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ON THE KINETICS OF OXIDATION CONTROLLED ADSORPTION OF A MODEL ALCOHOL ON A Pt+Au ALLOY ANODE

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ABSTRACT

The kinetics of 1,3-propanediol adsorption on a Pt+Au alloy of Au bulk content of 80 at. % was studied with the application of a linear potential sweep transient technique. The adsorption proceeded at a potential of 0.80 V, which coincided with the value of the anodic peak determined by the substrate oxidation as shown by the recorded voltammograms. The adsorption time t_{ads} *was varied in the range 1-500 ms. In accord with the preliminary investigations the study was carried out in a solution of 1,3-propanediol of* 4.10^{-4} *mol* l^{-1} *in 1.0 M KOH. The potential pulses following the adsorption step were run with a scan rate of 6.50 Vs-*^{1}*. The temperature was varied in the range from 287.7 K to 300.2 K. Activated chemisorption was observed. The temperature dependence of the initial adsorption rate was found to obey the empirical rate law suggested by Chia et. al. The values of the enthalpy and entropy of adsorption activation were found to be 35 kJ mol*$^{-1}$ *and -24 J mol*$^{-1}$ *K*$^{-1}$*, correspondingly. The adsorption kinetics studied was described by Roginskii-Zeldovich equation as well. The values of* $\Delta H^{\neq}_{ads}$ *and* $\Delta S^{\neq}_{ads}$ *were 35 kJ mol*$^{-1}$ *and -13 J mol*$^{-1}$ *K*$^{-1}$*, respectively. The enthalpy of adsorption activation equals that of the alcohol's electrooxidation activation showing that the rate-determining step of the overall process at the alloy anode refers to a reaction of the intermediate, produced in the substrate's chemisorption with the surface hydroxide coverage as is the case with Pt.*

Keywords : adsorption kinetics, initial adsorption rate, Roginskii-Zeldovich equation, 1,3-propanediol, Pt+Au alloys, electrooxidation mechanism.

INTRODUCTION

Many alloy and surface modified Pt electrodes have been tested for use as organic fuel cell anodes because they are well known to have unique catalytic properties for many important chemical transformations [1-7]. They have been a particularly active area of research in electrocatalysis [8-12]. The experimental results obtained show that the increased catalytic activity of these materials can be attributed to: (i) modification of the surface electronic properties resulting in changes of the adsorption properties; (ii) increased surface concentration of adsorbed oxygen containing species involved in the organic substances oxidation; (iii) suppression of the formation of strongly adsorbed intermediate species due to the "third body effect". These conclusions refer to *Pt+Au* alloys too [13-19]. Recent studies on the elecrocatalytic behavior of the latter electrode system focus on exploration of the effect of the alloys surface composition on the catalytic activity observed not only in alkaline [18] but in acidic media as well [19]. This factor is additionally elucidated in a comparative investigation [20] of the catalytic activity of *Pt+Au* alloys and *Au* electrodes modified by electroless deposition of *Pt*. The study, being in accord with the renewed interest towards *Au*'s future role in fuel cell systems [21, 22], shows that the electrooxidation of a model organic substance proceeds with a lower apparent activation energy at *Pt+Au* alloy electrodes when compared to the modified *Au* substrates if the surface content of *Au* is less than 0.70. The plausible explanations discussed refer mainly to the procedure of the apparent activation energy estimation, to the interaction between the adsorbate valence states and the metal surface resulting from the deposition, to the effect of *Pt* clusters' size and the type of the substrate.

There are numerous investigations on the electrocatalytic oxidation of mono- and polyhydric alcohols at *Au* and *Pt* [23 and refs. therein]. It is now well recognized that this surface multistage process is strongly *pH* dependent and follows a mechanism which is quite close for both metals. The rate-determining step of the process at *Pt* refers to a reaction of the intermediate, produced in the substrate's dissociative chemisorption, with $Pt\left(OH\right)_{ad}$. In case of *Au* the heterogeneous dehydrogenation of alcohol's molecules, involving electron transfer to the metal electrode determines the rate of the overall process. But unlike the case at *Pt* the hydrogen abstraction considered occurs via a transient adsorbate complex resulting from an interaction between adsorbed substrate molecules and hydroxide species on the electrode surface. Thus it is evident that in both cases alcohol molecules adsorption precedes the rate determining step. The same should be valid for the electrooxidation process at *Pt+Au* alloys. There is an experimental evidence that the presence of chemisorbed OH^- anions or/and partially oxidized Au atoms is required for the anodic process not only at *Au* [22] but at *Pt+Au* alloys as well [19]. But further investigations are required to support the idea advanced.

The aim of this work is to study the kinetics of a model alcohol's adsorption at a Pt+Au alloy. Unlike the adsorption investigations described in the literature the present one is carried out in the potential range of the substrate's oxidation, i.e. the adsorption studied is expected to be controlled by the subsequent oxidation step.

EXPERIMENTAL

The experiments were performed with a Pt+Au alloy electrode of Au bulk content of 80 *at.%*. Au counter and a hydrogen reference electrodes were used. All potential values cited in the text refer to *RHE*. The true electrode surface of the working electrode was measured prior to each experiment. The procedure used was previously described [24 and refs.therein]. The electrode pretreatment procedure involved pulsing in the potential range 0.05-1.55 *V* with a scan rate of 0.10 Vs^{-1} for a period of 30 *min*.

Linear potential sweep transient technique [25] was applied in this case as well (in fact it was used for the study of the same process but at *Pt*, *Au* and a *Pt+Au* alloy electrode of a different bulk composition [24]). The potential-time sequence included two cleaning pulses involving potential steps to: 1.70 *V* for 5 *s* and 1.10 *V* for 10 *s*. The adsorption proceeded at a potential of 0.80 *V*, i.e. at the value of the anodic peak determined by the substrate oxidation as shown by the recorded voltammograms. The adsorption time t_{ads} was varied in the range from 1 to 500 *ms*. Three subsequent potential pulses followed the adsorption step. Their lower limit was determined by the adsorption potential while the upper one reached the value of 1.80 *V* to provide complete adsorbate oxidation. The organic substance's concentration and the scan rate applied were adjusted to ensure that the second and the third transients coincided. Moreover, they had to coincide with the transient recorded under the same conditions but in the absence of the organic substrate. Thus it was possible to show that the adsorbate was removed by oxidation during the first sweep and the surface was left free within the following two sweeps. The coincidence showed as well that no re-adsorption occurred to a significant extent. Hence, the background current could be measured in the same solution by simply measuring the second and the third transient. Hence the same electrode could be used throughout the experiment without further electrochemical pretreatment.

The method yielded meaningful results if in general the transient duration provided complete oxidation of the adsorbate and no re-adsorption occurred. If either condition was not fulfilled, the charge Q_{ads} decreased with the increase of the scan rate,

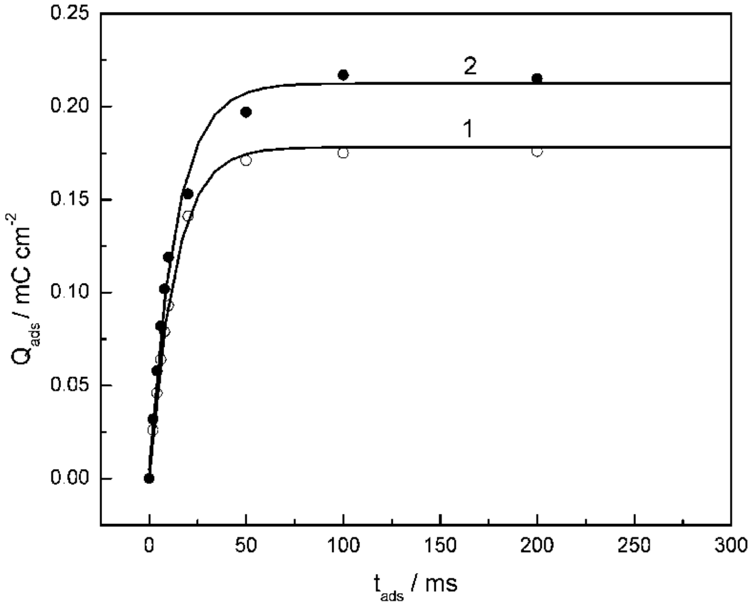

Fig. 1. Q_{ads} vs. t_{ads} obtained for the alloy electrode studied at 287.7 K (1) and 291.6 K (2) .

s. Under favorable conditions a plateau was observed in the plot $Q_{ads}\ vs.\ s$. Its limits were determined by the rate of adsorption and that of oxidation, respectively. The charge Q_{ads} due to the adsorbate oxidation was followed as a function of the scan rate and the width of the plateau observed was tested in solutions of varying both alcohol's concentration and temperature. In accord with the preliminary investigations the study was carried out in a solution of 1,3-propanediol of 4.10^{-4} *mol* l^{-1} in 1.0 *M KOH* . The scan rate applied was 6.50 Vs^{-1}.

The electrolyte solution was prepared from bidistilled water, 1,3-propanediol (*Fluka*, *purum*) and *KOH* (*Riedel-deHäen, pa*). Prior to each measurement the solution was deoxygenated with N_2. Bubbling was switched off 60 *s* prior to reaching the adsorption potential. All experiments were performed in a double walled Pyrex glass cell with electrochemical equipment of a conventional type. The studies were run at 4 temperature values in the range of 287.7 *K* to 300.2 *K*. The accuracy was ± 0.2 *K*.

RESULTS AND DISCUSSION

Two plots $Q_{ads}\ vs.\ t_{ads}$ for the adsorption process studied at two temperature values (287.7 K and 291.6 K) are presented for illustration in Fig. 1. It is seen that like in case of Pt and the other alloy investigated [24] Q_{ads} increases with t_{ads} and temperature. This indicates that the initial adsorption rate grows with temperature increase as expected for activated chemisorption [26, 27]. The temperature dependence of the initial adsorption rate is found to obey the empirical rate law suggested by Chia et. al. (eqn.(5) in reference [28]):

$$\left(\frac{\partial Q_{ads}}{\partial t_{ads}}\right)_{t_{ads}\to 0} = Kc_0\left({}_{L}Q_{ads} - Q_{ads}\right)\exp\left(\frac{\Delta S^{\neq}_{ads}}{R}\right)\exp\left(\frac{\Delta H^{\neq}_{ads}}{RT}\right) \qquad (1)$$

where the frequency factor $K = \dfrac{kT}{h}$, while the subscript *L* indicates the limiting value of Q_{ads} at bulk concentration c_0 . $\Delta H^{\neq}_{ads}$ and $\Delta S^{\neq}_{ads}$ are the enthalpy and entropy of adsorption activation, respectively. The values of the initial adsorption rate were determined graphically and the subsequent calculations were carried out with the maximum values of Q_{ads} reached at the longest t_{ads} and the highest temperature studied. In this study ${}_{L}Q_{ads} = 2.18\,Cm^{-2}$. The linear dependencies expected in correspondence with eqn. (1) provide to estimate the

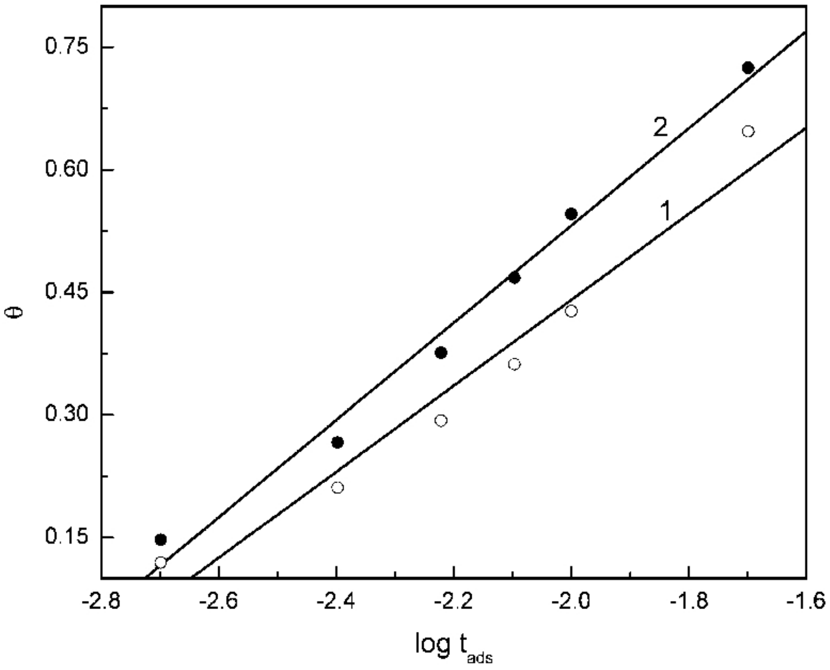

Fig. 2. θ vs. $\log t_{ads}$ obtained for the alloy electrode studied at 287.7 K (1) and 291.6 K (2).

values of $\Delta H^{\neq}_{ads}$ and $\Delta S^{\neq}_{ads}$, i.e. 35 *kJ mol*$^{-1}$ and -24 *J mol*$^{-1}$ *K*$^{-1}$, correspondingly.

The adsorption kinetics can be described by Roginskii-Zeldovich equation [29] as well in correspondence with the concepts of slow chemical adsorption proceeding on a non-uniform surface:

$$\theta = \left(2.303/g^{'}\right)\left[\log\left(g^{'}k_{ads}\,c_{ROH}\right)+\log t_{ads}\right] \quad (2)$$

where $g^{'} = ag/RT$ with a and g standing for the symmetry factor of adsorption enthalpy and the interaction coefficient, respectively. The linear relationship of θ on $\log t_{ads}$ provides the estimation of the adsorption rate constant, k_{ads}. This was done in a comparative investigation [29] of the adsorption of methanol and some other aliphatic alcohols on Pt in an acid medium. The same approach was used [30] to study 1,3-propanediol adsorption on a Pt+Au alloy electrode of different bulk composition. Some of the linear plots obtained in this case (the procedure of θ estimation is described elsewhere [30]) are presented for illustration in Fig. 2. The temperature dependence of k_{ads} is used to calculate the enthalpy and entropy of activation. The values obtained are 35 *kJ mol*$^{-1}$ and -13 *J mol*$^{-1}$ *K*$^{-1}$, respectively. It is important to underline the complete coincidence of the $\Delta H^{\neq}_{ads}$ - values determined with the application of two different equations. But another coincidence deserves even greater attention. The same value was reported for the enthalpy of electrooxidation activation for the same alloy electrode [18]. It is worth adding that in the latter case the standard rate constant of electrooxidation was determined and its temperature dependence was followed. The fact that the enthalpy of adsorption activation and the enthalpy of electrooxidation activation of the alcohol studied, coincide suggests that the adsorption step which precedes the oxidative transformation of the adsorbed residue is limited in this case, i.e. at this high anodic potential it is controlled by the rate at which the electrode surface is set free from both the adsorbed organic and hydroxide species. This interpretation is supported by the values of the entropy of activation pointed above. They are slightly different but in general much higher than those reported in ref. [18]. This shows that the degree of disordering at the alloy surface achieved at the adsorption potential is in fact less. This means that the alcohol's adsorption proceeds predominantly at surface sites which are set free in the course of the subsequent oxidation step. In fact these results were expected in view of the concepts of the mechanism of the alcohol's electrooxidation which should not differ from those for Pt and Au.

CONCLUSIONS

The study on the kinetics of 1,3-propanediol adsorption on a Pt+Au alloy of Au bulk content of 80 at. % shows that

- the degree of surface coverage grows with the increase of adsorption time and temperature, i.e. activated chemisorption takes place;
- the value of the enthalpy of adsorption activation is identical with that of the enthalpy of electrooxidation activation (found in a previous investigation) as the adsorption proceeds at the potential of the alcohol's electrooxidation peak.

Hence it can be concluded that the alcohol's adsorption taking place under the conditions pointed above is in fact controlled by the rate at which the electrode surface is set free from the adsorbed organic and hydroxide species. This means that the rate-determining step of the overall oxidation process at the alloy anode is identical with that at Pt .

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