The electrooxidation mechanism of formic acid on platinum and on lead ad-atoms modified platinum studied with the kinetic isotope effect

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HIGHLIGHTS

- Insight into mechanism of formic acid oxidation on Pt and Pt/Pb electrodes with kinetic isotope effect.
- Catalytic synergistic effect in direct oxidation of formic acid to CO_2 induced by upd-lead.
- Suppression of strongly bound CO-like species on upd-lead ad-atoms modified platinum electrode.
- The optimal conditions for monitoring of FA in acidic solution containing Pb^{2+} cations were specified.

ARTICLE INFO

ABSTRACT

Kinetics and mechanism of formic acid (FA) oxidation on platinum and upd-lead ad-atoms modified platinum electrodes have been studied using unlabelled and deuterated compounds. Poisoning of the electrode surface by CO-like species was prevented by suppression of dissociative chemisorption of FA due to a fast competitive underpotential deposition of lead ad-atoms on the Pt surface from an acidic solution containing Pb^{2+} cations. Modification of the Pt electrode with upd lead induced a catalytic effect in the direct electrooxidation of physisorbed FA to CO_2. With increasing degree of H/D substitution, the rate of this reaction decreased in the order: HCOOH > DCOOH ≥ HCOOD > DCOOD. HCOOH was oxidized 8.5-times faster on a Pt/Pb electrode than DCOOD. This primary kinetic isotope effect proves that the C—H- and O—H-bonds are simultaneously cleaved in the rate determining step. A secondary kinetic isotope effect was found in the dissociative chemisorption of FA in the hydrogen adsorption—desorption range on a bare Pt electrode after H/D exchange in the C—H bond, wherein the influence of deuterium substitution in the O—H group was negligibly small. Thus the C—H bond cleavage is accompanied by the C—OH and not the O—H bond split in the FA decomposition, producing CO-like species on the Pt surface sites.

1. Introduction

An effective way to enhance the catalytic activity of noble metals (Pt, Pd, Au) in electrochemical reactions (in particular oxidations) of organic molecules and CO is their modification with a second metallic component with a different strength of adsorption of hydrogen and/or oxygen, realized by electro-deposition of foreign metals [1–18] or by alloying [12,19–23]. Recently, much attention has been paid to nanostructured mono-, bi- and multi-metallic systems [12,24–46] including core-shell-structured nanoparticles [47–50] or self assembled monolayers on electrodes [51–56]. These reported investigations have been mainly concerned with the influence of composition, support effects and other structural details on their efficiency as catalyst in fuel cells. However, despite of many reports, further extensive adsorption and kinetic studies are desired for better understanding of the mechanism of the catalytic reactions at such electrodes.

The purpose of this work is to present data on the kinetic isotope effect caused by systematic H/D substitution of formic acid (FA) as a useful way to gain deeper insight into the mechanism of the rate determining step (rds) in the electrooxidation of this compound on platinum and upd-lead ad-atoms modified platinum electrodes. Taking into account our earlier investigation dealing with the kinetics of formaldehyde adsorption and oxidation on Pt and Pt/Pb

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electrodes in acidic medium [7], we now report results of experiments performed using cyclic voltammetry at moderate and fast sweep rates combined with chronoamperometry, aimed at further elucidation of the electrooxidation mechanism of FA at these electrodes.

2. Experimental

All measurements were performed at room temperature (298 K) in a conventional three compartment cell, separated by glass frits and equipped with a Luggin capillary at a distance of 2 mm from the working polycrystalline platinum (99.998%) sheet electrode of 1 cm^2 geometric area. A large area Pt sheet of the same purity was used as counter electrode. A hydrogen electrode filled with the supporting electrolyte solution (RHE) was used as reference [57]. Prior to each experiment, the working electrode was repeatedly activated in the deaerated supporting electrolyte solution by cycling (dE/dt = 5 V s^{-1}) in the potential range 0.025 V < E_{RHE} < 1.5 V until a reproducible voltammogram was obtained. Finally, the roughness factor of Pt (2.2 ± 0.2) was determined from the charge (Q_H = 0.46 mC cm^{-2}) corresponding to the hydrogen adsorption and/or desorption according to the well-known procedure [58], assuming that a hydrogen monolayer requires 0.21 mC cm^{-2}.

Cyclic voltammograms (CV) and chronoamperometric transients at E = const were obtained on a setup including a computer-controlled 9431 potentiostat (Atlas-Sollich, Poland) equipped with an IR-drop correction system coupled to a signal generator working in the triangular potential sweep mode with programmable potential sequences, potential ranges, number of cycles and scan rates as well as time periods with holding the electrode potential at a constant value. Current–potential–time dependencies were recorded and analysed with a computer-based system connected to a MC112-12 interface (Mescomp, Poland).

The following procedure was applied in the adsorption experiments. After a series of 8 potentiodynamic scans between 0.07 V and 1.65 V, the potential of the working electrode was held at E = 1.5 V for 5 ms and then switched (at dE/dt = 10 V s^{-1}) to different fixed E_{ad} values for various time periods, t_{ad}. Next, the species adsorbed on the Pt electrode were oxidized or reduced during the first positive or negative going potential sweep, respectively. The charge related to the electrooxidation of FA residues or upd-Pb ad-atoms (Q_{ox}) was determined by integration of the respective CVs recorded in the first and subsequent cycles. The coverage of the electrode surface with adsorbed species (θ) was evaluated from the difference (ΔQ_H) between the charge corresponding to the hydrogen desorption from Pt in the supporting electrolyte (Q_H^o) and after adsorption of FA (Q_H), according to the expression: $\theta = \Delta Q_H/Q_{ox} = (Q_H^o - Q_H)/Q_{ox}$. The rate of the electrode coverage was determined at various constant values of E_{ad} and different values of t_{ad} at constant values of $c_{Pb^{2+}}$ or c_{FA}. By comparing Q_{ox} with ΔQ_H, the number of electrons transferred per Pt site (n_{eps}) was calculated: $n_{eps} = Q_{ox}/\Delta Q_H$. It should be noted that the charge corresponding to the double layer or to the oxide layer formation in a supporting electrolyte solution was always subtracted from the total charge involved in the investigated electrode process. In chronoamperometric experiments the sequence of activating steps was followed by measurements of the current density–time (j–t) transients at constant electrode potentials, E_{ad}.

Electrolyte solutions were prepared using Millipore Milli-Q-water, HCOOH (p.a. LOBA, 99–100%), HClO$_4$ suprapur (Merck), Pb(ClO$_4$)$_2$ (SERVA, 50% sol.), DCOOD (p.a. MERCK, 100% D), DCOOH (99.85% D), p.a. DClO$_4$ and triply-distilled D$_2$O (IBJ Swierk, Poland). The concentrations of perchloric and formic acids were determined by titration. Argon 99.998% (BOC-Gas) was used for deaeration and

stirring of the investigated solutions. DClO$_4$ was used in preparation of electrolyte solutions with D$_2$O and perdeuterated compounds.

3. Results and discussion

Representative CVs in Fig. 1, obtained at fast sweep conditions (dE/dt = 5 V s^{-1}) after holding the electrode potential within the hydrogen adsorption-desorption region, at E_{ad} = 0.2 V for t_{ad} = 180 s, illustrate differences in the catalytic properties of the Pt/Pb and Pt electrode in a supporting electrolyte solution (0.2 M HClO$_4$) containing 10^{-2} M HCOOH, with and without Pb^{2+} cations. Note, that the sweep rate chosen was high enough to determine the charge related to the oxidation of adsorbed species present at the electrode/solution interface only without any interference of Pb^{2+} and FA diffusing from the bulk of the solution to the electrode surface.

Strong poisoning of the Pt surface with irreversibly adsorbed species, formed of FA in the absence of Pb^{2+} cations in solution, is clearly indicated (trace 1 in Fig. 1) by suppression of the current related to the hydrogen electrosorption/desorption at $E \leq 0.4$ V and by the appearance of the anodic current peak between 0.75 V < E < 1.5 V corresponding to the oxidation of the adsorbate, with a maximum around 1 V. Evidently, the saturation coverage of Pt surface sites ($\theta \approx 1$) with the strongly bonded species is achieved under the above-mentioned experimental conditions (E_{ad} = 0.2 V, t_{ad} = 180 s). Accordingly, the platinum electrode is inactive for the oxidation of FA within the double layer potential range. The influence of FA concentration (c_{FA}), on the surface coverage with the poisonous adsorbate during the first 15 s at a constant electrode potential (E_{ad} = 0.2 V) is illustrated by CVs in Fig. 2. The respective CVs after various adsorption times at constant c_{FA}, which allow determination of the rate of the electrode coverage with FA residues ($d\theta/dt$), are shown in Fig. 3.

There is a general agreement that the strongly bound adsorbate is generated on a Pt electrode via the dissociative chemisorption of FA. Several possible CO-like surface species of various monomeric and dimeric structures (CO, HCO, COH, C$_2$O$_3$, H$_2$C$_2$O$_3$, HC$_2$O$_3$, HC$_2$O), coexisting in equilibrium on a Pt surface, were identified [59–70] depending on experimental conditions determined by various applied experimental techniques. Taking into account the obtained n_{eps} values (electrons per Pt site) of 1.6–2 and the fact that
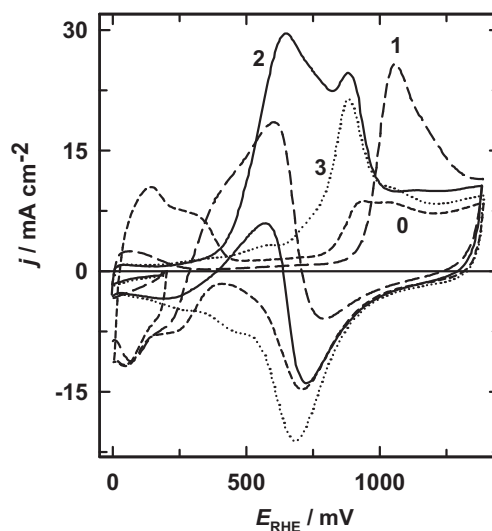

Fig. 1. CVs of a polycrystalline platinum electrode in solutions of 0.2 M HClO$_4$ (0), 0.2 M HClO$_4$ + 0.01 M FA (1), 0.2 M HClO$_4$ + 1 mM Pb(ClO$_4$)$_2$ + 0.01 M FA (2), 0.2 M HClO$_4$ + 1 mM Pb(ClO$_4$)$_2$ (3); dE/dt = 5 V s^{-1}, E_{ad} = 0.2 V, t_{ad} = 180 s.