

## **A time effect in the early stages of a surface oxidation of a Pt(111) plane in alkaline solution\***

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A time effect in the early stages of surface oxidation of a Pt(111) plane in 0.1 M NaOH solution was studied by examining the reduction parts of the  $j/E$  profile recorded after holding the potential for various times at several values at the end of anodic-going sweeps. The processes associated with the two peaks, which appear in the anodic part of the voltammogram, are assigned to the early stages of a surface oxidation. Two  $\text{OH}_{\text{ad}}$  states are suggested based on the existence of reversibly or weakly bound  $\text{OH}_{\text{ad}}$  species and irreversibly or strongly bound  $\text{OH}_{\text{ad}}$  species. The reversibly bound  $\text{OH}_{\text{ad}}$  species are involved in the "normal" structure of the butterfly peak, while the irreversibly adsorbed  $\text{OH}_{\text{ad}}$  species can be obtained only by the slow diffusion of a part of the initially electrosorbed OH species from sites with low to sites with higher binding energies. The irreversibly reduced  $\text{OH}_{\text{ad}}$  species cannot be completely removed from the surface causing, therefore, some permanent transformation of the initial state of the surface. This kind of species was not detected in the area of the second oxidation peak. The phenomena observed in the reduction part of the  $j/E$  profile induced by a time effect in the second peak could be associated with a place-exchange mechanism between oxygen containing species, whatever they are, and the platinum surface.

*Keywords:* Pt(111) surface oxidation, reversible  $\text{OH}_{\text{ad}}$  species, irreversible  $\text{OH}_{\text{ad}}$  species,  $j/E$  profile, time effect.

### INTRODUCTION

The role of surface states and of species generated during surface oxidation in the understanding of the electrocatalytic oxidation of alcohols at single crystal platinum electrodes has been indicated in a number of recently published papers.<sup>1–10</sup> Special attention was paid to the development of two peaks in the cyclic voltammograms for a Pt(111) plane in acid ( $\text{HClO}_4$ ) or alkaline (NaOH) solutions in the potential region relevant for alcohol oxidation. According to the rather coordinated results obtained, the ini-

\* Dedicated to Professor Dragutin M. Dražić on the occasion of his 70th birthday.

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tial-stage, characterised by the so-called butterfly peak, was associated with the reversible  $\text{OH}^-$  anion adsorption/desorption.<sup>1-6,9</sup> It was suggested by examining the kinetics and mechanism of  $\text{OH}^-$  anion adsorption in sodium hydroxide solution at a Pt(111) surface that this process is based on the simple fast charge transfer reaction:



while the adsorption itself obeys a Frumkin type isotherm.<sup>5</sup> The  $\text{OH}_{\text{ad}}$  species has been proposed as a reactive intermediate in the electrochemical oxidation of methanol<sup>1-4</sup> and  $\text{C}_2 - \text{C}_4$  alcohols.<sup>11</sup>

The nature of the species involved in the second oxidation peak occurring in the voltammogram of a Pt(111) plane is still unknown. These species were commonly referred to as surface "oxide".<sup>12,13</sup> However, bearing in mind the fact that the inhibition of alcohol oxidation takes place in the potential area coinciding with the area of the second oxidation peak, a detailed study of this stage in the surface oxidation should be undertaken.

This work deals with a distinctive feature of the adsorbed species involved in the early stages of the oxidation of a Pt(111) surface following their influence on the surface stage.

#### EXPERIMENTAL

The single crystal surfaces were prepared by annealing in a hydrogen flame and cooling in a hydrogen stream.<sup>14</sup> The almost cool crystal was protected by a drop of water and transferred into the electrochemical cell.

The sodium hydroxide solutions were prepared before each experiment from Merck analytical grade reagent and ultra pure water from a Millipore Milli-Q system (18 M $\Omega$ ).

The measurements were carried out in a conventional three compartment electrochemical cell with a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference. All the potentials were referred to SCE. Nitrogen was used to deaerate the solutions and to maintain the inert atmosphere over the solution during the measurements. All experiments were performed at room temperature.

The dipping method for keeping the electrode in contact with the solution at the starting potential was applied.

Conventional equipment for cyclic voltammetric and potential step measurements was employed (PAR Model 273 potentiostat/galvanostat and Houston Instrument Model 200 XY recorder).

#### RESULTS AND DISCUSSION

##### *Oxidation of Pt(111) surface*

The basal voltammogram for a Pt(111) surface in a sodium hydroxide solution, given in Fig. 1, shows two well-defined processes separated by a so-called double layer. The first process, seen as a flat reversible peak at  $-0.95 \text{ V} < E < -0.6 \text{ V}$  is associated with hydrogen adsorption/desorption. The second process is related to a surface oxidation taking place at  $-0.4 \text{ V} < E < 0.1 \text{ V}$ . The peaks, assigned as I and II, represent the different stages in the process of oxide layer formation. According to the shape of the basal voltammogram, it could be assumed that the early stage in surface oxidation is a reversible process, presented by the so-called butterfly peak (peak I), which is followed by an irreversible process giving rise to peak II.

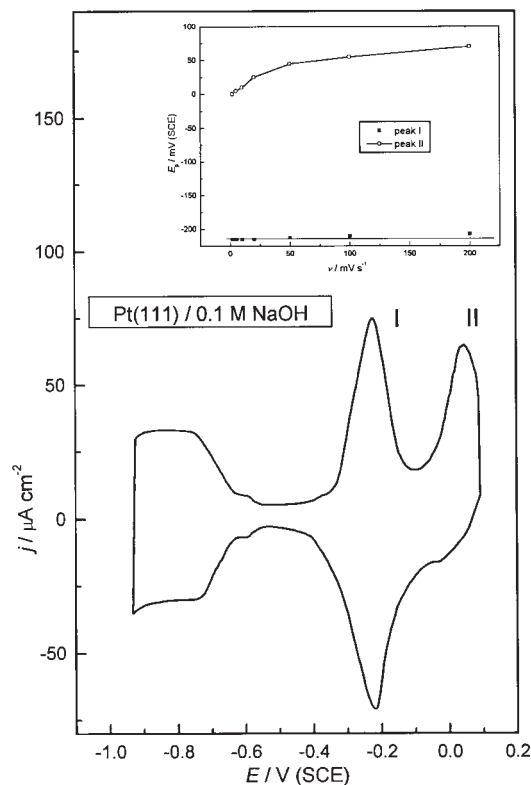


Fig. 1. Basal voltammogram of a Pt(111) electrode in 0.1 M NaOH solution. Sweep rate:  $v = 50 \text{ mV s}^{-1}$ ;  $t = 22 \text{ }^\circ\text{C}$ . Inset: Dependence of the peak potential on the sweep rate for a Pt(111) electrode in 0.1 M NaOH solution.

The dependence of the first and second peak potential on the sweep rate is given in the inset of Fig. 1. The peak potential for the first peak is independent of the sweep rate in the range  $0.001 \text{ V s}^{-1} - 0.2 \text{ V s}^{-1}$ , clearly indicating that the oxidation stage corresponding to this peak has the characteristics of a reversible process. However, the dependence of the second peak on the sweep rate suggests the presence of a slow irreversible process.

Two peaks can be generated if the existence of two kinds of oxygen containing species is assumed.<sup>15</sup> Consequently, the first peak, the so-called butterfly peak, was related to a fast, reversible  $\text{OH}^-$  ion chemisorption defined by the simple charge transfer reaction giving  $\text{OH}_{\text{ad}}$  species.<sup>5</sup> The second peak could be associated with further surface oxidation, producing other oxygen containing species.<sup>12,13</sup>

#### *Time effect in surface oxidation*

Time effect experiments were performed by adjusting the potential from the initial value  $E = -0.55 \text{ V}$  to different positive potential limits using the potential step method and subsequently holding the potential at these values. Then the electrode was subjected to a negative going linear sweep at  $v = 50 \text{ mV s}^{-1}$  whereby the  $j/E$  profile was recorded.

The results of such experiments are given in Fig. 2. They differ generally, depending on the holding potential and the holding time. When the potential was held in

the area of the butterfly peak (Fig. 2 a – c), the mutual characteristics at the reduction part of the obtained  $j/E$  profiles can be defined by a decrease of the coverage with reversibly adsorbed  $\text{OH}_{\text{ad}}$  species and by the development of a new peak at  $E = -0.45$  V. Quantitatively both phenomena are very dependent on the holding time and the positive potential limit, being particularly pronounced at the initial stage of surface oxidation at  $E = -0.3$  V (Fig. 2a).

On the other hand, when the potential is held in the region of the second oxidation peak, related to the formation of other oxygen-containing species (Fig. 2 d), the formation and reduction of the surface species occur without the two components in the reduction part of  $j/E$  profile being resolved.

By comparing the results presented in Fig. 2, it can be assumed that the appearance of the new reduction peak at  $E = -0.45$  V could be associated with the presence of an irreversibly reduced species originating from the reversible  $\text{OH}_{\text{ad}}$  species, initially adsorbed during holding the potentials in the area of the butterfly peak. These species seem to be more stable and more strongly bound to the surface than the reversible  $\text{OH}_{\text{ad}}$  species according to their less positive reduction potential. The fact, that the amount of irreversible reduced species decreases with increasing coverage by previously adsorbed  $\text{OH}^-$  anions from approximately  $\theta = 1/3$  (Fig. 2 a) to a monolayer value (Fig. 2 c), suggests that a diffusion process plays an important role. This means that under the conditions of a random surface arrangement, some of the reversibly adsorbed  $\text{OH}_{\text{ad}}$  species are able to reach sites with higher binding energies by a time dependent surface diffusion process (Fig. 2 a). Consequently, increasing the coverage by adsorbed  $\text{OH}^-$  ions up to a monolayer value causes a significant decrease of the peak at  $E = -0.45$  V (Fig. 2 c). Finally, this peak disappears after holding the potential at  $E = 0.1$  V in the area of peak II (Fig. 2 d). This means that irreversibly reduced species, responsible for the appearance of a peak at  $E = -0.45$  V, cannot be formed in the potential region of the second peak.

The cyclic voltammograms given in Fig. 3 demonstrate the effect of holding the potential for various times in the area of butterfly peak. They were recorded by applying the negative going sweeps up to  $E = -0.55$  V, *i.e.*,  $E = -0.95$  V (Figs. 3 a and 3 b, respectively) and subsequently positive going sweeps after holding the potential at  $E = -0.25$  V. The decrease of the reversibility between the formation and reduction of the  $\text{OH}_{\text{ad}}$  layer with increasing holding time can be clearly seen from the reduction part of the basal voltammogram which is resolved into two peaks. The continuing growth of the new peak at  $E = -0.45$  V is followed by continuing decrease of the peak at  $E = -0.3$  V. The irreversible species, associated with the peak at  $E = -0.45$  V, cannot be completely removed from the surface up to  $E = -0.55$  V (Fig. 3 a) causing a blocking effect of  $\text{OH}^-$  anion adsorption, as can be seen from the anodic part of the  $j/E$  profile. Lower potentials are needed for them to be further reduced but they still partially remain at the surface even in the hydrogen adsorption/desorption region (Fig. 3 b). The transformations of the basal voltammogram caused by the time effect are not qualitatively but are very much quantitatively dependent on the negative potential limit of scanning.

The cyclic voltammogram obtained after holding the potential at  $E = -0.25$  V does not change during further continuous cycling in the potential region  $-0.95$  V  $< E <$

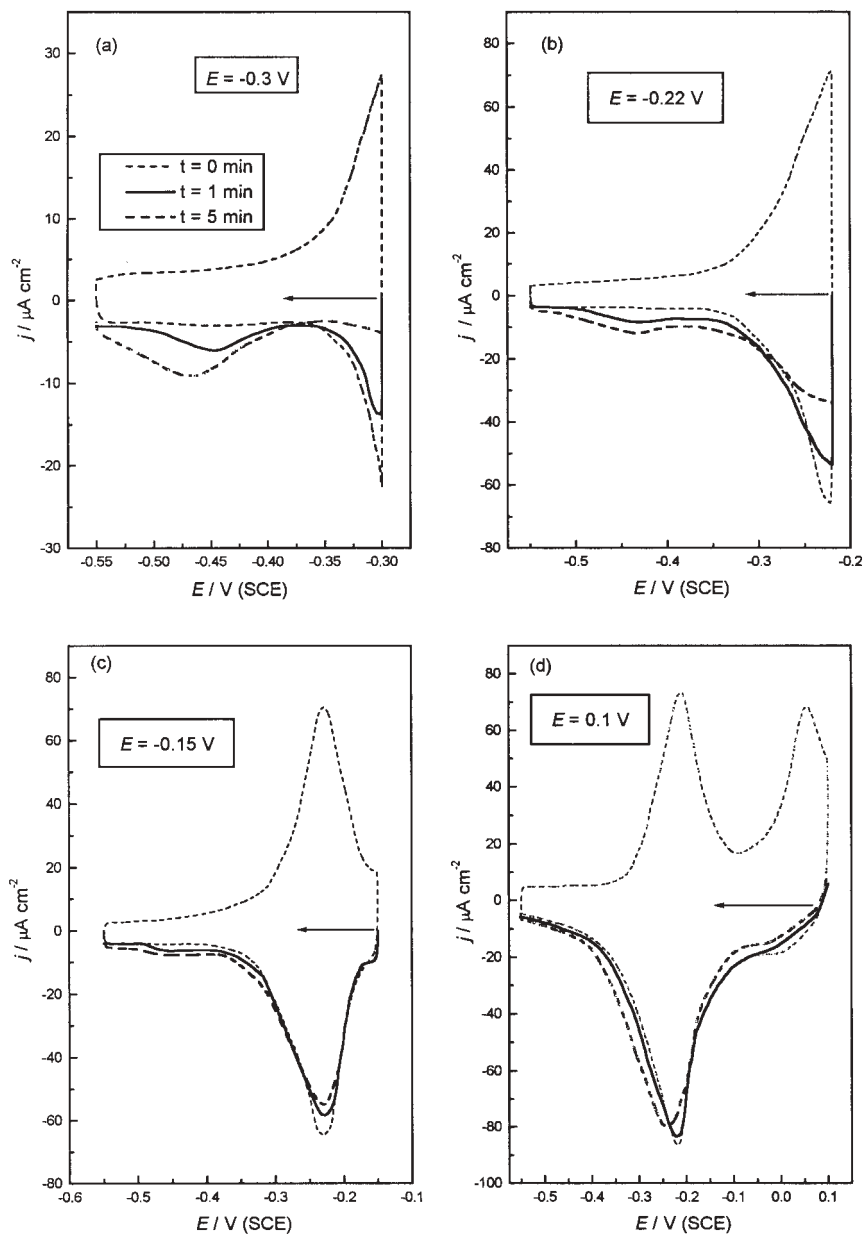


Fig. 2. Time effect in negative going sweeps for the reduction of oxygen containing species at a Pt(111) electrode in 0.1 M NaOH solution recorded after various holding times and potentials. Sweep rate:  $v = 50 \text{ mV s}^{-1}$ ;  $t = 22 \text{ }^\circ\text{C}$ .

$-0.1 \text{ V}$  indicating that a new surface condition had been established (Fig. 4). Some inhibition of the hydrogen and  $\text{OH}^-$  anion adsorption/desorption processes could be caused by the poisoning effect resulting from the presence of the irreversible species strongly

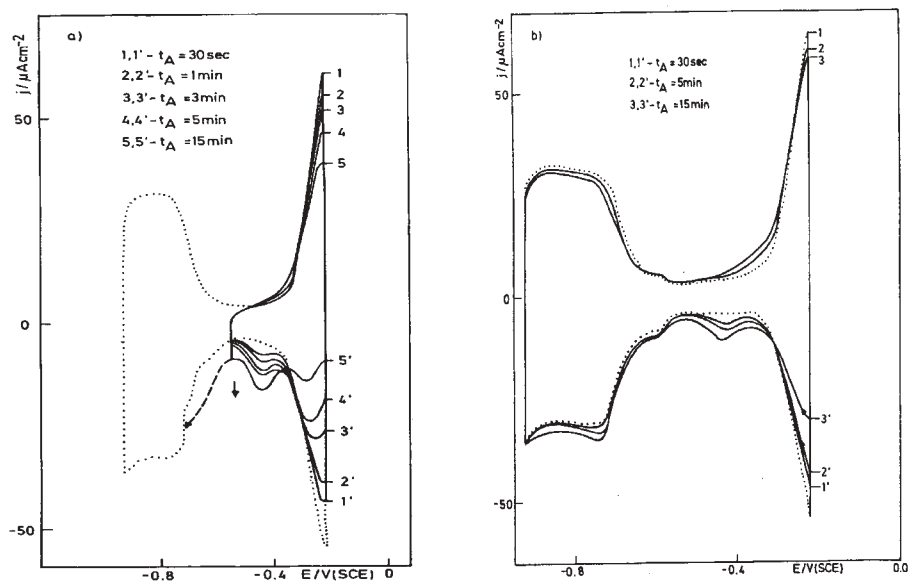


Fig. 3. Cyclic voltammograms of a Pt(111) electrode in 0.1 M NaOH solution recorded after holding the potential at  $E = -0.25$  V for various times ( $t_A$ ) up to the negative potential limit  $E = -0.55$  V (a) and  $E = -0.95$  V (b) (—) and the corresponding basal voltammograms (----). Sweep rate  $v = 50$  mV s<sup>-1</sup>;  $t = 22$  °C.

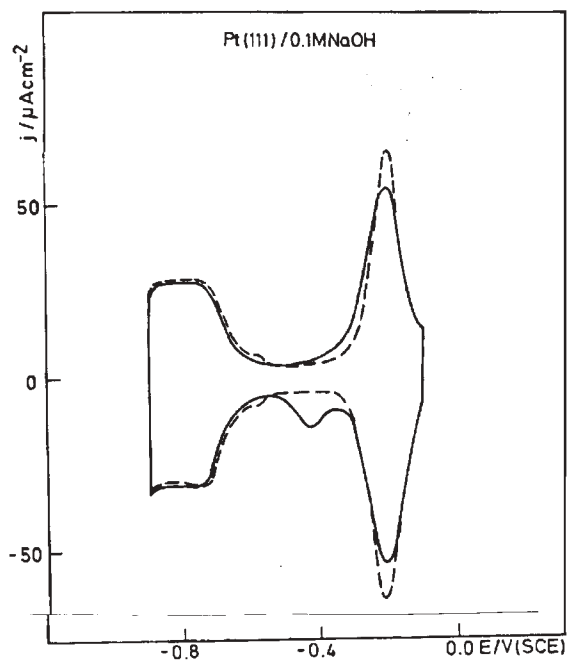


Fig. 4. Cyclic voltammogram recorded after holding the potential at  $E = -0.25$  V (—) and the basal voltammogram of a Pt(111) electrode (----) in 0.1 M NaOH solution.

bound to the surface. Bearing in mind that the transformations are permanent, a rearrangement of the surface by place exchange ( $\text{PtOH} \rightarrow \text{OHPt}$ )<sup>15</sup> cannot be taken into consideration.

Based on the results presented in Figs. 2, 3 and 4, it is suggested that the irreversible species originating from the initially reversibly adsorbed OH species are the same kind of species, *i.e.*,  $\text{OH}_{\text{ad}}$  species, which have the ability to be strongly bound to appropriate surface sites during the time dependent surface diffusion process.

#### *Nature of the irreversible species*

The cyclic voltammograms obtained by expanding the positive potential limits from  $E = 0.1$  V to  $E = 0.6$  V are given in Fig. 5 a. In the positive going sweeps, a kind of plateau is formed after the second oxidation peak, while a reduction peak in the opposite scan direction, which becomes progressively larger and shifted to less positive potentials, indicates an increase of the irreversibility in the surface oxidation followed by an overall destruction of the surface. Oxide species formed at higher positive potentials seem to be responsible for the surface reconstruction.

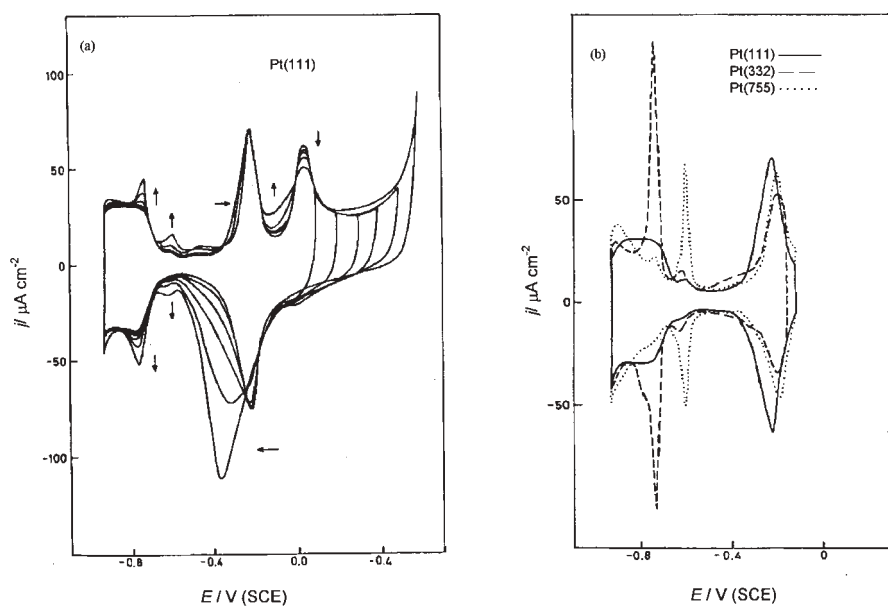


Fig. 5. (a) Cyclic voltammogram for a Pt(111) electrode recorded from  $E = -0.95$  V to various reversal potential in positive going sweeps. (b) Basal voltammograms of Pt(111), Pt(755) and Pt(332) electrodes in 0.1 M NaOH solution. Sweep rate  $\nu = 50$   $\text{mV s}^{-1}$ ;  $t = 22$   $^{\circ}\text{C}$ .

By comparing the voltammogram given in Fig. 5 a with the basal voltammograms for the stepped Pt(755) and Pt(332) planes given in Fig. 5 b, the nature of surface reconstruction, caused by higher oxide species, can be seen. The details observed in Fig. 5 a, such as the progressive development of peaks at  $E = -0.62$  V as on the Pt(755) (Fig. 5 b) and at  $E = -0.78$  V as on the Pt(332) surface (Fig. 5 b) and the current increase in the double layer region, as well as the shift of the onset of the butterfly peak to more positive val-

ues with respect to the basal voltammogram for the Pt(111) plane, show the transformation from a flat to a stepped surface consisting of (111) and (100) step sites. The absence of the peak at  $E = -0.45$  V in the reduction part of the Pt(111) voltammograms, obtained by cycling in the area of high oxide formation (Fig. 5 a), and on the basal voltammograms for stepped planes (Fig. 5 b), clearly suggests that the origin of this peak should be associated neither with a surface reconstruction nor with oxide species.

The new surface state established after holding the potential in the butterfly peak region could be caused by a new  $\text{OH}_{\text{ad}}$  state, *i.e.*, by strongly bound irreversible  $\text{OH}_{\text{ad}}$  species, which cannot be completely removed from the surface and consequently act as a poison in the hydrogen and  $\text{OH}^-$  ion adsorption processes.

#### CONCLUSIONS

The results obtained under the experimental conditions presented in this work imply that two  $\text{OH}_{\text{ad}}$  states, characterized by weaker or stronger interaction of the  $\text{OH}^-$  ions with the surface, exist. Reversible  $\text{OH}_{\text{ad}}$  species and irreversible  $\text{OH}_{\text{ad}}$  species correspond to the previously mentioned  $\text{OH}_{\text{ad}}$  states, respectively. Both kinds of species originate from the area of butterfly peak at a Pt(111) surface. The major differences between them are the time dependent formation of the irreversible  $\text{OH}_{\text{ad}}$  species and their incapability of being completely eliminated from the surface, causing a blocking effect of hydrogen and  $\text{OH}^-$  ion adsorption. The reversible  $\text{OH}_{\text{ad}}$  species was proposed as a reactive intermediate in the electrochemical oxidation of alcohols, while the irreversible  $\text{OH}_{\text{ad}}$  species act as a catalytic poison in these processes.

#### ИЗВОД

##### ВРЕМЕНСКИ ЕФЕКАТ У ОКСИДАЦИЈИ Pt(111) ПОВРШИНЕ У АЛКАЛНОЈ СРЕДИНИ

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Временски ефекат у току оксидације Pt(111) електроде у 0,1 М NaOH је испитиван у области првог и другог оксидационог пика који одговарају почетку оксидације површине, а појављују се на потенцијалима релевантним за оксидацију алкохола. Задржавањем потенцијала у области првог тзв. “лептир” пика детектоване су две врсте  $\text{OH}_{\text{ad}}$  честица. Реверзибилне  $\text{OH}_{\text{ad}}$  честице чине “нормалну” структуру “лептир” пика, док се иреверзибилне  $\text{OH}_{\text{ad}}$  честице могу добити само временски зависном дифузијом дела иницијално адсорбованих реверзибилних  $\text{OH}_{\text{ad}}$  честица. Иреверзибилне  $\text{OH}_{\text{ad}}$  честице су чврсто везане за површину и не могу се потпуно уклонити са површине узрокујући трансформацију површине у односу на њено иницијално стање. Задржавање потенцијала у области другог оксидационог пика нема за последицу стварање иреверзибилних  $\text{OH}_{\text{ad}}$  честица. Реверзибилне и иреверзибилне  $\text{OH}_{\text{ad}}$  честице имају значајну улогу у процесу оксидације алкохола. Реверзибилне  $\text{OH}_{\text{ad}}$  честице су активни интермедијери у реакцији, док иреверзибилне  $\text{OH}_{\text{ad}}$  честице делују као тзв. каталитички отрови.

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