decrease of potential, which gets the value 0.06 V in <0.2 s (line a). It reaches a plateau with an average value of 0.05 V for about 250 s and then decreases again reaching a value near 0.01 V after 2400 s. A similar behaviour (line b) is observed when HCOOH is substituted by H$_2$ (H$_2$ saturated 0.5 M H$_2$SO$_4$ solution), the potential decay being slower than in the previous case, requiring nearly 55 s to reach the plateau. In this context, it is well known that in the H$_2$ saturated solution the plateau with an average value of 0.05 V corresponds to the transition from α to β phase of the Pd-H system [18,19]. Thus, the comparison between both OCP decays evidences that the spontaneous adsorption of formic acid on Pd leads to the adsorption and subsequent absorption of hydrogen. Moreover, it is also demonstrated that the processes of HCOOH spontaneous decomposition and formation of H$_{ad}$ are two orders of magnitude faster than the hydrogen adsorption from molecular hydrogen. Finally, for the sake of comparison, the OCP transient (line c) was also recorded in the blank solution (N$_2$ saturated 0.5 M H$_2$SO$_4$).

Fig. 2B shows the profiles obtained from the voltammetric strippings applied in the blank solution after OCP measurements in HCOOH containing solution (line a) and H$_2$ saturated solution (line b). They are practically identical, exhibiting in the anodic sweep the peak at 0.09 V of the electrooxidation of absorbed hydrogen, the peak corresponding to the H$_{UPD}$ electrodesorption at 0.25 V and finally the characteristic process of oxide formation starting from 0.7 V. Moreover, the cathodic sweep shows the contributions of the reduction of Pd
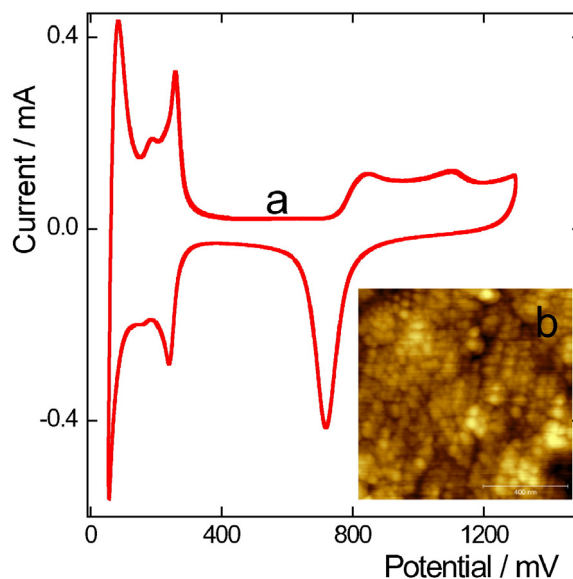

Fig. 1. a) Voltammetric profile of the Pd electrode in 0.5 M H$_2$SO$_4$ at 0.1 V s^{-1}; b) micrograph of nanostructured Pd obtained by AFM.