



# Investigation of methanol oxidation on unsupported platinum electrodes in strong alkali and strong acid

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## Abstract

Porous unsupported electrodes are made from platinum powder prepared by a room-temperature  $\text{NaBH}_4$  reduction method. Cyclic voltammograms (CVs) are recorded in different electrolytes of high and low pH in the presence and the absence of different concentrations of methanol. Various electrochemical processes occurring in different potential regions of the CVs are discussed. Steady-state galvanostatic polarisation measurements for the methanol oxidation reaction (MOR) on these electrodes in different electrolyte/methanol mixtures are also carried out. The MOR performance increases from a highly acidic range to a highly alkaline range. On increasing the KOH concentration above 6 M, however, the activity declines. Also, the MOR performance changes on changing the methanol concentration in a solution of a given pH. The highest MOR activity is obtained in a 6 M KOH + 6 M  $\text{CH}_3\text{OH}$  mixture. It is concluded that by choosing the proper ratio of  $\text{OH}^-$  ions and  $\text{CH}_3\text{OH}$  in solution, it is possible to remove completely the intermediate organic species and/or poisonous species that retard the MOR rate on the electrode surface. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Unsupported platinum electrode; Strong alkali; Strong acid; MOR activity; Intermediate organic poisonous species

## 1. Introduction

To date, there have been no detailed investigations of the variation of steady-state polarisation and the cyclic voltammogram (CV) characteristics of highly methanol oxidising unsupported Pt electrodes in electrolytes of different high and low pH. Also, the variation in the electrochemical properties of these electrodes in solutions that contain different quantities of methanol has not been systematically studied. In the present study, we have examined these aspects and discuss the various processes that occur on unsupported platinum electrodes in different potential regions of the CVs by extending the mechanistic pathways proposed for the methanol oxidation reaction (MOR) in alkaline and acidic solutions of low strength [1–7].

The steady-state polarization performances of these electrodes in strong alkaline and acidic solutions that contain different quantities of methanol are measured and

compared. The highest MOR activity is obtained in a 6 M KOH/6 M  $\text{CH}_3\text{OH}$  mixture for the platinum unsupported electrode. It is also inferred from this study that by choosing the proper ratio of  $\text{OH}^-$  ions and  $\text{CH}_3\text{OH}$  in solution, it is possible to remove completely the intermediate organic species and/or poisonous species that retard the MOR rate on the electrode surface.

## 2. Experimental

Platinum powder is prepared by reducing 1%  $\text{H}_2\text{PtCl}_6$  solution with 5%  $\text{NaBH}_4$  solution and washing the precipitate repeatedly with pure water until it reaches neutral pH. The powder is then dried in an air oven at  $110^\circ\text{C}$ . The dry metal powder is spread over the Pt mesh and pressed in a hydraulic press at a pressure of 450 psi at room temperature. The Pt electrode thus prepared offers a porosity of 60% void volume. The real area of the electrode has not been determined in the present study, and only the geometrical area has been utilised to calculate the current densities.

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A conventional, three-electrode system is employed for electrochemical measurements. A platinum exmet is used as the counter electrode. A Hg/HgO/OH<sup>-</sup> reference electrode is employed in the alkaline electrolytes and a Hg/Hg<sub>2</sub>Cl<sub>2</sub>/Cl<sup>-</sup> electrode in the acidic electrolytes. The electrode potentials are reported with respect to the normal hydrogen electrode (NHE).

The tip of the Luggin capillary is located close to the surface of the working electrode in order to minimize the IR drop. In all experiments, pure N<sub>2</sub> gas is purged through the electrolyte solution to eliminate the oxygen. Cyclic voltammograms (CVs) are recorded with a BAS model 100 B/W potentiostat interfaced to an IBM PXT microcomputer with a National Instruments IEEE-488 General Purpose Interface Card (GPIB). All the CVs are obtained at a scan rate of 25 mV s<sup>-1</sup>, unless stated otherwise. In the galvanostatic overvoltage measurements, the polarization anodic currents are controlled precisely with a d.c. constant-power supply and the electrode potentials are measured with a digital voltmeter.

### 3. Results and discussion

#### 3.1. Electrocatalysis in different pH solutions in the absence of methanol

##### 3.1.1. Cyclic voltammograms for platinum in alkaline solutions

Fig. 1a shows the first CV cycle recorded for an unsupported platinum electrode in 1 M KOH solution. During the first cycle, as soon as the forward scanning is started from  $E = -0.826$  V, the hydrogen absorption reaction occurs vigorously on the electrode. The absorption rate begins to decrease at  $E = -0.77$  V and reaches zero at  $-0.68$  V, beyond which desorption of hydrogen begins to take place. At the end of the first cycle, the hydrogen absorption rate is drastically reduced when the potential is taken to the negative region. On the second cycle, the rate decreases further, and after the third cycle, stable current values are established.

Fig. 1b shows the fourth CV cycle for an unsupported platinum electrode in 1 M KOH solution in the  $-0.826$  to  $0.4$  V range. This cycle is taken to represent the stabilized regime. Three symmetric peaks attributable to the occurrence of the hydrogen desorption reaction are present in the  $-0.75$  to  $-0.21$  V region during the forward sweep. At a slightly higher positive potential, i.e., about  $-0.16$  V, a less active PtO monolayer starts to form on the surface and the corresponding current plateau continues up to a potential of  $0.4$  V. The PtO layer is reduced during the backward sweep in the  $0.36$  to  $-0.27$  V region (peak current at  $E_p = -0.04$  V) and three cathodic peaks due to the hydrogen adsorption reaction are present in the  $-0.3$  to  $-0.8$  V region.

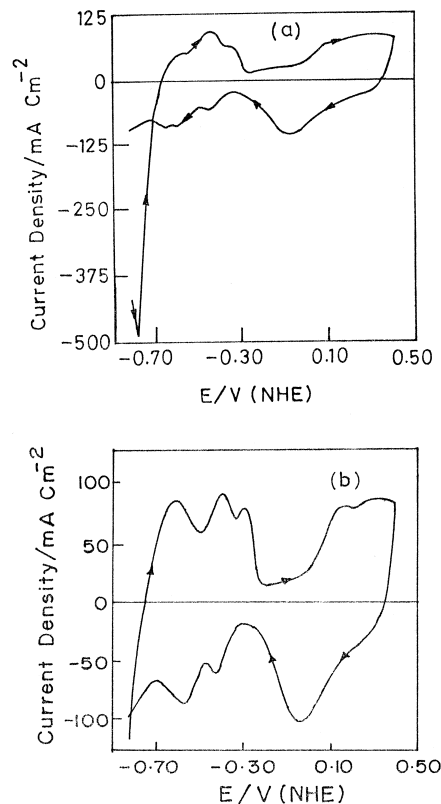
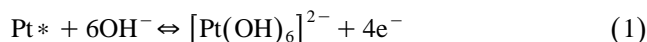


Fig. 1. CVs for unsupported platinum electrode in 1 M KOH solution at room temperature: (a) 1st cycle; (b) 4th cycle.

The CV features in different electrolyte OH<sup>-</sup> concentrations (6 M KOH and 11 M KOH) have also been recorded. In 6 M KOH solution, the potential for the onset of PtO layer formation is shifted negatively to  $-0.33$  V. The PtO layer reduction peak appears in the  $0.35$  to  $-0.4$  V region followed by the hydrogen adsorption reaction in the  $-0.4$  to  $-0.8$  V region. At high alkaline concentration, viz., 11 M KOH the onset potential for the PtO film formation and its reduction potential are shifted to even more negative values. Moreover, the double-layer region also slowly diminishes on increasing the OH<sup>-</sup> ion concentration.

It has been suggested by Burke and O'Dwyer [8] that when platinum electrodes are subjected to cycling between the hydrogen evolution and the oxygen evolution potential regions, a low level of hydrous oxide is formed on the platinum metal sites. Visintin et al. [9] have also similarly reported the observation of this phenomenon from surface morphological studies on platinum electrodes.

Burke and O'Dwyer [8] have proposed that the hydrous oxide species is present in the form of hexahydroxy platinum acid  $[\text{Pt}(\text{OH})_6]^{2-}$  and begin to form in the hydrogen desorption potential region, although the exact potential has not been detected. It has been argued that  $[\text{Pt}(\text{OH})_6]^{2-}$  is formed via the reaction:



which takes place as a result of an adatom/incipient hydrous oxide transition, which is dependent largely on the metal atom displacement effect that arises from the repetitive formation and reduction of a thin compact layer. The reaction given by Eq. (1) occurs as the metal atoms at the interface, perhaps at interfacial surface defects, decrease their lattice coordination numbers and attain adatom status.

The platinum powder used in this study has been prepared by a low-temperature method; hence, there is a high probability of having a large population of surface defects.

### 3.1.2. Cyclic voltammograms for platinum in acidic solutions

The CV for an unsupported platinum electrode in 1 M  $H_2SO_4$  is shown in Fig. 2. Two hydrogen oxidation peaks and a double-layer region are present in the potential regions 0 to 0.36 V and 0.44 to 0.82 V, respectively. Above  $E = 0.82$  V, a PtO monolayer is formed up to the potential 1.23 V [10]. The PtO layer is reduced during the backward sweep in the 1.19 to 0.6 V region and exhibits a cathodic peak ( $E_p = 0.76$  V). This is then followed by a double-layer region. The hydrogen adsorption reaction commences at about 0.34 V and is completed at 0 V.

A CV for this electrode in 2.5 M  $H_2SO_4$  solution has also been recorded. The hydrogen oxidation peaks now occur in the 0.03 to 0.44 V region, and the onset potential for PtO layer formation is 0.84 V. The  $E_p$  (0.82 V) of the PtO reduction peak is shifted positively by 60 mV; hydrogen adsorption starts at 0.44 V and finishes at 0.03 V. Burke et al. [11] have reported that the hydrous oxide formation and reduction reaction of Eq. (1) occurs between 0.2 and 0.5 V on platinum in acid solutions.

### 3.2. Electrocatalysis in different pH solutions in the presence of methanol

#### 3.2.1. Methanol oxidation on porous unsupported platinum in strong alkaline solutions

Beden et al. [1] have used a CV technique to study MOR electrocatalysis on a small platinum bead electrode (obtained by melting a platinum wire) in  $10^{-3}$ ,  $10^{-2}$ ,

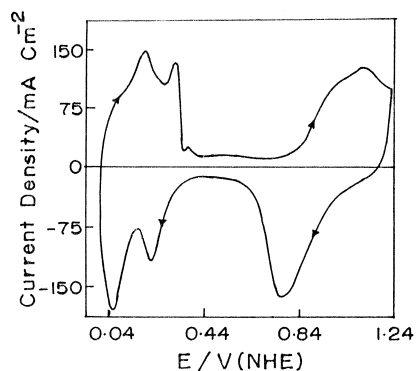
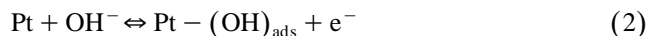


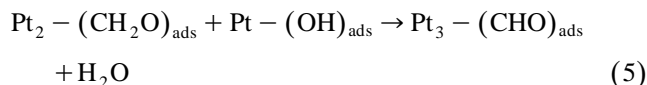
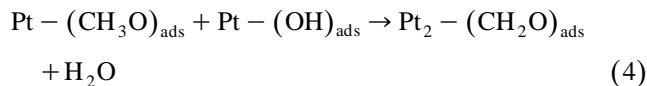
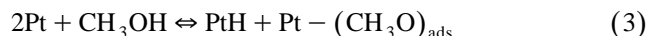
Fig. 2. CV for unsupported platinum electrode in 1 M  $H_2SO_4$  solution at room temperature (4th cycle).

$10^{-1}$ , 0.5 and 1 M NaOH solutions with different concentrations of methanol viz.  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$  and 1 M  $CH_3OH$ ). The following observations were made: (i) the presence of an anodic peak during the positive sweep and another anodic peak during the backward sweep for all the electrolyte/ $CH_3OH$  concentration mixtures investigated; (ii) a change in the magnitude of the oxidation current, as well as in the general shape of the voltammogram occur on varying the methanol concentration in the electrolyte; (iii) an increase in the MOR activity as the hydroxyl ion concentration in solution is increased for a given methanol concentration; (iv) a decrease in the MOR activity once the hydroxyl/methanol concentration ratio is greater than unity. From these results, Beden et al. [1] have suggested that the enhancement of the MOR activity is due to the greater availability of  $OH^-$  ions in solution and a higher coverage of  $OH^-$  ions on the electrode surface.

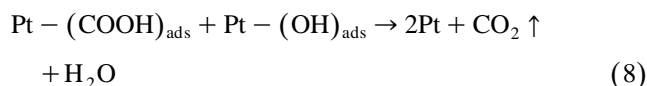
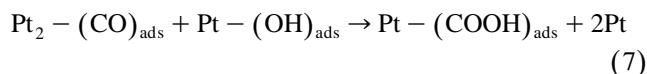
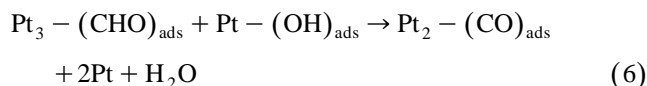
The MOR mechanistic pathways deduced from the proposal advocated by Beden et al. [1] for alkaline solutions of low concentration are as follows;



The  $OH^-$  ions required for this equilibrium are supplied by hydrous oxide formed in the hydrogen region, as well as by the solution  $OH^-$  ions at  $E > -0.2$  V.



The strength of the bonding of  $(CHO)_{ads}$  on the surface determines the entire rate of the reaction. The chemisorptive bonding of CHO on platinum in alkali is weak, such that further oxidation takes place without much difficulty, i.e., without irreversibly blocking the electrode active sites, namely:



The following reports the findings of cyclic voltammetric experiments to determine the MOR activity on unsupported porous platinum electrodes in electrolytes that contain different concentrations of alkali (1, 6 and 11 M KOH) and methanol (1, 6 and 11 M  $CH_3OH$ ). The different CV features observed in each of these solutions are discussed in light of the above mechanistic pathways.

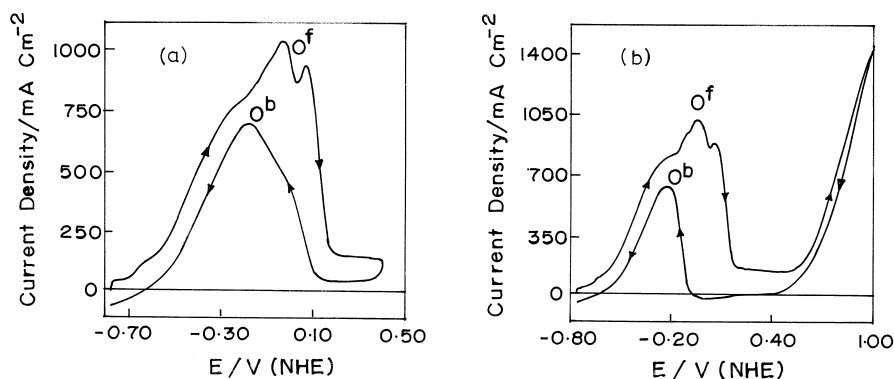


Fig. 3. CVs (4th cycle) for the MOR on unsupported platinum electrodes in 6 M KOH/1 M CH<sub>3</sub>OH solution in the potential range: (a)  $-0.775$  to  $0.4$  V; (b)  $-0.775$  to  $1.0$  V. Experiments performed at room temperature.

In Fig. 3a, the CV recorded for an unsupported Pt electrode in 6 M KOH/1 M CH<sub>3</sub>OH is shown. During the forward sweep, an anodic peak, O<sup>f</sup>, occurs at  $-0.60$  V; the maximum peak current,  $i_p$ , is observed at  $E_p = -0.04$  V. The current of this peak then declines exponentially until  $E = 0.2$  V where the less active PtO monolayer film inhibits the MOR. Reactions (2) to (8) appear to occur in the potential region of the peak O<sup>f</sup>. Steps (6) to (8) that involve the release of CO<sub>2</sub> gas seem to occur in the potential between  $-0.2$  and  $0.2$  V, as suggested by the presence of a potential hump. Any residual weakly bonded CHO species do not become oxidized at higher potentials; hence, another peak corresponding to the oxidation of organic species is not seen in the oxygen evolution reaction (OER) potential region, i.e., at  $E > 0.6$  V in the CV recorded separately in the  $-0.8$  to  $1.0$  V region, see Fig. 3b. By contrast, an anodic peak appears in the OER potential region, as will be seen later on in Fig. 7, for a platinum electrode in acid solution. In this case, the strongly bonded poisonous organic species persist and are oxidized to some extent in the high-potential region.

A shoulder is noted in the  $-0.6$  to  $-0.18$  V range on the left side of the O<sup>f</sup> peak in Fig. 3a. An analysis of the

variation of the maximum peak current of this shoulder with the square root of the scan rate indicates that the associated process is diffusion-controlled. It is speculated that the appearance of the shoulder could be due to oxidation arising out of the condition when OH<sup>-</sup> ions are available in excess and chemisorbed organic species availability is insufficient at the electrode surface in the given electrolyte.

During the backward sweep, an oxidation peak, O<sup>b</sup>, is present at  $0.13$  V where the PtO film is reduced; the  $E_p$  of the O<sup>b</sup> peak coincides with the potential region of the shoulder of the O<sup>f</sup> peak. In this potential region, the electrode can acquire a large quantity of active oxygen atoms from 6 M KOH solution and use them to burn off the residual weakly bonded CHO species that remain at the end of the forward sweep, as well as to oxidize the freshly chemisorbed methanol molecules.

When the electrolyte consists of equimolar concentrations of alkali and methanol, dissociatively chemisorbed methanol and OH<sub>ads</sub> species appear to cover the adjacent platinum sites simultaneously. Almost all the sites are covered in high equimolar mixtures, viz., 6 M KOH/6 M CH<sub>3</sub>OH and 11 M KOH/11 M CH<sub>3</sub>OH, and hence com-

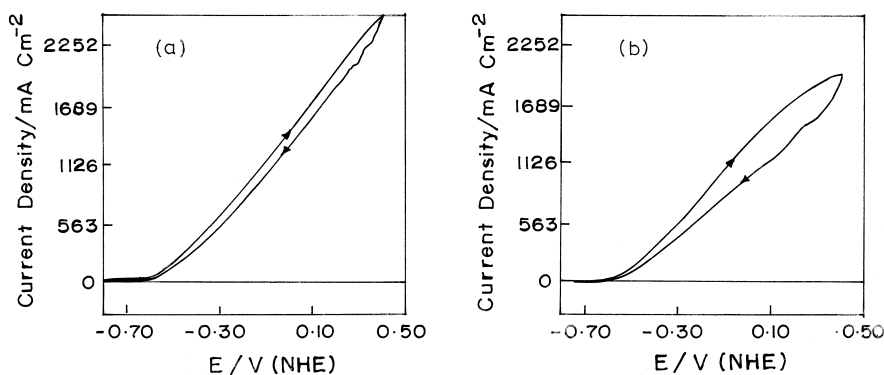


Fig. 4. CVs (4th cycle) for the MOR on unsupported platinum electrode in: (a) 6 M KOH/6 M CH<sub>3</sub>OH solution; (b) 11 M KOH/11 M CH<sub>3</sub>OH solution. Experiments performed at room temperature.

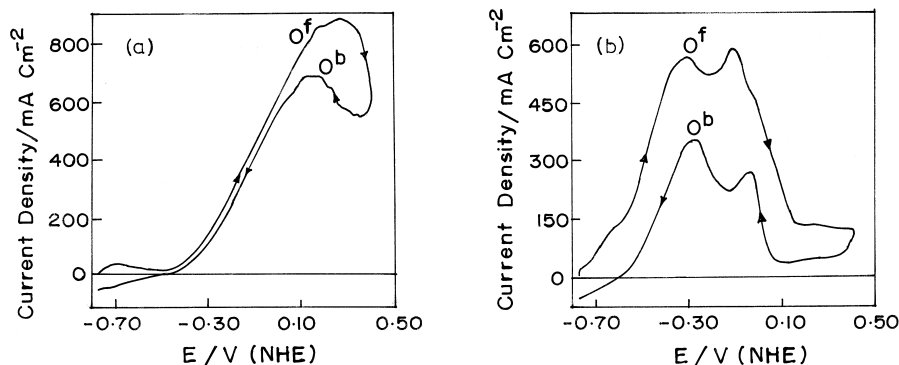


Fig. 5. CVs (4th cycle) for the MOR on unsupported platinum electrode in: (a) 1 M KOH/1 M CH<sub>3</sub>OH solution; (b) 11 M KOH/1 M CH<sub>3</sub>OH solution. Experiments performed at room temperature.

plete oxidation of chemisorbed organic species take place without permitting any CHO species to remain on the electrode surface. The O<sup>f</sup> and O<sup>b</sup> peaks are not formed in the CVs recorded in these solutions, and only a featureless polarization current–potential response is observed, as shown in Fig. 4a,b. For the 6 M KOH/6 M CH<sub>3</sub>OH mixture, a high current density of 2.53 A cm<sup>-2</sup> is obtained at  $E = 0.4$  V for a scan rate of 25 mV s<sup>-1</sup>. For the 11 M KOH/11 M CH<sub>3</sub>OH mixture, the current density at this potential is 1.97 A cm<sup>-2</sup> at the same scan rate. This decrease in current density may be due to the lower ionic conductivity of the 11 M KOH/11 M CH<sub>3</sub>OH mixture. The O<sup>b</sup> peaks are not observed because not even a trace of CHO species appears to remain on the electrode surface at the end of the forward sweep.

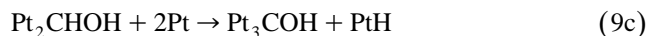
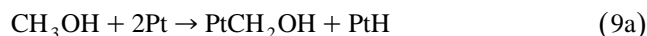
For the lower equimolar concentration mixture 1 M KOH/1 M CH<sub>3</sub>OH, the O<sup>f</sup> and O<sup>b</sup> peaks appear; their  $E_p$  values are 0.28 and 0.16 V, respectively (see Fig. 5a). Although this mixed solution is an equimolar concentrated solution, the CHO species have not been completely oxidized at the end of the forward sweep, possibly because 1 M KOH does not provide sufficient active oxygen atoms for burning off of the carbonaceous species. Nevertheless, only a small amount of the carbonaceous species may remain. Therefore, only a small O<sup>b</sup> peak is observed during the backward sweep in the CV in Fig. 5a, and that only in the high positive potential region. For an 11 M KOH/1 M CH<sub>3</sub>OH mixture, the O<sup>f</sup> and O<sup>b</sup> peaks are presented, but are shifted to more negative potentials (see Fig. 5b). The peaks are also observed in an 11 M KOH/6 M CH<sub>3</sub>OH mixture. This could be due to the fact that the excess coverage of OH<sub>ads</sub> species on the electrode surface oxidizes the chemisorbed organic species quickly and block the chemisorption of further methanol molecules at lower potentials. As the excess OH<sup>-</sup> ions are not utilized for burning off of the organic species, these ions could assist the rapid formation of the PtO layer in the higher potential range. As a result, a decrease in the rate of the MOR has been noted.

### 3.2.2. Methanol oxidation on porous unsupported platinum electrodes in acidic solutions

Organic intermediate species are strongly adsorbed on the platinum electrodes in acid solutions, and many attempts have been made to understand the nature of strongly bonded adsorbed intermediate species. Among these studies, an in situ infrared spectroscopy study by Kunimatsu [12] has identified the presence of linearly bonded =CO species on the surface of platinum electrodes in acidic electrolytes. These linearly bonded =CO species act as poisonous species.

The mechanistic pathways for the MOR on platinum in an acid medium are as follows [5].

At  $E < 0.5$  V, the dissociative chemisorption of methanol on Pt electrode takes place



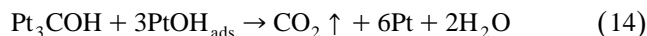
The PtH species are lost to the solution as H<sup>+</sup> ions, i.e.,



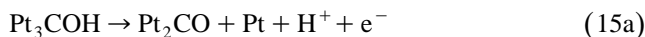
The equilibrium formation of OH<sub>ads</sub> at the surface occurs over the 0.3–0.9 V region [6,13,14]; a low level of hydrous oxide formation takes place at metal sites as a result of the surface equilibrium reaction (Eq. (1)) at about 0.2 V [11], namely:



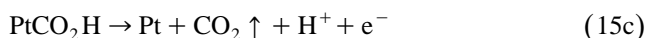
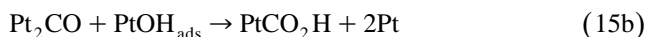
The product of each step of Eqs. (9a), (9b) and (9c) may react with OH<sub>ads</sub> to yield different oxidation products:



Over the 0.5–1.1 V range, the reaction



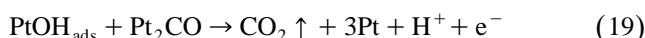
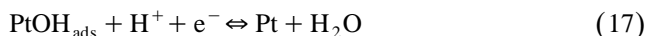
is followed by



The unreacted  $\text{Pt}_2\text{CO}$  may also rearrange to give a linearly bound species which acts as a poison



The linear species  $\text{Pt}=\text{C}=\text{O}$  can be oxidized via either of the following two processes: (i) during the cathodic sweep:



(ii) the potential region where the OER occurs, i.e., at  $E > 1.23$  V:

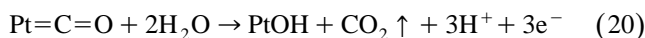


Fig. 6a presents the CV recorded in the 0.04 to 1.23 V region for an unsupported platinum electrode in 1 M  $\text{H}_2\text{SO}_4$ /1 M  $\text{CH}_3\text{OH}$ . During the positive sweep, the MOR begins at  $E = 0.06$  V, and after the initial anodic reactions of Eqs. (9a), (9b), (9c) and (10) have taken place at potentials below 0.44 V, the oxidation peak  $\text{O}^f$  appears in the potential range at a more positive value than that observed in alkaline solution. The  $E_p$  of  $\text{O}^f$  is 0.95 V. All the steps of Eqs. (11), (15a), (15b) and (15c) appear to occur in the potential region of  $\text{O}^f$ . The  $\text{O}^b$  peak ( $E_p = 0.77$  V) is present during the backward sweep. The magnitudes of the  $\text{O}^f$  and  $\text{O}^b$  peaks are more or less same and the peak  $\text{O}^b$  is associated with the removal of the linear species  $\text{Pt}=\text{C}=\text{O}$  according to the steps of the reactions (17) to (19) [6]. When the concentration of acid is increased to 2.5 M  $\text{H}_2\text{SO}_4$  and the methanol concentration is maintained at 1 M, the positions of the peaks  $\text{O}^f$  and  $\text{O}^b$  are shifted to

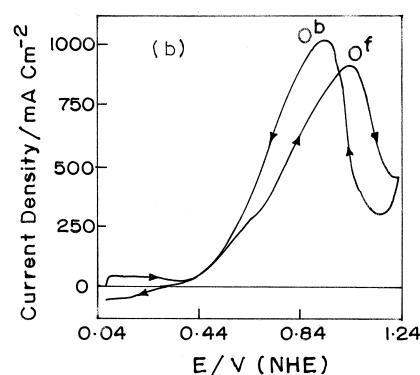
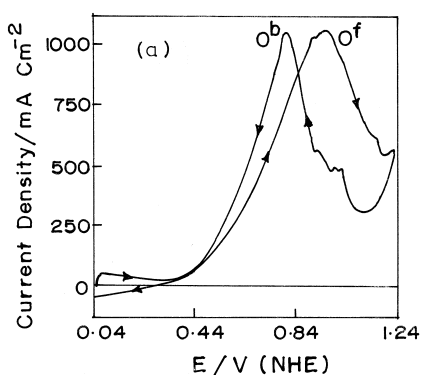


Fig. 6. CVs (4th cycle) for the MOR on unsupported platinum electrode in: (a) 1 M  $\text{H}_2\text{SO}_4$ /1 M  $\text{CH}_3\text{OH}$  solution; (b) 2.5 M  $\text{H}_2\text{SO}_4$ /1 M  $\text{CH}_3\text{OH}$  solution. Experiments performed at room temperature.

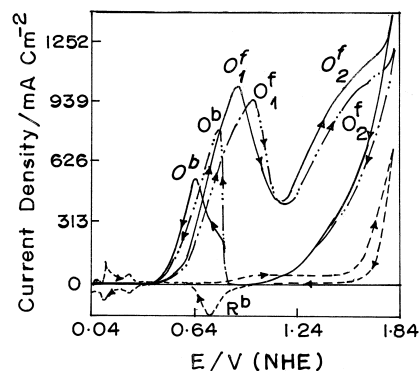


Fig. 7. CVs (4th cycle) for the MOR on unsupported platinum electrode in the potential range 0.04 to 1.825 V at room temperature. (—) in 1 M  $\text{H}_2\text{SO}_4$ /1 M  $\text{CH}_3\text{OH}$  solution (peak labels in italics), (---) in 2.5 M  $\text{H}_2\text{SO}_4$ /1 M  $\text{CH}_3\text{OH}$  solution and (· · ·) in 2.5 M  $\text{H}_2\text{SO}_4$  solution without  $\text{CH}_3\text{OH}$  at room temperature, records at a scan rate of  $10 \text{ mV s}^{-1}$ .

more positive potentials, see Fig. 6b. Also, the magnitude of the  $\text{O}^b$  peak becomes greater than that of the  $\text{O}^f$  peak.

The CVs recorded in the 0.04 to 1.825 V region for an unsupported platinum electrode in both acid solutions are shown in Fig. 7. In these CVs, an additional oxidation peak, namely  $\text{O}^f_2$ , appears at  $E > 1.23$  V as a result of a reaction (Eq. (20)) between species  $\text{Pt}=\text{C}=\text{O}$  and some fresh active surface oxygen atoms that become available at the electrode surface in the potential region between the  $E_{\text{rev}}$  for the OER and the onset of the OER, as has been already pointed out by Manoharan and Goodenough [6] from a study with a smooth platinum electrode. A CV recorded in the supporting electrolyte 2.5 M  $\text{H}_2\text{SO}_4$  solution (without  $\text{CH}_3\text{OH}$ ) is also included in Fig. 7 to substantiate the conclusion that the  $\text{O}^f_2$  is due to the reaction given by Eq. (20). It appears that the population of the poisonous  $\text{Pt}=\text{C}=\text{O}$  species increases on the electrode surface as the acid concentration is increased. This is supported by the observation that the  $i_p$  of the  $\text{O}^b$  peak in 2.5 M  $\text{H}_2\text{SO}_4$  is greater than that in 1 M  $\text{H}_2\text{SO}_4$ . It also appears that the CO in the  $\text{Pt}=\text{C}=\text{O}$  species is too strongly

bonded in stronger acid solution; thus, removal of these species at higher positive potentials is more difficult. This conclusion is supported by the fact that the current observed in the  $O_2^f$  peak region for 2.5 M  $H_2SO_4$  is smaller than that in 1 M  $H_2SO_4$  solution.

The current intensity of the  $O_2^f$  peak in 1 M  $H_2SO_4$  is higher than that in 2.5 M  $H_2SO_4$  for the following two reasons. First, lesser adsorption of the intermediate species takes place in higher pH electrolytes. Second, a large coverage of  $OH_{ads}$  species takes place on the electrode surface so that chemisorptively dissociated species are oxidized in somewhat less positive potential regions. In high acid concentration (2.5 M  $H_2SO_4$ ), the  $OH_{ads}$  coverage on the electrode surface takes place only at high positive potentials and also adsorption of  $HSO_4^-$  ions competes with  $OH^-$  ion adsorption in the MOR potential regions [15]. As a result, the availability of active  $OH_{ads}$  species to oxidize the organic species is lowered.

### 3.3. Steady-state polarization data for unsupported platinum electrodes

Steady-state polarization curves for the MOR on the porous platinum electrodes in electrolytes that contain various concentrations of alkali and methanol, and in 1 M  $H_2SO_4$  and 2.5 M  $H_2SO_4$  solutions containing 1 M  $CH_3OH$  are shown in Fig. 8. It is clear that the MOR performance increases on going from a highly acidic range to a highly alkaline range. Nevertheless, the activity increases only up to 6 M KOH solution; on increasing the KOH concentration further, the activity declines.

Also, the MOR performance is dependent on the methanol concentration for a given pH solution. It is of interest to note that of the three methanol concentrations examined, viz., 1, 6 and 11 M  $CH_3OH$  in 11 M KOH

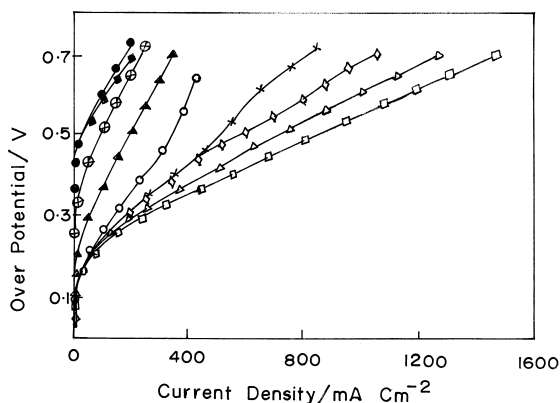


Fig. 8. MOR polarization curves for unsupported platinum electrode in various concentrated KOH and  $H_2SO_4$  solutions that contain different quantities of  $CH_3OH$ . ( $\Delta$ — $\Delta$ ) 6 M KOH/6 M  $CH_3OH$ , ( $\diamond$ — $\diamond$ ) 11 M KOH/6 M  $CH_3OH$ , ( $\times$ — $\times$ ) 11 M KOH/11 M  $CH_3OH$ , ( $\circ$ — $\circ$ ) 11 M KOH/1 M  $CH_3OH$ , ( $\blacktriangle$ — $\blacktriangle$ ) 6 M KOH/1 M  $CH_3OH$ , ( $\oplus$ — $\oplus$ ) 1 M KOH/1 M  $CH_3OH$ , ( $\blacksquare$ — $\blacksquare$ ) 1 M  $H_2SO_4$ /1 M  $CH_3OH$ , ( $\bullet$ — $\bullet$ ) 2.5 M  $H_2SO_4$ /1 M  $CH_3OH$ , all at room temperature, and ( $\square$ — $\square$ ) 6 M KOH/6 M  $CH_3OH$  at 50°C.

solution, the solution containing 6 M  $CH_3OH$  yields maximum activity. Similarly, of the two methanol concentrations (1 M and 6 M  $CH_3OH$ ) tested in 6 M KOH solution, 6 M  $CH_3OH$  gives the better performance. In fact, of all the solutions tested, the 6 M KOH/6 M  $CH_3OH$  mixture yields the best performance ( $i = 1.27 \text{ A cm}^{-2}$  at  $\eta = 0.7 \text{ V}$ ). On increasing the solution temperature to 50°C, still higher activity has been obtained ( $i = 1.45 \text{ A cm}^{-2}$  at  $\eta = 0.7 \text{ V}$ ).

## 4. Conclusions

The activity for the methanol oxidation reaction (MOR) on an unsupported platinum in both alkaline and acidic media can be summarised as follows.

(1) The MOR performance increases on going from a highly acidic range to a highly alkaline range. The activity increases, however, only up to 6 M KOH solution. At higher concentrations, the activity declines. Also, the MOR performance alters on changing the methanol concentration of a given pH solution.

(2) Higher equimolar concentrations of alkali and methanol yield higher MOR current densities. The 6 M KOH/6 M  $CH_3OH$  mixture yields the highest MOR performance.

(3) Generally, the  $O^f$  peaks observed in the CVs obtained in alkaline and acid solutions are due to the chemisorption of methanol molecules and to the oxidation of the intermediate organic species.

The  $O^b$  peaks in alkaline solution are due to the oxidation of the residual weakly bonded CHO species during the backward (i.e., negatively going) sweep.

The  $O^b$  peaks of the CV in acid solution are due to the oxidation of linearly bonded Pt=C=O species during the backward sweep.

(4) It appears that CHO species do not become bonded on the platinum electrodes in the equimolar mixture 6 M KOH/6 M  $CH_3OH$ . This suggests that by choosing the proper ratio of  $OH^-$  ions and  $CH_3OH$  in solution, it is possible to obtain maximum MOR performance while at the same time completely removing the intermediate organic species and/or the poisonous species on the electrode surfaces.

(5) The intermediate organic CHO species are weakly bonded on the platinum electrodes in all KOH/ $CH_3OH$  mixtures, except in 6 M KOH/6 M  $CH_3OH$  and 11 M KOH/11 M  $CH_3OH$ . The platinum electrodes exhibit lower performance in acidic solutions than in alkaline solutions because the CO species are linearly bonded on the electrode surface in acidic media and, accordingly, suppress the rate of the reaction.

(6) The poisonous species on platinum electrodes in acid can be oxidized to some extent by going to the OER potential region.

(7) A shoulder is always observed on the left-hand side of the  $O^f$  peaks in the CVs obtained in 6 M KOH/1 M  $CH_3OH$  solution. This has been interpreted as due to the availability of excess  $OH^-$  ions and insufficient chemisorbed organic species for oxidation at the electrode surfaces.

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