Possibilities of prevention of formation of poisoning species on direct methanol fuel cell anodes

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Abstract

Porous unsupported Pd, Pt and Pt–Ru single phase alloy electrodes with different compositions viz. 9:1, 7:3 and 5:5 were prepared by $NaBH_4$ reduction method at room temperature.

Extensive cyclic voltammetric investigations in different solutions have been performed on these electrodes, as well as on smooth electrodes, with the aim of identifying suitable combinations of electrode structure and electrolyte/methanol mixtures which can prevent the formation of organic poisoning species.

Various electrochemical processes occurring in different potential regions are discussed. Meanings of the appearance/disappearance of oxidation peaks during both forward and backward sweeps on the present electrodes are pointed out. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fuel cells/alkaline electrolyte; Fuel cells/acid electrolyte; Noble metal catalysts; Methanol oxidation: formation of poisoning species

1. Introduction

The formation of intermediate organic poisoning species during the course of the methanol oxidation reaction (MOR) on noble metals and their alloy electrodes in aqueous solutions of alkali and acid is considered to be a common phenomenon and has been posing a problem for developing direct methanol fuel cell anodes [1–9]. These intermediate organic poisoning species has been identified by in situ IR spectroscopic studies and found to exist in the form of $(CHO)_{ads}$ in alkaline solution and in the form of linearly bonded $=C=O$ in acid solution on smooth Pt and Pt-based alloy electrodes [4,10–14]. On smooth Pd, it has been identified that the bridge bonded $>CO$ is the poisoning species [15]. With the aim of avoiding the formation of these poisoning species on the electrodes surfaces, binary Pd-based alloy catalysts and binary, ternary and quartenary Pt alloy catalysts have been employed for the MOR. However, the complete removal of these species has not been completely realised [14–25] in these studies. In the present investigation, extensive cyclic voltammetric (CV) measurements for the MOR on several smooth and carbon unsupported porous Pd, Pt and Pt–Ru alloy electrodes of compositions 9:1, 7:3 and 5:5 in different aqueous electrolytes of high and low pH that contain different quantities of methanol have been carried out.

The CVs of the porous unsupported Pt and Pt–Ru alloy electrodes in different alkaline and acidic solutions and those of the Pd electrodes in different alkaline solutions have exhibited both featured curves (i.e. the curves with the formation of anodic oxidation peaks namely O^f and O^b) and featureless polarisation curves (i.e. the curves without forming the O^f and O^b peaks). In the case of the smooth Pt and Pd electrodes, only featured CV curves have been obtained in all the electrolyte/methanol combinations tested in the present study. The various processes that occur on the unsupported porous electrodes and the smooth electrodes are discussed [1,3,4,21,26].

It is inferred from this study that by choosing the proper porous electrode structure and the proper ratio of OH^- and CH_3H in solution, it may be possible to avoid completely the intermediate organic species and/or poisoning species that retard the MOR rate on the electrode surface.

2. Experimental preparation of the porous unsupported Pd, Pt and Pt–Ru alloy electrodes

The porous unsupported Pd, Pt and Pt–Ru (9:1), (7:3) and (5:5) single phase alloy electrodes were prepared from the

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metal powders by the compaction method. These metal powders were prepared by aqueous phase reduction method as reported elsewhere [27]. The Pd, Pt and Pt–Ru alloy electrodes, thus, prepared offered a porosity of 60–65% 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 current densities.

Foils of Pt and Pd were used as smooth working electrodes. The smooth Pt electrode was pre-treated with acetone and 5% solution of aqua regia followed by washing with demineralised water. The smooth Pd electrode was pre-treated by mildly abrading with fine grade emery paper followed by washing with demineralised water. The Pt smooth electrodes were scanned in the region between -0.25 and 1.8 V and the Pd smooth electrodes in the region between 0.3 and 1.8 V at 25 mV s^{-1} initially to ensure that the expected CV behaviour of the system is observed.

A conventional, three-electrode system was employed for electrochemical measurements. All the CVs were obtained at a scan rate of 25 mV s^{-1}, unless stated otherwise, as reported in [27]. The electrode potentials are reported with respect to reversible hydrogen electrode (RHE).
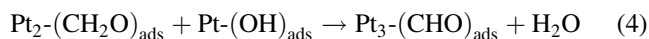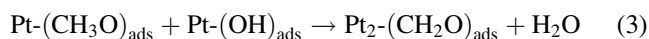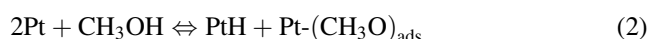
3. Results and discussion

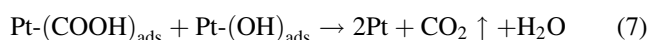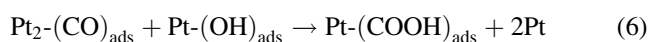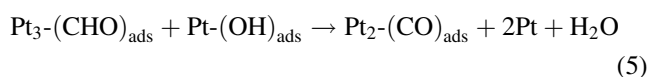### 3.1. Cyclic voltammograms for the oxidation of methanol on Pt and Pt–Ru electrodes in alkaline solutions[1]

The MOR mechanistic pathways in alkaline solutions are as follows [3]:

$$Pt + OH^- \Leftrightarrow Pt\text{-}(OH)_{ads} + e^- \tag{1}$$
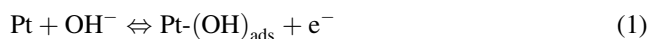
The OH$^-$ ions required for this equilibrium are mainly supplied by the solution OH$^-$ ions at $E > 0.3$ V [28].

$$2Pt + CH_3OH \Leftrightarrow PtH + Pt\text{-}(CH_3O)_{ads} \tag{2}$$

$$Pt\text{-}(CH_3O)_{ads} + Pt\text{-}(OH)_{ads} \rightarrow Pt_2\text{-}(CH_2O)_{ads} + H_2O \tag{3}$$

$$Pt_2\text{-}(CH_2O)_{ads} + Pt\text{-}(OH)_{ads} \rightarrow Pt_3\text{-}(CHO)_{ads} + H_2O \tag{4}$$

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's active sites.

$$Pt_3\text{-}(CHO)_{ads} + Pt\text{-}(OH)_{ads} \rightarrow Pt_2\text{-}(CO)_{ads} + 2Pt + H_2O \tag{5}$$

$$Pt_2\text{-}(CO)_{ads} + Pt\text{-}(OH)_{ads} \rightarrow Pt\text{-}(COOH)_{ads} + 2Pt \tag{6}$$

$$Pt\text{-}(COOH)_{ads} + Pt\text{-}(OH)_{ads} \rightarrow 2Pt + CO_2 \uparrow + H_2O \tag{7}$$

A low level of hydrous oxide, which may be formed at metal sites and surface defects [29] via the reaction of

Eq. (8), may also contribute the active oxygen atoms responsible for "burning off" the organic species in the reactions of Eqs. (2)–(7).

$$Pt^* + 6OH^- \leftrightarrow [Pt(OH)_6]^{2-} + 4e^- \tag{8}$$
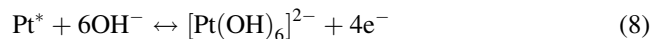
CVs have been recorded on the unsupported porous Pt, Pt–Ru and the smooth Pt electrodes in electrolytes that contain varying concentrations of alkali and methanol.

In Fig. 1, the CVs recorded for the porous unsupported Pt electrode in 6 M KOH solutions that contain varying concentrations of methanol (1, 3, 6, 9 and 11 M CH$_3$OH) are shown. During the forward sweep, the MOR begins at 0.18 V for all the electrolyte/methanol mixtures. For the 6 M KOH/1 M CH$_3$OH mixture, the anodic peak O^f occurs in the region 0.18–0.92 V with $E_p = 0.7$ V. The reactions (1–4) occur in the early potential region of the O^f peak and the reactions of Eqs. (5)–(7) occur in the region 0.18–0.92 V. A less active PtO monolayer film is formed at $E > 0.8$ V during the forward sweep. It blocks the supply of the active oxygen atoms and hence further occurrence of the MOR is suppressed.

During the backward sweep, the oxidation peak O^b, appears in the region 0.8–0.17 V with $E_p = 0.5$ V. In this region, the oxide layer becomes reduced and gives room for the electrode surface to acquire a large quantity of active oxygen atoms from the solution. These atoms then oxidise the weakly bonded residual CHO species that remain at the end of the forward sweep as well as freshly chemisorbed methanol molecules and give rise to the O^b peak.

On increasing the methanol concentration to 3 M, the electrode tries to oxidise the organic species completely but it does not quite succeed in doing so. The formation of the less active PtO is not completely suppressed in this case. At $E > 1.05$ V, some PtO is formed during the forward sweep and it reduces the rate of oxidation of the organic species. This accounts for the current-declining portion of the CV
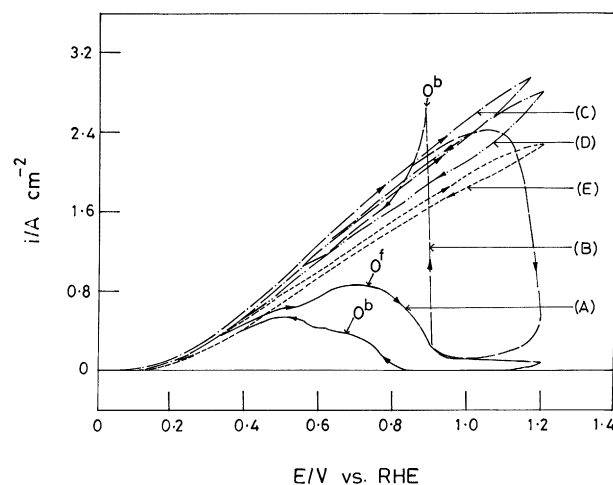

Fig. 1. CVs for the MOR on porous unsupported Pt electrodes in 6 M KOH solutions that contain varying concentrations of CH$_3$OH: (A) 1 M; (B) 3 M; (C) 6 M; (D) 9 M; (E) 11 M.

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[1] In the case of the Pt–Ru alloy electrodes, the active oxygen atoms are supplied via some of the Pt and some Ru sites.

curve. During the backward sweep, the PtO is reduced in the potential region 1.2–0.9 V and the remaining CHO species are immediately oxidised. Following this, freshly chemisorbed methanol molecules are oxidised at $E < 0.8$ V.

On increasing further the methanol concentration to 6 M, it appears that complete oxidation of chemisorbed organic species takes place without permitting any CHO species to remain on the electrode surface and the peaks O^f and O^b are not observed [30]. Instead, a featureless polarisation curve is obtained (3 A cm^{-2} at 1.17 V). The active oxygen atoms, provided by the porous network of the unsupported carbon catalytic electrodes, seem to be greatly efficient oxidisers. It is noteworthy that no previous work has discussed such featureless CV curves for the MOR.

For higher methanol concentrations viz. 9 and 11 M, the featureless polarisation curves are again noted. However, in these higher concentrations, relatively lower current densities are obtained.

On recording the CVs in 1 M KOH solutions containing varying concentrations of methanol (1, 3 and 6 M), small O^f and O^b peaks are observed for the 1 M KOH/1 M CH$_3$OH and 1 M KOH/3 M CH$_3$OH mixtures in the higher potential region. On increasing the methanol concentration to 6 M, the formation of these peaks is suppressed and the featureless polarisation curve is formed.

In the case of 11 M KOH with 1, 3, 6, 9, 11 and 13 M CH$_3$OH, the O^f and O^b peaks are formed in concentrations up to 9 M. Upon further increasing the methanol concentration (11 and 13 M), the featureless polarisation curves are obtained.

In the case of the porous unsupported Pt–Ru alloy electrodes, the active oxygen atoms are supplied by both Pt and Ru atoms, the ratio of supply being governed by the alloys' compositions. The anodic peaks O^f and O^b appear in the CVs in the 6 M KOH/1 M CH$_3$OH and 3 M CH$_3$OH mixtures. On raising the methanol concentration to 6 M, the featureless polarisation curves are obtained for all of the Pt–Ru compositions [31].

Fig. 2 presents the CVs recorded for the smooth Pt electrodes in 6 M KOH solutions that contain 1, 3, 6, 9, 11, 13, 15 and 18 M CH$_3$OH. For all of these mixture combinations, onset of the MOR takes place at 0.37 V, which is 190 mV more positive than for the porous unsupported Pt electrodes. The O^f and O^b peaks appear in all the CVs.

For the 6 M KOH/1 M CH$_3$OH mixture, the E_p values of the O^f and O^b peaks are 0.73 and 0.55 V, respectively. On gradually increasing the methanol concentration (1–18 M) in the solution, the positions of both the O^f and O^b peaks shift slightly in the positive direction. The current densities of the O^f peaks increase up to 13 M CH$_3$OH and on further increasing the methanol concentration (15 and 18 M), the current densities of the peaks decline.

On recording the CVs in 1 M KOH solutions containing varying concentrations of methanol (1, 3, 5, 7, 9 and 11 M), only featured curves are recorded. The 1 M KOH/9 M
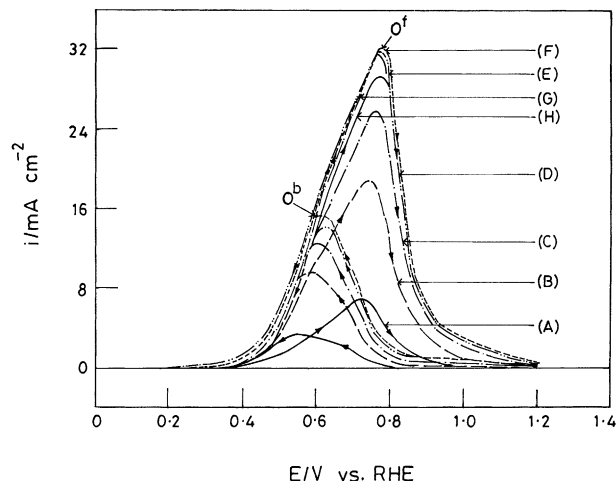

Fig. 2. CVs for the MOR on smooth Pt electrodes in 6 M KOH solutions that contain varying concentrations of CH$_3$OH: (A) 1 M; (B) 3 M; (C) 6 M; (D) 9 M; (E) 11 M; (F) 13 M; (G) 15 M; (H) 18 M.
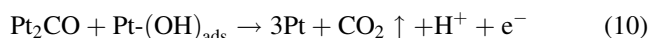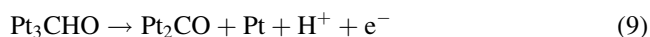
CH$_3$OH mixture has yielded the highest current density peak.

Similarly the O^f and O^b peaks have only been observed in the CVs recorded in highly concentrated (11 M) KOH solutions containing varying concentrations of methanol (1, 3, 6, 9 and 11 M).

From the observations of the appearance of the O^f and O^b peaks and higher MOR polarisations in all KOH/methanol mixtures, it can be inferred that the oxidation of the intermediate organic species (CHO)$_{ads}$ does not take place easily and completely on the smooth Pt electrodes. Population of the active sites that are present on the smooth electrodes are lower compared to those in the porous electrodes. Hence inadequate amounts of the active oxygen atoms may be extracted from the electrolyte on the smooth Pt electrodes to completely oxidise the (CHO)$_{ads}$ species in the lower potential region and these organic species remain as the "poisoning species" on the surface of the electrodes.

### 3.2. Cyclic voltammograms for oxidation of methanol on Pt and Pt–Ru alloy electrodes in acid solutions

The dehydrogenation of methanol molecules occurs in acid solutions via the reactions (1–4) and the (CHO)$_{ads}$ species are further oxidised as follows [32]:

$$Pt_3CHO \rightarrow Pt_2CO + Pt + H^+ + e^- \tag{9}$$

$$Pt_2CO + Pt\text{-}(OH)_{ads} \rightarrow 3Pt + CO_2 \uparrow + H^+ + e^- \tag{10}$$

The unreacted Pt$_2$CO may also rearrange to give a linearly bonded CO species which acts as poison

$$Pt_2CO \Leftrightarrow Pt=C=O + Pt \tag{11}$$

On reversing the sweep, the linear species Pt=C=O are oxidised according to the following reactions:
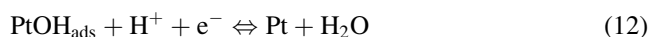
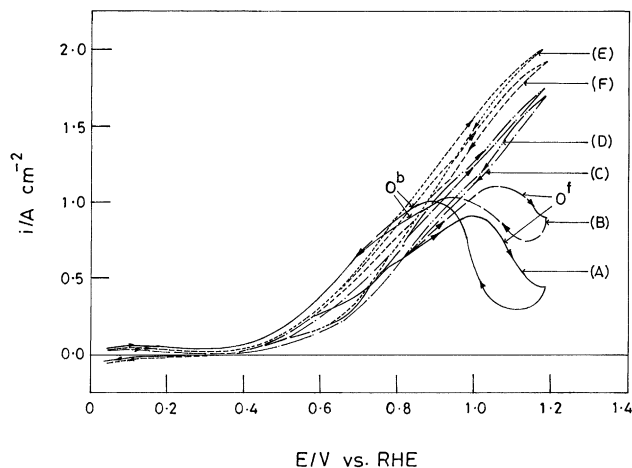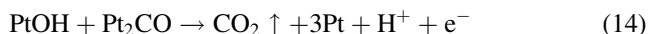$$PtOH_{ads} + H^+ + e^- \Leftrightarrow Pt + H_2O \tag{12}$$

Fig. 3. CVs for the MOR on porous unsupported Pt electrodes in 2.5 M H_2SO_4 solutions that contain varying concentrations of CH_3OH: (A) 1 M; (B) 2.5 M; (C) 4 M; (D) 6 M; (E) 8 M; (F) 10 M.

$$Pt=C=O + Pt \rightarrow Pt_2CO \qquad (13)$$

$$PtOH + Pt_2CO \rightarrow CO_2 \uparrow + 3Pt + H^+ + e^- \qquad (14)$$

The active oxygen atoms may also be provided by the Ru atoms during the occurrence of the reactions of Eqs. (10) and (11) while employing the Pt–Ru electrodes.

The CVs recorded for the unsupported porous Pt electrode in 2.5 M H_2SO_4 solutions that contain 1, 2.5, 4, 6, 8 and 10 M methanol are shown in Fig. 3. For the 2.5 M H_2SO_4/1 M CH_3OH mixture, the MOR begins at 0.06 V, and after the initial anodic reactions of Eqs. (1)–(4) have taken place at potentials below 0.44 V, the peak O^f appears at potential 150 mV more positive than that observed in alkaline solutions. The E_p of O^f is 1 V.

The reactions of Eqs. (9) and (10) occur in the potential region of the O^f peak. The appearance of the O^b peak ($E_p = 0.85$ V) during the backward sweep suggests that all the Pt_2CO species are not reacting completely during the forward sweep; some Pt_2CO species remain unreacted and they rearrange themselves into a linear Pt=C=O structure. The peak O^b is associated with the removal of the linear species Pt=C=O according to the reactions of the Eqs. (12)–(14) [26].

When the methanol concentration is raised to 2.5 M, small O^f and O^b peaks are observed at $E > 0.8$ V. On further raising the methanol concentration (up to 10 M), the featureless CV curves are observed [27]. It is apparent that on raising the methanol concentration above 2.5 M, all the linearly bonded poisoning PtCO species are completely oxidised by the active oxygen atoms supplied by the porous network of the unsupported catalytic electrodes. The current densities of these CV curves increase on adding further quantity of methanol (4–8 M). On increasing the methanol concentration above 8 M, the current densities of the peaks decline.

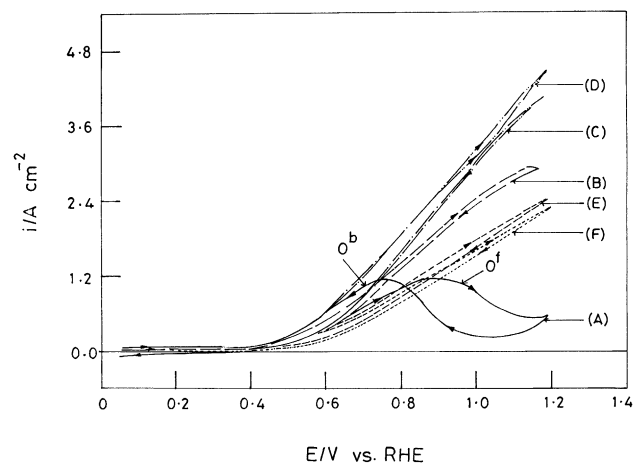In the case of 1 M H_2SO_4 solutions with varying concentrations of methanol (1, 2, 4, 6, 8 and 10 M), the O^f and

Fig. 4. CVs for the MOR on porous unsupported Pt–Ru (7:3) electrodes in 2.5 M H_2SO_4 solutions that contain varying concentrations of CH_3OH: (A) 1 M; (B) 2.5 M; (C) 4 M; (D) 6 M; (E) 8 M; (F) 10 M.

O^b peaks appear only in the 1 M H_2SO_4/1 M CH_3OH mixture. On increasing the methanol concentration, the featureless CV curves are obtained. The current densities of the peaks increase only up to 3 M, and above this concentration, the current density falls down.

In higher concentrations of acidic solutions (up to 5 M H_2SO_4), only the featureless CV curves are obtained.

The porous unsupported Pt–Ru alloy electrodes of all the compositions show featureless polarisation curves in all acidic solutions except in 2.5 M H_2SO_4/1 M CH_3OH and 1 M H_2SO_4/1 M CH_3OH [31]. The CVs recorded for the best performing 7:3 electrode in 2.5 M H_2SO_4 solutions with varying concentrations of methanol (1, 2.5, 4, 6, 8 and 10 M) are shown in Fig. 4.

Fig. 5 shows the CVs for the smooth Pt electrodes in 2.5 M H_2SO_4 solutions containing varying concentrations of methanol 1, 3, 6, 8 and 10 M CH_3OH. During the forward sweep, the MOR begins at 0.6 V in all these mixtures, which
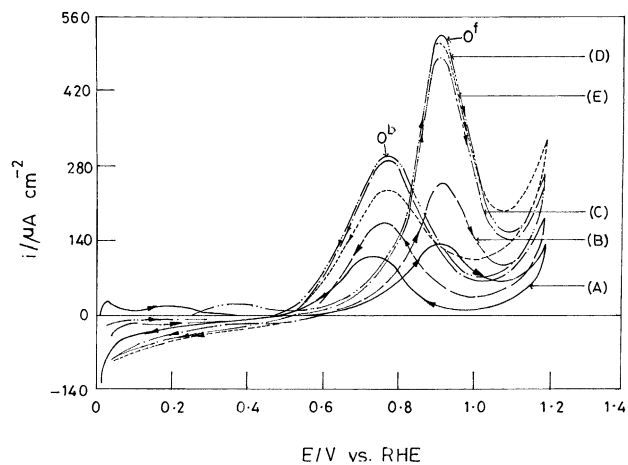

Fig. 5. CVs for the MOR on smooth Pt electrodes in 2.5 M H_2SO_4 solutions that contain varying concentrations of CH_3OH: (A) 1 M; (B) 3 M; (C) 6 M; (D) 8 M; (E) 10 M.

is 250 mV more positive than with the porous Pt electrodes. The maximum current density for the O^f peak is observed for the 2.5 M H_2SO_4/8 M CH_3OH mixture and on further increasing the methanol concentration to 10 M, the current density decreases.

In the case of 1 M H_2SO_4 with varying concentrations of methanol (1, 3 and 6 M), all the CVs show O^f and O^b peaks. The 1 M H_2SO_4/1 M CH_3OH mixture has yielded the highest current density among these combinations. On raising the methanol concentration beyond 1 M, the current density of the O^f peak declines.

It can be surmised from the investigation on the smooth Pt electrodes in acid solutions that the oxidation of the poisoning =C=O does not take place completely on these electrodes.

3.3. Cyclic voltammograms for the oxidation of methanol on Pd electrodes in alkaline solutions

The MOR on the Pd electrodes in alkaline solutions proceeds via chemisorptive dissociation pathways and the strongly held intermediate organic species is bridge bonded Pd_2CO [15].

Fig. 6 shows the CVs for the porous unsupported Pd electrodes in 6 M KOH solutions that contain 1, 3, 5, 6, 8 and 9 M CH_3OH. The O^f and O^b peaks are observed up to 5 M CH_3OH; probably the process of formation of less active PdO dominate in these mixtures [33].

On increasing further the methanol concentration to 6 M, the O^f and O^b peaks are not observed, and the featureless CV curve is observed. In this mixture, dissociatively chemisorbed methanol and OH_{ads} cover the Pd sites in such a way that the complete oxidation of chemisorbed organic species take place without permitting any CO species to remain on the electrode surface [34]. On raising the methanol concen-
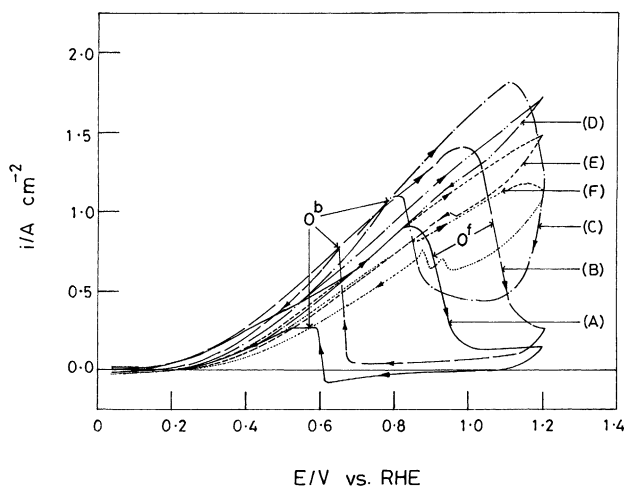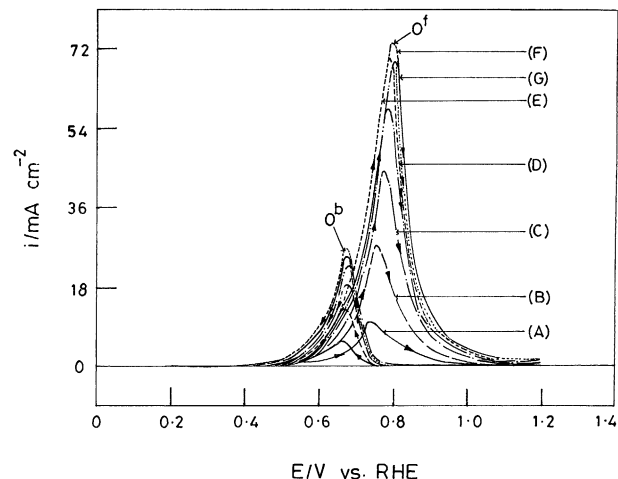

Fig. 7. CVs for the MOR on smooth Pd electrodes in 6 M KOH solutions that contain varying concentrations of CH_3OH: (A) 1 M; (B) 3 M; (C) 6 M; (D) 9 M; (E) 11 M; (F) 13 M; (G) 15 M.

tration above 6 M (i.e. 8 and 9 M), again small O^f and O^b peaks appear in the CVs and, also, the current densities of these peaks decrease. This suggests that the active oxygen atoms extracted by the Pd electrodes from 6 M KOH solution are not able to oxidise completely the bridge bonded CO species that arises from the excess methanol.

The CVs recorded for 1 and 11 M KOH solutions containing varying concentrations of methanol show only O^f and O^b peaks.

Fig. 7 shows the CVs recorded for the smooth Pd electrodes in 6 M KOH solutions that contain 1, 3, 6, 9, 11, 13 and 15 M CH_3OH. All these mixtures show O^f and O^b peaks. The current densities of the peaks increase up to the concentration of 13 M. In 15 M, the current density is lower.

On lowering the KOH concentration to 1 M and on adding various amounts of methanol (1, 3, 6 and 9 M) the positions of the O^f and O^b peaks are shifted in the positive direction.

In the case of 11 M KOH solutions with 1, 3, 6, 9 and 11 M CH_3OH, the positions of the O^f and O^b peaks are slightly shifted in the negative side suggesting that the MOR may take place somewhat more easily on increasing the KOH concentration in the electrolyte/methanol mixtures.

It is learnt from these investigations that on the smooth Pd electrodes, the intermediate bridge bonded >CO species does not become completely oxidised in the KOH/methanol mixtures of all concentrations and they remain as poisoning species on the surface of the electrodes.

The Pd electrodes corrode in acid solutions and hence they do not catalyse the MOR [27,34].

4. Conclusions

From the extensive cyclic voltammetric investigations of the MOR on the porous unsupported Pd, Pt and Pt–Ru alloy

Fig. 6. CVs for the MOR on porous unsupported Pd electrodes in 6 M KOH solutions that contain varying concentrations of CH_3OH: (A) 1 M; (B) 3 M; (C) 5 M; (D) 6 M; (E) 8 M; (F) 9 M.

electrodes of compositions 9:1, 7:3 and 5:5 and the smooth Pt and Pd electrodes in different aqueous electrolytes of high and low pH, the following conclusions have been drawn:

The CVs recorded for the porous unsupported Pd, Pt and Pt–Ru alloy electrodes in some electrolyte/methanol mixtures exhibit featureless polarisation curves. If O^f and O^b peaks do not appear in the CVs, then it can be inferred that the poisoning species do not arise under such circumstances and that the intermediate organic species are rapidly oxidised by the active oxygen atoms provided by the porous network of the catalytic electrodes.

The anodic peaks O^f and O^b appear in the CVs in some electrolyte/methanol mixtures. Appearance of these peaks in the CVs mean that both the methanol and the active oxygen atoms do not meet at the electrodes surface in a suitable ratio and the complete oxidation of chemisorbed organic species does not take place. The strongly bonded organic species persist as the "poisoning species" on the surface of the electrodes during the forward sweep.

On the smooth Pt and Pd electrodes where a porous structure does not exist, the poisoning species seem to persist in any electrolyte/methanol combination. The O^f and O^b peaks appear in all the CVs. On the smooth electrodes, the number of active sites are lower. Adsorption of the active oxygen atoms and methanol takes place in ratios such that the complete oxidation of the intermediate organic species do not take place.

It is concluded that it is possible to prevent the formation of the poisoning species provided unsupported porous structured methanol anodes are chosen and a suitable combination of electrolyte/methanol is employed. In situ IR spectroscopic investigations would be desirable to further corroborate these findings.

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