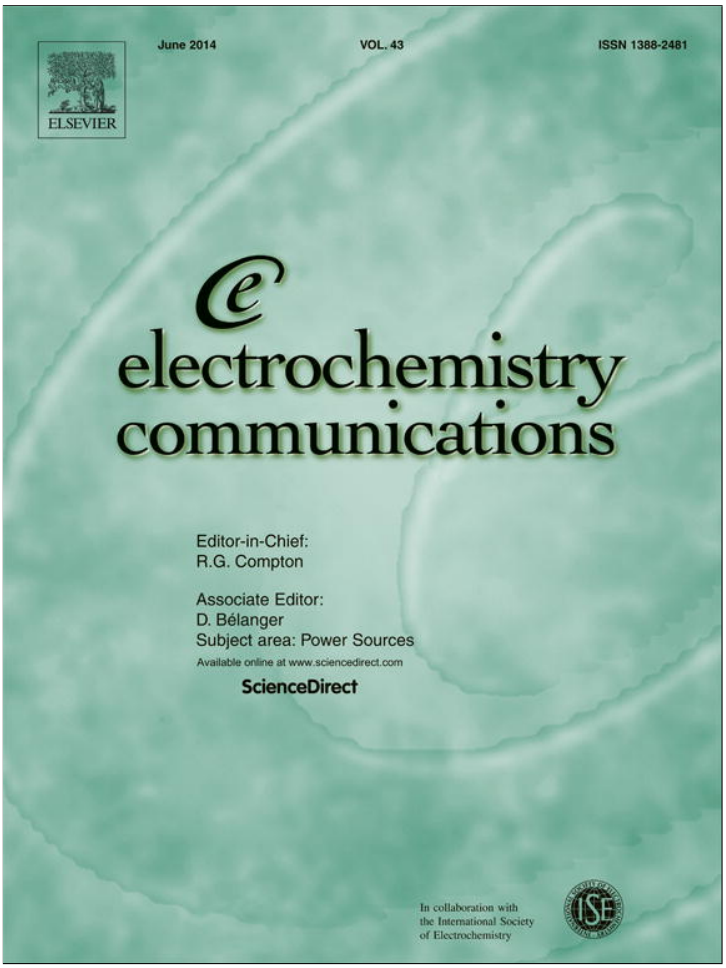

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Short communication

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.

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

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 ν = 25 mV·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.

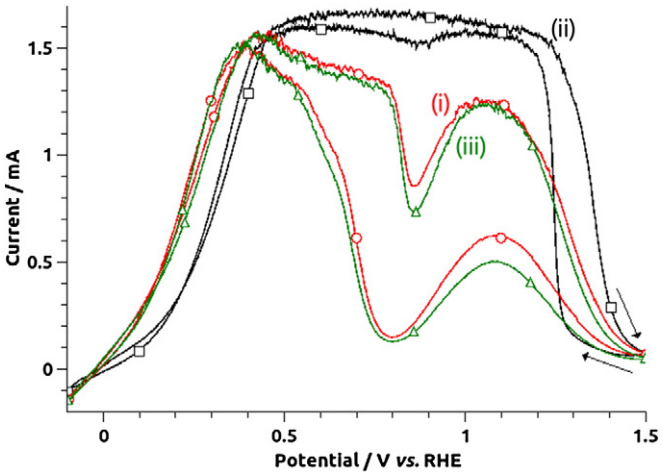

Fig. 1. RDE voltammograms of a Pt disk electrode in 10 mM $NaBH_4$ + 1 M NaOH electrolyte solution, ν = 25 mV·s^{-1}, Ω = 1000 rpm. Influence of the electrode preparation procedure: (i) polishing and ultrasonic cleaning, (ii) polishing, ultrasonic cleaning and 100 cycles in 1 M NaOH between −0.1 and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

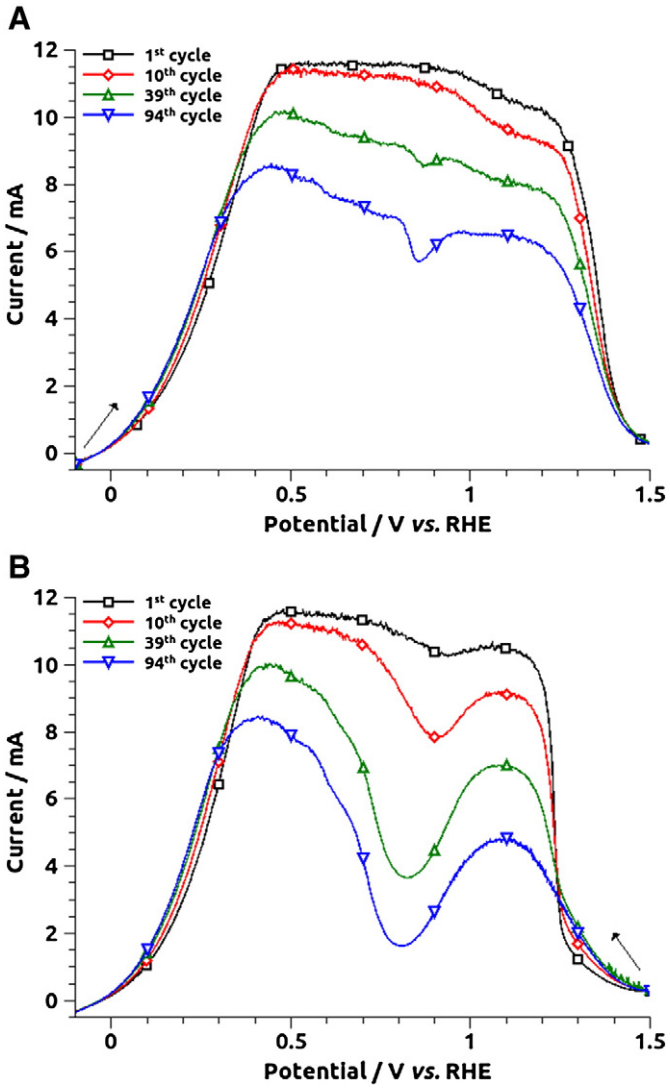

Fig. 2. RDE (A) anodic sweep and (B) cathodic sweep of the voltammograms performed in 1 M NaOH + 10 mM $NaBH_4$ electrolyte solution at a Pt disk electrode cycled 100 times in 1 M NaOH electrolyte beforehand between −0.1 and 1.5 V *vs.* RHE, ν = 25 mV·s^{-1}, Ω = 1000 rpm.

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.

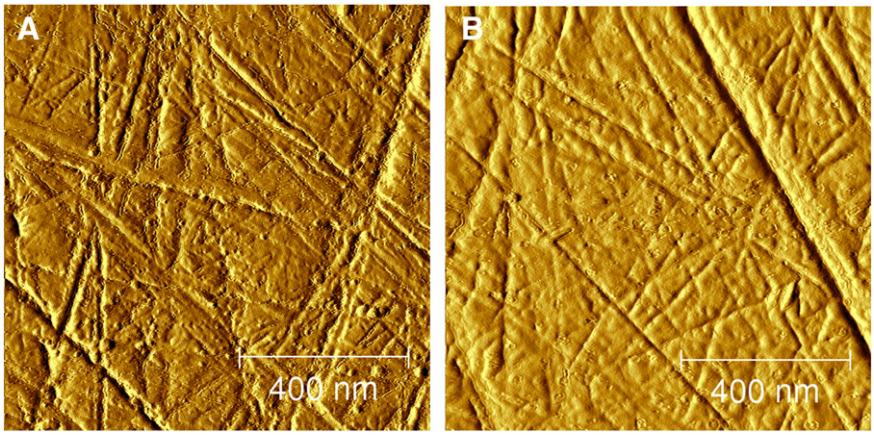

Fig. 3. Tapping-mode AFM amplitude images of a polycrystalline Pt surface electrode (A) before and (B) after 100 voltammetric cycles in 1 M NaOH electrolyte between −0.1 and 1.5 V *vs.* RHE. Same amplitude scale for the two images.

Pt electrode prepared as described in case (ii) displays in Fig. 1 a clearly different voltammogram shape compared to cases (i) and (iii). Performing a cyclic voltammetry in 1 M NaOH + 10 mM $NaBH_4$ electrolyte directly after 100 cycles in 1 M NaOH electrolyte (*i.e.* without any polishing between these two procedures) yields a peculiar result. The voltammogram consists of a mass-transport limited oxidation where the limiting current plateau is well-defined in the anodic sweep between 0.5 and 0.9 V *vs.* RHE, followed by a slight decrease of oxidation current from 0.9 to 1.2 V *vs.* RHE and a sharp decrease from 1.2 to 1.5 V *vs.* RHE. The cathodic sweep displays the same two potential regions with mass-transport limited oxidation, and does not exhibit the sharp hysteresis observed in cases (i) and (iii) at potential below *ca.* 1.2 V *vs.* RHE. This shows that a smooth Pt electrode prepared according to the procedure of case (ii) does not undergo a severe blocking by Pt oxides, compared to cases (i) and (iii). To the best of our knowledge, it is the first time that this kind of voltammogram is presented in the literature.

From Fig. 1, one can conclude that cycling a Pt electrode in NaOH electrolyte apparently changes the structure of the Pt surface, which then behaves differently than the smooth Pt surface classically used in most BOR studies (*i.e.* prepared without any cycling in NaOH beforehand) towards the oxidation of BH_4^-. This particular Pt surface is nevertheless brought back to the classical one by mechanical polishing, as illustrated in Fig. 1: the BOR voltammogram in 1 M NaOH + 10 mM $NaBH_4$ electrolyte of the Pt electrode prepared as described in case (iii) is almost superimposed to that of the Pt electrode prepared as described in case (i).

A Pt electrode has been prepared following the procedure of case (ii) to get this particular state of surface. After plotting the CV that corresponds to case (ii) in Fig. 1, this electrode has then been cycled in 1 M NaOH + 10 mM $NaBH_4$ electrolyte between −0.1 and 1.5 V *vs.* RHE. Some voltammograms of this experiment are presented in Fig. 2. Cycling in this strongly reducing electrolyte takes back the Pt surface from the particular structure presented in case (ii) of Fig. 1 to the classical one of cases (i) and (iii). Note that the electrolyte composition gradually changes during cycling, due to the progressive consumption of BH_4^- as a result of its irreversible electrooxidation and hydrolysis: the BH_4^- concentration is lower on the 94th cycle than on the 1st one. This accounts for the large differences in mass-transport limiting oxidation currents monitored in Fig. 2.

A first attempt to physically observe a possible modification of the smooth Pt surface after the voltammetric cycling in 1 M NaOH has been performed. The smooth Pt electrode was prepared as described before and its surface was observed using tapping mode atomic force microscopy (AFM Veeco Dimension 3100) before and after the 100 voltammetric cycles in 1 M NaOH between −0.1 and 1.5 V *vs.* RHE. From Fig. 3, apart from the polishing scratches, there are indisputably no notable differences to be observed within the AFM range between the polycrystalline Pt surfaces before and after the voltammetric cycling in 1 M NaOH. Indeed, the root mean square roughness (RMS) of the surface does not change with the voltammetric cycling in 1 M NaOH (*c.a.* 1.6 nm RMS in both images of Fig. 3).

This result could suggest that our voltammetric cycling does not change considerably the surface morphology like other more brutal treatments where the growth of a relatively thick Pt oxide layer occurs, but more likely leads to surface disorder of the polycrystalline Pt induced by oxygen place-exchange [3,12–14]. This disordering, not visible by AFM, could induce a difference of reactivity towards the BOR as the type of Pt sites available on the surface for the reaction is likely to change and to behave differently towards, for example, OH or BH_x adsorption. However, this discussion is merely a hypothesis as the phenomena that are supposed to occur on these smooth polycrystalline surfaces cannot be directly observed by imaging techniques. The first results presented in this paper can therefore be seen as an introduction for a future study using well-defined Pt single crystals, where it is expected to learn more about the influence of the atomic structure arrangement of the Pt on the BOR.

4. Conclusions

These results demonstrate the dramatic sensitivity of the Pt surface towards the BOR. Cycling the Pt electrode beforehand in NaOH between −0.1 and 1.5 V *vs.* RHE likely changes the Pt surface structure. This particular state of Pt surface favors a BOR pathway that differs to that occurring on “classical” Pt surfaces (*i.e.* surfaces not extensively cycled in NaOH electrolyte). Elucidating the reason of this particular behavior could help to improve the understanding of the BOR mechanism on Pt. Another interest of these results is to point out the influence of the Pt surface preparation on the reproducibility problems inherent to BOR studies. Indeed, as it is difficult to control perfectly the surface structure of a polycrystalline Pt electrode, two different experimenters would much probably work on two different Pt surfaces that behave differently towards the BOR. Among other variables, this phenomenon likely explains the observed discrepancies of results presented in the literature for the BOR on polycrystalline Pt under similar conditions.

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