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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],

$$HCOOH \rightarrow HCOO_{ad} + H^+ + e^- \quad (1)$$

the direct route is completed by,

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

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

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

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

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],

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

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

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.

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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_2SO_4 saturated with N_2. The other contains 0.5 M H_2SO_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_2SO_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_2SO_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_2SO_4 solution, as well as in the blank solution (N_2 saturated 0.5 M H_2SO_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_2SO_4 solution and H_2 saturated 0.5 M H_2SO_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_2SO_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_2SO_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_2SO_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_2SO_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_2SO_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_2SO_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_2SO_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

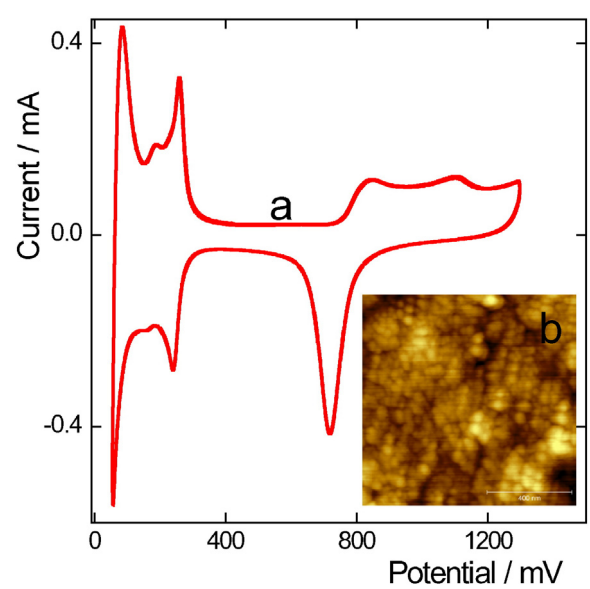

Fig. 1. a) Voltammetric profile of the Pd electrode in 0.5 M H_2SO_4 at 0.1 V s^{-1}; b) micrograph of nanostructured Pd obtained by AFM.

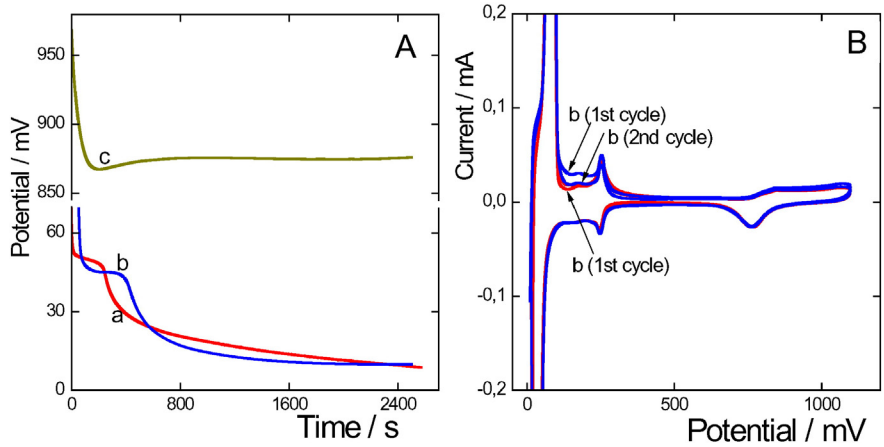

Fig. 2. A) OCP vs. time responses after polarization at 1.0 V in a) N_2 saturated 1 M HCOOH - 0.5 M H_2SO_4; b) H_2 saturated 0.5 M H_2SO_4; c) N_2 saturated 0.5 M H_2SO_4; B) voltammetric stripping at 0.01 V s^{-1} in N_2 saturated 0.5 M H_2SO_4 after OCP a) and b).

oxide, the adsorption of H_{UPD} and finally the hydrogen absorption and evolution. The most important conclusion from line a is that there is not any evidence of electrooxidation processes of carbon containing adsorbed species, including CO_{ad}, which produces a sharp peak near 0.90 V [20].

Furthermore, Fig. 3A shows the response corresponding to the second type of voltammetric stripping recorded in the blank solution, after a potential holding ($E_s = 0.3$ V) in HCOOH containing solution. The profile resembles those of Fig. 2B, showing only the presence of absorbed hydrogen and H_{UPD}. This behaviour is repeated for the different values of E_s ($0.10 \le E_s/V \le 0.50$). This result strengthens the idea that on Pd in HCOOH solutions the adsorbed species containing carbon are not significant, which is in agreement with spectroscopic evidence [21], and emphasizes the key role played by H_{ad} in the HCOOH electrooxidation.

Taking into account that the absorption of hydrogen on Pd needs its previous adsorption on the surface [22,23], the process during the OCP decay in the solution containing formic acid can be described by,

$$HCOOH \rightarrow HCOO_{ad} + H_{ad} \tag{6a}$$

As $HCOO_{ad}$ is not detected in the voltammetric stripping, it is considered that quickly decomposes according to,

$$HCOO_{ad} \rightarrow CO_2 + H_{ad} \tag{6b}$$

H_{ad} resulting from steps (6a) and (6b) is absorbed, as it is demonstrated by the presence of phase transition α-Pd/H → β-Pd/H (Fig. 2A, line a).

Finally, Fig. 3B shows the current-potential response corresponding to a potentiodynamic sweep run at 0.01 V s^{-1} in 1 M HCOOH - 0.5 M H_2SO_4 solution. It can be observed that both anodic and cathodic current profiles are almost coincident. An exponential increase takes place between 0.056 V and 0.35 V, then continues an almost linear increase until reaching a maximum at 0.46 V, followed by a significant current decrease. It can be appreciated that the oxidation process takes place at lower potentials compared with those observed for other simple organic molecules (methanol, acetaldehyde, CO, etc.) [6–8]. This result, together with the absence of adsorbed species different from hydrogen in the potential region $0.10 \le E/V \le 0.50$, leads to the conclusion that the anodic current corresponds basically to the electrooxidation of H_{ad}, produced by the spontaneous HCOOH dissociative adsorption, through the Volmer step,

$$H_{ad} \rightarrow H^+ + e^- \tag{6c}$$

Consequently, the kinetic mechanism for the HCOOH electrooxidation on Pd should be established by the steps 6a–c. It can be appreciated that the proposed mechanism involves H_{ad}, which establishes a fundamental difference in the kinetic analysis of the reaction with respect to a recent study [24]. Moreover, it can also explain the formation of molecular

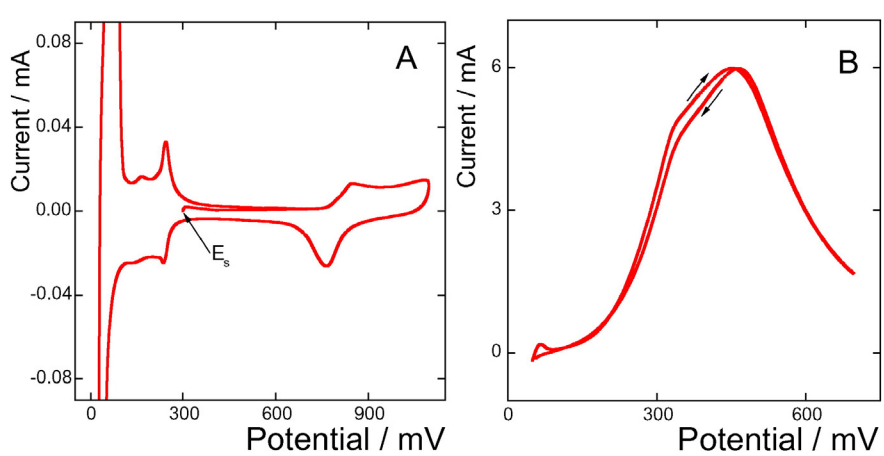

Fig. 3. A) Voltammetric stripping at 0.01 V s^{-1} in N_2 saturated 0.5 M H_2SO_4 after polarization at 0.3 V in N_2 saturated 1 M HCOOH–0.5 M H_2SO_4; B) potentiodynamic sweep at 0.01 V s^{-1} in N_2 saturated 1 M HCOOH–0.5 M H_2SO_4.

hydrogen from H_{ad} recombination (Tafel step) in the spontaneous decomposition.

Furthermore, the high rate of hydrogen adsorption on the OCP transient also explains the fact that the profiles corresponding to the anodic and cathodic sweeps of Fig. 3B are almost overlapped. The current decrease from 0.46 V can be explained by the inhibition of active sites due to the reversible water electroadsorption,

$$H_2O \rightleftharpoons OH_{ad} + H^+ + e^- \quad (6d)$$

as it was observed previously in the studies of the hydrogen oxidation reaction on Pt [25] and Ru [26] in the same conditions, together with the bisulphate adsorption [21].

4. Conclusions

New evidences related to the formic acid oxidation reaction on palladium electrode were found through different experimental measurements carried out in a flow cell, which allowed the electrolytic solution holding the electric circuit closed to be changed. Under these conditions, stripping voltammetry, coupled with open circuit potential and chronoamperometry, were applied, as well as slow potentiodynamic sweeps. The results obtained demonstrate that the HCOOH oxidation to CO_2 on Pd involves the spontaneous dissociative adsorption of formic acid producing adsorbed hydrogen, which is electrooxidized to protons at potentials lower than those expected for the electrooxidation of carbon containing adsorbed species.

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