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PROPANOL OXIDATION ELECTROCATALYSIS BY UNDERPOTENTIAL DEPOSITED METAL ATOMS

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ABSTRACT

In the present study the electrocatalytic effect of foreign metal monolayers deposited on platinized platinum electrode on the oxidation mechanism of propanol was investigated. The explanation of the results were made by the comparision of current-potential curves obtained in the absence and presence of up to monolayers of Cd, Tl, Bi, Hg and Au on Ptz-Pt electrode. It was found that Au, Cd and Au monolayers have good catalytic effects, But Bi, Hg, Tl inhibit the oxidation of propanol. At the same time, experiments confirm the previously postulated mechanism of propanol oxidation. The absorption energy or bond strenth of Pt-H or Pt-Me is an important factor that determine the oxidation rate of propanol.

INTRODUCTION

In recent years the fuel cells have been developed as an alternative high efficiency energy source and there have been intensive studies in order to utilisation of fuel cells depends upon the development of efficient, stable and cheap electrocatalyst (Bockris, 1970 b). Although the study submitted here is not directly related to fuel cells, it is directed to contribute their improvement.

The effect of the surface state upon the electrode reactions taking place at phase boundary is an undeniable fact. The electrocatalytic properties of an electrode surface can be modified and therefore the rate of electrode reaction can be change by depositing a monolayer of another metal upon it (Rand and Woods, 1973).

Platinum was shown to be a very good electrocatalyst for the oxidation of many small organic molecules (Bockris and Amulya, 1970

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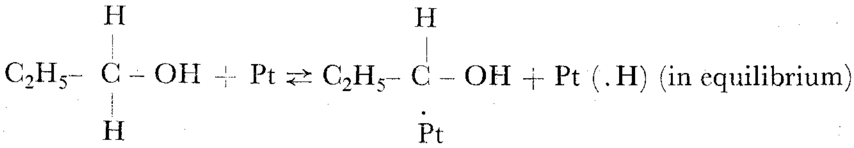
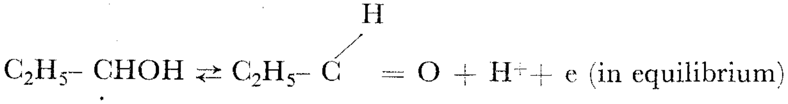
a) In this study the effects of monolayer Cu, Ag, Cd, Hg, Tl and Au deposited on the platinized platinum electrode, upon the kinetics of the oxidation of propanol were investigated. The purpose was to determine which Pt-based metal couple was the most suitable for the oxidation of propanol.

The oxidation kinetics of propanol upon the platinized platinum (Ptz-Pt) was investigated before (Bengüdeniz and Kabasakaloğlu, 1982). According to this study propanol is oxidized in three different regions. The first oxidation takes place in the double layer region of Pt during the anodic sweep. The reaction rate in this region is determined by the hydrogen discharge following the dissociative adsorption of propanol. We called this process I.



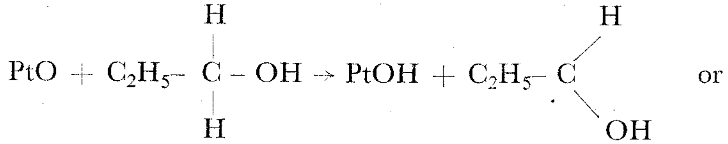
$$C_2H_5-\overset{H}{\underset{H}{C}}-OH + Pt \rightleftarrows C_2H_5-\overset{H}{\underset{\dot{Pt}}{C}}-OH + Pt(.H) \text{ (in equilibrium)}$$

$H (Pt) \rightarrow H^+ + Pt + e$ (rate determining step)

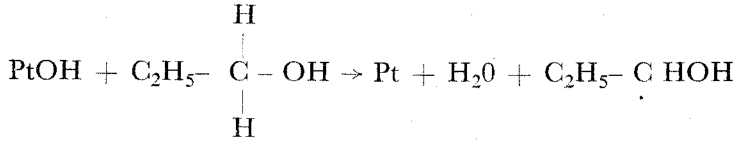


$$C_2H_5-\underset{\bullet}{C}HOH \rightleftarrows C_2H_5-\overset{H\diagup}{C}=O + H^+ + e \text{ (in equilibrium)}$$

The second which we called process II again takes place in the potential region created by the oxygen layer adsorbed upon platinum. In this region propanol is chemically oxidized by the aid of PtO. The rate determining step is either

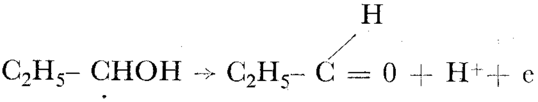


$$\text{a. } PtO + C_2H_5-\overset{H}{\underset{H}{C}}-OH \rightarrow PtOH + C_2H_5-\underset{\cdot\;\diagdown OH}{\overset{\diagup H}{C}} \quad \text{or}$$



$$\text{b. } PtOH + C_2H_5-\overset{H}{\underset{H}{C}}-OH \rightarrow Pt + H_20 + C_2H_5-\underset{\bullet}{C}HOH$$

followed by



$$C_2H_5-\underset{\bullet}{C}HOH \rightarrow C_2H_5-\overset{H\diagup}{C}=0 + H^+ + e$$

There was another anodic process which took place after the reduction of PtO during the cathodic potential sweep when the current-potential curves were plotted by cyclic voltammetry. We explained this by the discharge of adsorbed hydrogen formed by the dissociative adsorption of propanol at the sites vacated by oxygen (Process III). Let us also emphasize that propanol prefers the strong binding sites of hydrogen on platinum during its adsorption occurs at Langmuir conditions (Bengüdeniz and Kabasakaloğlu, 1982).

According to proposed mechanism the strength of Pt-H and the strength of Pt-0 or Pt-OH bonds play the most important roles for process I and process II respectively. The adsorbed layers which change the strength of these bonds also change the reaction rate.

The common feature of all the metals adsorbed upon the Ptz-Pt are that they all inhibit the adsorption of hydrogen on platinum and do not adsorbe any hydrogen themselves. Therefore they are expected to effect the process I. The effects of adsorbed layer upon the process II depend upon two different factors. The first one is the stability of Pt-Me couple. Under this situation the coverage of Pt with oxygen is delayed. The other one is the formation of the respective oxides of the metals adsorbed on the surface. The effect of Pt-Me couple upon the oxidation of propanol under both of these conditions are different and highly significant.

EXPERIMENTAL

The experiments were conducted with a cell having three compartments for the counter, working and reference electrodes separated from each other with stopcocks. Working and counter electrodes were made of platinum covered with platinum black (Ptz-Pt). Saturated calomel electrode was used as a reference. The potentials in the figures and the text were given with respect to hydrogen electrode.

The solutions were prepared with conductance water and freed oxygen by bubbling nitrogen before and throughout the experiment. Current-potential measurements were performed under potentiostatic control using Tacussel 30.01 potentiostat in combination with Tacussel UAP-3 unit and EPL 2 recorder.

The electrode surface was cleaned electrochemically as described in the previous study (Bengüdeniz and Kabasakaloğlu, 1982) before each experiment and the reactive compound was added after obtaining reproduciple Pt/H_2SO_4reference curve. The potential range and potential sweep rate used in these experiments were 0.0V-1.42V and 2.5 mV/s respectively.

The metal couples were prepared by adding metal saltz at a concentration level of 10^{-4}M to the solution and depositing metal upon Ptz-Pt electrode. The metal saltz used for these purpose were $CuSO_4$, $AgNO_3$, $CdSO_4$, Bi $(NO_3)_3$, Hg $(NO_3)_2$ and $TlNO_3$. Pt-Au couple was obtained by dissolving pure Au wire (Johnson Matthey 99.99) in admiralty solution and placing appropriate amount of this solution into the experimental cell. All the metals except gold can be electrolitically removed from the Pt surface. This was taken into account during the study. In the figures of the text the curves recorded at the third or fourth scans where steady state condition was assumed to be reached were given. The electrode surface area was determined by integrating the hydrogen region of steady i-E curves obtained in 1 N H_2SO_4. The charge required to cover the polycrystaline Pt surface with a single layer hydrogen atoms is 210 μC/cm²(Biegler et al. 1971). Therefore the surface area of the electrode can be found by dividing the charge obtained by the integration to 210. The electrode surface area could be redetermined before each experiment since the electrode cleaning process was repeated before every experiment. The current densities in the figures were calculated by using these values.

The metal coverage ratio of the surface, P_{Me} can be determined from

$$P_{Me} = \frac{Q_{Me}}{n.Q^{\circ}_{H}} \quad \text{or} \quad P_{Me} = \frac{Q^{\circ}_{H} - Q_{H}^{Me}}{Q^{\circ}_{H}}$$

$Q^{\circ}_{H}$and $Q_{H}^{Me}$are the charges necessary to cover the surface with mono molecular hydrogen or desorbing the adsorbed hydrogen from the surface in the absence and in the presence of metal atom upon the surface respectively. n and Q_{Me}show the number of electrons and charge passed during the desorption of deposited metal atoms respectively.

RESULTS AND DISCUSSION

a. Electrocatalysis by copper atoms.

The I-E behaviour of small amounts of copper deposition on Ptz-Pt electrode in 1 N H_2SO_4 medium is shown Fig. 1 (a). The

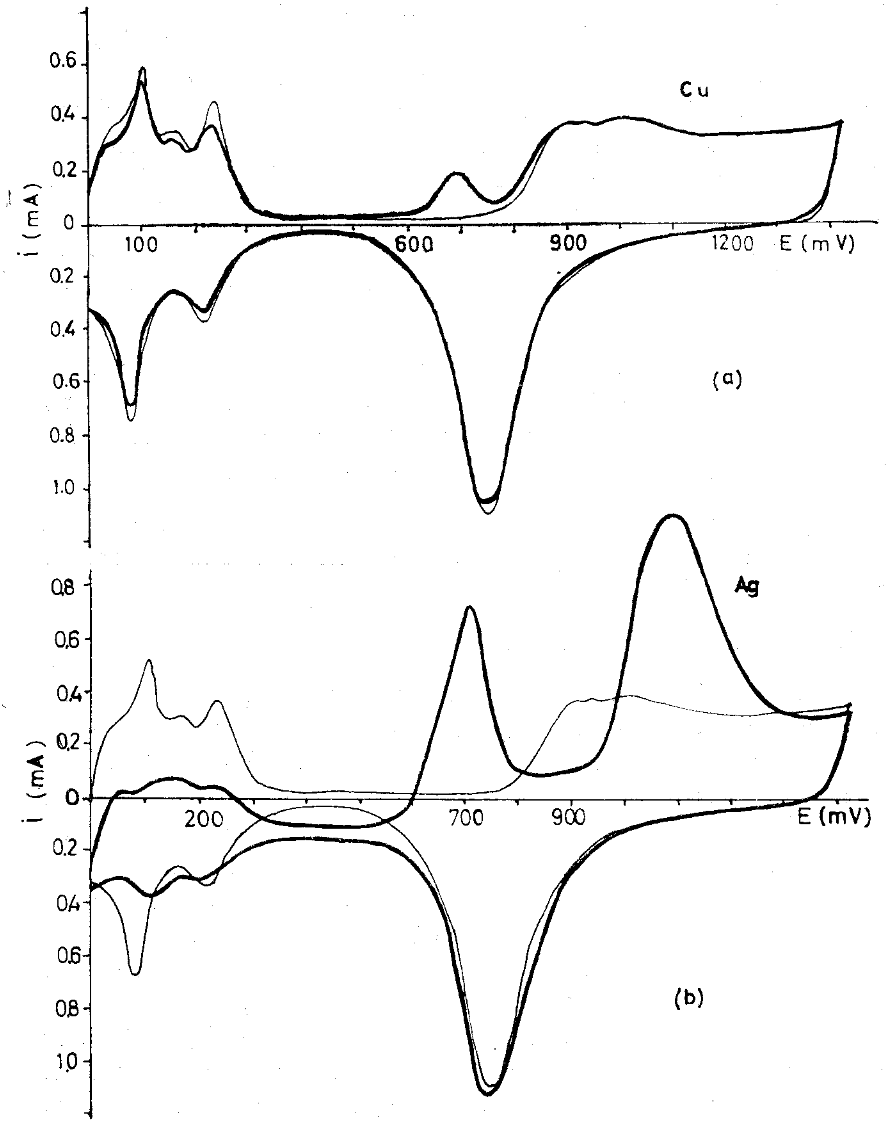


Figure 1. The I-E curves obtained for Cu and Ag deposition on Ptz-Pt in the medium of H_2SO_4. Sweep rate 2.5 mV/s

— Pt – Ptz/H_2SO_4 (a) ▬ Pt-Cu/H_2SO_4

(b) ▬ Pt-Ag/H_2SO_4 P_{Cu}= 0.087 P_{Ag}= 0.72

reference curve is also shown on the same figure for the comparision. The figure shows that copper reduces the hydrogen adsorption but have no effect upon the oxygen chemisorption. Figure 2, shows the curves obtained by the addition of increasing concentration of propanol at constant copper coverage ratio. As in the case of medium without copper, the current peaks belong to the process I which starts at 0.55 V, the process II which takes place in the region of platinum oxide formation (0.8-1.4 V) and process III in the anodic direction after the PtO reduction peak which appears at 0.75 V in the cathodic sweep were observed to increase.

The curves in figure 3 were obtained at 5.10^{-3}M propanol concentration for different copper coverage ratios. As it is clearly seen from these curves that the copper deposition have no inhibitive effect in any region and all three process accelarated.

Figure 4a shows the change in maximum current densities in all these three process with copper coverage ratio at constant propanol concentration 5.10^{-3}M.

b. Electrocatalysis by silver atoms.

In silver deposition the weak hydrogen binding sites of Pt surface is preferred. But as the P_{Ag}increases both weak and strong hydrogen binding sites are equally occupied (Szabo and Nagy. 1976). The desorption of monomoleculer Ag layer takes place at 0.7 V in anodic sweep. The Ag coverage ratio was calculated from the area of the silver desorption peak appeared at 0.7 V in Fig. (Ib). Since Ag-Pt and Ag-Ag-Pt structures are stable (Stucki, 1977; Tindall and Bruckenstein, 1971), the coverage of platinum with oxygen can only occur after the dissolution of adsorbed silver atoms. Thus the peak at 1.1 V in Fig. (Ib) corresponds to the retarded oxygen coverage of Pt. Figure 5 shows the i-E curve for Pt-Ag couple at $P_{Ag}=0.06$ for various propanol concentrations. The current belonging to process I which goes through dissociative adsorption of propanol appears to be constant at a very small value at 0.50-0.60 V. But the peak corresponding desorption of silver at 0.7 V appeared to increase slightly with the increasing propanol concentration in spite the silver concentration in the solution was kept constant. This can be explained by the reaction of propanol on Ag or the dissociative adsorption of it to the sites vacated by silver atoms. The situation may be much more complicated than it appears, since the dissolution of silver takes

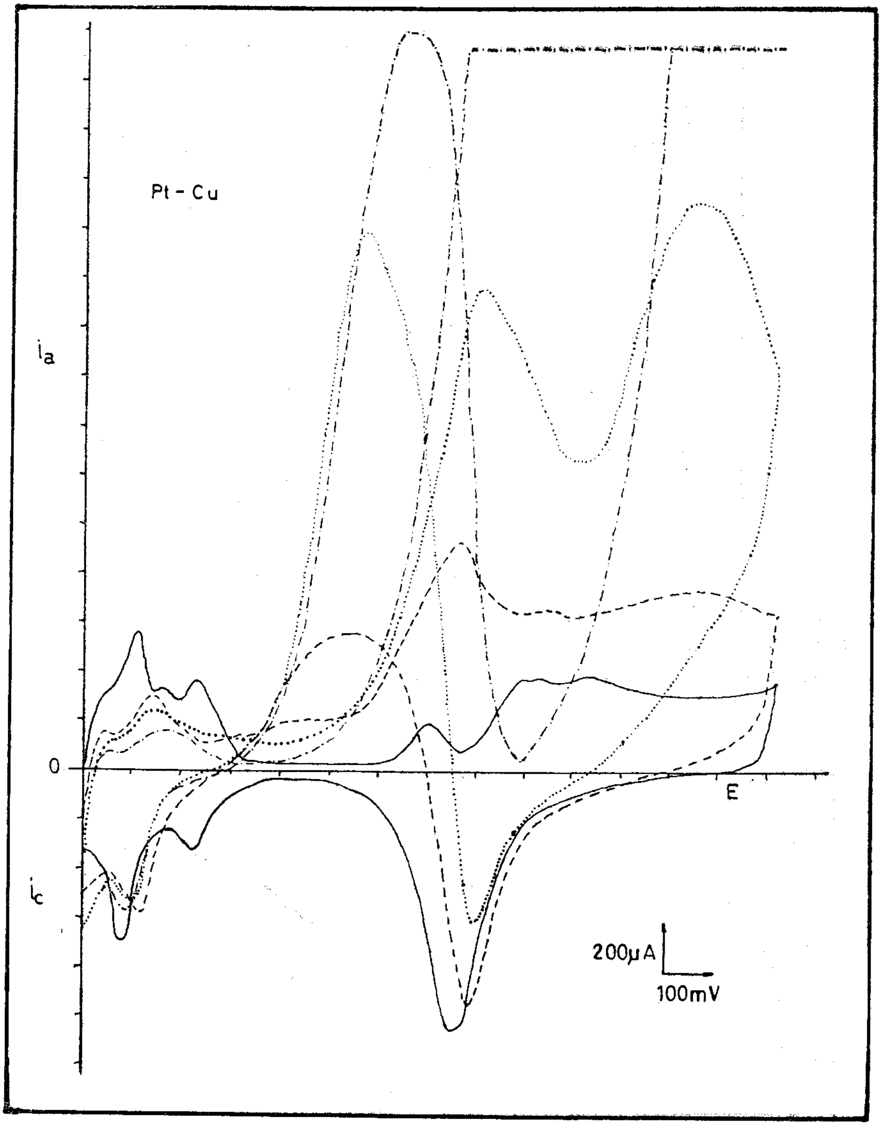


Figure 2. The I-E curves obtained in 1 N H_2SO_4 at various propanol concentration for Pt-Cu couple.

$P_{Cu} = 0.087$ $v = 2.5$ mV/s

— 0.000 M, - - - - 0.001 M: .... 0.005 M; -.-. 0.01 M propanol..

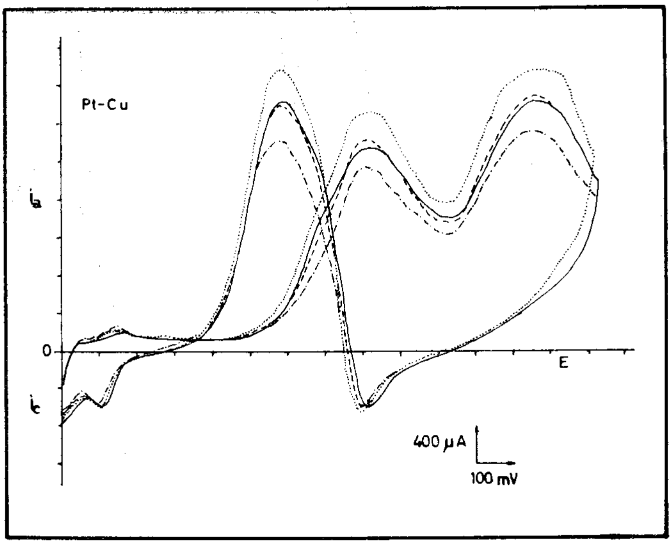


Figure 3. The I-E curves at 5.10^{-3}M propanol concentration for different Cu coverage ratios in H_2SO_4.
— P_{Cu} = 0.017; ..... P_{Cu} = 0.036, - - - P_{Cu} = 0.065 -.-. P_{Cu} = 0.087 v = 2.5 mV/s

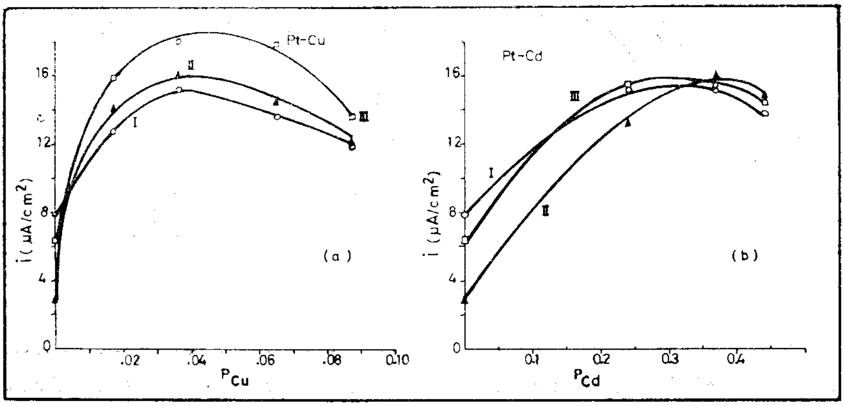


Figure 4. The changes in rates of each process with the metal deposition at constant propanol concentration of 5 10^{-3} M in Pt-Cu and Pt-Cd systems.
(0) Process I (▲) Process (II) (☐) Process III (a) i ↔ P_{Cu} (b) i ↔ P_{Cd}

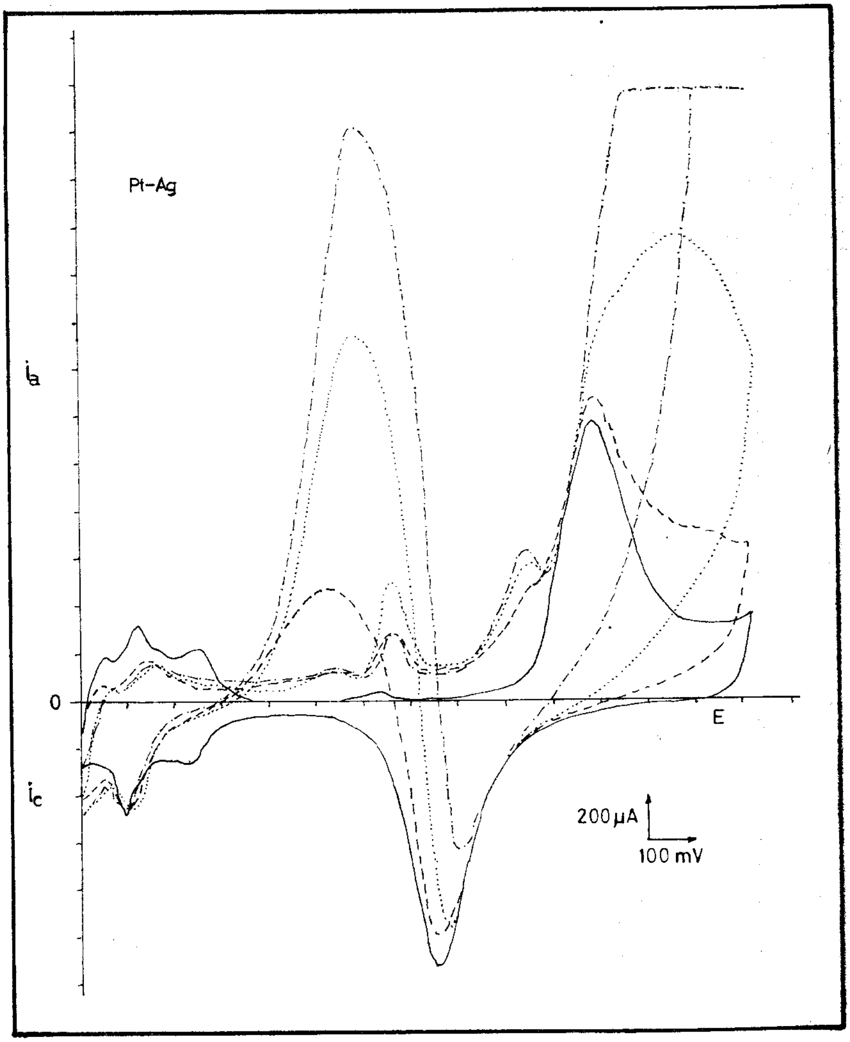


Figure 5. The I-E curves obtained in 1 N H_2SO_4 at various propanol concentration for Pt-Ag couple v = 2.5 mV/s P_{Ag} = 0.06
— 0.000 M; - - 0.001 M, ... 0.005 M, -.-. 0.010 M propanol

place in H_2SO_4 and the solubility of Ag_2SO_4 formed is quite low. The Ag_2SO_4 formed, deposits upon Pt and blocks the surface (Kabasakaloğlu, 1981; Stucki, 1977). That is the reason why we will not try to make further evaluation about the process I. The currents belong to process II and III increased as the propanol concentration is increased.

The i–E curves obtained by increasing P_{Ag} ratio at constant propanol concentration of 5.10^{-3} M are shown in Fig 6. Process I stops completely as the Ag coverage is increased. So much so that the peak seen near 0.5 V becomes very weak and the current passes in cathodic direction at $P_{Ag} \geq 1.25$. Figure 7b shows the change in current density for every process with increasing silver deposition at constant propanol concentration. One can say that propanol

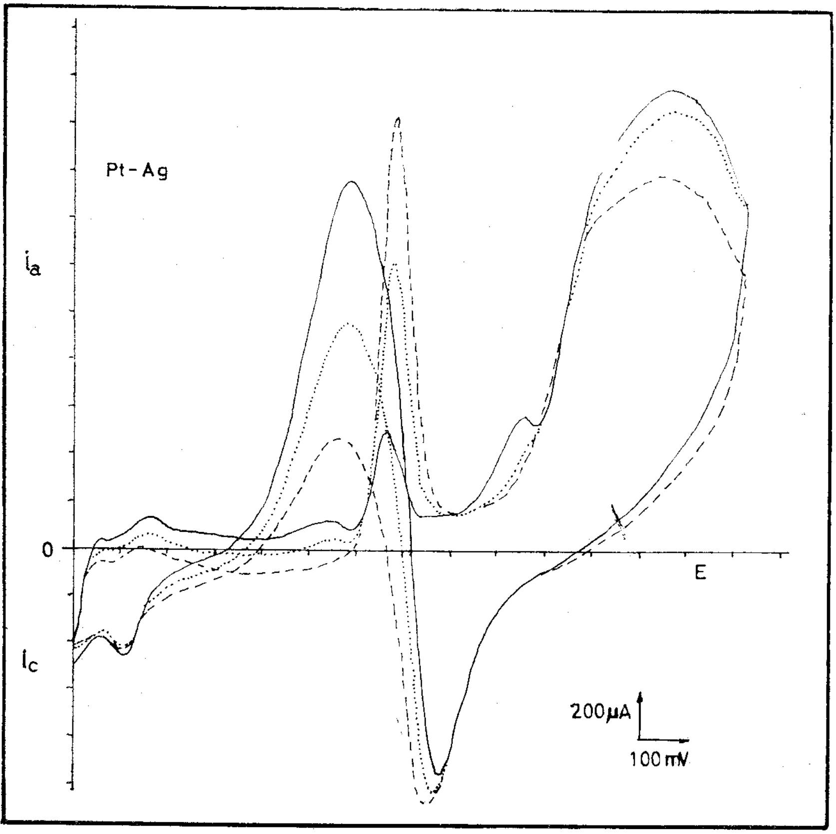


Figure 6. The changes in I-E curves with Ag coverage for Pt-Ag system obtained in 1 N H_2SO_4 and at a propanol concentration of 5 10^{-3} M. v = 2.5 mV/s
— P_{Ag} = 0.33, ... P_{Ag} = 0.72, - - - P_{Ag} = 1.25

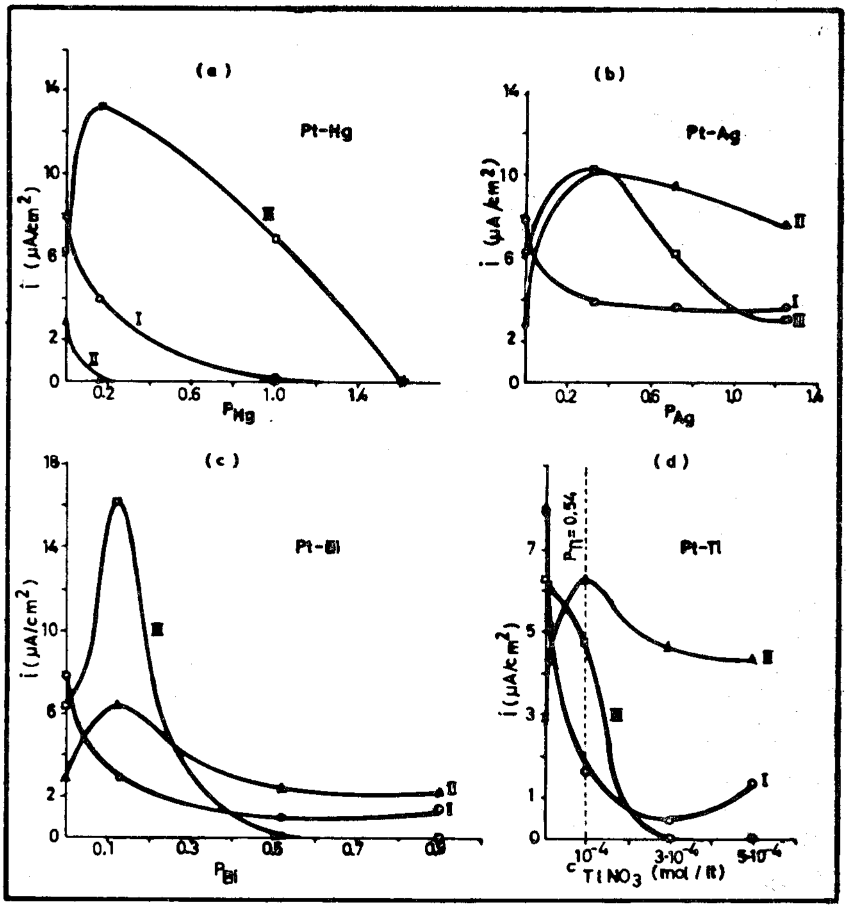


Figure 7. The changes in the rate of each process with various metal deposition at constant propanol concentration of 5.10^{-3} M.
(0) Process I (▲) Process II (□) Process III
(a) i ↔ P_{Hg} (b) i ↔ P_{Ag} (c) i ↔ P_{Bi} (d) i ↔ C_{TlNO_3}

oxidation is inhibited due to stability of Pt-Ag structure. The oxidation after the dissosiative adsorption of propanol, in otherwords process I, is seen to remain constant for $P_{Ag} \geq 0.33$. This constant value is due to the propanol oxidation which takes place at 0.7 V at the desorption peak of silver. The peak belonging to process II is seen to increase with P_{Ag}. But the current density is insignificant when it is compared with Pt based metal couples (Pt-Au, Pt-Cu, Pt-Cd) which show catalytic effect. Although the current density of process III increases at low P_{Ag} values it shows a rapid decrease at high covrage ratios.

c. Catalytic effect of mercury

The effect of mercury deposition upon the smooth platinized platinum electrode and its influence upon hydrogen adsorption and hydrogen evolution have been widely investigated (Markov et al. 1973; Vandrak and Balej, 1971; 1973). The mercury deposition does not take place in single layers but it occurs as small droplets. There remains vacant platinum sites between these droplets. It needs four single layers of mercury atoms in order to poison the smooth platinum surface completely. But it only requires 1.5 layers of mercury for Ptz-Pt electrode.

The current-potential relation for low and high mercury coverage in Pt-Hg system is shown in Fig 8. The mercury layer is desorbed at 0.9 V and the retarded coverage of Pt surface with oxygen can only take place after that. The coverage ratio of mercury has been calculated from the peak area at 0.9 V by assuming that only the one valency oxide is formed. At high coverages the peak at 1.25 V following the peak at 1.1 V due to oxygen chemisorption shows the oxidation of Hg I oxide to Hg II oxide. The enlargement of Pt-O reduction peak confirms the presence of Hg oxides on the surface. The peak seen at 0.65 V belongs to dissolution of multilayer mercury according to following reaction.

$$Hg \rightarrow Hg^{2+} + 2e^- \qquad E = 0.788 + 0.0295 \log (Hg^{2+})$$

In Pt-Hg couple process I and process III partly occurs but process II stops completely (Fig 9). Since mercury causes the retarted PtO formation it may be resembled to Pt-Ag system. Therefore one would expect that process II to be catalysed as in Pt-Ag system. But the presence of mercury oxides inhibits process II. Figure 10 shows the I-E curves at varying coverage ratios with mercury at constant propanol concentration. Figure 7a shows the relation of current density to mercury coverage ratio for each process. According to these curves process I is inhibited in every coverage ratio. Process II never takes place. The peak belonging to peak III shows a slight increase. But process III is inhibited as P_{Hg} is increased. At very high coverages

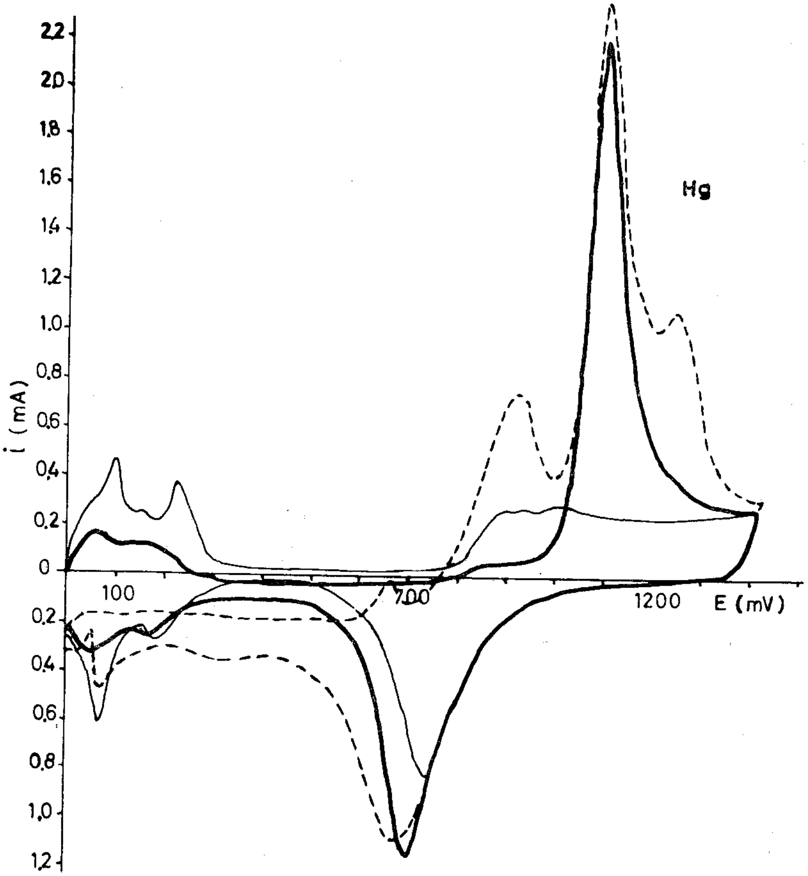


Figure 8. The I-E curves for Pt-Hg system in 1 N H_2SO_4 v = 2.5 mV/s
— P_{Hg} = 0, — P_{Hg} = 0.166, - - - P_{Hg} = 1.63

($P_{Hg} \geq 1.63$ the broken line in Fig. 10) the I-E curve is similar to that 1 N H_2SO_4 without propanol. In conclusion Pt-Hg system cannot be regarded superior to platinum.

d. Catalytic effect of bismuth.

The adsorption of bismuth has been investigated by many workers (Adzic et al. 1975; Bowles, 1970; Szabo and Nagy, 1978a; 1978b;

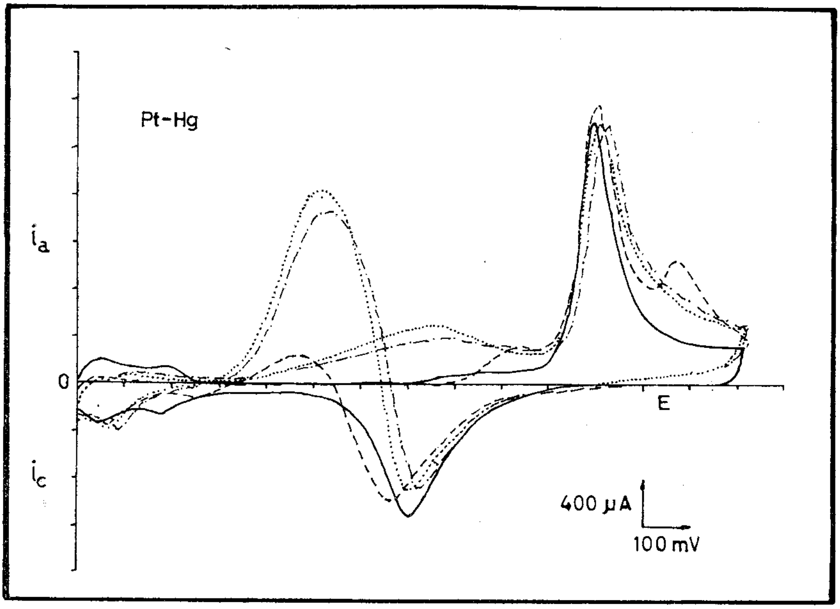


Figure 9. The I-E curves obtained in 1 N H_2SO_4 at various propanol concentrations for Pt-Hg system. v = 2.5 mV/s P_{Hg} = 0.166
— 0.000 M, – – – 0.001 M ..... 0.005 M, –.–. 0.007 M propanol.

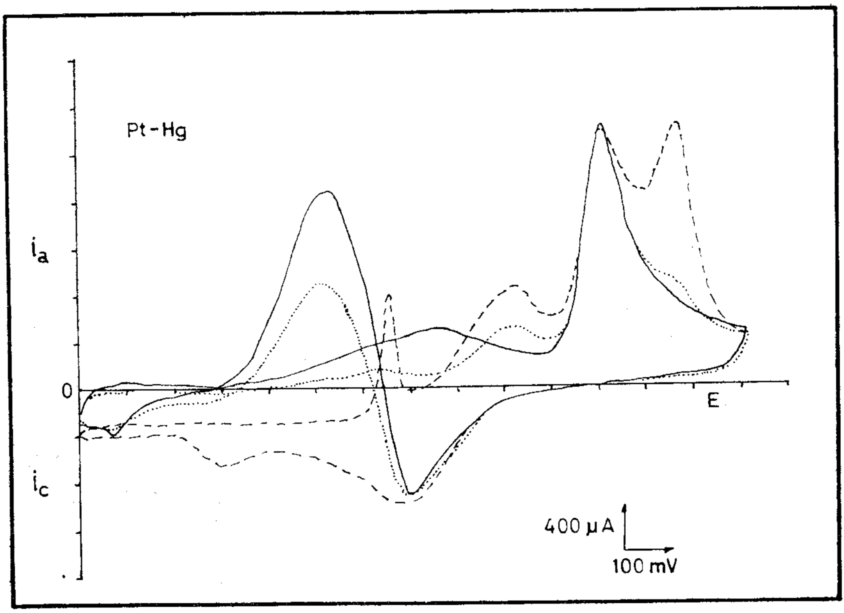


Figure 10. The changes in I-E curves with mercury deposition obtained in 1 N H_2SO_4 + 5.10^{-3} M propanol for Pt-Hg system v = 2.5 mV/s
— P_{Hg} = 0.166, ... P_{Hg} = 1.06 – – – P_{Hg} = 1.63

Williams and Wright, 1976). According to these studies Bi atoms diminishes the hydrogen adsorption upon Pt surface and changes the hydrogen evolution mechanism (Adzic et al. 1975). Bismuth deposition closely resembles the silver deposition and there forms stable Bi adsorbed atoms. The number of hydrogen atoms displaced by bismuth atoms is three at low coverage and two at high coverage ratios (Szabo and Nagy, 1976; 1978a; 1978b). Before coverage ratio reaches to unity, the three dimensional growth starts with the formation of BiO. The I-E behaviour if Pt-Bi system is shown in Fig. 11. Bismuth

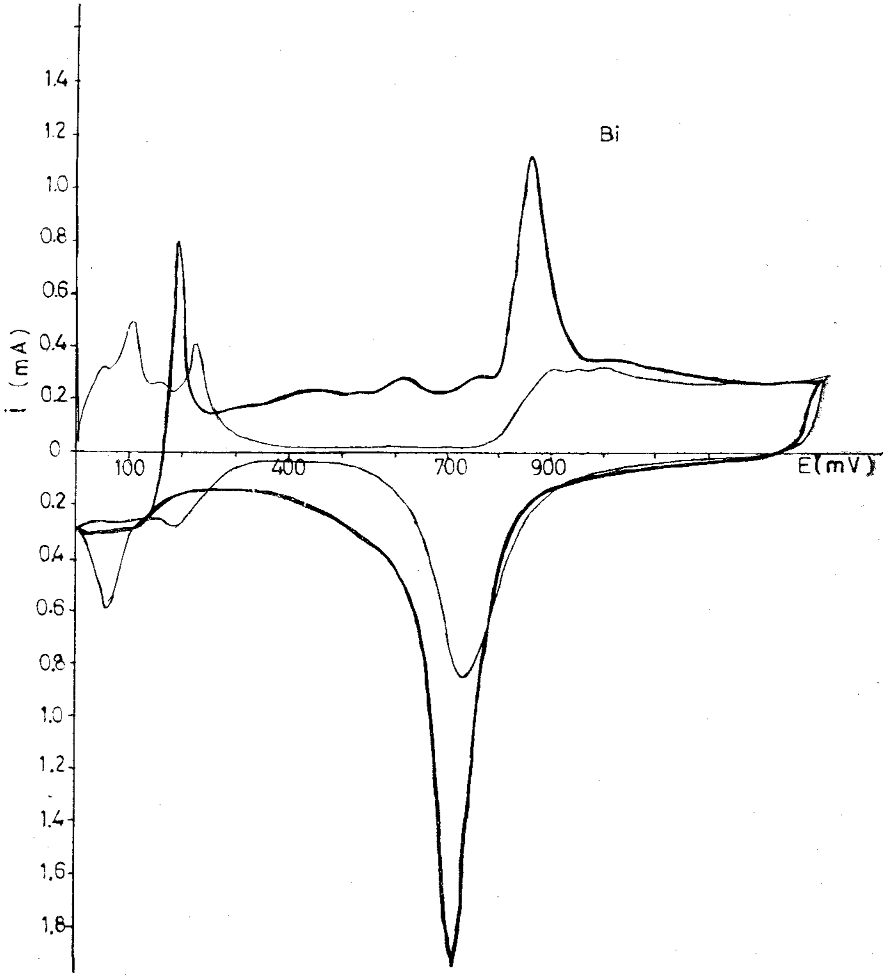


Figure 11. The I-E curve of Bi deposition on Ptz - Pt in 1 N H_2SO_4 v = 2.5 mV/s
— P_{Bi}= 0, — P_{Bi}= 0.521

deposition shows two characteristic region. The number of electrons transfered in the first peak and the PtO region are one and three respectively (Adzic et al. 1975; Bowles, 1970). BiO dissolves as BiO^+ at the peak appeared at 0.2 V with one electron transfer. This process continues in the double layer region with the dissolution of Bi ads and BiO ads. The second peak appears at 0.84 V corresponds to the formation of Bi_2O_3 from Bi_{ads}. The presence of this oxide at the surface can be understood from the increase in PtO desorption peak. The coverage ratio of the surface with bismuth was calculated by assuming that one adsorbed bismuth atom displaces two hydrogen atoms and the concentration of bismuth atoms dissolved in double layer is negligible and all the Bi ads atoms converted into Bi_2O_3 at 0.84 V. The P_{Bi} ratio can then be calculated from the area of the peak at 0.84 V.

Figure 12 shows the I-E curves at various propanol concentrations and constant bismuth coverage ratio. Pt-Bi couple shows a similar behaviour to those of Pt-Ag and Pt-Hg, process I completely stops at $P_{Bi} = 0.126$ as in the case Pt-Ag. Also the peak corresponding to three electron transfer dissolution of Biads at 0.84 V increases with propanol concentration, as in the case of silver desorption. These increase can be explained in various ways:

1. The oxidation of propanol after the dissosiative adsorption of it at the vacant platinum sites. 2. The oxidation of propanol on Bi atoms. 3. The oxidation of propanol by the help of Bi_2O_3. But one cannot say anything which of these explanations is true according to these study.

The effect of bismuth coverage ratio upon the propanol concentration is shown in Fig. 13 and 7. Process II and III are only seen at low coverage ratios.

Pt-Bi couple shows a stable structure as in Pt-Ag and Pt-Hg. This means that Bi deposition and desorption is dominant to propanol oxidation. There is a critical coverage Bi value where BiO starts to deposit. At low Bi coverage the curve obtained for $P_{Bi} = 0.126$ in (Fig 12) there seen no BiO dissolution. The change in the number of hydrogen atoms which Bi diplaces, occurs after this critical coverage value at which BiO begins to form. Therefore there are two different structure in Pt-Bi system. When BiO involves, the catalytic effect changes.

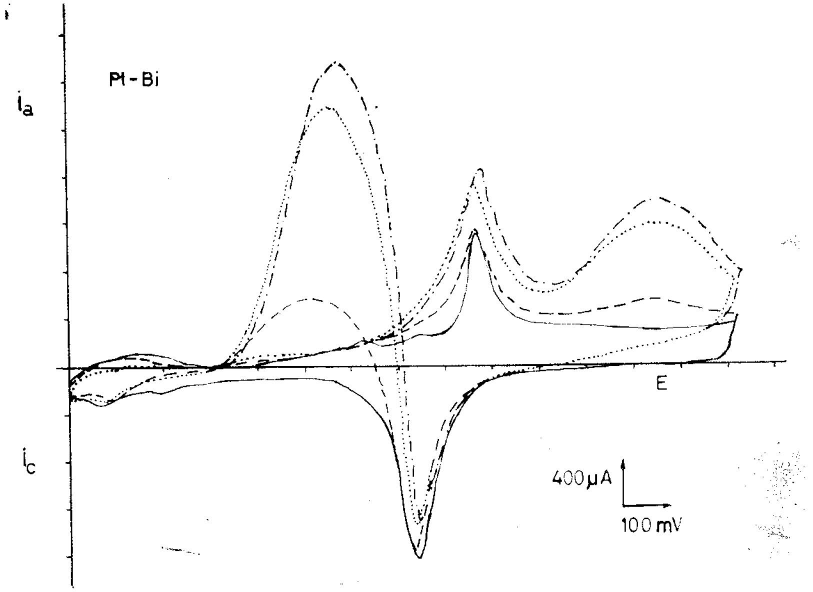


Figure 12. The I-E curves obtained for Pt-Bi couple for various propanol concentrations in 1 N H_2SO_4. v = 2.5 mV/s P_{Bi} = 0.126
— 0.000 M, – – – 0.001 M, ... 0.005 M, –.–.– 0.007 M propanol.

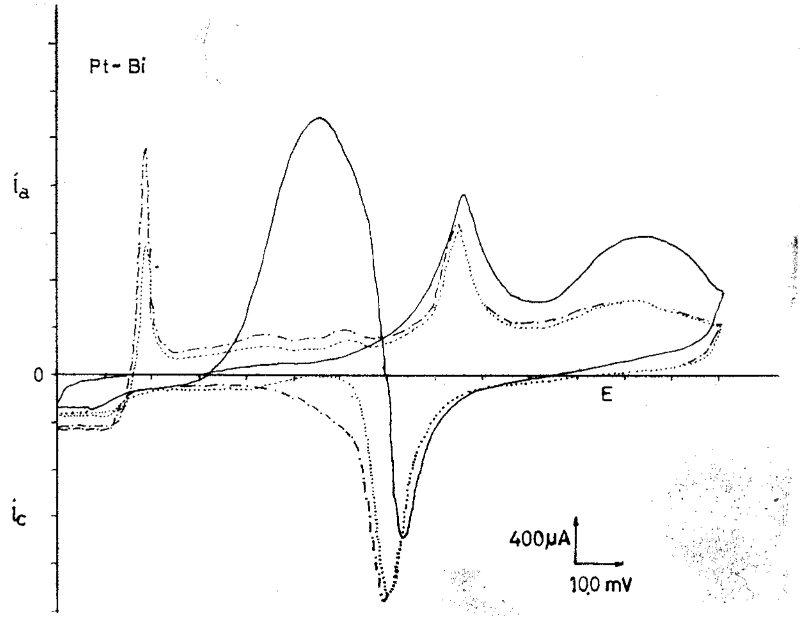


Figure 13. The changes in I-E curves with Bi deposition in 1 N H_2SO_4 + 5.10^{-3}M Propanol.
v = 2.5 mV/s
— P_{Bi} = 0.126, ... P_{Bi} = 0.521, –.–. P_{Bi} = 0.901

At low coverages proces II and III accelarate and where at high coverages, all three processes stop.

e. Thallium deposition and its electrocatalytic effect.

As in other metals, the hydrogen adsorption decreases with Tl deposition. But Tl, does not inhibit hydrogen adsorption at the sites where thallium has not deposited (Adzic el al. 1975; Szabo and Nagy, 1977; 1978a; 1978b). Deposited thallium desorption is observed in the oxygen region (0.9 V-1.1 V Fig. 14). At more positive potentials $Tl_2 0_3$ formation begins. This oxide is reduced before Pt-O at 1.1 V. Figure 14 b shows I-E curves for Pt-Tl couple.

There is a significant difference between the electronic characters of thallium and platinum. Their work functions, zero charge potentials, sublimation heats are significantly different (Table II). That is why Pt-Tl couple shows different catalytic effect than Pt itself. Another important feature of thallium deposition is that even at very low solution concentrations saturated coverage is reached, so P_{Tl} value could not be determined.

Figure 15 shows the I-E curves obtained by increasing the propanol concentration. The surface coverage of thallium is greater than unity. Process I does not take place on the surface covered with thallium. The current in the PtO region increases with propanol concentration. Thus the presence of Tl catalysis the process II (Fig. 7d). But $Tl_2 0_3$ is formed at Pt0 region. The decrease in the reduction current of $Tl_2 0_3$ with increasing propanol concentrations (Fig. 15), makes one think that $Tl_2 0_3$ participates in the propanol oxidation.

The I-E curves obtained with increasing Tl concentration at constant alcohol concentration is shown in Fig. 16. In this figure there is a step at 0.55 V which can be attributed to process I. The current at this step decreases as the thallium concentration is increased. Process III occurs only at low Tl deposition. Its rate decreases to zero with increasing Tl coverage. In conclusion Tl is a bad catalyst.

f. Cadmium deposition and its electrocatalytic effect.

Cadmium deposition on various sub-layers has been widely investigated (Joviceviz et al. 1977; Szabo and Nagy, 1977). Cadmium desorption coincides with hydrogen desorption and finishes before

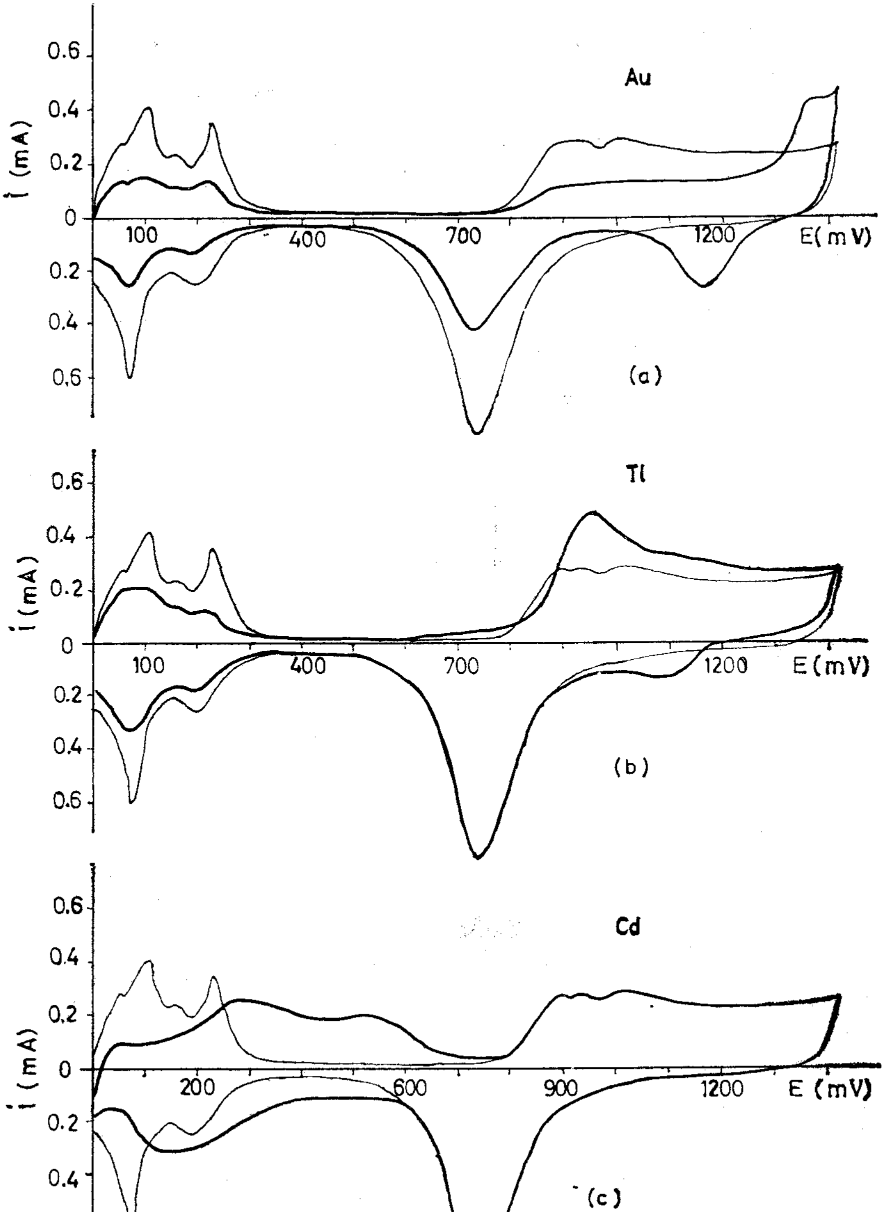


Figure 14. The change in Pt/H_2SO_4 curve with the deposition of Au, Cd and Tl. v = 2.5 mV/s

Thin line shows the curve for pure Ptz – Pt, thick curve shows the curve for metal couple. a) Pt-Au, P_{Au} = 0.563 b) Pt-Tl, P_{Tl} = 0.154 c) Pt-Cd, P_{Cd} = 0.37

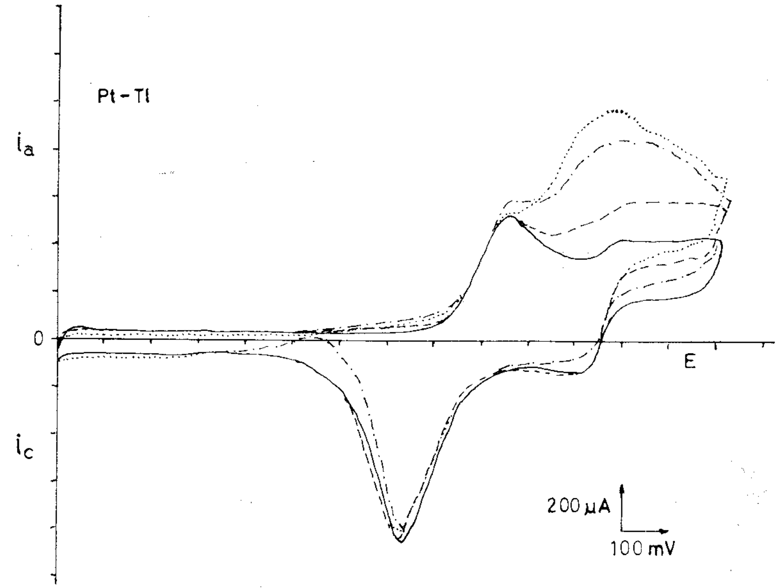


Figure 15. The I-E curves obtained for Pt-Tl system in 1 N H_2SO_4 and various propanol concentrations. v = 2.5 mV/s, Tl concentration 3.10^{-3}M, $P_{Tl} > 1$
— 0.000 M, - - - 0.001 M, ... 0.005 M -.-., 0.007 M propanol.

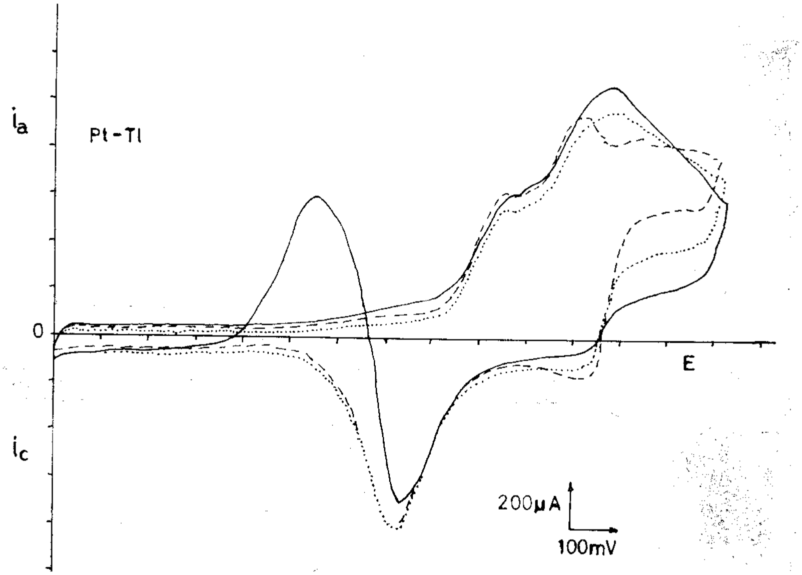


Figure 16. The I-E curves for Pt-Tl system in 1 N H_2SO_4 + 5 10^{-3} M propanol concentration. v = 2.5 mV/s
— 10^{-3}M TlN0$_3$(P_{Tl} = 0.54), ... 3.10^{-4} TlNO$_4$(P_{Tl} > 1) - - - 5 10^{-4} M TlNO$_3$, $P_{Tl} > 1.0$.

the coverage of platinum with oxygen. The cadmium deposition preferably occurs at the sites of weakly bounded hydrogen atoms as seen in Fig. 14c. The ionic character of adsorbed cadmium atoms causes them to be weakly adsorbed on the surface. The electrosorption valency of Cd which has a valency of two reaches to only a value of 0.3 (Schultze and Koppitz, 1976).

The Pt-Cd system is highly different than other metal couples with respect to electrocatalytic effect. The oxidation of propanol with its dissosiative adsorption (process I) starts at more negative potential, at the desorption potential of cadmium and its rate is also increased (Figure 17). Cd catalysis the oxidation in each of those three regions in the same way.

Figure 18 shows the I-E curves at constant propanol concentration with increasing Cd coverage. The best catalytic effect was obtained for $P_{Cd} \geq 0.3$–0.4. The increase of the rate of process I can be explained as follows. The bonding energy of Pt–H decreases because Cd_{ad} an atom which weakens the hydrogen binding. Since the Pt-H binding energy formed after the dissosiative adsorption of propanol decreases, the rate of hydrogen discharge which is the rate determining step of process I also increases. Therefore the total rate of reaction increases.

The increase in the rate of process II is surprising, Because cadmium is completely desorbed in this region. The increase in process III can be attributed to the decrease in the adsorption energy of platinum and consequently the decrease in the Pt-H bonding energy by the cadmium atom which deposit after the reversal of current.

The cadmium coverage was calculated from the cadmium desorption peak which appears at 0.55 V. This peak is mixed with the hydrogen desorption peak as seen in Fig. 14c. In order to find an average value for P_{Cd}, the peak at 0.55 V extrapolated towards the hydrogen region. The P_{Cd} value was calculated from the peak obtained by this extrapolation.

g. Gold deposition and its electrocatalytic effect.

Pt-Au couple has received a very big interest due to its electrocatalytic capability, its inertness towards the environmental conditions and other specific features.

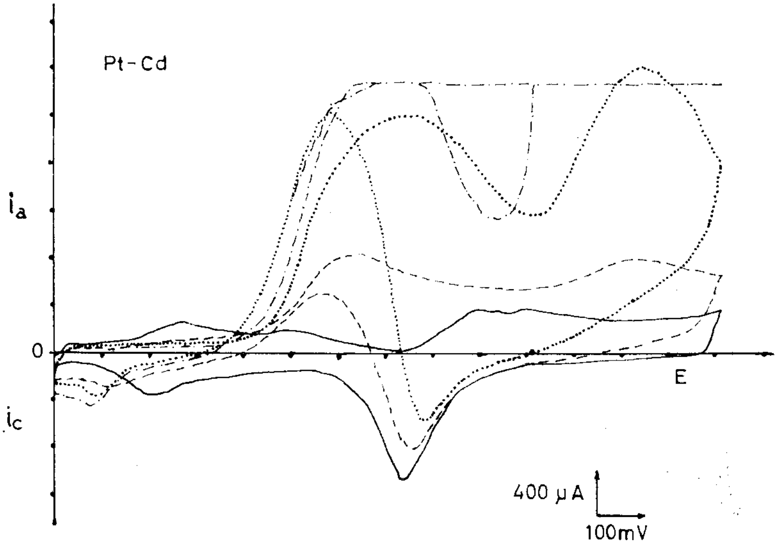


Figure 17. The I-E curves obtained for Pt-Cd system in 1 N H_2SO_4 at various propanol concentrations. v = 2.5 mV/s P_{Cd} = 0.44
— 0.000 M, - - - 0.001 M, ... 0.005 M, -.-. 0.01 M Propanol.

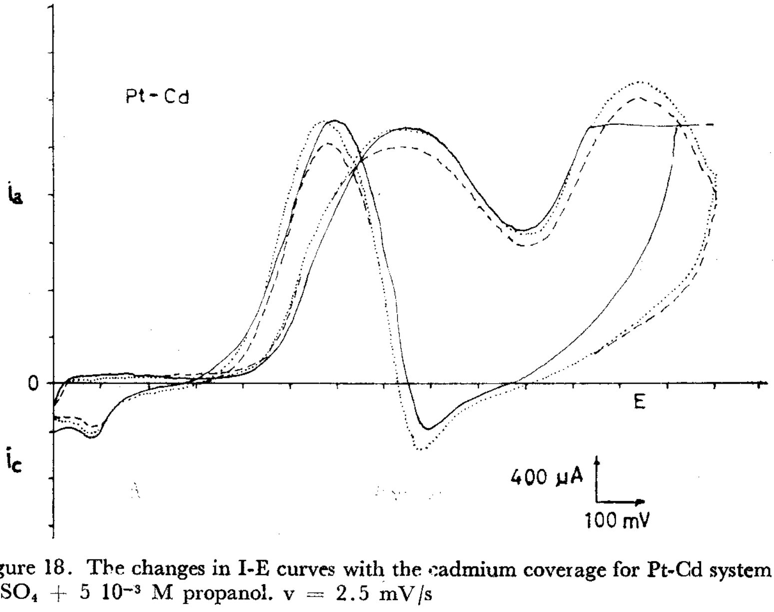


Figure 18. The changes in I-E curves with the cadmium coverage for Pt-Cd system in 1 N H_2SO_4 + 5 10^{-3} M propanol. v = 2.5 mV/s
— P_{Cd} = 0.24, ... P_{Cd} = 0.37, - - - P_{Cd} = 0.44

The adsorption of Au on Pt is an irreversible process (Cadle and. Brukenstein, 1979). As other metals gold also inhibites the hydrogen adsorption on Pt and does not adsorb hydrogen itself. But it was shown to adsorb small amount of hydrogen under specific conditions (Ruetschi and Delahey, 1955). The number of hydrogen displaced by gold is 2.5 at low and 1.25 at high coverage ratios (Szabo and Nagy, 1977). This number for Pt-Au couple which i-E behaviour is shown in Fig. 14, was found to be 1.25 using the data obtained in this study by the way given in Furuya and Motoo (1978). Another important effect of gold is its ability to decrease the bonding energy of the adsorption which Pt makes with other components in the solution. The empty orbitals in the d bands of platinum is filled with the electrons of gold and the adsorption energy of Pt atom is decreased (Beltowska, 1979).

There is a gold oxide formation together with platinum-oxide during the anodic oxidation of Pt-Au system. Figure 14 a shows that the formation of this oxide takes place at 1.5 V and it is reduced before the reduction of Pt-0. P_{Au} value can be determined from the charge corresponding the desorption of this gold oxide. There are studies claiming that the structure of gold oxide is Au_20_3 (Tacconi et al. 1977). Also figure 14 a shows that the deposition of gold inhibits the hydrogen adsorption on platinum electrode and oxygen chemisorbtion takes place at the vacant platinum sites not occupied by gold. Figure 19 shows the I-E curves obtained for various propanol concentrations and Figure 20 shows the I-E curves for Pt-Au where P_{Au} values were changed at a constant propanol concentration of 10^{-3} M. In figure 21 the current density of each process is plotted as a function of P_{Au}. The fact that gold oxide is also used in process II is understood from the disappearance of gold oxide reduction peak upon the addition of propanol. Although the increasing gold upon the surface slightly decreases the rate of process I compared with pure platinum, this is very insignificant. This can be explained as follows. As in many other metals there is no dissosiative adsorption of propanol on gold in acidic media (Bilgiç and Kabasakaloğlu, 1985. Since the dissosiative adsorption of propanol can only take place, on the vacant platinum sites, the rate of process I decreases. But this decrease occurs gradually due to decrease of Pt-H bonding energy by gold atoms. The plateau observed in Fig. 21 for the $P_{Au} \geq 0.1–0.5$ can be attributed to this effect. The decrease in the oxidation rate due

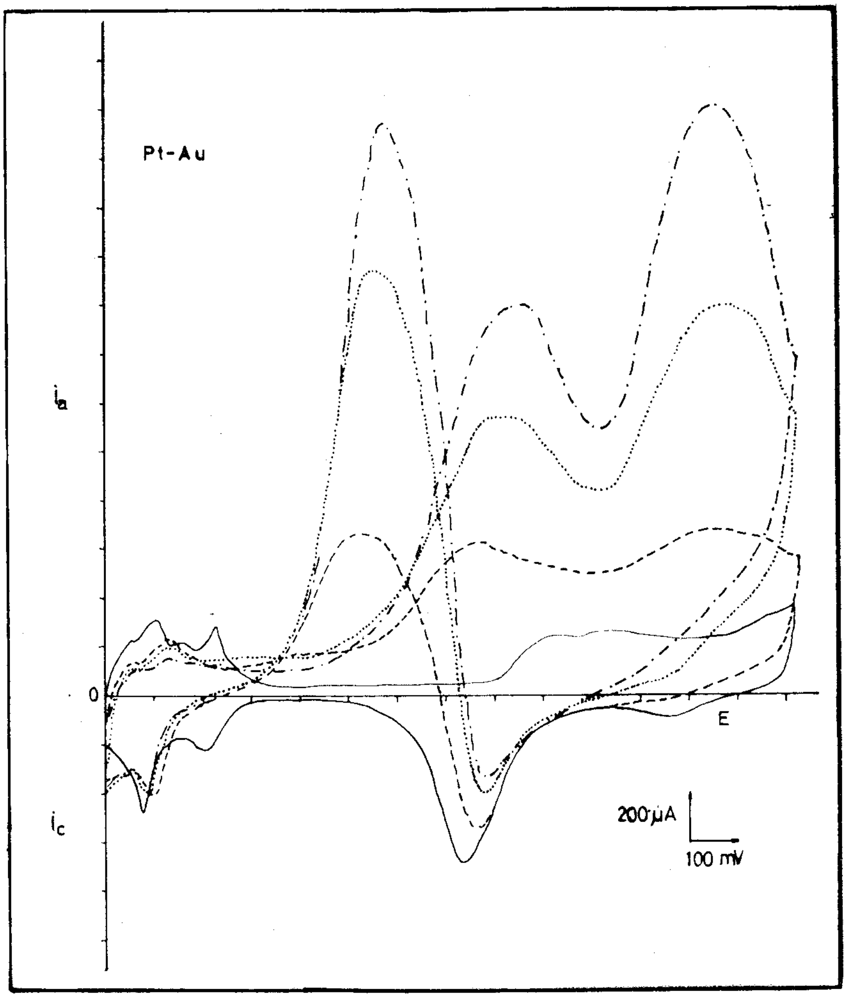


Figure 19. The I-E curves for Pt-Au system in 1N H_2SO_4 at various propanol concentration. v = 2.5 mV/s P_{Au} = 0.125.
— 0.000 M, – – – – 0.001 M, ... 0.005 M –.–. 0.007 M propanol.

to diminishing vacant platinum sites is equal to the increase due to decrease in the Pt-H bonding energy by gold atoms. Outside this range the decrease in the number of vacant platinum sites is the dominant factor upon the oxidation rate which shows a significant decrease.

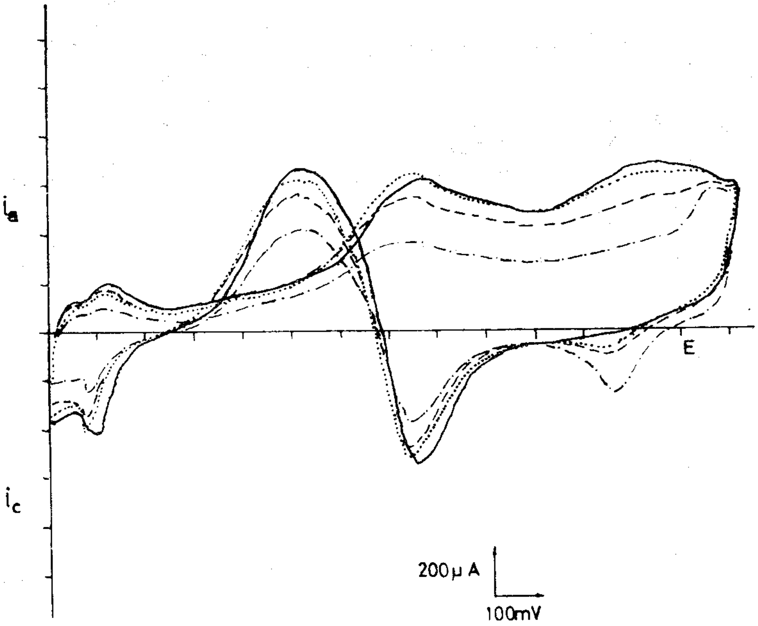


Figure 20. The changes in I-E curves with Au deposition in 1 N H_2SO_4 + 10^{-3}M propanol. v = 2.5 mV/s.
— P_{Au} = 0.125, ... P_{Au} = 0.250, - - - P_{Au} = 0.453 -.-.- P_{Au} = 0.563

The current values for process II and process III were found to be higher with Pt-Au system than Ptz-Pt. Therefore this system is a better electrocatalyst for process II and III than Ptz-Pt. Since the presence of Au on the surface decreases both Pt-organic and PtO bonding energy it is much easier to remove the products such as alcohol radicals. This also facilitates the reaction of PtO with propanol. Some of the organic radicals were shown to be oxidized faster on Pt-Au couple. (Beltowska, 1979). Also the gold oxide film can easily give the oxygen which it holds much weaker than Pt for the oxidation process. Therefore one expects the chemical oxidation in process II with Pt-O increase with the help of gold oxide. This is the reason for the constant increase in the current density of process II up to high gold coverage ratios.

The increase in process III, can be explained by the decrease in the bonding energies of Pt-H and Pt-Org. adsorptions by the gold atoms as in process I. The decrease in the bonding energy of Pt-H causes the rate of hydrogen discharge increases after the dissosiative adsorption of alcohol. The alcohol radical can easily be removed

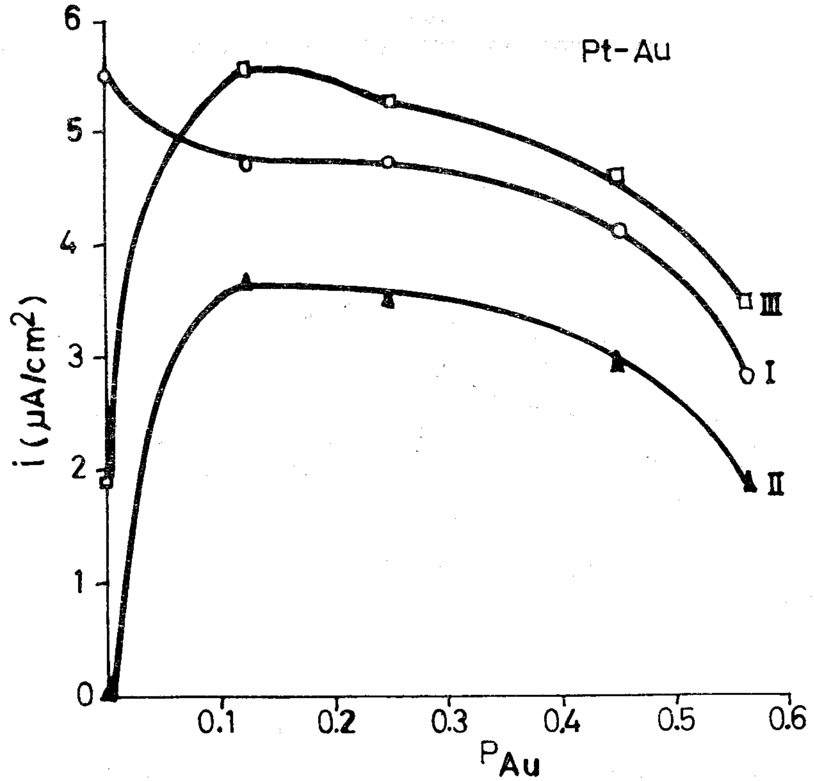


Figure 21. The changes in the rate of each process with gold deposition in 1 N H_2SO_4 + 10^{-3} M propanol.
(0) Process I, (▲) Process II, (□) Process III

from the surface due to decreased Pt-Org bonding energy. Also, the surface diffusion rate of gold atoms is quite low. Since the deposition takes place randomly, the unstable structure is constantly maintained (Szabo and Nagy, 1976). This unstable structure causes the surface to show a better electrocatalytic effect.

h. The comparision of metal couples with respect to their catalytic effects.

It was thought that it would be possible to determine which metal couples accelarate and which metal couples decelarate the propanol oxidation by establishing the catalytic order of these metal couples. The order can be established at constant saturated or most effective coverage ratios. We established this order at constant propanol concentration of 5.10^{-3} M by comparing the effective coverage ratios. Table I shows the maximum current densities of each process for the Pt-Me systems, P_{Me} shows the most effective coverage ratios. According to this table the order of the metals which show good catalytic and inhibitive effects are Cu > Cd > Au and Ag < Bi < Hg < Tl respectively.

All metals except Cu, Cd and Au inhibit process I compared with pure Ptz-Pt. Process II is accelarated by all metals except mercury.

This accelaration is highly significant for each metal except those Tl and Bi. Hg completely inhibits process II. All the metals except Tl increases the rate of process III. According to table I following order can be given:

For process I Cu ≥ Cd > Au, Pt > Hg ≥ Ag > Bi > Tl
For process II Cd ≥ Cu > Au ≥ Ag > Bi ≥ Tl > Pt > Hg
For process III Cu > Bi > Cd > Au > Hg > Ag > Pt > Tl

One of the interesting point in these series is different catalytic effect of Bi on process I and process III, although the same electrochemical mechanism was proposed. Bi inhibits process I but shows almost the same catalytic effect on process III as Cu and Cd atoms. The reason for that is most probably the unstable structure of initially formed Bi_{ad} atoms. The unstable adsorbed Bi atoms formed after the reduction of Pt-0 in cathodic direction increases the rate of process III which takes place in the same potential region. Bi_{ad} attains a stable structure at the potential range where process I occurs and the desroption of Bi_{ad} atoms takes place first. The second thing to be done is to determine which metallic properties causes these variations. This requires the establishment of the relations between the values given in this table and the work functions, Φ (Koch et all, 1979), zero point potentials of PtMe couples, Epzc, (Lackmann and Moller, 1975). adsorption energies of Me-H (Ruetschi and Delahey, 1955a), Me-OH (Rüetschi and Delahey, 1955b) and Me-Org, süblimation energies of metals (Lackmann and Moller, 1975) hydrogen and oxygen, overpotentials, Fermi energies etc. Some of the quantities mentioned collected from literature are tabulated in table II. We tried to establish a relation between the quantities given in this table and the values of current density given in Table I. Unfortunately it was not possible to establish these relations due to inadequate number of the metals studied and the uncertainty in quantities such as zero point potentials and work functions and the necessity of knowing the values of the quantities mentioned above at our working conditions. Although some changes confirming these relations have been obtained, there exists significant deviations especially with Pt-Cd couple. Koch et al. (1979) claimed that the catalytic effect of metal couples to the oxidation of organic molecules is related to oxide potentials. But they were not to establish any theoretical base for their claim. There is a definite relation between the catalytic effects of metal couples and some of their properties. The reason for the failure to establish such a relation between these properties and the catalytic effect is due to these properties belonging to pure metal. Because the electronic character of the sublayer changes towards to the elecronic character of the metal deposited upon it. The electrodes with various coverage have entirely new electronic character.

One can say thay Me-H bonding energy is very important for process I and M-OH for process II. It can also claimed that the electronic work functions and zero point potentials are important factors in catalytic effect.

Table 1 The current densities obtained at constant propanol concentration of 5.10^{-3} M in Pt-Me system.

Metal Couple	P_{Me}	$\mu A/cm^2$		
		Process I	Process II	Process III
Pt – Cu	0.036	15.13	15.97	18.01
Pt – Cd	0.376	15.12	16.10	15.40
Pt – Au	0.125	8.86	11.16	14.36
Pt – Ag	0.330	3.81	10.18	10.31
Pt – Bi	0.126	2.81	6.36	16.27
Pt – Hg	0.166	3.98	—	13.13
Pt – Tl	0.540	1.67	6.20	4.77
Pt – Ptz	—	7.90	2.89	6.36

Table II Some of the basic properties of the metals used in the preparation of Pt-Me couples

Metal	Φ Me (eV)	E_{pzc} (V)	M-Hads Kcal/mol	M.-OHads Kcal/mol	Ls süb Kcal/mol
Pt	5.40	0.02	62.9	53.7	172.2
Au	4.78	0.18	59.3	43.4	77.2
Tl	3.84	-0.75	55.3	—	38.9
Hg	4.50	-0.19	52.9	—	20.0
Bi	4.29	-0.39	—	—	43.7
Cd	3.97	-0.72	53.9	76.8	25.3
Ag	4.30	-0.44	57.6	60.0	63.6
Cu	4.55	0.09	58.5	63.2	75.9

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