



Enhanced catalytic activity and stability for the electrooxidation of formic acid on lead modified shape controlled platinum nanoparticles



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ARTICLE INFO

Article history:

Received 17 May 2016

Received in revised form 29 July 2016

Accepted 3 August 2016

Available online 4 August 2016

Keywords:

Shape-controlled Pt nanoparticles

Pb adsorption

Pb modified electrodes

Formic acid oxidation

SECM

ABSTRACT

High catalytic activity for formic acid oxidation reaction (FAOR) is demonstrated in Pb modified shape-controlled Pt nanoparticles (NPs). Cyclic voltammetry is used to follow the effective modification of Pt NPs by Pb. Octahedral shaped Pt NPs (having a (111) preferential surface structure) modified by Pb are proved the most active electrocatalyst studied towards FAOR and display a catalytic activity of c.a. 7 mA cm^{-2} at 0.5 V in 0.1 M formic acid solution. This current density represents an enhancement factor of 29.5 with respect to the unmodified Pt NPs and this is 2.7 and 2.3 times higher than that found on $\text{TiO}_2/\text{100-Pt}$ NPs and $\text{SbO}_3/\text{111-Pt}$ NPs, respectively, some of the most active electrocatalysts based on adatoms modified Pt NPs reported so far. This outstanding activity is displayed at maximum Pb coverage and also confers a wide electrocatalyst stability over the entire potential range studied. FAOR is also studied using scanning electrochemical microscopy (SECM) by the micropipette delivery/substrate collection (MD/SC) working mode as a preliminary rapid test to identify active electrocatalysts. In particular, the remarkable activity enhancement exhibited by a Pt ultramicroelectrode (100 μm diameter) modified by Pb is rapidly imaged by SECM providing preliminary catalyst performance information. Thus, this technique emerges as a suitable and fast method to test, and in some cases quantify, catalyst activity for reactions of interest in fuel cell applications.

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1. Introduction

Formic acid oxidation reaction (FAOR) represents a very important reaction in electrocatalysis, since it can be used as a model in fundamental studies for other small organic molecules (SOMs) such as methanol or ethanol [1]. Moreover, formic acid has been proposed as a fuel for direct liquid fuel cells (DLFCs), which can be used as small power supply [2,3] in electronic devices, since FAOR presents fast oxidation kinetics, safety in the manipulation and less fuel crossover through the ionic exchange membrane than other fuels such as methanol [4]. In a direct formic acid fuel cell (DFAFC) [5], the thermodynamic cell potential is 1.428 V, which makes it more interesting than hydrogen fuel cells from an available energy point of view. Nevertheless, the overpotential for the

FAOR at present needs to be improved in order to reach commercial applications.

Pt is one of the most studied metals in electrocatalysis [1]. In particular, FAOR on Pt electrodes has been widely studied over the last decades due to the high activity of this metal for the oxidation of different SOMs. Since FAOR has probably the simplest oxidation mechanism among all different SOMs, a deep understanding of the FAOR mechanism on Pt should be very useful for other important electrocatalytic oxidation reactions. It is well accepted that FAOR on Pt electrodes follows two different reaction pathways [6–8]. One of them, the so-called indirect via, involves the formation of CO on the electrode surface, which acts as a poison intermediate. The other pathway is known as the direct via, and implies the formation of an active intermediate, which is immediately oxidized into CO_2 . On the other hand, it is also well-known that FAOR is a surface sensitive reaction [9,10]. Studies on Pt single crystal electrodes (Pt(*hkl*)) have allowed a better comprehension of some of the elementary steps in FAOR, proving that Pt(100) is the most active electrode for both paths, while Pt(111) is least active one, in spite of the fact that the formation of CO is almost negligible on this electrode [11].

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The modification of the surface chemical composition on the Pt(*hkl*) electrodes is one of the most widely employed methods to increase the catalytic activity for the FAOR. This strategy is mainly based on the incorporation of different adatoms, which can be either metals or semi-metals, on the surface of the Pt(*hkl*) electrodes. This epitaxial adsorption and deposition of a sub-monolayer of adatoms on a foreign metal substrate is usually performed either by irreversible adsorption at open circuit potential or by underpotential deposition (UPD). These two interesting methods to modify noble metals may generate surface alloys in some cases [12]. In the case of modified Pt electrodes, the UPD method [13] is based on the electrodeposition of an adatom monolayer from a solution containing the adatom dissolved as a cation at potentials significantly less negative than that for the bulk electrodeposition of the adatom [14]. The main difference between UPD and irreversible adsorption methods is the fact that irreversible adsorbed adatoms remain stable on the Pt surface in the absence of the adatom cation in solution [1,15–19], but on the contrary, UPD adatoms are not stable on the Pt surface unless the solution contains the adatom cation in low concentration. Moreover, irreversible adsorption allows achieving adatom coverages independently of the applied potential, as far as it remains within the adatom electrochemical stability limits. In addition, this approach also avoids the problem of accuracy in the coverage quantification that appears when the UPD method is used, due to its dependency with the applied potential and solution composition. The well accepted positive effect of the presence of some adatoms on the electrocatalytic activity of Pt electrodes towards FAOR is visualized by an evident shift to lower potential values on the onset oxidation potential and/or by increasing current densities of the oxidation reaction. In this sense, it is proposed that adatoms may act following three main different mechanisms; *i*) the *third body* effect in which the foreign adatom modifies the reaction mechanism by steric interference, since it blocks specific adsorption sites on the Pt surface preventing CO formation [20], *ii*) the *electronic* effect [21,22], where the modification of the Pt electronic structure due to the presence of foreign adatoms enhances the activity of the surface and *iii*) the *bi-functional* effect [23], in which the adatom and the Pt surface sites have distinct roles in the oxidation mechanism [24].

Over the last decades, adatoms such as bismuth (Bi) [25,26], arsenic (As) [27], antimony (Sb) [28], palladium (Pd) [29] and lead (Pb) [19,30,31] adsorbed on Pt(*hkl*) electrodes has been studied, showing an important improvement in the FAOR activity, by following at least one of the proposed mechanisms mentioned above. Nowadays, the next challenge is to transfer all that knowledge from single crystal electrodes to nanoparticles (NPs) with a preferential surface structure. In this sense, the role of some adatoms such as Bi [32], Sb [33] and Ti [34] modifying shape-controlled Pt NPs have been already reported. Particularly, Bi adatom has shown a significant enhancement in the activity of the (111) preferential Pt NPs towards FAOR [35], which agrees with previous studies using Bi modified Pt single crystal electrodes [36]. Some new approaches in the study of FAOR on modified Pt NPs electrode also include trimetallic systems [37] and graphene–Pt NPs hybrid materials [38].

Despite the number of adatoms already studied modifying Pt NPs, there are still some of them untested. This is the case of Pb adatom on shape-controlled Pt NPs for FAOR, which is studied herein. However, Pb has been already used in Pt–Pb bimetallic alloys [39–41] to improve conventional spherical Pt NPs activity towards FAOR, as well as intermetallic Pb–Pt catalysts [42,43]. The main goal of this article is to address that question in order to explore the feasibility of using Pb modified shape-controlled Pt NPs as catalyst for fuel cell applications. The use of conventional Pb or PtPb NPs in real electrochemical filter press reactors either for electroorganic synthesis [44] or DFAFCs [45] have been already demonstrated in the literature.

Finally, the use of novel electroanalytical techniques for studying the reaction mechanism in electrocatalytic reactions provides new tools for electrocatalyst interrogation [46–50]. Among of them, the scanning electrochemical microscopy (SECM) [51], which is based on the steady-state diffusion controlled regime provided by either an ultramicroelectrode (UME) or a micropipette, has already demonstrated its utility for studying FAOR [52–54]. However, no SECM imaging studies have been devoted to prove the activity improvement of adatoms modifying Pt electrodes in FAOR. So far, only a voltammetric study of FAOR on Bi modified Pt UME has been reported [55]. In the present work, we use SECM images to provide some additional information in the comparison of the activity for FAOR on pristine Pt and Pb modified Pt (Pb–Pt).

2. Experimental section

2.1. Chemicals

1,2-dichloroethane (CH₂Cl–CH₂Cl, DCE) anhydrous 99.8%, octyltriethoxysilane 97.5%, lead (II) perchlorate hydrate Pb(ClO₄)₂·H₂O (Aldrich® 99.995%), H₂SO₄ (Merck KGaA Suprapur® 96%), HCOOH (Merck KGaG 98%), polyethylene glycol dodecyl ether (Brij® 30), *n*-heptane (ACROS Organics, Analysis), sodium borohydride (Aldrich® 99.99%), sodium polyacrylate (Aldrich®), K₂PtCl₄ (Aldrich® 99.99%), H₂PtCl₆·6H₂O (Aldrich® 37.50%), HCl (Aldrich® 37%), NaOH (Merck, Pellets for analysis). All solutions were prepared with ultrapure water (18.2 MΩ cm, Purelab Ultra system, Elga-Vivendi).

2.2. Electrochemical experiments

Cyclic voltammetry (CV) and chronoamperometry (CA) were performed using a conventional electrochemical glass cell of 3 electrodes at room temperature and a potentiostat-galvanostat AUTOLAB PGSTAT302N (Metrohm Autolab B. V.) or a potentiostat CHI 760E. The working electrode was prepared by adding 4 μL of each type of Pt NPs (2 μL for 100-Pt NPs) coating a 3 mm diameter gold (Au) disk electrode, which is used as a NPs support and current collector, and allowing the water solvent to be evaporated before entering the electrode in the cell. The sample volume of 4 μL was selected after performing a calibration curve that proved no diffusion limitations for FAOR due to the thickness of that layer of NPs deposited on the gold disk electrode. Each Pt NPs suspension was sonicated for 2 min before being used. A gold wire was used as a counter electrode, and a reversible hydrogen electrode (*RHE*) within a Luggin capillary was employed as a reference electrode. All potentials used in this paper are referred to *RHE*. CVs for Pt surface area quantification were carried out in a deaerated 0.5 M H₂SO₄ solution. CVs and CAs for studying the electrocatalytic activity for FAOR were carried out in deaerated 0.1 M HCOOH and 0.5 M H₂SO₄ solution. An electrochemical pre-treatment for removing the CO_{ads} accumulated at the electrode surface from previous FAOR experiments was performed before starting each CA. This consists in holding the electrode potential at 0.8 V for 5 s. The potential window where it is possible to work avoiding structure modifications on the shape-controlled Pt NPs surface is between 0.05 V and 0.8 V [56,57].

2.3. Pb modified shape controlled Pt NPs (Pb_θ/Pt NPs)

Three types of shape-controlled Pt NPs dispersed in water with surface area to volume ratios of 0.03 cm² μL⁻¹ for cubic 100-Pt NPs and 0.017 cm² μL⁻¹ for octahedral 111-Pt NPs and quasi-spherical poly-Pt NPs were used. The chemical synthesis of those NPs was carried out as previously described in detail [58]. The Pt NPs morphology/shape was confirmed by transmission electron

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