Electrochemical Oxidation of Methanol, Formic Acid & Hydrazine at Pt-Ni, Pt-Au & Pt-Pd Electrodes

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Electrochemical oxidation of methanol, hydrazine and formic acid has been studied on a pure platinum electrode and platinum which has been co-deposited with Au, Pd or Ni from a platinizing solution containing about 10% of latter metal. The polarization characteristics of the electrodes indicate that in their electro-oxidation process, the co-deposited Pt-Au, Pt-Pd, Pt-Ni act as better electrodes than platinum alone and the catalytic activity increases in the order Pt<Pt-Ni<Pt-Pd<Pt-Au. The rate determining step in these electrochemical oxidation using different electrodes is the chemisorbed dissociative step which results in adsorbed hydrogen which is subsequently oxidized through a fast step. It is seen that electrodes possessing higher values of heat of adsorption for hydrogen act as better electrocatalyst.

METHANOL, formic acid and hydrazine are important fuels because of their electrochemical reactivity. Several studies have been reported on the mechanism of anodic oxidation at platinum electrode of methanol[1-4], formic acid[5-7] and hydrazine[8].

A comparison of activity of noble metal alloys for anodic oxidation of methanol has been made by Breiter[9], and Dahms and Bockris[10]. They explained the difference in activities of the metal by a difference in metal organic bond strengths which may be related to the distinct difference of heats of sublimation for the metals and the difference in work function, the metal with the higher work function exhibiting the faster reaction.

Frumkin[11] observed that an alloy made by simultaneous deposition of platinum and ruthenium from a mixture which contained 10% or less ruthenium was 100 times as active as pure platinum in oxidation of methanol. Grimes and Spengler[12] showed that the use of mixed Pt-Pd electrode brought about complete oxidation of methanol to carbonate. McKee and Pak[13] observed that Pt containing up to 10.2% nickel acted as a better electrode than platinum alone in anodic oxidation of H_2 and CO mixture containing up to 10% CO. According to them, Pt-5% Cu, Pt-5% Sb are also better than platinum alone in the above reaction.

The present investigation has been undertaken to study the activity of Pt mixed with Pd, Au or Ni in electrochemical oxidation of methanol, formic acid and hydrazine.

Materials and Methods

The experimental scheme followed was similar to that described by Wynveen[14] and Masaru and Hironosuke[15]. The galvanostatic circuit[16] employed consisted of high voltage stabilized D-C power supply connected in series to a variable resistance. The direct current source was connected to the auxiliary platinum electrode (cathode) and the working electrode (anode) in a conventional H-type glass cell, anode and cathode compartments being separated by fritted glass. In the galvanostatic procedure followed, the steady state was assumed such that the system varied negligibly with time when measurement was taken. Under these conditions, it was possible to control the current externally and measure the resulting potential. The potential (mV) of the anode against SCE or Hg/HgO (1N KOH) electrode was measured with the help of a Cambridge pH-meter. A Luggin capillary was used to minimize IR drop. The current through the anode was varied stepwise, the corresponding potential being determined. The four electrodes used in the present study were prepared as follows: platinized Pt prepared from platinizing solution containing chloroplatinic acid in HCl (2N). The second one was prepared co-deposition of Pt and Au on a platinum foil from the solution of chloroplatinic acid and auric chloride in HCl (2N). The solution contains platinum and gold in the ratio of 10:1 by wt of metals. The third and fourth electrodes were prepared similarly by co-deposition of Pt/Ni and Pt/Pd respectively. Nickel chloride or palladium chloride along with chloroplatinic acid in HCl (2N) were used in the preparation of the last two electrodes respectively. A current density of 15 ma/cm² for 25 min was used during electrodeposition for all the electrodes. Basic solution of platinic chloride (1%) with lead acetate (0.01%) in HCl (2N) was used in all the cases.

The electrochemical oxidation of methanol and hydrazine was studied in KOH solution (1N) and that of formic acid in H_2SO_4 medium (0.5N). Estimation of Ni in the co-deposit was done polarographically[17] and the amount was found to be 0.479 $\times 10^{-4}$ g/cm². All the chemicals used were of BDH AR grade. Triply distilled conductivity water was used.

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The anodic charging curves of the electrodes in the presence of hydrogen were recorded following the procedure of Delahay and Berzins[18] using Tektronix-547 oscilloscope. The glass cell was provided with a stopper through which 6 electrodes were introduced and dipped into $2.5N$ H_2SO_4 (AR H_2SO_4). The sulphuric acid solution was preelectrolysed with 15-50 ma current for 24 hr. Two electrodes were platinized platinum foil (1 cm²) of which one was used as the reference electrode and the other as counter electrode. The remaining four electrodes (exposed length 0·8 cm., diameter 0·05 cm) were platinized platinum electrode, Pt-Ni, Pt-Au and Pt-Pd electrodes used as anodes. The cell was also provided with an inlet and outlet for purified hydrogen gas. A constant current was passed through the anode and the counter electrode by means of a mercury switch. The input attenuater of 'Y' amplifier was set at 0·5 V/cm and the time base switch at 5 msec/cm. The potential of the experimental electrode was referred to that of a platinized platinum electrode in the same solution, which might be considered as hydrogen electrode. The oscilloscopic trace was photographed by means of Du Mont oscilloscopic camera type 2615.

Results and Discussion

Current-voltage curves at 30° for anodic oxidation of N_2H_4 (0·5M), and CH_3OH (1M) both in KOH (1M) at Pt-Au, Pt-Pd, Pt-Ni and platinized platinum electrodes and that of formic acid (1M) in H_2SO_4 (0·5N) are shown in Fig. 1. The results indicate that the activity of Pt in the oxidation of these fuels increased in the order: Pt<Pt-Ni<Pt-Pd<Pt-Au. It was found that higher temperature reduces the polarization in each case for all electrodes.

In acidic solution methanol could be oxidized at the platinum electrode to carbon dioxide and water, and in alkaline solution the main oxidation product was reported to be formate ion[2]. A mechanism of electrochemical oxidation of methanol was proposed by Pavela[1] and later supported in a similar form by Buck and Griffith[2]. The mechanism of oxidation proposed for alkaline media may be written as:
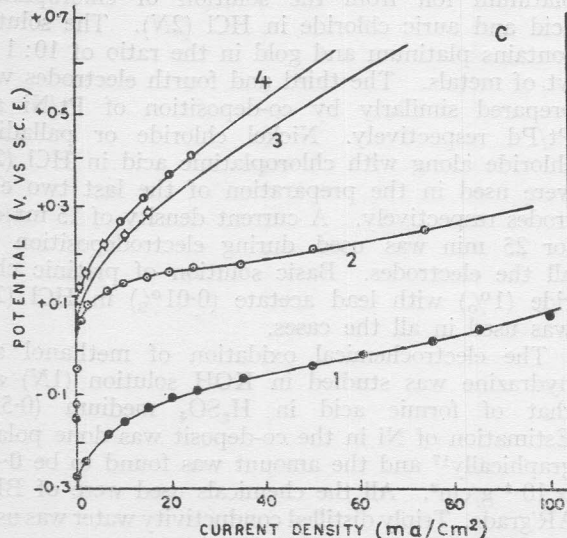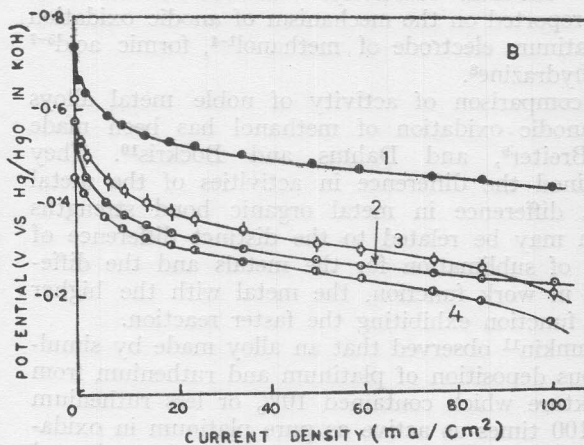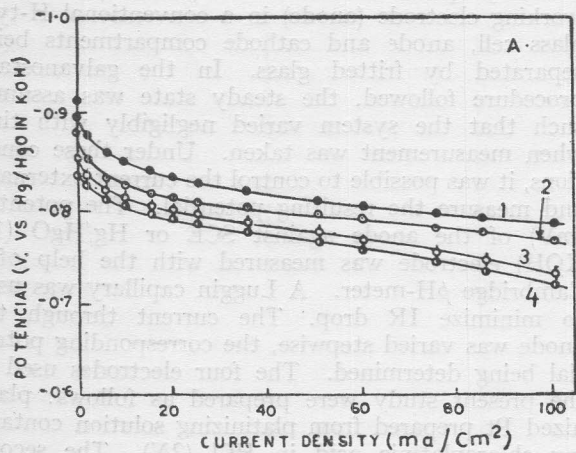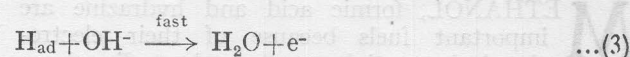
$$CH_3OH + OH^- \rightleftharpoons CH_3O^- + H_2O \quad \text{...(1)}$$

$$CH_3O^- \xrightarrow[\text{slow}]{Pt} CH_2O^-(ad) + H_{ad} \quad \text{...(2)}$$

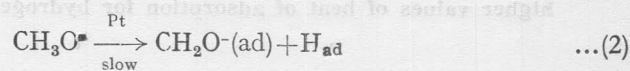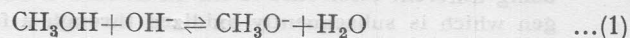$$H_{ad} + OH^- \xrightarrow{\text{fast}} H_2O + e^- \quad \text{...(3)}$$
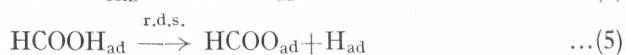

Fig. 1 — Current-voltage curves for anodic oxidation of (A) N_2H_4 (0·5M), (B) CH_3OH (1M) and (C) HCOOH (1M) at different electrodes A and B in KOH (1M) and C in H_2SO_4 (0·05N) at 30° [(1) Pt-Au; (2) Pt-Pd; (3) Pt-Ni; and (4) platinized Pt]

From the experimental observation of Langmuir type adsorption and a Tafel slope of $2RT/F$, the first electron transfer[19] is indicated as the rate determining step, where dissociative chemisorption step is involved.

In the decomposition of formic acid, Schwab[6] proposed a mechanism which consisted of adsorption of molecular formic acid, decomposition to carbon dioxide and adsorbed hydrogen, and hydrogen desorption. Gottlieb[7] reported Tafel slope of $2RT/F$ in oxidation of formic acid in H_2SO_4 and proposed preliminary decomposition of formic acid and subsequent oxidation of hydrogen. The mechanism may be represented by Eqs. (4-7)[6,20].

$$HCOOH_{soln} \rightleftharpoons HCOOH_{ad} \qquad ...(4)$$

$$HCOOH_{ad} \xrightarrow{r.d.s.} HCOO_{ad} + H_{ad} \qquad ...(5)$$

$$H_{ad} \rightarrow H^+ + e^- \qquad ...(6)$$

$$HCOO_{ad} \rightarrow CO_2 + H^+ + e^- \qquad ...(7)$$

Conway *et al.*[8] proposed a mechanism for the oxidation of N_2H_4 at platinum involving free radical intermediates and successive dehydrogenation. According to them initial adsorption equilibrium may involve the electrochemical dehydrogenation step (Eq. 8).

$$N_2H_4 + M \rightleftharpoons M.N_2H_3 + H^+ + e^- \qquad ...(8)$$
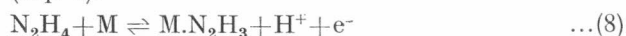
with rate determining step as (Eq. 9).

$$M + M.N_2H_3 \rightarrow M.N_2H_2 + MH(MH \xrightarrow{fast} H^+ + e^-)...(9)$$

A similar step involving N_2H_2 or N_2H (by progressive dehydrogenation) may follow. They reported that the Tafel slope is 0·10-0·12 V in acid or alkali with low current density.

Thus in the foregoing discussion it appears that in electrochemical oxidation of CH_3OH, $HCOOH$ and N_2H_4, the rate determining step is chemisorbed dissociative step which results in adsorbed hydrogen which is subsequently oxidized through a fast step. So different metals having different d-character and heat of adsorption (ΔH_{ads}) for hydrogen would behave differently. It is expected that the metal which possesses higher value of ΔH_{ads} will act as a better electrocatalyst for the oxidation of the above fuels. Experimental values of ΔH_{ads} reported[21] on metals Pt, Pd, Ni are 65·7, 65·2, 67·2 kcal/mole respectively and the spectroscopic values[22] for Ni

and Au are 71·4 and 71·3 kcal/mole respectively. So it is expected that ΔH_{ads} will increase by the presence of any of these metals along with platinum during co-deposition.

The increase in activity of platinized platinum electrode co-deposited with any of the three metals Au, Ni and Pd is indicated from the reduced polarization of the electrode, the order being: $Pt < Pt-Ni < Pt-Pd < Pt-Au$. If dissociative chemisorption is the rate determining step, it is expected that the presence of Au, Pd or Ni in Pt will increase the rate of oxidation of above species since ΔH_{ads} would increase by the presence of these elements with platinum. ΔH_{ads} values may be compared at zero coverage (free surface) with respect to the reacting species.

Results of anodic charging curves of the different electrodes are represented in oscilloscopic traces (Fig. 2). The chemisorbed hydrogen ionization region increased in the order for electrodes: platinized $Pt < Pt-Ni < Pt-Pd < Pt-Au$, which is the same for the activity of the electrodes. There may be two reasons for the greater extent of hydrogen ionization region in the charging curves for the electrodes of alloy systems than that for Pt alone. One reason may be that the roughness of electrodes of the alloy system is increased and the other may be that the coverage of the electrode by hydrogen is increased due to stronger affinity of the surface of the alloy system for hydrogen. The evidence for the latter is found in the work of McKee and Pak[13]. Two types of adsorption (one weak and the other strong bond) have been indicated by work of Schuldiner[23]. It is likely that the coverage of the electrode by hydrogen will be greater if ΔH_{ads} on the alloy system becomes more than the corresponding value on platinum alone. The values of ΔH_{ads} on the metals correspond to this experimental fact.

The apparent anomalous activity of Pt-Pd and the greater amount of chemisorbed hydrogen on Pt-Pd surface (Fig. 2c) may be related to ΔH_{ads} value of metals, the roughness of the electrode surface and the probable decrease of activation energy of adsorption of hydrogen depending on inter atomic spacing[24]. It is to be noted that Pt-Au surface is modified in respect to hydrogen chemisorption as this region is absent in Au-electrode[25].

In this connection the report of this is also in accord with the findings of Frumkin (loc. cit.).
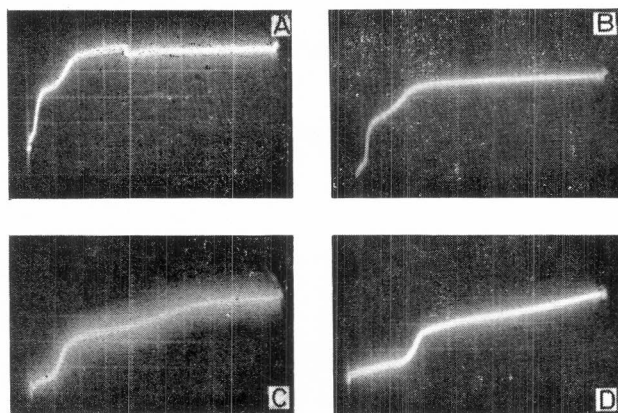

Fig. 2 — Potential-time oscillograph for the oxidation of hydrogen in $2·5N$ H_2SO_4 from the surface of (A) platinized Pt, (B) Pt-Ni, (C) Pt-Pd and (D) Pt-Au electrodes [Current density 0·502 a/cm². Potential scale (vertical) is 0·5 V per large division and time scale (horizontal) is 5 msec per large division]

It is to be noted that ΔH_{ads} for Ru is comparatively greater[26] than that for Pt. Masaru and Hironosuke[15] also found higher activity of Au or Pd than Pt in oxidation of HCHO in alkaline medium. The order of activity found was: Au>Pd>Pt.

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