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Short communication

Influence of the surface morphology of smooth platinum electrodes for the sodium borohydride oxidation reaction

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ABSTRACT

In this study, we show that the platinum electrode preparation procedure influences its behavior towards the borohydride electrooxidation reaction (BOR) mechanism. Cycling a smooth polycrystalline Pt electrode in alkaline electrolyte within the water stability domain prior to the BOR characterization radically changes the shape of the BOR voltammogram obtained in hydrodynamic conditions using the rotating disk electrode (RDE) setup, compared to the "classical" one measured on a smooth polycrystalline Pt electrode just polished before the BOR RDE study. This particular BOR voltammogram is reversibly brought back to the "classical" one after voltammetric cycling in borohydride alkaline media. These changes in the BOR voltammogram highlight the sensitivity of the BOR mechanism towards the Pt surface morphology. A first comparison of the Pt electrode surface before and after the voltammetric cycling in alkaline media using tapping mode atomic force microscopy (AFM) shows no morphological differences between the two surfaces within the AFM observation range, suggesting a very fine atomic structure disordering of the Pt surface. Such strong dependence of the BOR mechanism on Pt regarding the electrode atomic structuring opens the way to future studies focusing on the BOR on well-defined Pt single crystals.

1. Introduction

Platinum has been extensively studied in electrocatalysis as it is one of the most active surfaces for oxygen reduction reaction (ORR) or hydrogen evolution reaction (HER). The use of well-defined Pt single crystals has enabled to shed light on the existence of structural effects of the Pt(*hkl*) surface on the oxidation mechanism of small organic compounds or for the ORR [1]. Indeed, reaction mechanisms can for instance involve intermediates that are adsorbed specifically at particular Pt(*hkl*) planes, or at defects between planes [2,3]. As polycrystalline electrode surfaces exhibit lower definition than single crystals, a relevant comparison between two studies of the same complex electrochemical reaction but using different polycrystalline electrode preparations is a sensitive issue. Indeed, depending on the polishing procedure of the electrode or on the pre-treatment (*e.g.* electrochemical cycling in acidic or alkaline media, pre-oxidation or pre-reduction), the roughness and the surface structure of the polycrystalline Pt electrode surface may change, leading to different reaction mechanisms/kinetics for the studied reaction and therefore to different results/conclusions. This might especially be the case for complex reaction mechanisms like the BH_4^- oxidation reaction (BOR) [4]. In that context, this study focuses on the dependence of the BOR mechanism with the surface morphology of polycrystalline Pt electrodes.

Ideally, the direct and complete oxidation of BH_4^- (Eq. (1)) is an eight-electron reaction ($E° = -1.24\ V_{NHE}$) but this theoretical value is hard to reach in practice due to non-faradic competitive reactions.

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \qquad (1)$$

Numerous studies have enabled unveiling the mechanism of the BOR at Pt surfaces in NaOH media, but no general consensus has been reached to date. The literature is for example rich in attempts to evaluate the number of electrons involved in the oxidation of BH_4^-, which may vary from 2 to 8 electrons for Pt surfaces, pointing out possible reproducibility problems between the different studies [5–10]. Indeed, the BOR mechanism at Pt surfaces is complex: it involves adsorbed species and reaction intermediates and the BOR competes with the heterogeneous hydrolysis of the BH_4^- anion that produces H_2 gas. Regarding the

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complexity of the BOR, it is clear that its mechanism is very sensitive to experimental conditions such as the purity of the reagents, NaOH and $NaBH_4$ concentrations, time management of the experiment and the structure of the electrode [11]. This complexity opens the way to strong effects of the Pt surface morphology, and therefore of the Pt surface preparation procedure that precedes the BOR characterizations. In that frame, this study presents two different behaviors exhibited by smooth Pt electrodes towards the BOR, for the same rotating disk electrode (RDE) experimental procedure of BOR characterization; these behaviors depend on the nature of the smooth Pt electrode surface preparation.

2. Experimental

The chemicals used were sodium hydroxide monohydrate (Merck, Suprapur) and sodium borohydride (Merck, Suprapur). Solutions were prepared in 18.2 MΩ cm and <3 ppb Total Organic Carbon (TOC) water (Elix + Milli-Q Gradient system, Millipore). All experiments were performed at room temperature and pressure (*c.a.* 25 °C, 1 atm).

The electrochemical experiments were controlled using a VSP (Bio-Logic) potentiostat in a three-electrode cell; a gold plate was used as counter-electrode and the reference electrode was a freshly prepared reversible hydrogen electrode (RHE).

The geometrical area of the Pt working electrode (mounted into an OrygaLys RDE setup) was equal to 0.0314 cm^2 (2 mm diameter) for experiments of Fig. 1 and 0.196 cm^2 (5 mm diameter) for experiments of Fig. 2 (it was checked that the features observed in Figs. 1 and 2 do not depend on the Pt electrode dimensions).

Concerning the electrode preparation, the Pt electrode was polished using a diamond paste (Mecaprex, Presi) on polishing cloth (Presi) in the following sequence: 6, 3, 1 and 0.1 μm and was then washed in an ultrasonic bath of acetone, 1–1 ultrapure water–ethanol, and ultrapure water (30 min for each bath) to remove any trace of impurities.

3. Results and discussion

Fig. 1 shows three typical voltammograms that can be obtained for a given smooth Pt electrode in 1 M NaOH + 10 mM $NaBH_4$ electrolyte, when different Pt electrode preparation procedures are employed prior the BOR characterizations (see the experimental section for details about polishing and ultrasonic cleaning). The Pt electrode was either (i) polished and cleaned in ultrasonic bath, or (ii) polished, cleaned in ultrasonic bath and cycled 100 times in 1 M NaOH electrolyte between −0.1 and 1.5 V *vs.* RHE (RDE rotated at Ω = 1000 rpm, voltammetry sweep rate $\nu = 25\ mV \cdot s^{-1}$) or (iii) polished, cleaned in ultrasonic bath, cycled 100 times in 1 M NaOH electrolyte between −0.1 and 1.5 V *vs.* RHE, polished and cleaned in ultrasonic bath again.

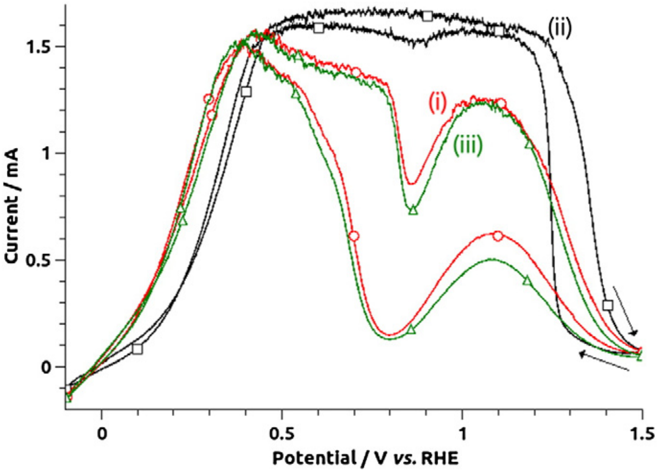

Fig. 1. RDE voltammograms of a Pt disk electrode in 10 mM $NaBH_4$ + 1 M NaOH electrolyte solution, $\nu = 25\ mV \cdot s^{-1}$, Ω = 1000 rpm. Influence of the electrode preparation procedure: (i) polishing and ultrasonic cleaning, (ii) polishing, ultrasonic cleaning and 100 cycles in 1 M NaOH between −0.1 and 1.5 V *vs.* RHE, (iii) polishing, ultrasonic cleaning, 100 cycles in 1 M NaOH between −0.1 and 1.5 V *vs.* RHE, polishing and ultrasonic cleaning again.

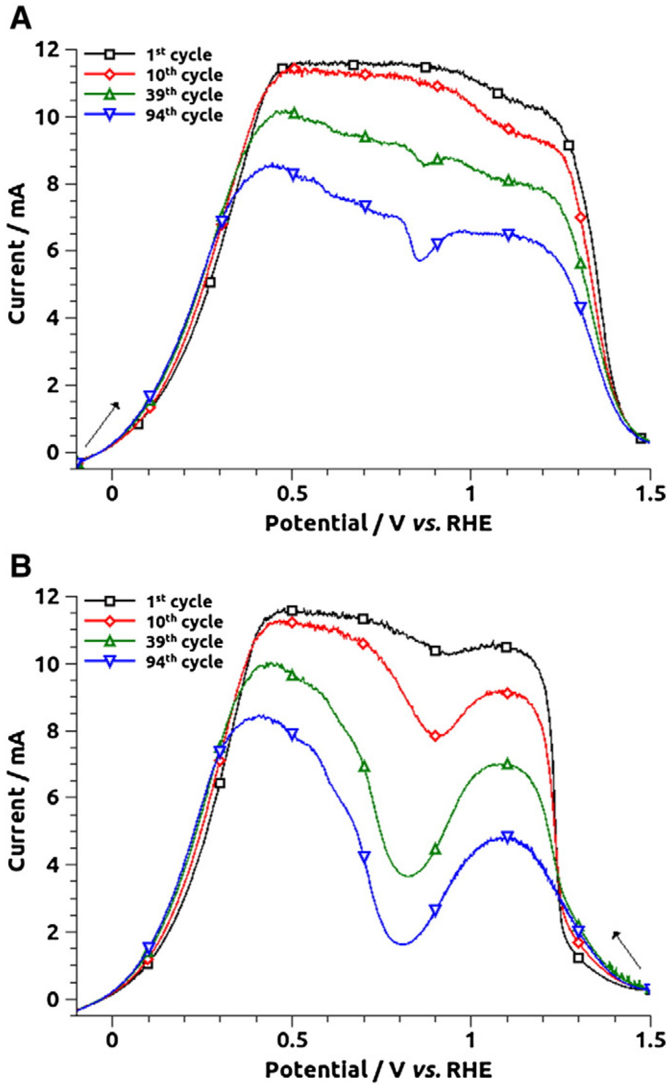

Fig. 2. RDE (A) anodic sweep and (B) cathodic sweep of the voltammograms performed in 1 M NaOH + 10 mM $NaBH_4$ electrolyte solution at a Pt disk electrode cycled 100 times in 1 M NaOH electrolyte beforehand between −0.1 and 1.5 V *vs.* RHE, $\nu = 25\ mV \cdot s^{-1}$, Ω = 1000 rpm.

Pt electrodes prepared as described in cases (i) and (iii) display in Fig. 1 a typical voltammogram shape for smooth Pt in comparable conditions [11,8,4]. The onset potential of oxidation is about −30 mV *vs.* RHE. Two distinguishable potential regions can be observed on these voltammograms. The first region between the onset potential and 0.9 V *vs.* RHE is a mass-transport limited oxidation where the limiting current gradually decreases with the increase of the potential from 0.4 to 0.9 V *vs.* RHE. This decrease of the limiting current is likely due to the progressive adsorption of oxygen-containing species that block the Pt active surface. In other words, the reaction proceeds on bare Pt in this potential region, not on OH_{ad}-covered Pt. The second region, between 0.9 and 1.5 V *vs.* RHE, is another mass-transport limited oxidation where the Pt surface is progressively and ultimately completely blocked by oxide formation (boron oxides or/and platinum oxides) from 1.1 to 1.5 V *vs.* RHE. The existence of these two regions reveals that Pt (low potential region) and Pt oxides (high potential region) both possess some activity towards the BOR.