

Studies of the electrochemical oxidation of methanol on platinum in phosphoric acid solution

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Abstract

The oxidation behaviour of methanol on platinum at room temperature in a low concentration of phosphoric acid ($\approx 5\%$) has been studied. Voltammetric behaviour in phosphoric acid medium is compared with that in perchloric acid. The effect of a bismuth underpotential deposition (upd) layer on the oxidation of methanol is also reported.

Introduction

Electrochemical oxidation of small organic molecules for fuel-cell applications has attracted constant attention. Among the various organic fuels, methanol has the distinction of being associated with a high charge (viz., 6 electrons) during its complete oxidation. Attempts have been made to study the oxidation of methanol on platinum in different acids [1–4], especially phosphoric acid because of its high temperature stability. Usually, phosphoric acid of concentration as high as 85% is employed as the electrolyte in fuel-cell systems [5]. Interestingly, studies [5] on the oxidation of formic acid, an organic fuel similar to methanol, have revealed that 40% phosphoric acid can yield oxidation currents higher than those obtained from 85% phosphoric acid at room temperature. Hence, efforts to explore the possibility of using still lower concentrations of phosphoric acid are worthwhile, since material requirements of the acid will be significantly reduced and the corrosive attack will be lessened. A study of methanol oxidation on polycrystalline platinum employing a low phosphoric acid concentration, viz., 0.5 M ($\approx 5\%$), is described in this paper. Other work reported is directed towards increasing the catalytic activity of the electrode surface through *in situ* modification of platinum with an underpotential deposition (upd) bismuth layer. It should be noted that the presence of upd metal layers has been found to greatly assist the oxidation of formic acid on platinum [6–8].

Experimental

A glass three-electrode cell was used. The working electrode was a polycrystalline platinum disc of area 0.283 cm^2 . The electrode surface was

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polished by successive application of 3/0, 4/0 and 5/0 emery paper, degreased with acetone, and washed thoroughly with water. A platinum foil was used as the counter electrode. Cyclic voltammograms were performed at 28 ± 1 °C using a potentiostat (Wenking, model POS 73) and an X-Y recorder (Rikadenki, model RW-201T). Potentials were recorded against a normal calomel electrode and are reported against the RHE. The electrolyte was prepared from AR grade chemicals and double-distilled water.

Results and discussion

The cyclic voltammetric (CV) behaviour of the oxidation of methanol (1.0 M) in a very low concentration of phosphoric acid (0.5 M) is shown in Fig. 1(a). Three stages of oxidation (I, II, III) – two during the anodic sweep and one during the cathodic sweep – are observed. These are very similar to those reported for the oxidation of methanol in acids such as HClO_4 and H_2SO_4 [9, 10] and in 85% (high concentration ≈ 8.5 M) H_3PO_4 [5]. The three stages are attributed, respectively, to the oxidation of adsorbed methanol, of methanol from the bulk on an oxygen-covered surface, and of methanol on a reduced surface. Subsequent discussion is confined to the first stage of methanol oxidation. Furthermore, in order to determine the specific influence of H_3PO_4 , the data are compared with those obtained in HClO_4 of the same concentration (0.5 M), see Fig. 1(b).

It is found that in H_3PO_4 as opposed to HClO_4 : (i) oxidation of methanol is decreased; (ii) the peak potentials corresponding to the oxidation are

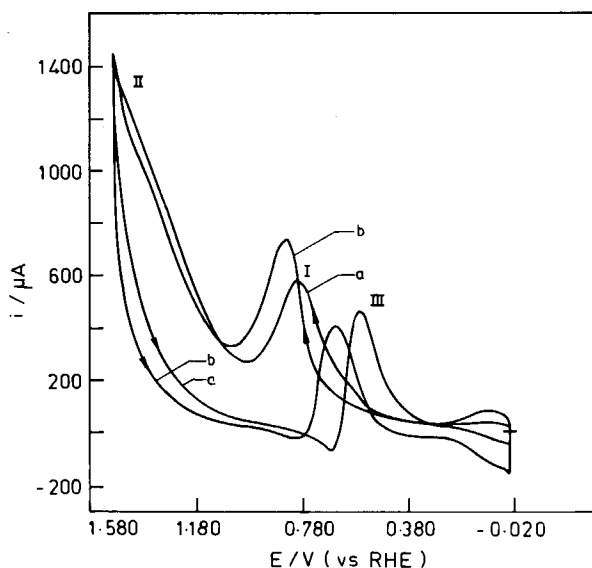


Fig. 1. Cyclic voltammograms for oxidation of CH_3OH (1 M) on platinum in: (a) 0.5 M H_3PO_4 ; (b) 0.5 M HClO_4 . Scan rate = 100 mV s^{-1} .

shifted to more negative values. In an attempt to understand this difference in behaviour, voltammograms were obtained in the two background electrolytes in the absence of methanol (Fig. 2). Clearly, the oxidation and reduction peak currents are higher in H_3PO_4 . Further, oxide formation and reduction are shifted to more negative potentials. This observed difference in behaviour between the two acids may arise from the following: (i) the phosphate anion is a good adsorbate [11, 12] while perchlorate anion is practically non-adsorbing; (ii) the pH of 0.5 M H_3PO_4 acid is higher than that of perchloric acid of the same concentration, i.e., 1.54 versus 0.44. Accordingly, a cyclic voltammogram (Fig. 3(a)) was recorded using HClO_4 (≈ 0.04 M) with the same pH as that of 0.5 M H_3PO_4 . It is seen (cf., Fig. 3(a) and (b)) that the increase of pH has resulted in an enhancement of the oxide reduction peak and also in a negative shift of the oxide formation and reduction potentials. The change in pH alone does not seem, however, to be adequate to account for the discrepancy in behaviour mentioned earlier. Again, this possibly suggests that the adsorption of phosphate anion may also exert some influence.

In another series of experiments, the voltammetric behaviour of platinum was studied in phosphoric acid of concentration between 0.5 and 5 M ($\approx 5\%$ to 50% aqueous solutions). The oxide formation and reduction characteristics were found to be practically identical except for a small positive shift in the oxide reduction potential with increase in acid concentration. The absence of a conspicuous change in behaviour with variation in acid concentration (viz., variation in pH), unlike that observed above between perchloric and phosphoric acids, suggests the influence of phosphate anion. The adsorption of phosphate anion on platinum surfaces from phosphoric acid solution has

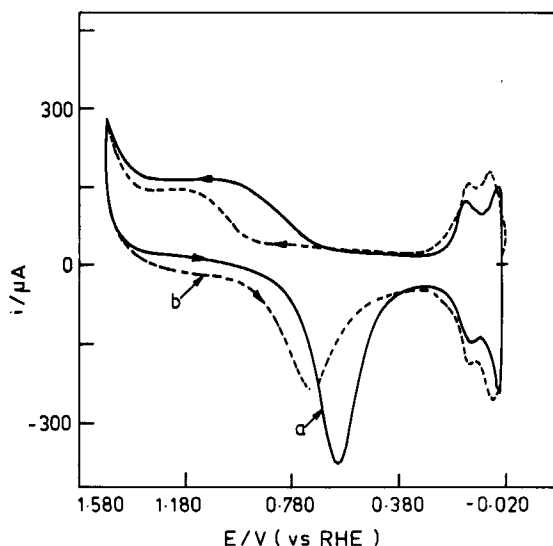


Fig. 2. Cyclic voltammetric behaviour of platinum in: (a) 0.5 M H_3PO_4 (pH=1.54); (b) 0.5 M HClO_4 (pH=0.44). Scan rate = 100 mV s^{-1} .

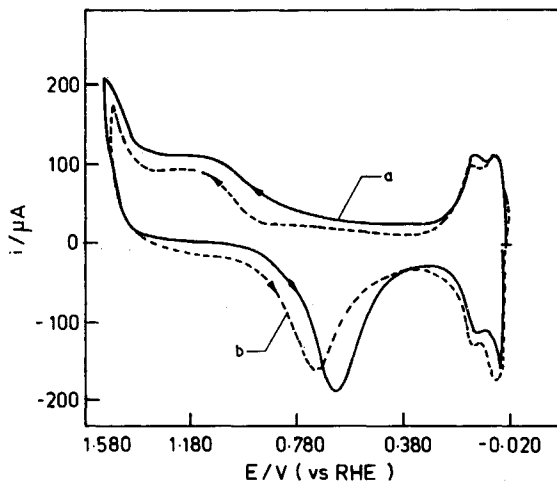


Fig. 3. Cyclic voltammetric behaviour of platinum in: (a) 0.04 M HClO_4 ($\text{pH}=1.54$); (b) 0.5 M HClO_4 ($\text{pH}=0.44$). Scan rate = 100 mV s^{-1} .

been well reported [12, 13]. Hence, it appears that both the adsorption of phosphate anion and the pH value impart appreciable effects on the behaviour of oxide formation and reduction on platinum.

In the light of the above observations, the decrease in peak current observed for the oxidation of methanol in phosphoric acid (Fig. 1(a)) compared with perchloric acid, can be expected to result from the adsorption of phosphate anion and pH change. Since the oxidation is known to involve adsorbed methanol, competitive adsorption of phosphate anions may result in decreased methanol coverage and, consequently, a decrease in peak current. Further, such a decrease can also arise on account of the higher pH of phosphoric acid, since increase in pH is known to decrease the rate of methanol oxidation [14].

It is interesting to note that the peak current for the oxidation of methanol in 0.5 M H_3PO_4 as revealed by the present studies is slightly higher than that reported [5] for the methanol oxidation in 85% H_3PO_4 . This establishes clearly the efficiency of 0.5 M H_3PO_4 as an electrolyte for methanol oxidation.

The addition of a small quantity of Bi^{3+} is found to enhance the oxidation of methanol (cf., Fig. 4(b)). This improvement in activity can be expected to result from modification of the platinum surface through a bismuth upd layer, as evidenced by a characteristic peak in the potential range of +0.78 to 0.48 V versus RHE (cf., Fig. 5). The latter agrees very well with the expected upd behaviour of bismuth on platinum in perchloric acid [15]. The enhancement of catalytic activity through upd adatoms observed in the present studies is rather marginal compared with that obtained for formic acid in similar acidic media [5].

It is relevant to note that in other acidic electrolytes, the catalytic influence of upd layers on methanol oxidation is also reported [16] to be

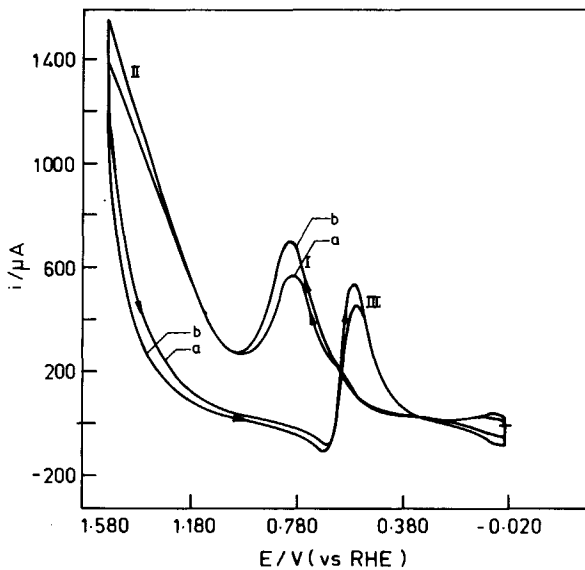


Fig. 4. Cyclic voltammograms for oxidation of CH_3OH (1 M) on platinum in: (a) 0.5 M H_3PO_4 ; (b) 0.5 M H_3PO_4 containing 10^{-5} M Bi^{3+} . Scan rate = 100 mV s^{-1} .

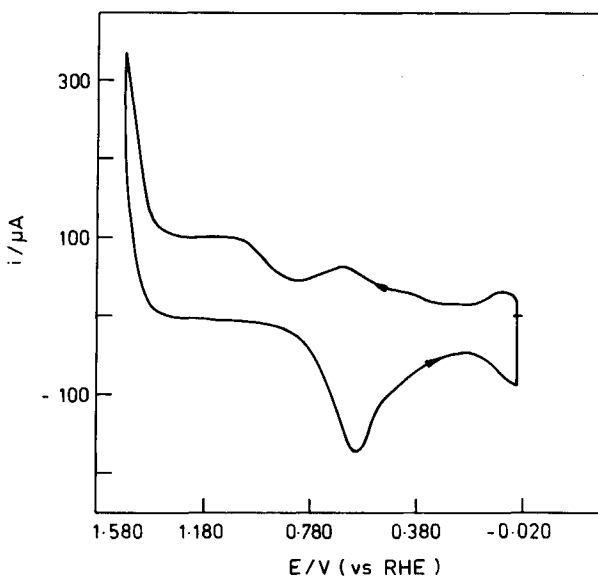


Fig. 5. Cyclic voltammometric behaviour of platinum in 0.5 M H_3PO_4 containing 10^{-5} M Bi^{3+} . Scan rate = 100 mV s^{-1} .

very small. This appears rather surprising since upd modification is known to impart very high catalytic activities to platinum for the oxidation of organic materials such as formic acid. Hence, further studies in this direction are

needed to pave the way for enhancing the catalytic activity of platinum for methanol oxidation.

Conclusions

1. Lower concentrations (0.5 M) of phosphoric acid for methanol oxidation yield currents that are comparable with those resulting from the use of high acid concentration (85%) hitherto reported at room temperature (293 K).

2. Addition of a small quantity of bismuth (that forms a bismuth up layer on platinum) imparts only a marginal increase in the catalytic activity of platinum for the oxidation of methanol in H_3PO_4 .

3. The observed decrease in currents for methanol oxidation in 0.5 M phosphoric acid compared with those in 0.5 M perchloric acid may be attributed to adsorption of phosphate ions and change in pH.

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