

Figure 5 – "Plotter Window" showing a cyclic voltammogram for an ECE anodic process recorded at (a) 200 mV/s and (b) 500 mV/s.

At the "Potentiostat Window" we can choose the adequate potential range and the scan rate (200 mV/s), turn the cell on and start the cycle. In the "Plotter Window" we can see the voltammogram appearing and notice that the cathodic counterpart for the first wave is smaller than the anodic peak, due to the chemical reaction (see figure 5a).

A second oxidation wave is observed, corresponding to the oxidation of the product of the chemical reaction. Unlike the first wave this peak is mainly reversible. Looking at the same system at a higher scan rate, as shown in picture 5b, we can see that the height of the first wave increases, due to the increase in scan rate. At the same time the intensity of the second wave decreases, since the time interval for the chemical reaction to proceed has decreased.

Stored voltammograms can also be saved to disk for future reference and to import to other applications, such as spreadsheets.

This programme is available, upon request, to anyone interested in using it.

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ELECTRO-OXIDATION OF METHANOL ON POROUS UNSUPPORTED Pt-Ru ALLOY ELECTRODES IN STRONG ALKALI AND STRONG ACID

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Abstract

Porous unsupported Pt-Ru single phase alloy electrodes with different compositions viz., 9:1, 7:3 and 5:5 are prepared by NaBH₄ reduction method at room temperature. The reactivity of these alloy electrodes towards the methanol oxidation reaction (MOR) is systematically investigated in different electrolytes of high and low pH with various quantities of methanol at room temperature by using cyclic voltammetric (CV) and steady-state galvanostatic polarisation techniques. Various electrochemical processes occurring in different potential regions are discussed. The highest activity of the MOR is obtained for a 7:3 electrode in 2.5 M $H_2SO_4 / 2.5$ M CH₃OH and in 6 M KOH / 6 M CH₃OH mixtures, respectively. It is concluded that by choosing the proper ratio of OH ions and CH₃OH in solution, it is possible to remove completely the intermediate organic species and/or poisonous species that retard the MOR.

Key words: unsupported Pt-Ru electrode, strong alkali, strong acid, MOR activity, intermediate organic poisonous species.

Introduction

While Pt-Ru binary alloy electrodes have been extensively studied for methanol oxidation reaction (MOR) in acid solutions [1-9], very little work has been done in alkaline solutions [10,11]. And that too, these prior studies have focussed mainly on high surface area carbon supported Pt-Ru alloys [10,11] and unsupported arc melted smooth Pt-Ru alloys [6]. The MOR on porous unsupported Pt-Ru alloy in alkaline as well as in acid solutions have not yet been investigated systematically, despite the fact that these alloy electrodes might provide the best activity for the MOR [2,7]. Very recently, Chu and Gilman [7], have prepared unsupported Pt-Ru alloy electrodes and investigated the MOR over a range of temperatures (between 25 and 60° C) by using only 0.5 M H₂SO₄ with 1 M CH₃OH; they have concluded that the Pt-Ru (5:5) provides the highest activity for the MOR.

In this paper, the activity of porous unsupported Pt-Ru single phase alloys with different compositions viz., 9:1, 7:3 and 5:5 is reported. The reactivity of these alloy electrodes towards the MOR was evaluated in different electrolytes of high and low pH that contain various quantities of methanol at room temperature (~25°C) by using the cyclic voltammetric (CV) and steady-state polarisation techniques. It is inferred that the highest activity for the MOR is obtained for the 7:3 alloy electrode in 2.5 M H₂SO₄ / 2.5 M CH₃OH mixture and in 6 M KOH / 6 M CH₃OH mixture at lower overpotentials. The CVs recorded for all the electrodes, exhibit anodic featureless curves for almost all equimolar electrolyte / CH₃OH mixtures and this could be due to complete oxidative removal of poisonous organic species chemisorbed on Pt sites.

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Experimental

The Pt-Ru alloy powders of different atomic compositions 9:1, 7:3 and 5:5 were prepared by reducing the required stoichiometric amount of 1 % H_2PtCl_4 solution and 1 % $RuCl_3 \times H_2O$ solution with 5% NaBH₄ solution and by washing the precipitate repeatedly with pure water until it reaches neutral pH. The powders were then dried in an air-oven at 110°C. The single phase formation of these alloys was characterised by XRD analysis. The alloy electrodes were prepared by spreading the alloy powders over a Pt mesh and pressing at room temperature. The real surface area of the electrode was not determined in the present study and only the geometrical area was utilised to calculate the current densities. A scanning electron microscopic examination of these electrodes indicated uniform inter-pore structure.

A conventional, three electrodes electrochemical cell with Hg/HgO/OH and Hg/Hg₂Cl₂/Cl reference electrodes for alkaline and acid electrolyte solutions, respectively and a high surface area Pt expanded metal as counter electrode were employed. N₂ gas was purged for 2 hours prior to the measurement. All CVs, were recorded at a scan rate of 25 mV s⁻¹. All potential values of CVs and steady-state polarisations were converted with respect to the reversible hydrogen electrode (RHE). CVs were recorded with a BAS model 100 B/W potentiostat interfaced to an IBM PC-XT microcomputer with a National Instruments IEEE-488 General Purpose Interface Card (GPIB). The BAS electrochemistry software was used to derive the measurements, process the data and display all the CV curves.

Results and Discussion

Cyclic Voltammograms for Pt-Ru alloy electrodes in alkaline solutions

The CVs of the Pt-Ru alloy electrodes in alkaline solution demonstrate that the atomic composition contributes to modifications in the hydrogen adsorption/desorption characteristics of Pt. Fig. 1 shows the CVs recorded for the unsupported Pt-Ru alloy electrodes in high pH (6 M KOH) solution. In the CV of 9:1 electrode, three hydrogen desorption peaks occur in the region 0 to 0.44 V. The surface oxide layer commences at 0.53 V, during the forward sweep. Upon reversing the scan, a broad oxide reduction peak with Ep = 0.71 V, followed by three hydrogen adsorption peaks in the region 0.43 to 0 V are observed.

In the case of 7:3 electrode, only two hydrogen desorption peaks are observed in the initial hydrogen adsorption region. Noticeably, adsorption of oxygen atoms (OH and O atoms) occur in the early potential i.e., at about 0.33 V. Also, an increased double-layer current is observed probably due to absorption of increased quantity of the oxygen species adsorption on Ru atoms.

When the percentage of Ru in the alloy is increased to 50%, the resolved current-potential profile becomes similar to that obtained for an elemental Ru electrode [12,13]. Ru has a greater affinity for oxygen and it tends to form irreversible thick RuO₂ oxide layer on its surface at potentials higher than 0.9 V. During cycling, this surface RuO₂ coated Ru electrodes are known to exhibit three quasi reversible peaks that are attributable to changes in the Ru valence states (Ru²⁺/Ru³⁺, Ru³⁺/Ru⁴⁺, Ru⁴⁺/Ru⁵⁺). The CV recorded for a well cycled 5:5 electrode in the present study presents three quasi reversible peaks which suggest that the irreversible RuO₂ coating is formed on the 5:5 electrode.



Potential / V vs RHE

Figure 1. CVs for the 9:1 (——), 7:3 (——) and 5:5 (----) electrodes in 6 M KOH solution at room temperature.

On lowering the concentration of the electrolyte (1 M KOH), the potentials for the onset of surface oxide layer formation and the reduction of oxides are shifted positively for the 9:1 and 7:3 alloy electrodes.

Cyclic voltammograms for Pt-Ru alloy electrodes in acid solutions

Fig. 2 shows the CVs recorded for the unsupported Pt-Ru alloy electrodes in strong acid solution (2.5 M H_2SO_4). For the 9:1 electrode, two hydrogen desorption peaks occur in the region ca. 0.05 to 0.32 V, and the monolayer surface oxide forms at E > 0.85 V during the forward sweep. On reversing the sweep, a broad oxide reduction peak (Ep = 0.80 V) is observed that is followed by a double-layer and two hydrogen adsorption peaks in the region 0.30 to 0.04 V.

In the case of 7:3 electrode also, two hydrogen desorption peaks are observed in the hydrogen region. The monolayer surface oxide form at E > 0.72 V during the forward sweep. This oxide is reduced in the region 1.10 to 0.68 V and the hydrogen adsorption reactions occur in the region 0.33 to 0.02 V during the backward sweep.

On increasing the Ru concentration in the alloy to 50 atomic % the rate of hydrogen adsorption/desorption on/from the electrode increases [14]; only one hydrogen desorption peak appears and, moreover, this peak becomes overlapped with the oxygen species adsorption profile at substantially negative potential ~ 0.34 V. The oxygen species adsorption on Ru at potential as low as 0.2 V has been reported by Ticianelli *et al* [15] in their ellipsometric studies on a 5:5 alloy electrode in 0.5 M H₂SO₄ solution. At E > 0.62 V, higher oxides of Pt and Ru are formed [16,17].



Potential / V vs RHE

Figure 2. CVs for the 9:1 (_____), and 7:3 (____) and 5:5 (----) electrodes in 2.5 M H₂SO₄ solution at room temperature.

On lowering the acid concentration (1 M H_2SO_4 solution), a cathodic shift in potentials for the reduction of surface oxides is noticed for all the compositions of Pt-Ru electrodes.

On increasing the concentration of acid solution (5 M H_2SO_4), relatively low intensive hydrogen and oxygen adsorption/desorption peaks are observed. Also, a slight cathodic shift in potentials for the reduction of surface oxides is noted.

Cyclic voltammograms for methanol oxidation on Pt-Ru alloy electrode in alkaline solutions

The mechanistic pathways proposed for the Pt electrodes in alkaline solution could be extended to the Pt-Ru alloy electrodes in alkaline solutions [11, 18, 19];

The discharge of water molecules takes place on all Ru atoms and some Pt atoms at E > ca. 0.3 V,

(1)

(2)

 $M + OH^- \iff M-(OH)_{ads} + e^-$

where M represents a Pt and/or Ru site.

The dehydrogenation of methanol molecules occurs on Pt sites in the region 0 to 0.26 V :

$$2Pt + CH_3OH \iff PtH + Pt-(CH_3O)_{ads}$$

$PtH + M-(OH)_{ads} \longrightarrow$	$Pt + M + H_2O$	(3)
Pt-(CH ₃ O) _{ads} + M-(OH) _{ads}	$\longrightarrow Pt_2-(CH_2O)_{ads}+H_2O$	(4)

$$Pt_{2}-(CH_{2}O)_{ads} + M-(OH)_{ads} \longrightarrow Pt_{2}-(CHO)_{ads} + H_{2}O$$
(5)

The organic products that appear on the R.H.S of the reactions (4) and (5) are adsorbed on adjacent Pt atoms that are available in the M sites.

Over the potential region 0.3 to 1.18 V, the CHO species are burnt off by active oxygen atoms.

$$Pt_{3}-(CHO)_{ads} + 3M-(OH)_{ads} \longrightarrow 3Pt + 3M + CO_{2} \uparrow + 2H_{2}O$$
(6)

The strength of the bonding of $(CHO)_{ads}$ on the surface determines the entire rate of the reaction. Generally, the chemisorptive bonding of CHO on Pt in alkali is weak, thus their oxidation by active oxygen atoms adsorbed on Ru and some Pt atoms take place without much difficulty, i.e., without irreversibly blocking the electrode active sites.



Potential / V vs RHE

Figure 3. CVs for the MOR on the 9:1 (------), 7:3 (------) and 5:5 (------) electrodes in 6 M KOH / 1 M CH₃OH solution at room temperature.

The CVs recorded for the alloys of different compositions in 6 M KOH / 1 M CH₃OH (Fig. 3) show up two anodic peaks O^{f} and O^{b} during the forward and the backward sweeps, respectively. The reactions (1) to (5) occur in the early potential region of the O^{f} peak and the step (6) occur in the region 0.15 V to 0.9 V. In this mixture, the concentration of OH ions is much greater than the concentration of organic species and hence monolayer oxide is easily formed in

the higher potential region during the forward sweep. This oxide layer blocks the supply of active oxygen atoms and reduce the rate of oxidation of the organic species. This could account for the current declining portion of O^f peak. However, during the backward sweep the oxide layer becomes reduced and gives to the electrode surface an opportunity to acquire a large quantity of active oxygen atoms from the solution. These atoms, then, burn off of 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.



Potential / V vs RHE

When the electrolyte contains equimolar mixtures of KOH and CH₃OH, as soon as the methanol molecules are chemisorptively dissociated in the early potential, required amount of active oxygen atoms are rapidly supplied by the solution to burn off of the weakly bonded organic species. This may account for the occurrence of featureless curves (i.e., curves without the appearance of O^{f} and O^{b} peaks) in the CVs of Figs. 4 & 5 recorded in 6 M KOH / 6 M CH₃OH and 1 M KOH / 1 M CH₃OH mixtures. The oscillations observed in the high potential region of the CV in Fig. 5 are due to the disturbances of the potential on the electrode caused by the release of CO₂ gas.





Figure 5. CVs for the MOR on the 9:1 (-----), 7:3 (-----) and 5:5 (-----) electrodes in 1 M KOH / 1 M CH₃OH solution at room temperatures.

The 5:5 composition has consistently shown a lesser activity for the MOR than the 7:3 composition for each of the alkali/methanol mixtures. This may be attributed to the formation of electrocatalytically inactive surface oxide film.

Cyclic voltammograms for methanol oxidation on Pt-Ru electrode in acid solutions

Fig. 6 shows the CVs for the unsupported 9:1, 7:3 and 5:5 electrodes in the 2.5 M $H_2SO_4/$ 2.5 M CH₃OH mixture. All the CVs do not show up O^f and O^b peaks. In the case of lower concentrated equimolar mixture (1 M $H_2SO_4/$ 1 M CH₃OH), totally featureless curves are not observed (see Fig. 7). Instead, i –V profiles with anodic oxidation peaks, O^f and O^b occurring at E > 0.8 V, are observed for all the electrodes.

The pathways for the dissociative chemisorption of methanol in acid solutions occur via the reactions (1) to (5). The (CHO)_{ads} species in acid solutions are further oxidised as follows [2,3,6,7,20,21];

$$Pt_3CHO \longrightarrow Pt_2CO + Pt + H^+ + e^-$$

(7)

It appears that in 2.5 M H_2SO_4 / 2.5 M CH₃OH equimolar mixture, all the organic species (Pt₂CO) become completely oxidised by the OH_{ads} species covering the Ru and Pt sites over the 0.37 to 1.15 V range

$$Pt_2CO + M-(OH)_{ads} \longrightarrow 2Pt + M + CO_2 + H^+ + e^-$$
(8)

The CVs recorded after altering the methanol concentration in 2.5 M H₂SO₄ solution have indicated that the activity of the MOR decreases both when increasing (4 M) and decreasing (1 M) methanol concentration. The CVs recorded in 2.5 M H₂SO₄ / 4 M CH₃OH do not exhibit O^f and O^b peaks and those recorded in 2.5 M H₂SO₄ / 1 M CH₃OH only exhibits these peaks.



Potential / V vs RHE

Figure 6. CVs for the MOR on the 9:1 (\longrightarrow), 7:3 (\longrightarrow) and 5:5 (-----) electrodes in 2.5 M H₂SO₄/2.5 M CH₃OH solution at room temperature.

The CVs recorded in various other acid/methanol mixtures such as $1 \text{ M H}_2\text{SO}_4 / 1 \text{ M}$ CH₃OH, $1 \text{ M}_2\text{SO}_4 / 0.5 \text{ M}$ CH₃OH have shown that the active oxygen atoms supplied by 2.5 M H₂SO₄ electrolyte possesses the highest strength. They are not only capable of burning off of the organic residual species completely; they are also capable of yielding highest activity for the MOR at a given electrode.



Potential / V vs RHE

Figure 7. CVs for the MOR on the 9:1 (-----), 7:3 (-----) and 5:5 (-----) electrodes in $1 \text{ M H}_2\text{SO}_4/1 \text{ M CH}_3\text{OH}$ solution at room temperature.

The CVs recorded in acid solutions of higher concentrations 5 M $H_2SO_4 / 5$ M CH₃OH and 5 M $H_2SO_4 / 2.5$ M CH₃OH do not show up O^f and O^b peaks. But the i_{max} values at E = 1.2 V (the maximum MOR oxidation current recorded in the CV) were lesser than those observed for the 2.5 M H₂SO₄ / 2.5 M CH₃OH mixture. The i_{max} values at E = 1.2 V for the different mixtures of electrolytes are shown in Table 1.

Table 1. i_{max} values at $E = 1$.	2 V at	scan rate 25 mV s	¹ in different	mixtures of electrolytes
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	Pt – Ru Electrode	i _{max} , A cm ⁻²				
SI.	Compositions	2.5 M H ₂ SO ₄ /	5 M H ₂ SO ₄ /	5 M H ₂ SO ₄ /		
INO.	1	2.5 M CH ₃ OH	2.5 M CH ₃ OH	5 M CH ₃ OH		
1	9:1	2.10	1.62	1.33		
2	7:3	4.90	1.56	2.60		
3	5:5	3.50	3.00	2.60		

These results indicate that on increasing the acid concentration above 2.5 M, the electroactivity decreases.

The occurrence of O^{f} and O^{b} peaks of higher magnitude in the 2.5 M H₂SO₄/1 M CH₃OH mixture are probably due to the fact that the Pt₂CO species are not completely oxidised during the forward sweep as the formation of monolayer oxides in the higher potential region may block the

supply of active oxygen atoms. Subsequently, the Pt₂CO species rearrange themselves to form linearly bonded species which act as poison.

(9)

 $Pt_2CO \iff Pt=C=O + Pt$

On reversing the sweep in 2.5 M H_2SO_4 / 1 M CH₃OH these poisonous species undergo oxidation and form O^b peak according to the reactions (10) to (12)

Pt-OHada	$+ H^{+} +$	e	$Pt + H_2O$	(10
PI-OHade	+ H +	e	$P_1 + \Pi_2 O$	(1)

 $Pt=C=0 + Pt \longrightarrow Pt_2CO$ (11)

$$Pt_2CO + M_{-}(OH)_{ads} \longrightarrow 2Pt + M + CO_2^{\uparrow} + H^+ + e^-$$
(12)

A close comparison of the activity for the MOR of the 5:5 composition with that of the 7:3 composition reveals out the fact that the activity of the former electrode is always lesser than the latter in all the acid/methanol mixtures. It may be speculated that the strength of active oxygen atoms that are extracted by the 5:5 composition for burning of the organic residues is weaker than the oxygen atoms extracted by the 7:3 composition in acid solutions.

Steady-state polarisation data for the unsupported Pt-Ru electrodes

Steady-state polarisation curves for the electrodes 9:1, 7:3 and 5:5 in various electrolyte/methanol mixtures are shown in Fig. 8a and 8b. These results clearly demonstrate that the highest performance of the MOR can be obtained with 7:3 electrode composition ($i_L = 3.2 \text{ A} \text{ cm}^{-2}$ at $\eta = 0.7 \text{ V}$) in the mixture 2.5 M H₂SO₄ / 2.5 M CH₃OH. Nevertheless, for the same electrode, higher activity is noted in the lower potential region in 6 M KOH / 6 M CH₃OH mixture ($i = 1.2 \text{ A} \text{ cm}^{-2}$) when compared to 2.5 M H₂SO₄ / 2.5 M CH₃OH mixture ($i = 0.2 \text{ A} \text{ cm}^{-2}$) at $\eta = 0.4 \text{ V}$. For all the compositions studied, Pt-Ru (7:3) yields the best MOR performance both in higher concentrated alkaline and acid solutions.





Figure 8. The MOR polarisation curves for the unsupported Pt-Ru electrodes. (a) In different concentrated KOH solutions that contain different quantities of methanol. 6 M KOH / 6 M CH₃OH: (\oplus — \oplus) 9:1, (\Box — \Box) 7:3 and (\diamond — \diamond) 5:5, 1 M KOH / 1 M CH₃OH: (\blacksquare — \blacksquare) 9:1, (\Box — \Box) 7:3 and (\diamond — \diamond) 5:5; (b) in different concentrated H₂SO₄ solutions that contain different quantities of methanol. 5 M H₂SO₄ / 5 M CH₃OH : (\oplus — \oplus) 9:1, (+—++) 7:3, and (\diamond — \diamond) 5:5, 2.5 M H₂SO₄ / 2.5 M CH₃OH : (\Box — \Box) 7:3 and (Δ — Δ) 5:5.

Conclusions

The present study allows the following conclusions

1. Generally, in KOH / CH₃OH mixtures, the intermediate organic CHO species are weakly bonded on the Pt sites and are easily oxidised by the active oxygen atoms covering the Ru and some Pt sites. In the case of non-equimolar mixtures the concentration of OH ions becomes greater than the concentration of organic species and hence monolayer oxides are easily formed in the high potential regions during the forward sweep. This oxide layer blocks the supply of active oxygen atoms and reduce the rate of oxidation of organic species. This in turn lead to the formation of O^f peak. On reversing the sweep, the oxides become reduced and give room for the electrode surface to acquire a large quantity of active oxygen atoms that oxidise the residual CHO species, and causes the occurrence of the O^b peak. Contrarily, in the equimolar mixtures, the CHO species are oxidised completely by the appropriate amount of active oxygen atoms supplied by the solution and lead to the formation of featureless i-V curves i.e., curves without the appearance of O^f and O^b peaks in the CVs during the forward sweep.

2. In the H_2SO_4 / CH_3OH mixtures, the intermediate organic species Pt_2CO [19,22,23] is strongly bonded on the electrode surface. In non-equimolar and equimolar mixtures of lower concentrations, the Pt_2CO species are not completely burnt off during the forward sweep as the monolayer oxides block the supply of active oxygen atoms. They rearrange themselves into linearly bonded PtCO species and act as poison. During the backward sweep, the PtCO species undergo oxidation by taking active oxygen atoms from the electrolyte and shows the O^b peak. In equimolar mixtures of higher concentrations all the Pt_2CO species are completely oxidised by the active oxygen atoms covering the Ru and some Pt sites and therefore featureless i-V curves are obtained. The maximum MOR current is obtained in the 2.5 M H_2SO_4 / 2.5 M CH_3OH mixture, and it may be due to the fact that the active oxygen atoms formed in this solution possess the highest strength to burn off completely the Pt₂CO species.

3. The unsupported Pt-Ru(7:3) alloy electrode shows the overall highest MOR activity in a highly acidic 2.5 M H₂SO₄ / 2.5 M CH₃OH and highly alkaline 6 M KOH / 6M CH₃OH equimolar mixtures. The higher Ru containing alloys show a lesser activity for the MOR probably due to the formation of inactive RuO₂ film in alkali and to their ability to extract relatively weaker active oxygen atoms from the acid solutions.

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