VOLTAMMETRIC STUDY OF THE ANODIC OXIDATION OF ETHYL ALCOHOL

K. Venkateswara Rao

Department of Applied Chemistry, Indian Institute of Technology, Kharagpur-721302

(Received April 1978 ; accepted June 1978)

The oxidation of ethyl alcohol and acetaldehyde on platinized platinum has been studied along with electrolytically co-deposited Pt-Au electrode in 1N sulphuric acid solution using slow sweep cyclic voltammetric method. Anodic sweeps showed two peaks, one at about 700 mV and the other at about 1200 mV The first peak was predicted to be due to oxidation of adsorbed ethyl alcohol to acetaldehyde and the other due to adsorbed acetaldehyde to acetic acid. The increase of active surface area by the presence of gold to platinum increased the electrocatalytic activity of Pt.

In recent years a great amount of experimental material has been accumulated dealing with chemisorption and electrochemical oxidation of various organic compounds on metals of the platinum group. In this communication an attempt has been made to study the electrochemical oxidation of ethyl alcohol and the chemisorbed species that are present in the process of oxidation. The galvanostatic and chronopotentiometric study of the oxidation of ethyl alcohol at platinized platinum in acid medium was done previously[1]. This study was limited to lower potential region. Now the study has been extended to cyclic voltammetry in an attempt to elucidate the adsorbed organic species and the mechanism of oxidation.

In the earlier studies on the electrolytic oxidation of ethyl alcohol Shlygin and co-workers[2] observed that acetal dehyde alone was formed on platinized platinum at high ethyl alcohol concentrations at 0.65 V; at more highly anodic potentials a mixture of acetic acid and acetaldehyde was formed and at potential values greater than 1.9V conditions were produced for pure acetic acid formation. In the latter studies they[3] observed a drop in current in the potential range 1.0 to 1.5V. This drop was assumed to result from relatively strong chemisorption of intermediates, thereby blocking or poisoning, part of the surface. In the case of electrolytic oxidation of acetaldehyde, when the potential curve passed through maximum, the drop in the current was attributed by Shlygin et al[4] to be due to the formation of adsorbed oxygen on the electrode. From the studies of the charging curves by Sokol'skii and Shamina[5] it was observed that the hydrogen plateau on recorded curves shortened with increasing concentrations of ethyl alcohol, but another plateau appeared at the same time in the potential range 450 - 500 mV which was assumed to be due to oxidation of ethyl alcohol to acetaldehyde.

Hollnagel et al[6] observed that under approximately equal conditions at cantrolled potentials, there exist convection-independent current maxima at 850 mV (ethyl alcohol) and 1200 mV (acetaldehyde). At 800 mV ethyl alcohol is mainly oxidized to acetaldehyde. Daniel Bek and co-workers[7] observed that only hydrogen obtained by the result of dehydrogenation is oxidized. In their studies Blake et al[8] observed that ethyl alcohol forms two types of adsorbed species one cathodically desorbable and the other non-desorbable; but the species were not specified. In the previous studies[1] it was found that the ethyl alcohol that is adsorbed on the surface of the electrode at open circuit potential is completely getting oxidized to acetaldehyde in the lower potential region, i.e., below the oxide layer formation potential. The value of θ_{org} was calculated to be approximately 0.8 at open circuit.

Experimental

The electrolytic cell used for measuring the slow sweep cyclic voltagrams was made up of a glass vessel provided with a stopper through which the required number of electrodes were introduced and dipped into the electrolyte (preelectrolysed 1N sulphuric acid solution). The reference electrode was a platinized platinum foil electrode whose geometric area was 2 cm^2. The test electrode was a platinized platinum wire electrode whose geometric area was 0.1 cm^2. The cell was provided with an inlet and an outlet for the gas.

To get the experimental voltagrams, the test electrode was made anode and the reference electrode

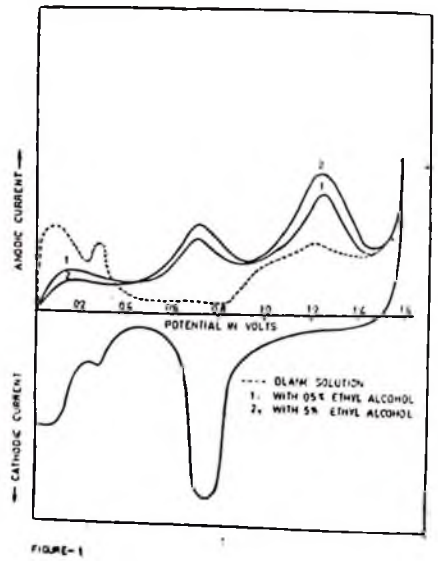
as cathode. The potential variation that was used in the present experimental studies was of 400mV/ min. The changes that occur at the anode were noted on the automatic X-Y recorder against time. The chart speed was regulated depending upon the current maximum.

The chloroplatinic acid and chloroauric acid that were used for the electrodeposition were obtained from Johnson Matthey Chemicals Ltd. The sulphuric acid used was of BDH AnalaR quality. The procedure adopted for purification of ethyl alcohol was mentioned earlier[1]. The instrument used for the study was 'Polarograph LP7, Laboratorni Pristroje Praha'. All the readings were taken in IN H_2SO_4 at 27°C.

Results and Discussion

a) VOLTAMMETRIC OBSERVATIONS

An initial examination of the adsorption of ethyl alcohol on platinized platinum in IN sulphuric acid solution using a continuous cyclic scan of the electrode potential between 0.4 and 1.6V (NHE) to analyse the surface, showed that the oxidation of adsorbed ethyl alcohol occurred as though two distinct and separate entities were involved. The maxima in the oxidation rates for the two species were

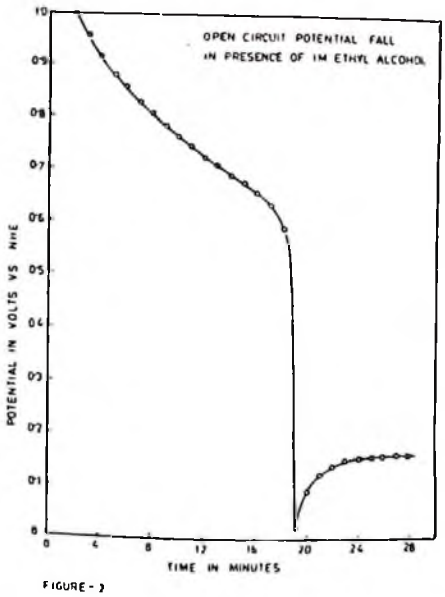


1. Cyclic voltagrams of oxidation of adsorbed ethyl alcohol at two different concentrations.

separated by some 500 mV. Fig. (1) shows the representative oxidation curves of adsorbed ethyl alcohol at different concentrations on platinum such that the different oxidation peaks can be seen clearly. The relative surface concentrations of two species were dependent upon the absolute coverage of the surface by ethyl alcohol. To separate and understand the relevance of these two species, a detailed analysis of the coverage of platinum surface by adsorbed hydrogen and the two adsorbed entities was made.

The true surface area of the electrode was determined from the anodic hydrogen desorption peaks between 0 and 0.4 V. In the voltammetric study the coulombic charge from anodic stripping of the adsorbed hydrogen was used rather than the deposition of hydrogen on the platinum surface favoured by other workers[9–11]. There is about ten percent difference in the surface area determination by the two methods.

Ethyl alcohol coverages were measured from the cathodic deposition of hydrogen peaks, correcting for the difference in double-layer capacitance and oxide formation on the original surface. Coverage by ethyl alcohol was calculated using one electron per site for the deposition of hydrogen on the surface. The adsorbed hydrogen coverage decreased with the total coverage by ethyl alcohol. Similar type of results were observed by Sokol'skii and Shamina[5].



2. Open circuit potential fall in the presence of 1M ethyl alcohol.

Fig. (2) shows the fall of open circuit potential when the electrode previously anodized to 1.6 V was kept in a solution containing ethyl alcohol. Here the potential falls below the steady open circuit potential to very nearly about 0 V and there the potential rises once again abruptly to open circuit potential which remains steady. This potential minimum, similar to that of formic acid, formaldehyde etc[12,13] was found to be highly dependent on the pretreatment of the electrode. The minimum in the open circuit potential can be attributed to a mixed potential between hydrogen, resulting from the dissociation of ethyl alcohol, and some organic species. The following scheme can be drawn to explain the above observations[1].

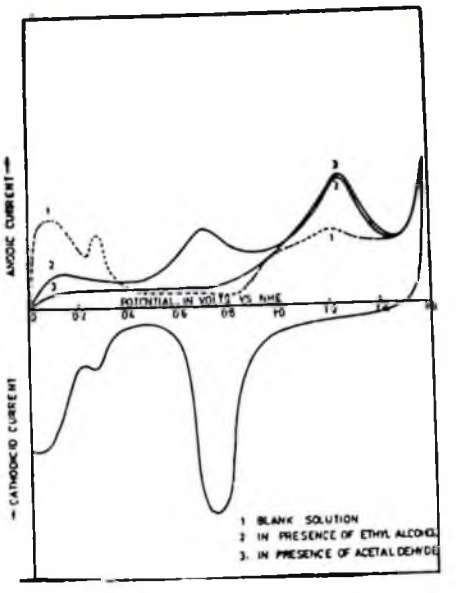
$$Pt - O + CH_3.CH_2OH_{soln} \rightarrow CH_3.CHO + H_2O + Pt$$
$$Pt + CH_3.CH_2OH_{soln} \rightarrow CH_3.CH_2OH_{ad}$$
$$CH_3.CH_2OH_{ad} \rightarrow CH_3.CHOH_{ad} + H_{ad}$$
$$H_{ad} \rightarrow H^+ + e$$

So at open circuit potential when the electrode was anodized previously, the adsorbed species that are possibly present on the surface of the electrode will be :

$CH_3.CH_2OH_{ad}$, $CH_3.CHOH_{ad}$, $CH_3.CHO_{ad}$ and H_{ad}.

According to Frumkin and co-workers[14] the products were ethane and methane. The occurrence of these methane and ethane as detectable products derived from ethyl alcohol arises when alcohol comes into contact with a platinized platinum electrode saturated with hydrogen. Reduction occurs to a hydrocarbon containing as many carbon atoms as the alcohol. If an outgassed platinized platinum is used, breaking along the C_1-C_2 bond occurs. They postulated that the adsorbate consisted partially at least of CH_{ad} fragments, the result of cracking The other process that will be taking place mainly when the electrode is covered with hydrogen was the replacement reaction i e., ethyl alcohol present in the solution replaces the hydrogen present on the surface of the electrode.

Fig. (3) which is the voltagram of blank solution, ethyl alcohol, and acetaldehyde indicates that the first peak which was observed, only for the system when the electrode is covered by ethyl alcohol, at 0.7V corresponds to the oxidation of adsorbed ethyl alcohol to acetaldehyde and the second peak which



3. Cyclic voltagrams of oxidation of adsorbed ethyl alcohol, and adsorbed acetaldehyde.

was observed for both ethyl alcohol and acetaldehyde at about 1.2 V corresponds to the oxidation of acetaldehpde to acetic acid.

As was known already[1,15] ethyl alcohol adsorbs on the surface of the electrode to a large extent. θ_{org}, the fractional coverage by the adsorbed organic was given as approximately 0.8. So at the open circuit potential 80% of the surface is covered by ethyl alcohol and the remaining portion may be assumed to be covered by the reduced and cracked species along with adsorbed hydrogen. Now when the potential is increased from open circuit potential, the oxidation of the adsorbed ethyl alcohol species ($CH_3.CH_2OH_{ad}$) takes place. This reaction is dissociative chemisorption of the adsorbed organic

$$CHC_2H_2OH_{ad} \rightarrow CH_3CHOH + H_{ad}$$
$$H_{ad} \rightarrow H^+ + e$$

which forms CH_3 CHOH and H_{ad}; of these two reaction steps the second one proceeds with high rate especially as the potential is increased to higher values. So the two reactions can be combined as :

$$CH_3\,CH_2OH_{ad} \rightarrow CH_3.CHOH + H^+ + e$$

The small peak observed in the hydrogen oxidation region in the presence of ethyl alcohol in the voltagram corresponds to the oxidation of the dissociated

hydrogen. The marked difference between the blank solution and in the presence of ethyl alcohol shows that the adsorbed species are of different type. For blank solution the oxidation of adsorbed hydrogen shows two typical peaks corresponding to the oxidation of loosely bound hydrogen and strongly bound hydrogen where in the ethyl alcohol system the peak was not subdivided; only one peak was observed. The results of Daniel-Bek[7], that only hydrogen obtained by the result of dehydrogenation of ethyl alcohol is oxidized, also supports the above proposition. Since the species CH_3CHOH is a chemisorbed species it needs more energy to get oxidized than that of CH_3. CH_2OH_{ad}. So the oxidation of the former species takes place at higher potentials. This means, first the dissociative chemisorption of $CH_3.CH_2OH_{ad}$ species takes place and when this is completed the chemisorbed $CH_3.CHOH$ species gets oxidized. The peak observed at about 0.7V in the ethyl alcohol voltagram corresponds to the oxidation of the chemisorbed species to acetaldehyde

$$CH_3.CHOH \rightarrow CH_3.CHO + H^+ + e.$$

Frumkin and co-workers[14] in their studies deduced that the initial chemisorption step is rate determining step. In addition, slow charging curves demonstrated that the chemisorbed species oxidized at a rate two orders of magnitude lower than did ethyl alcohol itself and therefore regarded as a poison rather than an adsorbed intermediate in the overall reaction. In the previous study[1] also it was found that the dissociative chemisorption of ethyl alcohol is the rate determining step.

The occurrence of another peak for ethyl alcohol at about 1.2 V indicates that the acetaldehyde present on the surface of the electrode undergoes further oxidation. The voltagrams of both ethyl alcohol and acetaldehyde show second peak at the same potential region indicating that the species getting oxidized is the same in both cases.

The fall of current observed after the peak (at 0.8 V) indicates that after complete oxidation of the chemisorbed species CH_3CHOH to CH_3CHO the current falls down indicating that the species present on the electrode is not getting oxidized. They remain as they are on the surface of the electrode. This process can be said to be blocking of the surface by the intermediates. But once the oxide layer formation starts taking place on the electrode surface the current increases again compared to that of the blank voltagram. This indicates that in the presence of the adsorbed acetaldehyde, in addition to oxide layer formation some other reaction is taking place which causes an increase in the current. If acetaldehyde is inactive even in this potential region the blank voltagram should give higher currents than does the other voltagrams, because in the latter case a part of the surface is inactive or not utilized for oxide layer formation. Now the excess current can be considered to be due to the electrochemical reaction between adsorbed acetaldehyde and oxide layer which can be represented as :

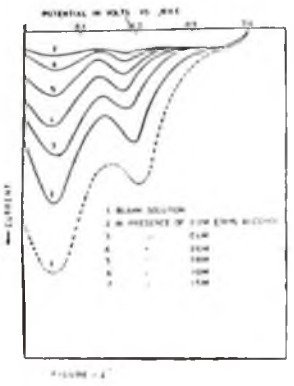
$$CH_3.CHO_{ad} + Pt - OH \rightarrow CH_3.COOH + H^+ + e$$

This oxidation process starts occurring from the potential where oxide layer formation commences to the potential where oxygen gas evolution begins. Here by the time the oxygen evolution starts the whole acetaldehyde present on the surface of the electrode gets oxidized to acetic acid and will be removed from the surface of the electrode. If any small amount of acetaldehyde is left over even at the oxygen evolution potential, chemical reaction between acetaldehyde and molecular oxygen takes place forming acetic acid : $CH_3.CHO + \frac{1}{2}O_2 \rightarrow CH_3COOH$. The observations of Shlygin and co-workers[2], that acetaldehyde alone was formed upto 0.65 V, at more highly anodic potentials a mixture of both acetic acid and acetaldehyde was formed and at potentials greater than 1.9 V pure acetic acid was formed, also supports the above said oxidation process.

In this way qualitatively the possible reactions that are occurring in the process of anodic oxidation of ethyl alcohol can be explained with the help of voltammetry.

In order to get θ_{org}, the fractional surface covered by the adsorbed organic the cathodic sweep was made use of. In this study the potential of the test electrode was kept at 0.4V and was taken out of the 1N sulphuric acid solution and was kept in a solution containing different concentrations of ethyl alcohol (ethyl alcohol and 1N sulphuric acid solution) for about 60 seconds. At 0.4V the electrode surface will be free of adsorbed species. After this the electrode was taken out and washed with distilled water and

then kept in the test solution. The cathodic sweep was taken starting from 0.4V to 0.0V. Fig. (4) shows the shapes of the cathodic sweeps at different con-

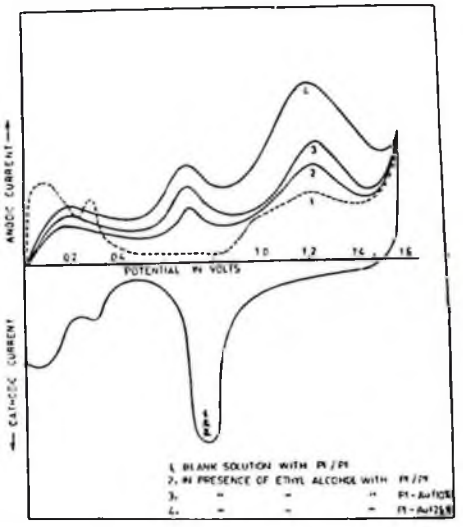


4. Cathodic sweeps of cyclic voltagrams at different concentrations of ethyl alcohol.

centrations of ethyl alcohol. From the measurements of the hydrogen deposition peak areas one can get θ_H, the fractional surface area covered by hydrogen, which was obtained by comparison of the hydrogen deposition regions of voltagrams of blank system and in the presence of adsorbed ethyl alcohol. Now the surface area which is not utilized for hydrogen deposition directly gives the value of θ_{org} $(1-\theta_H)$. In this method of determination of θ_{org} value, it was assumed that the interaction between the adsorbed organic and hydrogen is not taking place and if at all it is negligible. From this figure it can be observed that as the concentration of ethyl alcohol is increased the θ_H value (or Q_H value) falls down, finally reaching zero. At this stage one can assume that the surface is completely covered by the ethyl alcohol adsorbed and this concentration in termed as limiting concentration, which is same as the limiting concentration which was observed[1] above which the order of reaction with respect to the concentration of ethyl alcohol is zero.

(b) ELECTROCATALYTIC ACTIVITY OF Pt-Au ELECTRODES

An alloy electrode was taken and studied along with platinized platinum electrode in order to check whether the binary system also behaves in the same way or it differs in the process of oxidation, because the observations of galvonostatic method indicated that the basic mechanism will be the same for the alloy systems also. In the previous studies on the anodic oxidation of methanol, formic acid and hydrazine[16] and formamide[17] in both acid and alkaline media it was observed that electrolytically co-deposited Pt-Au electrode shows a better electrocatalytic activity than that of platinized platinum in spite of its well known poor catalytic activity in all the electro oxidation processes mentioned in the the literature [18,19]. Now the same binary system was taken and studied to check its electrocatalytic activity.



5. Cyclic voltagrams of oxidation of adsorbed ethyl alcohol at (1) platinized platinum, (2) Pt-Au at 10 atomic % gold and (3) Pt-Au at 25 atomic % gold.

Fig. (5) shows the anodic sweeps of cyclic voltagrams of adsorbed ethyl alcohol on platinized platinum and Pt-Au (10 and 25 atomic% Au) electrode. Here the two different compositions were taken in order to verify the results of one composition by the other. This figure shows that the peak heights are increased from platinized platinum to Pt-Au of 10 atom% gold and then to Pt-Au of 25 atomic% gold. From this figure one can observe that the peaks due to acetaldehyde (at 0.7 V) and the other due to acetic acid (1.2 V) occurs strikingly at the same potential. The only difference found was a considerable increase in the peak currents and correspondingly peak areas. The results indicate that exactly the same type of reactions are occurring on the platinum-gold electrodes also. There is no change

of mechanism. Since there is no shift in the peak potential one can assume that not only the mechanism is same in both the cases but the basic catalytic properties are also unaltered. Considerable increase in the peak area suggests that the active surface area of the Pt-Au system is only increased. This increase in the active surface area causes an increase in the catalytic activity. The results of the charging curves[16], in which the catalytic activities of the co-deposited binary systems were determined from hydrogen oxidation region, also shows that Pt-Au electrode has got quite a high active surface area than does platinized platinum.

This increase in the active surface area of platinum by the presence of gold atoms is unexplainable on the basis of d-band character. Pure gold is basically inactive for hydrogen adsorption[20] and also organic adsorption[21]. From these results one can conclude that the presence of gold decreases the available surface for the adsorption to take place. So theoretically there should be a linear fall in the active surface area Inspite of this, the experimental results show an increase in the catalytic activity of platinum by the presence of gold. This can be explained assuming that even though pure gold is inactive in the adsorption and oxidation processes, in the presence of platinum gold also exhibits the electrocatalytic activity. Stephens[22] in his oxygen chemisorption studies on Pd-Au films observed an increase in the total uptake of oxygen by the alloys even though there was no oxygen chemisorption on pure gold films. He explained this observation as the presence of palladium has made it possible for oxygen to react with gold atoms in the surface, although oxygen would not adsorb on pure gold films. This discussion of the results in terms of the properties of individual surface atoms rather than holes in the d-band was unusual at the time, though, as can be seen[23] the individual surface atom approach has been used to explain high activity on Cu-rich copper-nickel alloys in which the d-band is expected to be full. The difference in the electrocatalytic activity by Pt-Au system which was observed in our studies[14,15] and in the previous studies[16,17] mainly due to the method of preparation. As was known very well the method of preparation of the catalyst has got pronounced influence on the activity.

REFFERENCE

1. K. Venkateswara Rao and C.B. Roy, J. Ind. Chem. Soc., In Press.
2. G. A. Bogdanovskii and I.A. Shlygin, Zhur. Fiz. Khim., 31 (1957) 2428.
3. A. I. Shlygin and G.A. Bogdanovskii, Trudy Chetvertogo Soveshchaniya po Elektrokhimi, Moscow 1956, 282.
4. G.A. Bogdanovskii and A.I. Shilygen, Zhur. Fiz. Khim., 33 (1959) 1769.
5. D.V. Sokil'skii and L. T. Shamina, Tr. Inst. Khim. Nauk, Akad. Nauk Kaz SSR 8 (1962) 37.
6. M. Hollnagel and U. Lohse, Z. Physik. Chem., 232 (1966) 237.
7. G.V. Vitvitskaya and V.S. Daniel-Bek, Sb. Rab. Khim. Istochnikam Toka 1966, 174.
8. A.R. Blake, A.T. Kuhn and J.G. Sunderland, J. Electrochem Soc., 120 (1973) 492.
9. S. B Brummer, J. Phys. Chem. 69 (1965) 1363.
10. S Gilman, J. Phys. Chem., 66 (1962) 2657.
11. P. Stonehart Electrochimica Acta., 18 (1973) 63.
12. J.E. Oxley, G. K. Johnson and B. T. Buzaiskii, Electronchim. Acta., 9 (1964) 897.
13. A.N. Frumkin, and B. I. Podlovchenko, Dokl. Acad. Nauk SSSR., 150 (1963) 349.
14. B. I. Podlovchenko, O. A. Petrii, A.N. Frumkin and Hira Lal, J. Electroanal. Chem. 11 (1966) 12.
15. E. Gileadi and B. J. Piersma, in 'Modern Aspects of Electrochemistry', Vol. 4, Ed. J.O'M. Bockris, Butterworths, London, 1966.
16 C. B. Roy, S.C. Das and H. R. Kundu, Ind. J. Chem., 14A (1976) 315.
17. K. Venkateswara Rao, S. C. Das and C.B. Roy, J. Electrochem Soc. Ind., In Press.
18. M. W. Breiter J. Phys. Chem., 69 (1965) 3327.
19. M. Watanabe and S. Motoo. J. Electroanal. Chem., 60 (1975) 259.
20. M. W. Breiter, J. Phys. Chem., 69 (1965) 901.
21. B. M. W. Trapnell, "Chemisorption", Butterworths, London, 1955.
22. S. J. Stephens, Nat. Symp. Vac Technol., Trans 4 (1958) 34.
23. R. L. Moss and L. Whalley, in 'Advances in Catalysis', Vol. 22. Ed. D. D. Eley, H. Pines and P. B. Weisz, Academic Press, New York and London, 1972.