Study In The Electrochemical Behavior Of Wo₃-Pt Coating: A Cyclic Voltammetric Approach

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Abstract: *Cyclic voltammetric studies were made on platinum in slightly alkaline solution (pH 8.) containing platonic chloride, sodium tungstate, dimethylsulphoxide, ethanolamine, sodium chloride and boric acid. Spectral U.V absorption studies indicate the complexation of Pt^{4+} with ethanolamine. The deposition of platinum involves a stepwise electron transfer mechanism involving platinum complex. Stripping voltammetric curves revealed the existence of intermediate species rich in tungsten. The concentration of ethanolamine affected the preferential deposit of W from the alloy. X-ray diffraction data further confirmed the phases of Pt_2W alloy.*
Key words: *Elecrodeposition, WO₃-Pt coating, cyclic voltammetry, U.V. absorption, XRD studies.*

I. Introduction

Tungsten forms hard alloys / composites with iron group metals, retaining some of its unique functional properties even at elevated temperatures [1, 2]. Electroplated Pt/WO_3 coatings are used as effective anode material for methanol fuel cell [3, 4]. These electrodes are free from de-activation by surface adsorption of reaction intermediates: CO, formaldehyde etc, which is likely to occur on platinum electrode surface [5].

Cyclic voltammetry is a versatile experimental technique used in the understanding of reaction pathways [6]. However, its use for alloy deposition process is found to be limited [7-9]. The objective of the present work is to analyze the plating bath solution used for deposition of WO_3-Pt alloys by cyclic voltammetric technique. The understanding of the electrochemical reduction of WO_3 from aqueous solution is still not well understood [10]. However, in this direction the deposition of Co-W [7, 8] and Cr-P [11] alloys has been successfully carried out using cyclic voltammetric technique. In our earlier paper the electroplating parameters are optimized to get quality cost effective and stable WO_3-Pt composite coating having good electrocatalytic for methanol oxidation [12]. Platinum microelectrode is used to decrease the effects of uncompensated IR drops, charging currents and enhance the mass transport process. These make it possible to work in the high bath concentration range associated with the plating process and obtain currents controlled by diffusion in the presence of convective mass transport [13].

The present communication reports a cyclic voltammetric study in understanding the electrochemical behavior of WO_3-Pt coating from plating bath solution containing ethanolamine (ETA) and dimethylsulphoxide (DMSO). The complex nature of the plating bath solution is being discussed by the UV spectral data. Free energy change for composite formation and phase present in the crystal lattice at various WO_4^{2-}, Pt compositions in the solution are given.

II. Experimental part

Apparatus

Experiments were carried out in an all glass single compartment cell of 50 ml capacity at 298K. A micro platinum electrode was used as a working electrode along with a large platinum foil and saturated calomel electrode as auxiliary and reference electrodes respectively. A luggin capillary was used to minimize the IR drop. The platinum electrodes were precleaned by a standard procedure [14]. Cyclic voltammograms were obtained at various scan rates (10-100 mV/sec) by monitoring the desired potential using a potentiostat (EG & G PAR 362) and only reproducible CV responses were recorded. Ultraviolet absorption studies were made using a spectrometer (Hitachi 150 – 20, Japan). An X-ray diffractometer [(Phillips, PW 1140/90) CuK$_{\alpha}$ radiation] was used to characterize the deposited alloy phases.

Reagents

All solutions were prepared by using double distilled water and AR grade chemicals. ETA after distillation was used to prepare a known concentration (0.01M < x < 0.1M) along with H$_2$PtCl$_6$ (0.01M), DMSO (0.05M), Na$_2$WO$_4$(0.025 < x < 0.025M), NaCl (10 g/L) and H$_3$BO$_3$ (20 g/L). The pH of the medium was maintained at 8.0 using H$_2$SO$_4$ / NaOH.

III.   Results and discussions

The experiments were conducted in the presence of NaCl used as a conducting salt. Hydrogen overpotential values on Pt and W were sufficiently low [15]. Under these conditions, the deposition of WO$_3$-Pt involves co-deposition of H$_2$ gas, which complicates the deposition process. In order to overcome this problem all the experiments
were carried out in the presence of H$_3$BO$_3$ (20 g/L) and NaCl (10 g/L) [16].

Electrochemical Behavior of H$_2$PtCl$_6$ - Influence of ETA and DMSO

When polarized from – 1000mV to +1500 mV in a solution containing H$_2$PtCl$_6$, NaCl and H$_3$BO$_3$ the forward scan exhibited an anodic peak at -670 mV (I) which predominates with sweep rate (Fig. 1). Another anodic peak at -400 mV (II) remained unchanged with sweep rate. In the reverse scan a cathodic peak (IV) appeared at -170 mV. Above 25 mV/s, another cathodic peak (III) appeared at -550 mV. Cathodic peak potentials (IV) became marked with sweep rate and varied with 30 mV /decade change of sweep rate.

Fig. 2 presents the cyclic voltammograms obtained in presence of DMSO. Forward scan exhibited an anodic peak (I) at -660 mV whose peak potentials were nearly constant. Above 50 mV/s, additional anodic peak (II) appeared at 750 mV. While reversing the scan cathodic peaks appeared at -180 mV (III) and at -470 (IV).Cathodic peak potential (IV) became significant with sweep.

When polarized from -1000 mV to+ 1500 mV in a solution containing DMSO and ETA, the forward scan exhibited an anodic peak (I) at -720 mV while reversing the scan a cathodic peak (III) appeared at -180 mV. Above 25 mV/s scan rate, an additional anodic peak appeared at 325 mV (II). At 100 mV/s, three anodic peaks were seen to be followed by a cathodic peak at 900 mV in the reverse scan. Anodic peak (I) potential became nobler with increase in sweep rate (Fig. 3).

Electrochemical behavior of WO4^{2-} - influence of DMSO

Fig. 4 represents the electrochemical behavior in tungstate solutions. Forward scan exhibited an anodic peak (I) at -600 mV whose peak potentials became nobler with sweep rate. While reversing the scan cathodic peaks appeared at 940 mV (II) and at -10 mV (III). The appearance of cathodic peak (II) may be due to the reduction of adsorbed oxygen followed by the reduction of multivalent tungstate ions. Cathodic peak potentials tend to become nobler with sweep rate.

Electrochemical behavior of WO4^{2-} and H$_2$PtCl$_6$ – effect of ETA concentration

In a solution containing H$_2$PtCl$_6$ and ETA in a molar concentration ratio 1:1 the forward scan exhibited and anodic peak at -810 mV whose peak potential was invariant with sweep rate (Fig. 5A). Reverse scan exhibited cathodic peaks at -190 mV and -620 mV. Cathodic peak potentials became nobler with sweep rate. At 50 mV/s, an additional cathodic peak appeared at 1050 mV due to the reduction of adsorbed oxygen.

Fig. 5B represents the cyclic voltammograms with H$_2$PtCl$_6$: ETA molar ratio 1:2. Forward scan exhibited anodic peak at -780 mV whose peak potential became nobler with sweep rate. While reversing the scan a cathodic peak appeared at -240 mV and whose peak potentials became nobler with sweep rate. Only at 25 and 50 mV/s scan rate and additional peak at -700mV appeared. The appearance of multiple peaks suggest the reduction of platonic and tungstate complexes.
when the H$_2$PtCl$_6$: ETA molar ratio was raised to 1:5 (Fig. 5C) the forward scan exhibited anodic peak at -600 mV whose peak potentials became nobler with sweep rate. Cathodic peak potentials were nearly invariant with sweep rate. Above 25 mV/s, additional cathodic peaks were seen at 475 mV and at 1125 mV. These cathodic peaks were attributed to the reduction of adsorbed oxygen and platinum complex respectively.

When the H$_2$PtCl$_6$: ETA molar ratio was to 1:10, forward scan exhibited and anodic peak at -790 mV (Fig. 5D). Anodic peak potentials became nobler with increase in sweep rate. Reverse scan exhibited a cathodic peak at -570 mV. A cathodic peak appeared at -220 mV which remained nearly constant with sweep rate.

Electrochemical behavior of H$_2$PtCl$_6^-$ - Influence and H$_2$PtCl$_6$ of WO4^{2-} concentration

When the WO$_4^{2-}$: H$_2$PtCl$_6$ molar ratio was 1: 1 the forward scan exhibited an anodic peak at -600 mV (Fig. 6B). Anodic peak potentials were nearly invariant. Above 25 mV/scan rate, cathodic peaks appeared at 1075 mV, 525 mV and at 50 mV. All the peaks suggest the reduction of adsorbed oxygen, tungsten and platinum complexes.

Fig. 6A presents the cyclic voltammograms obtained from solution of WO^{2-}_4 H_2PtCl_6 in a molar ratio of 2.5 :1. Forward scan exhibited an anodic peak at -790 mV. Reverse scan exhibited cathodic peaks at -220 mV and at -570 mV. Above 25 mV/s scan rate, additional anodic peaks appeared at 325 mV and cathodic peak at -570 mV disappeared. Cathodic peak potential at -220 mV did not vary with sweep rate.

When polarized from -1000 mV to + 1500mV, the forward scan exhibited an anodic peak at -770 mV. (Fig. 6C) in WO^{2-}_4 H_2PtCl_6 molar ratio of 5:1. On reversing the scan a cathodic peak was seen at -250 mV. Above 50 mV/s scan rate, additional anodic peaks were obtained at 379 mV. Cathodic peak potentials at -250 mV became active with sweep rate.

Fig. 6D presents the electrochemical characteristics obtained from WO^{2-}_4 and H_2PtCl_6 in a molar ratio of 10:1. Anodic peak was seen at -700 mV. While reversing the scan cathodic peaks appeared at -150 mV and at -575 mV. Cathodic peak potentials became significant with sweep rate.

UV absorption spectral studied

In supporting the results obtained by cyclic voltammetric studies of the plating bath solution for its complex nature, electronic spectra of the solution containing Pt^{4+}, WO^{2-}_4 with ETA have been recorded. Electronic absorption spectrum of solution containing Pt^{4+} and ETA exhibits a strong band at 38230 cm⁻¹ (Fig. 7) which is characteristics if $\Pi \rightarrow e^g$ transitions. This corresponds to first chloride to meal charge transfer band of the complex octahedral geometry [17]. Under the present experimental conditions, WO^{2-}_4 ions do not form complex with ETA.

IV.   Discussion

In ETA solution H_2PtCl_6, the observed cathodic peak at -180 mV (Fig. 3) is due to the reduction of platinic complexes. If the form $[PtL_2Cl_2]^{2-}$ where L is the ETA ligand, reduction occurs as

$$[PtL_2Cl_2]^{2-} + e \longrightarrow [PtCl_2]^- + 2L \qquad (1)$$

$$[PtCl_2]^- + e \longrightarrow Pt + 2Cl \qquad (2)$$
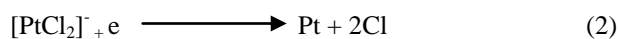
Many theories and mechanisms have been proposed for the deposition of reluctant metal like W in the presence of transition metals. However, some of these theories have no supportive experimental evidence. In the present case, the second cathodic peak current (Table 1) varied with ETA concentration, indicating that ETA aids the deposition of WO_3 Pt by complexing with Pt. Second cathodic peak current did not vary uniformly with tungstate concentration at all sweep rates. This suggests that tungsten may not form complex with ETA. This is in accordance with the UV spectral data (Fig. 7).

The dissolution of tungsten from the alloy was found to depend on the concentration of ETA present in solution. Presence of ETA favored dissolution, which is in support of the observed results i.e., increasing of anodic peak current and peak potential becoming nobler with ETA concentration (Table 2).

The reversible potential of W / WO^{2-}_4 ions in solution,

$$W + 8 OH^- \longrightarrow WO^{2-}_4 + 4 H_2O + 6e \qquad (3)$$
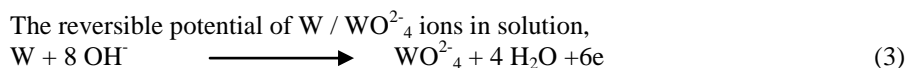
At pH 8.0 can be calculated from

$$E_{r,W} = E^o_W + (RT/6F) \ln [a_{WO4}^{2-}] \qquad I$$

Where E^o_W is the standard potential for tungsten and a_{WO4}^{2-} is the activity of tungstate ions.

$$E_{r,W-aloy} = E^o_W + (RT/6F) \ln [a_{WO4}^{2-}/ a_{W, alloy}] \qquad II$$

$E_{r,Walloy}$ is the reversible potential of W in the intermetallic compound (it is assumed that the surface energy contribution at the inter face of the alloy / electrolyte is negligible).
$a_{W, alloy}$ is the activity of the W in the intermetallic compound.

The difference,

$$-\Delta E = E_{r,W} - E_{r, W-alloy}$$
$$= (RT/6F) \ln [a_{WO4}^{2-}]$$
$$-6F\Delta E = (RT/6F) \ln [a_{WO4}^{2-}] = \Delta G \qquad III$$

As a first approximation, $\Delta G = -6F \Delta E$. The free energy of alloy formation can be calculated from the anodic peak intersection potential. Variation of ΔG with increase in W content indicates the formation of intermetallic phases (Table 3).

Table 4 gives the X-ray diffraction data obtained on the alloy deposit on copper obtained from various solutions. When the alloy contained more tungsten, more phases were seen. Full width at half maximum (FWHM) values of these deposits revealed higher crystallanity with particle diameter $\approx$ 8 nm (WO^{2-}_4 Pt = 10: 1 in the bath solution) obtained by Debye- Scherrer equation [19]. The appearances of oxides of platinum and W are due to the formation of air formed films on the deposit.

V.   Conclusions.

ETA preferentially forms complex with Pt^{4-} ions, which undergoes stepwise reduction to platinum. During deposition, the hydrogen evolution is reduced considerably by using H$_3$BO$_3$ and NaCl in the plating bath solution. The dissolution of W from the alloy favoring in the presence of appreciable concentration of ETA. The variation of negative free energy change with the change in W concentration indicates the formation of intermetallic phases rich in W, XRD pattern revealed the presence of varying phases.

VI.   Acknowledgement

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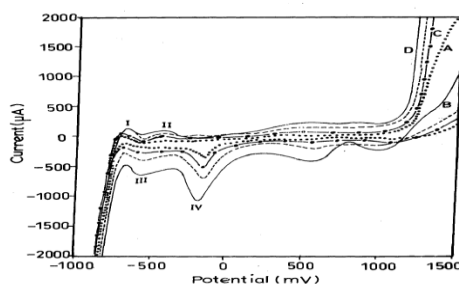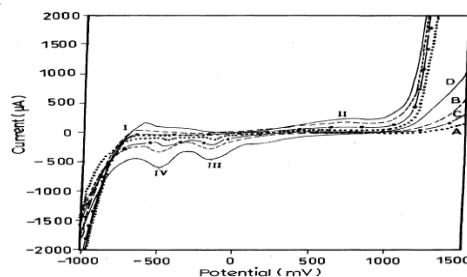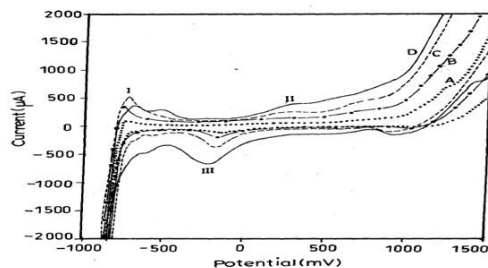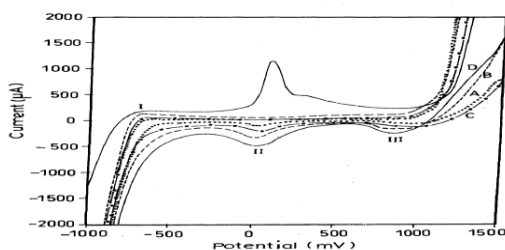
Figure 1

Figure 2
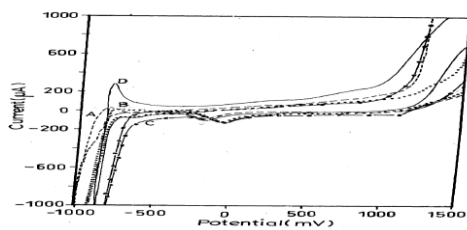
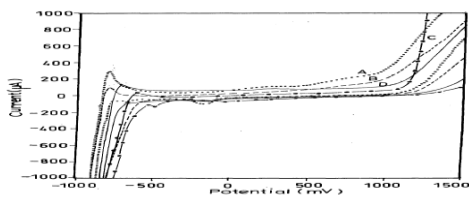**Figure 3**

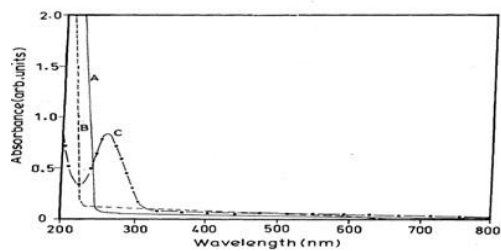**Figure 4**

Figure 5

Figure 6

Figure 7

Table 1. Parameters derived for the deposition of alloy form cyclic voltammograms – effect of ETA concentration.

Concentration of ETA (M)	Second cathodic peak current (µA)	
	(a)	(b)
10^{-2}	----	385
2×10^{-2}	344	535
5×10^{-2}	547	915
1×10^{-1}	2500	3515

(a) sweep rate at 50 mV/s (b) sweep rate 100 mV/s.

Table 2. Parameters derived for the dissolution of alloy form cyclic voltammogramsat 50 mV/s.

Concentration of ETA (M)	anodic peak Potential (MV)	anodic peak intersection potential (mV)
10^{-2}	-800	96
2×10^{-2}	-750	131
5×10^{-2}	-650	213
1×10^{-1}	-600	1500

Table 3. Parameters derived form cyclic voltammograms.

Solution Molar ratio (WO_4^{2-}-Pt)	anodic peak potential (MV)	anodic peak intersection potential (mV)	ΔG free energy change (kJ/mole)
1:0	-655	-750	--------
1:1	-700	-778	-7.5
5:1	-775	-833	-22.2
10:1	-800	-850	-26.8

Table 4. XRD data obtained *on WO₃-Pt (< 2% Pt) coatings

Solution composition Molar ratio (WO_4^{2-}: Pt)	2θ	STD ASTM #d (A⁰)	d (A⁰)	phase
	39.980	2.2555	2.2555	Pt_2W (101)
1:1	54.698	1.680	1.678	WO_3 (420)
	62.360	1.480	1.480	PTO (222)
	33.732	2.662	2.657	WO_3 (420)
5:1	40.110	2.248	2.248	Pt_2W (031)
	46.649	1.949	1.947	Pt_2W (130)
	62.500	1.480	1.486	PTO (222)
	23.668	3.761	3.759	WO_3 (200)
10:1	40.073	2.248	2.250	Pt_2W (031)
	45.925	1.949	1.949	Pt_2W (130)
	62.288	1.480	1.482	PTO (222)
	67.921	1.379	1.380	Pt_2W (132)
	82.088	1.176	1.174	Pt_2W (231)

*CuK_α

#Ref.18

Legends to figure

Figure 1. Cyclic voltammogramsobtained in solution (with 20 g/L H_3BO_3 at pH 8.0) 10 mM H_2PtCl_6 at various sweep rates: (a) 10 mV/s, (b) 25 mV/s (c) 50 mV/s (d) 100 mV/s.

Figure 2. Cyclic voltammogramsobtained in solution (with 20 g/L H_3BO_3 at pH 8.0) 10 mM H_2PtCl_6 + 0.05 M DMSO at various sweep rates: (a) 10 mV/s, (b) 25 mV/s, (c) 50 mV/s and (d) 100 mV/s.

Figure 3. Cyclic voltammograms obtained in solution (with 10 g/L NaCl and 20 g/L H_3BO_3 at pH 8.0) 10 mM H_2PtCl_6 + 0.05 M DMSO+ 0.1 M ETA at various sweep rates: (a) 10 mV/s, (b) 25 mV/s, (c) 50 mV/s and (d) 100 mV/s.

Figure 4. Cyclic voltammograms obtained in solution (with 10 g/LNaCl and 20 g/L H_3BO_3 at pH 8.0) 0.1M Na_2WO_4 + 0.05 M DMSO at various sweep rates: (a) 10 mV/s, (b) 25 mV/s, (c) 50 mV/s and (d) 100 mV/s.

Figure 5. Cyclic voltammograms obtained in solution (with 10 g/LNaCl and 20 g/L H_3BO_3 at pH 8.0, sweep rate ʋ =10 mV/s) 0.025M Na_2WO_4 + 0.05 M DMSO+ 10 mM H_2PtCl_6 containing different concentrations of ETA: (a) 0.01M, (b) 0.02M (c) 0.05M (d) 0.1M.

Figure 6. Cyclic voltammograms obtained in solution (with 10 g/LNaCl and 20 g/LH_3BO_3 at pH 8.0, sweep rate ʋ=10 mV/s) 0.1M ETA+ 0.05 M DMSO+ 10 mM H_2PtCl_6 containing different concentrations of Na_2WO_4: (a) 0.025M, (b) 0.01M, (c) 0.05M and (d) 0.1M.

Figure 7. Ultraviolet spectra of solutions: (a) 0.1M ETA, (b) 0.1M ETA + 10 mM Na_2WO_4 and (c) 10 mMH_2PtCl_6 + 0.1M ETA.