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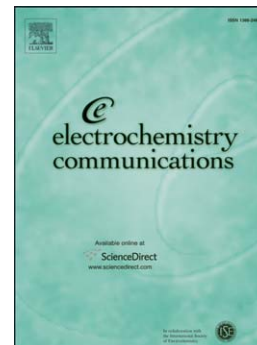
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Borohydride electro-oxidation on Pt single crystal electrodes

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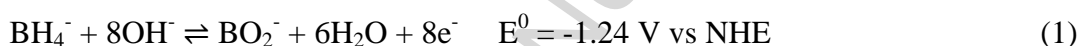
Abstract

The borohydride oxidation reaction on platinum single-crystal electrodes has been studied in sodium hydroxide solution using static and rotating conditions. The results show that borohydride electro-oxidation is a structure sensitive process on Pt surfaces. Significant changes in the measured currents are observed at low potentials. In this region, the Pt(111) electrode exhibits the lowest activity, whereas the highest currents are measured for the Pt(110) electrode. The behavior of the different electrodes is discussed taking as reference the observed behavior on the blank electrolyte and the possible formation of weakly adsorbed intermediates.

Keywords: Platinum; single crystal electrodes; borohydride oxidation; fuel cell; surface sensitive.

1. Introduction

Borohydride (BH_4^-) oxidation is currently attracting interest as an alternative anode reaction for fuel cells since it exhibits several advantages, such as a low thermodynamic potential ($E^0 = -1.24 \text{ V vs NHE}$) which allows a high theoretical cell potential (1.64 V using O_2 as oxidant) [1], high capacity (5.7 Ah g^{-1}), high energy density (9.3 Wh g^{-1} at 1.64 V) [2] and absence of CO poisoning [3]. However, the borohydride oxidation reaction (BOR) is a complex 8-electron process (1) [3] which occurs in several steps and therefore involves numerous intermediates.



Moreover, this reaction competes with the heterogeneous hydrolysis of BH_4^- on the electrode surface of the electrocatalysts with the best reactivity (Pt or Au) [1], [4]. Although numerous studies have been devoted to the understanding of the reaction mechanism of the BOR at Pt surfaces [5-8], this mechanism is not clear yet. By using in situ Fourier Transform Infrared Spectroscopy (FTIR) coupled with electrochemical measurements and Differential Electrochemical Mass Spectrometry (DEMS), Chatenet and co-workers have proposed possible initial elementary steps of the BOR with the participation of intermediates with BH_2 and BH_3 moieties [1,9]. In the potential range between 0.18 and 0.6-0.7 V intermediates with BH_3 groups are formed by heterogeneous hydrolysis or direct BOR, and these groups are rapidly oxidized to BH_2 . At higher potential values ($0.6-0.7 \text{ V} < E < 1.10 \text{ V}$) there is quantitative formation of BO_2^- from BH_2 oxidation, and above 1.10 V, BH_2 oxidation reaction becomes very fast. At the open circuit potential, a fast heterogeneous hydrolysis of BH_4^- species is detected.

Additionally, the mechanism of the BOR is very sensitive to experimental conditions [10]. At this respect, the effect of the surface structure on the BOR has not been studied in detail at the time. The effects of the surface structure are easily studied with single crystal

electrodes, which also facilitates the untangling of the reaction mechanism, since a direct correlation between site and reactivity can be established. In a polycrystalline surface, with several type of sites with different reactivity at a given potential, such study cannot be done. Single crystal electrodes have been previously used to determine the reactivity of the different site for several reactions, including oxygen reduction [11], methanol oxidation [12], formic acid oxidation [13] and hydrazine oxidation [14]. Thus, the aim of this work is to study the borohydride oxidation reaction using Pt single crystal electrodes to investigate the possible effect of the surface structure for this process, and the relationship between the adsorbed species on the surface electrode and the reactivity.

2. Experimental

The experiments were carried out following the general procedure described in [15]. The working solutions were prepared using NaOH·H₂O (Merck, Suprapur, 99.99%) and NaBH₄ (Sigma-Aldrich, 99.99%). Ultrapure water (Elga PureLab Ultra, 18.2 MΩ cm) was used for the preparation of solutions and glassware cleaning. The working electrodes were different Pt single crystal electrodes: the three basal planes (Pt(111), Pt(110) and Pt(100)), the three *turning points* in the stereographical triangle (Pt(331), Pt(311) and Pt(210)) and two *kinked* surfaces (Pt(321)^R and Pt(531)^R). A signal generator EG&G PARC 175 and eDAQ EA161 potentiostat with a eDAQ e-corder ED401 recording system were used for the electrochemical measurements. Hanging meniscus rotating disk electrode (HRMDE) configuration experiments were performed using an EDI101 rotating electrode and rotation rate was controlled by a Radiometer CTV 101 apparatus. All experiments were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the cyclic voltammograms for the different studied Pt single crystal electrodes in 0.1 M NaOH containing 5 mM of NaBH₄. It can be seen that the activity of the different electrodes for the borohydride oxidation reaction is significantly different. Therefore, this reaction is clearly a structure sensitive process, which points out the presence of adsorbed species in the relevant steps of the mechanism.

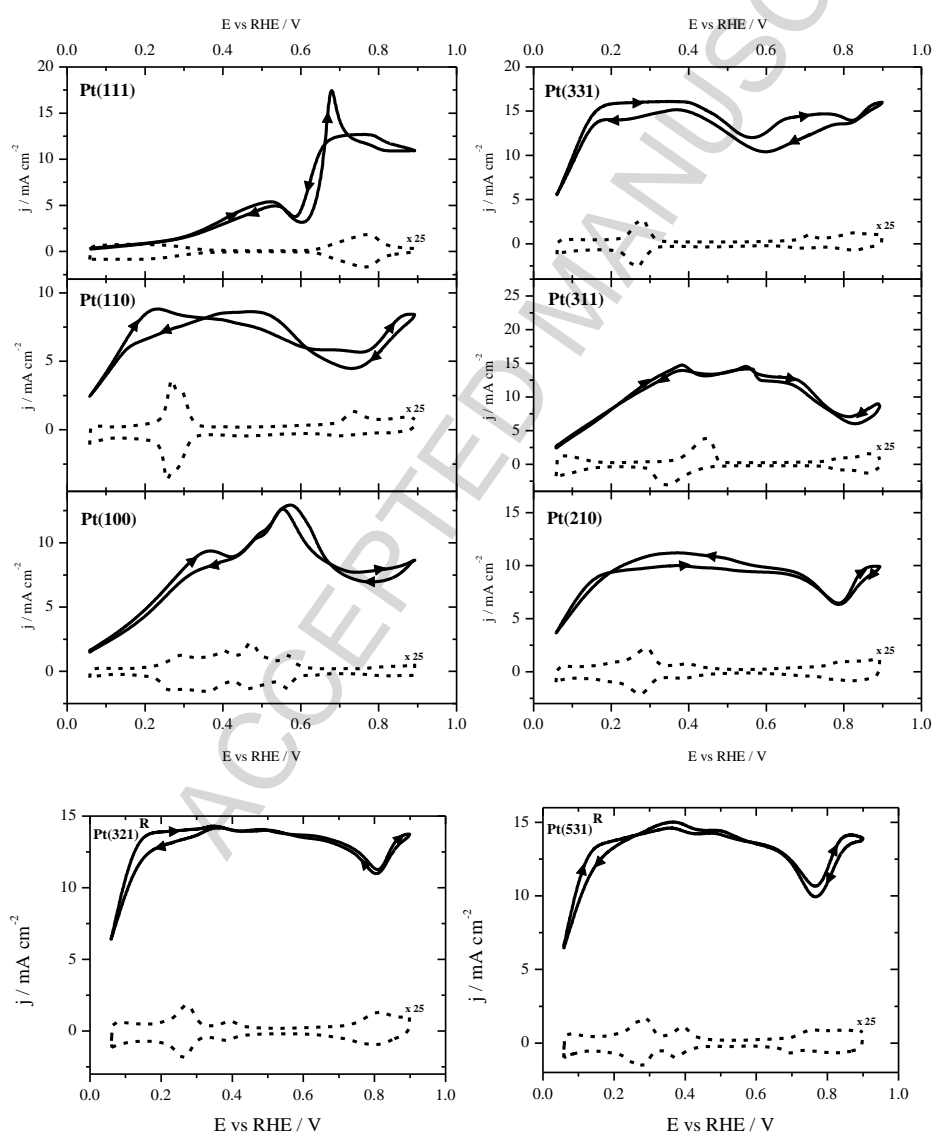


Fig.1. Cyclic voltammograms for the different Pt single crystal electrodes in 0.1 NaOH in the absence (dotted lines) and presence of 5 mM NaBH₄. The voltammograms in the absence of NaBH₄ are multiplied by a factor of 25 to allow comparison. Scan rate: 50 mV s⁻¹.

In spite of the small differences, all the voltammograms have similar features: At 0.06 V, oxidation currents are always detected, and this current increases until a maximum is reached. After that, a clear diminution in the currents is observed between 0.6-0.9 V (except for the Pt(111) electrode). The point at which the maximum current is reached can be related to the onset of OH adsorption on the electrode [16,17]. Thus, for the Pt(111) electrode, peak currents are achieved at ca. 0.6 V, which is the onset of OH adsorption. For the Pt(100) electrode, the onset for OH is ca. 0.45 V [16], and peak currents are obtained in this region. For the other surfaces, the peaks in the blank voltammograms at ca. 0.26 and 0.40 V (figure 1) corresponds to the competitive process of hydrogen desorption/OH adsorption, and peak currents for BOR are obtained approximately in these regions.

On the other hand, the decay in current densities at ca. 0.6-0.9 V can be associated with the oxide formation. As can be seen in the voltammograms of figure 1, the current diminution in the BOR currents coincides with the region where incipient oxides are being formed on the surface, as the blank voltammograms show. This oxide formation is marked by the presence of a small current increase in the blank voltammogram. The only exception in the decay trend is the Pt(111) electrode, for which, the oxide formation occurs above 1 V. The activity of this electrode is the lowest at low potentials. In contrast high activities are measured for the Pt(321) electrode, a kinked surface with chiral sites [18].

As aforementioned, the BOR has already started at 0.06 V for most electrodes, which is the usual initial potential at which the voltammograms of platinum electrodes are recorded. For this reason, it is interesting to determine the effects of the lower potential limit in the process (Figure 2). The experiments were performed using two different lower potential limits: 0.06 V and -0.10 V. For both potential limits, the reactivity order is the same. However, currents are remarkably higher when the lower potential limit is set to -0.1 V for Pt(100) and Pt(110) electrodes. In the case of the Pt(111) electrode, currents are very similar

to the previous case. The increase in current can have two different origins: the removal at $E < 0$ V of some adsorbates that block the surface as has been proposed in [1,9] or the accumulation of borohydride hydrolysis products at those potentials, which are easily oxidized at $E > 0$ V [9]. In order to determine the cause, experiments in HMRDE configuration were carried out (figure 3A). In this configuration, the lower potential limit has no effect on the measured currents. When the initial potential is 0.06 V (not shown), currents are virtually identical to those measured in figure 3A with a lower potential limit of -0.1 V. This fact indicates that the accumulation of borohydride hydrolysis products is the cause of the current increase in static conditions, since those products are not adsorbed on the surface and are easily removed in forced diffusion conditions. Similar results have been obtained in complex electrodes when the residence time of the borohydride molecules are changed [19].

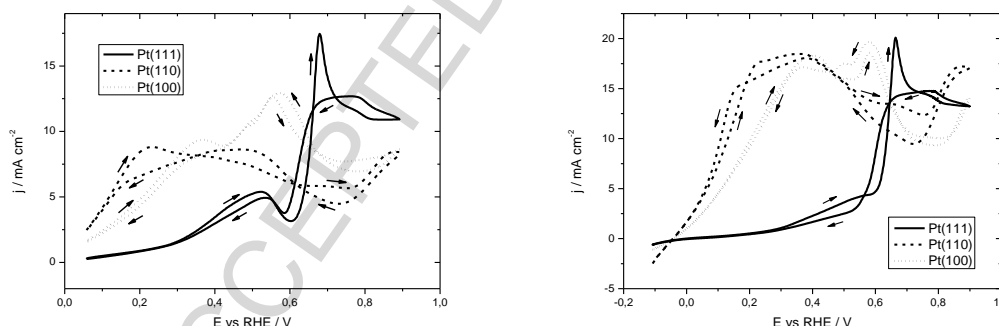


Fig. 2. Comparison of the cyclic voltammograms for the Pt basal planes in 0.1 M NaOH + 5 mM NaBH₄ with two different initial potentials for the scan. Scan rate: 50 mV s⁻¹.

The experiments using a rotating disk configuration can also help to establish the contribution of transport controlled steps in the BOR in other potential regions. Figure 3 compares the results obtained in hanging meniscus static and rotating (2500 rpm) configurations. As can be seen, the current density values are higher when the electrode is rotated, but the voltammetric profiles are very similar. The most significant difference is observed for the Pt(111) electrode, for which the currents at low potential is significantly increased. This fact suggests that some reversibly adsorbed species coming from a reaction product are poisoning the surface. The effect of the forced convection created by the rotation

eliminate the reaction product from the interfacial region and thus adsorption of these species cannot take place. For the other two electrodes, the differences are much smaller and those differences can be explained by the enhanced transport to the surface. However, diffusion controlled conditions are never fulfilled, indicating that the limitations in the currents are due to adsorbents. As a conclusion, in the oxidation process some blocking species are formed and those species can be removed from the surface either by potential excursion in the hydrogen evolution region (Pt(110) and Pt(100)) or using forced convection (Pt(111)).

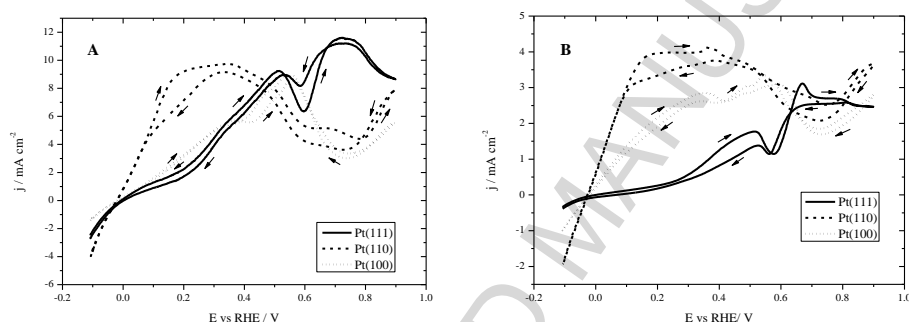


Fig. 3. Cyclic voltammograms for the Pt basal planes in 0.1 M NaOH + 1 mM NaBH₄ (A) using a HMRDE configuration ($\Omega = 2500$ rpm) and (B) in static conditions. Scan rate: 50 mV s⁻¹.

Once the behavior of the basal electrodes have been established, the behavior of the Pt polycrystalline electrode can be understood. In a previous study [10], it was shown that representative BOR voltammograms at smooth polycrystalline Pt electrodes before and after cycling the electrode 100 times in 1 M NaOH between -0.1 V and 1.5 V vs RHE were significantly different. The major difference is that voltammogram for the fresh electrode has a current decay near $E \sim 0.7$ V that does not appear in the voltammogram of the electrode that was cycled 100 times in NaOH. It is known that the repetitive cycling in the oxide region causes the loss of the wide (111) and (100) domains initially present on the polycrystalline Pt surface [20,21], leaving a more disordered surface. This surface disorder is induced by oxygen place-exchange, which forms islands on the previously ordered terraces leading to a more disordered structure [22-24]. Chatenet and co-workers propose that the disappearance of the inhibition near $E \sim 0.7$ V in the voltammogram in presence of BH₄⁻ for the cycled

electrode is caused by this structural change, which would lead to a different pathway for the BOR. However, in our study we observe an inhibition in the voltammograms for all of the well-defined surfaces in different potential regions, even for the *kinked* surfaces, which should be considered similar to the cycled polycrystalline Pt, but without the necessity of the large potential excursions. Therefore, the reason for the presence of the decay should be different. As aforementioned, the decay seems to be related to the onset of oxide formation, which results in an initial diminution of the currents, and after that point, currents increase again to reach the initial values. The repetitive cycling will create a surface in which the defects have a (110) symmetry [25,26]. The most similar surface structure in the single crystal surfaces is the Pt(331) electrode, which have monoatomic (111) terraces and monoatomic (110) steps (or viceversa) and for this surface, the decay around 0.6-0.8 is the lowest one of all the studied surfaces. Since the voltammogram of a Pt poly electrode can be considered as the sum of the contributions of the different domains and sites present on the surface, the disappearance of the decay should be then associated to a change in the contributions, in which, most of the sites behave in a similar way to the Pt(331) electrode, which has a very small decay.

4. Conclusions

The study of the borohydride oxidation reaction using Pt single crystal electrodes in alkaline media reveals that it is a structure sensitive reaction. Among the basal planes, the Pt(110) shows the highest current density values at low potentials, whereas the lowest activity is observed for the Pt(111) electrode. The studies using different lower potential limits or forced transport indicates that some intermediate species are formed at low potentials and are weakly adsorbed, hindering the oxidation. The observed current decay at high potentials can be related to the incipient oxide formation, but not to the presence of ordered (111) or (100) domains.

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Highlights

- Borohydride oxidation reaction is a structure sensitive reaction.
- The activity for low index planes at low potential are Pt(110)>Pt(100)>Pt(111)
- OH adsorption and oxide formation affects the reactivity.

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