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Methanol oxidative fuel cell: electrochemical synthesis and characterization of low-priced WO₃-Pt anode material

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Abstract Electroplating of WO₃-Pt has been carried out using a suitable plating bath solution and optimum working conditions. X-ray and SEM studies of the deposit reveal a smooth and uniform distribution of micro-particles on the surface. New phases of the plated material appear on heat treatment. The electrocatalytic activity of the WO₃-Pt co-deposit is considerably higher than for platinum alone. WO₃ in the WO₃-Pt co-deposit reduces the retardation effect of methanol oxidation by the reaction intermediate observed in the case of Pt alone. WO₃-Pt co-deposits exhibit low overpotential for methanol oxidation in both acidic and alkaline media at low temperature and have good corrosion resistance in electrolytic media. The electrochemical parameters for methanol oxidation of these co-deposits depend on trace amounts of the platinum, heat treatment and the microstructure of the coating.

Keywords Anode material · Fuel cell · Methanol oxidation · Overpotential · WO₃-Pt coating

Introduction

The methanol oxidative fuel cell is a prospective power source since it has an easily refuelable power stack in electrically driven vehicles [1]. It is almost on the verge of abandonment because of the following facts: (1) the high cost of the Pt group metals used as the electrodes, (2) electrode surface poisoning by reaction intermediates during the oxidation [2] and (3) the inadequacy of the membrane that removes the cross-leaks of methanol to the air electrode [3]. To overcome these problems to some extent, composites of Pt with Ru [4], WO₃ [5] and alloys of Ni [6] are used as the electrodes. However, the

preparation of these electrodes involves tedious procedures and is not cost effective. By eliminating Pt completely, or using it only in trace amounts in the electrodes, it is possible to reduce the cost of making the electrodes for the fuel cell by 20% [7]. In this direction, attempts have been made to prepare and characterize cost-effective Co-W and Cu-Ni alloys as anode materials for the methanol oxidation fuel cell in both H₂SO₄ and KOH media [8, 9].

The results pertaining to the electrochemical preparation and characterization of WO₃-Pt as an anode for the methanol oxidative fuel cell is reported in the present communication. The anode material developed is low priced, the method of preparation is simple and the electrode exhibits low overpotential for the reaction under normal working conditions.

Experimental

All solutions were prepared using analytical reagent grade chemicals and double distilled water. The WO₃-Pt coatings were made on copper foils (99.9%, 20 mm×10 mm×0.25 mm). The copper surface was pre-cleaned with trichloroethylene followed by water. The surface was mechanically polished with emery paper down to grade 6/0 and washed with dilute H₂SO₄, then with water and finally chemically polished [10]. The details of the pretreatment of the electrode surface and experimental procedure have been described earlier [11]. The deposition was carried out using a three-compartment glass cell of 50 mL capacity at 323 K for 1–3 h. The pH of the bath solution was maintained at 8.0 using dilute NaOH/H₂SO₄. The deposition of the WO₃-Pt coatings and subsequent polarization studies in CH₃OH+H₂SO₄ and CH₃OH+KOH mixtures were carried out using a potentiostat/galvanostat (PAR 273 EG&G, Princeton, NJ, USA) against a stainless steel (SS 316) counter electrode and a saturated calomel electrode as the reference electrode. A Luggin capillary minimized the IR drop.

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The surface morphology and microstructures of the coatings obtained under optimum deposition conditions were examined using a scanning electron microscope (JOEL, JSM-840A) and an X-ray diffractometer (Siemens D-5005, Cu K radiation). The coatings were stripped in 1:4 HNO₃ and their compositions were determined using an atomic absorption spectrometer (Perkin-Elmer 10000). The WO₃-Pt coatings were used as an anode in a methanol oxidation cell containing H₂SO₄ (0.5 M) and KOH (3 M) electrolytes.

Results and discussion

Bath composition and operating parameters

The complexing agents in the plating solution produce good quality coatings during electroplating [12]. Keeping in view our knowledge of the solution chemistry of W and Pt, a few complexing agents were screened at pH 8.0 using UV-visible spectrophotometry. An aqueous solution containing Pt⁴⁺ ions with sodium potassium tartarate (SPT) showed a weak peak (Fig. 1) at 385 nm. This is assigned as a ¹A_{1g} → ³T_{1g} transition with an octahedral d⁶ system of the complex type [Pt(CHOHCOO)₂(H₂O)₂]. Similar studies with the solution containing ethylenediamine (EDA) or dimethyl sulfoxide (DMSO) did not produce any band, indicating non-complexing behavior. On the basis of these results, preliminary experiments were carried out under potentiostatic conditions (−1000 to −1800 mV) using a bath solution containing known concentrations of Na₂WO₄, platinum(IV) chloride and SPT. The conductivity of the plating bath solution was enhanced by using NaCl. DMSO was used to obtain good quality WO₃-Pt coatings. Experiments were conducted at different deposition potentials, bath compositions, pH values and working temperatures. Based on the experimental observations, the bath composition and working conditions were optimized (Table 1) to obtain good quality WO₃-Pt coatings. The W takes the form of WO₃ during elec-

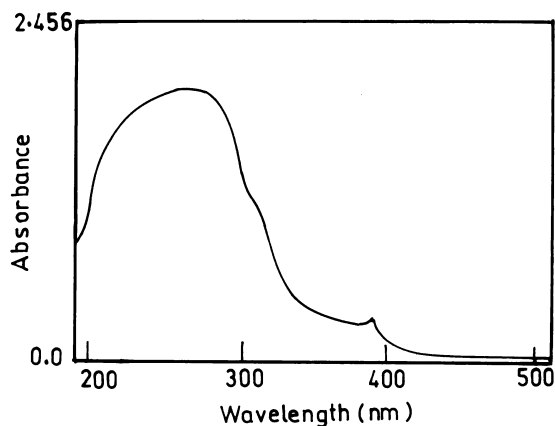


Fig. 1 UV-visible spectra of platinum with SPT

Table 1 Bath composition and plating conditions

Bath component	Concentration (M)	Plating parameters
Sodium tungstate	0.05	Cathode: copper foil
Dimethyl sulfoxide	0.10	Anode: stainless steel
Sodium potassium tartarate	0.20	Deposition potential: −1500 mV
Platinum(IV) chloride	1–20 ^a	pH: 8.0
Ethylenediamine	0.10	Time: 1–3 h
Sodium chloride	0.15	Temperature: 323 K

^amM

trodeposition [13]. It is therefore presumed that traces of Pt are dispersed in WO₃ in the coatings.

Surface and structural analyses

The coatings obtained under optimum experimental conditions were subjected to EDAX analysis, which confirmed the presence of traces of Pt (~2%) in the coatings. The SEM microphotographs were taken for the deposited as well as the heat-treated coatings. The SEM microphotograph of the deposit surface (Fig. 2A) shows non-uniform features, which become smoothed after heat treatment (Fig. 2B). The dot mapping of Pt in the coating (Fig. 2C) shows uniform distribution of Pt on the surface. Figure 3 shows the XRD patterns for the

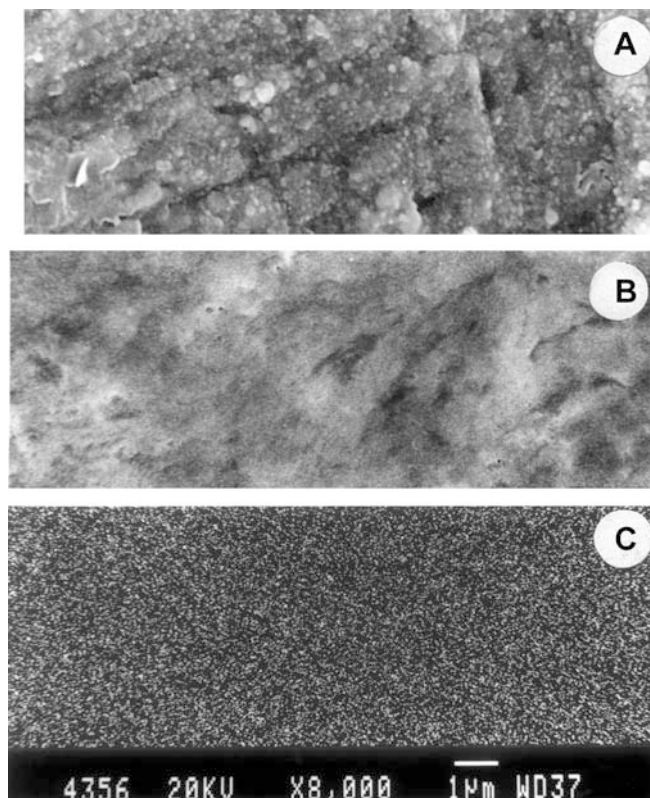


Fig. 2 SEM microphotographs of (A) as-deposited WO₃-Pt (>2% Pt) coatings, (B) after heat treatment (623 K for 5 h under 10^{−6} mbar air) and (C) EDAX Pt dot mapping

as-deposited (Fig. 3A) and heat-treated (Fig. 3B) WO₃-Pt coatings. The XRD data are given in Table 2. The diffraction peaks of the as-deposited coatings exhibit only a few phases, along with a partially amorphous feature. On heat treatment, more new phases appear in the coating and the crystallinity percentage also increases.

Polarization and cyclic voltammetric studies

The electrocatalytic activity of the WO₃-Pt coatings during oxidation of 1 M methanol in 0.5 M H₂SO₄ and 3 M KOH was studied using the galvanostatic polarization technique in the current density range 1–100 mA cm⁻² at 323 ± 1 K. Figure 4 shows the galvanostatic anodic polarization of the as-deposited and heat-treated WO₃-Pt coatings in H₂SO₄ and KOH media. The electrochemical parameters are given in Table 3. It was observed that the overpotentials for methanol oxidation on WO₃-Pt coatings in both H₂SO₄ and KOH are relatively less than that observed with Pt alone as the working electrode, suggesting that traces of Pt in a dispersed state with WO₃ serves as a better electrocatalyst for the methanol oxidation than Pt itself. A decrease in sulfuric acid concentration or an increase in methanol concentration decreased the overpotential. The polarization data (Table 3) show that heat treatment of the coatings enhanced the catalytic activity by

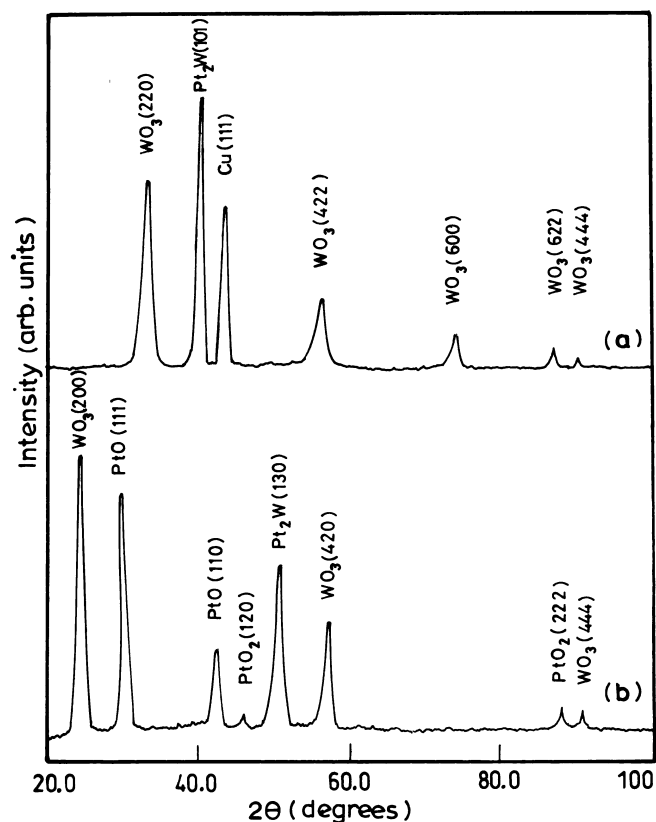


Fig. 3 XRD patterns of WO₃-Pt coatings: (a) as-deposited and (b) after heat treatment

Table 2 XRD data obtained^a for WO₃-Pt (>2% Pt) coatings

2θ	Observed d (Å)	Std. ASTM d (Å) ^b	Phase
As deposited			
33.719	2.658	2.662	WO ₃ (220)
39.940	2.256	2.255	Pt ₂ W (101)
43.440	2.083	2.092	Cu (111)
59.523	1.553	1.534	WO ₃ (422)
75.443	1.260	1.253	WO ₃ (600)
87.089	1.119	1.118	WO ₃ (622)
91.089	1.080	1.088	WO ₃ (444)
After heat treatment ^c			
24.000	3.707	3.761	WO ₃ (200)
30.476	2.933	2.970	PtO (111)
42.229	2.140	2.176	PtO (110)
44.799	2.023	2.023	PtO ₂ (120)
46.930	1.936	1.949	Pt ₂ W (130)
54.769	1.676	1.680	WO ₃ (420)
87.875	1.111	1.118	PtO ₂ (222)
89.708	1.093	1.008	WO ₃ (444)

^aCu K_α

^b1997 JCPDS, International Centre for Diffraction Data, PCPDFWIN, v. 1.30

^c623 K for 5 h under 10⁻⁶ mbar air

exhibiting a low overpotential (η) when compared to the uncatalyzed reaction. This may be due to the formation of new phases (Table 2) resulting from surface modification on heat treatment. The WO₃-Pt coatings exhibited a low overpotential even at 100 mA cm⁻² up to 100 h, which is comparatively lower than other

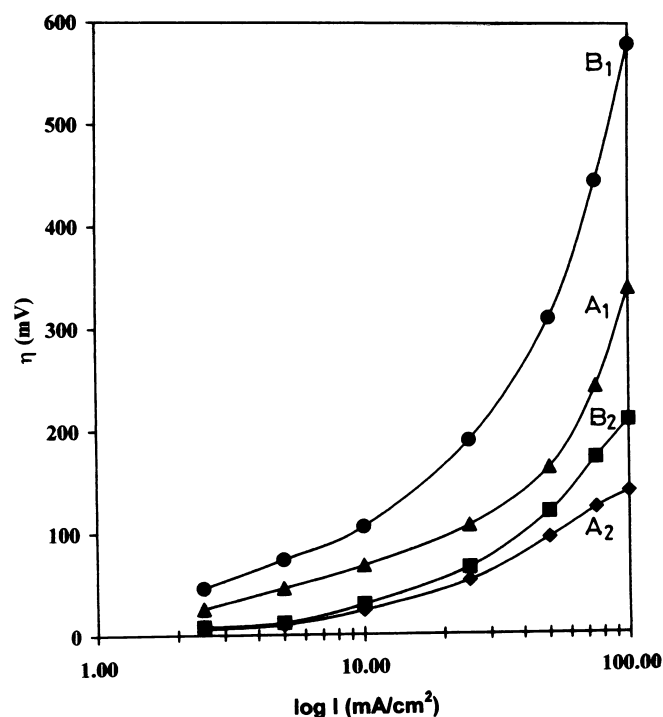


Fig. 4 Galvanostatic polarization diagrams for methanol oxidation on WO₃-Pt coatings: as-deposited [A₁ (triangles) and B₁ (circles)] and after heat treatment [A₂ (diamonds) and B₂ (squares)] in 0.5 M H₂SO₄ (A₁, A₂) and 3 M KOH (B₁, B₂) at 323 K

Table 3 Electrochemical parameters obtained during methanol oxidation in 0.5 M H₂SO₄ and 1 M KOH for WO₃-Pt (>2% Pt) coatings at 323 ± 1 K^a

Medium	b_a (mV decade ⁻¹)	i_{corr} (μA cm ⁻²)	$i_{\text{corr rate}}$ (mpy)	$\eta_{100\text{mA}}$ cm ⁻² (mV)
1 M CH ₃ OH + 0.5 M H ₂ SO ₄	67 (46)	16 (4)	3 (1)	340 (140)
1 M CH ₃ OH + 1 M KOH	98 (41)	80 (14)	16 (4)	580 (210)

^aThe values with the heat-treated samples are given in parentheses

electrodes used for the methanol oxidation reaction under comparable conditions [14].

The WO₃-Pt coatings also exhibited better corrosion resistance in H₂SO₄ medium than in KOH (Table 3). The heat treatment of the coating further improved the corrosion resistance, as evident from the prolonged polarization experiments (up to 100 h) that were conducted in both 0.5 M H₂SO₄ and 3 M KOH containing 1 M methanol at a current density of 100 mA cm⁻². The anode was stable with a steady potential of ±10 mV (Fig. 5).

Cyclic voltammetric experiments with heat-treated WO₃-Pt coatings as the working electrode in aqueous solution containing 1 M methanol and 0.5 M H₂SO₄ were carried out at different scan rates (10–100 mV s⁻¹) in the potential range –1600 to 1400 mV in order to compare the results obtained from the polarization studies. The cyclic voltammogram takes the shape at a particular scan rate which is a characteristic of an electrochemical reaction at the electrode. In the present system a scan rate of 50 mV s⁻¹ was found to give a good cyclic voltammogram. The results were compared with Pt as the working electrode under comparable experimental conditions (Fig. 6). The anodic peak current obtained with Pt was very small (1.83 μA) but increased significantly (to 4712 μA) with the WO₃-Pt

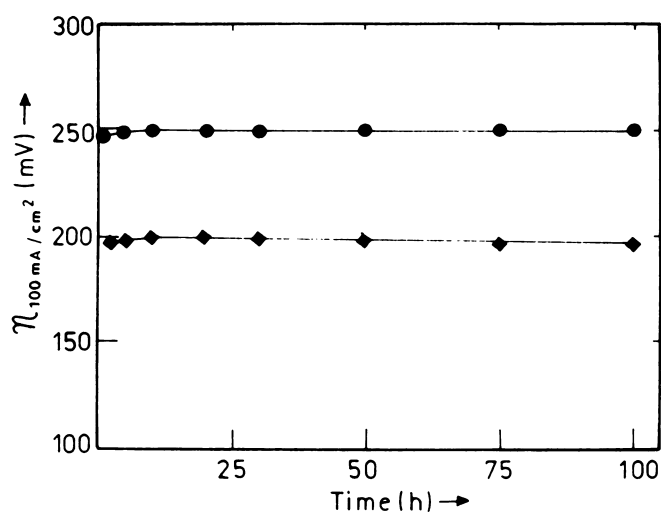


Fig. 5 Variation of overpotential (at 100 mA cm⁻²) with time on WO₃-Pt coating in 1 M CH₃OH + 0.5 M H₂SO₄ (diamonds) and 1 M CH₃OH + 3 M KOH (circles) at 323 K

electrode. From these results, the increase in the relative rate of oxidation ($I_{p(\text{WO}_3\text{-Pt})}/I_{p(\text{Pt})}$) was calculated to be 2574.

The electro-oxidation of methanol is a complex process, which is retarded by the adsorption of reaction intermediates such as CO, formaldehyde, formic acid, etc., on the electrode surface [15]. In aqueous solution under slightly acidic conditions, zinc sulfate in the presence of formaldehyde gives a characteristic cyclic voltammogram [16]. These earlier findings are used to identify the intermediate species in the present system. Cyclic voltammograms were obtained on the WO₃-Pt microelectrode using an oxidized methanol mixture along with zinc sulfate in 0.5 M H₂SO₄. The cyclic voltammograms obtained were comparable with those obtained in acidic zinc sulfate solution containing formaldehyde. The identical results obtained (Fig. 7) confirmed the involvement of formaldehyde as an intermediate during oxidation of methanol on the WO₃-Pt coating.

Methanol is ultimately oxidized [15] to carbon dioxide at the platinum electrode in acidic solution, with several intermediates: (1) detectable adsorbate CO, (2) dissolved formaldehyde and formic acid and (3) dehydrogenated adsorbates HCHO_{ads} and CH₂OH_{ads}. On the basis of estimated rates for the oxidation of intermediate (1), its oxidation is very slow compared with the overall methanol oxidation. These facts suggest that the reaction intermediate is mainly HCHO.

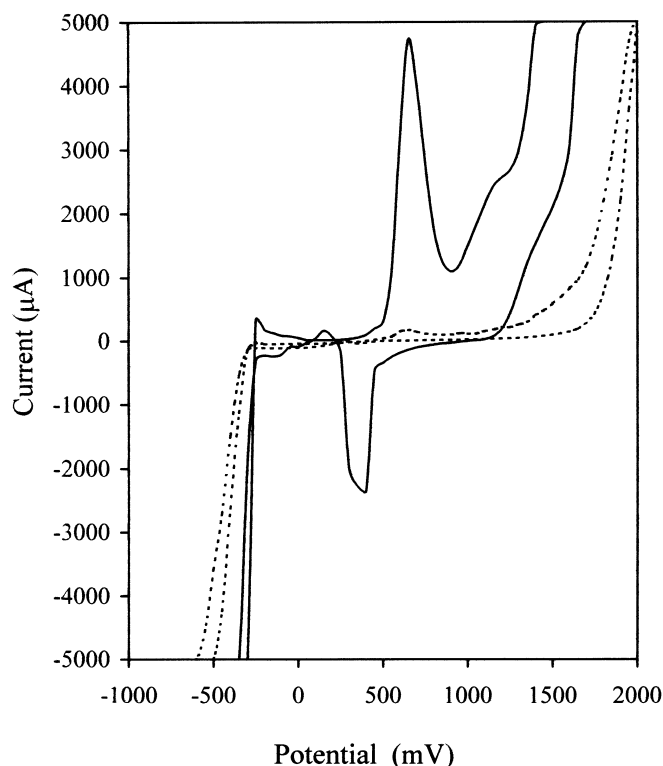


Fig. 6 Cyclic voltammograms obtained in a sulfuric acid/methanol mixture at a scan rate of –50 mV s⁻¹ and temperature of 298 K: the WO₃-Pt coating (full lines) and platinum alone (dashed lines)

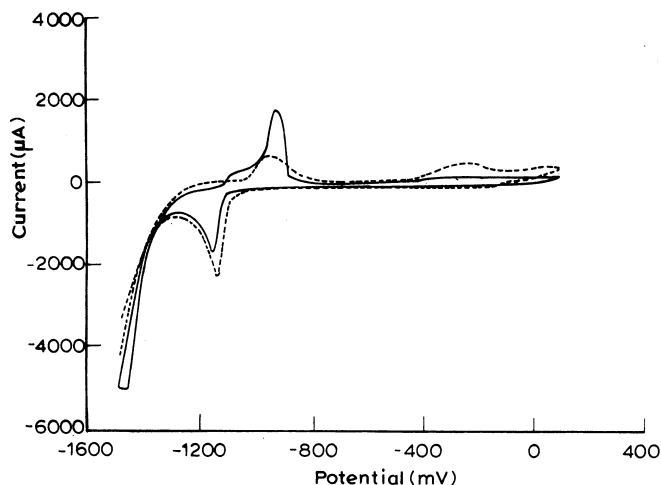


Fig. 7 Cyclic voltammograms obtained in acidic (pH 3.0) ZnSO₄ and Na₂SO₄ at a scan rate of 100 mV s⁻¹ and at a temperature 298 ± 1 K with formaldehyde (*full lines*) and with the oxidized reaction mixture (methanol and H₂SO₄) (*dashed lines*)

This is confirmed using the cyclic voltammetric technique. The rate of oxidation of methanol depends on several parameters, namely the concentrations of methanol/H₂SO₄/KOH, the nature and the composition of the electrode surface [17]. One of the important parameters in the evaluation of electrocatalytic behaviour is the real surface area. In the present system, however, it is not the case and the enhancement of the electrocatalytic activity upon heat treatment may be due to changes in the surface morphology. XRD data with heat-treated samples show the presence of new phases, which perhaps modify the electronic and structural properties of the surface, which in turn assist the electrocatalytic activity during methanol oxidation.

Conclusion

A plating bath and working conditions were developed to obtain good quality WO₃-Pt co-deposits. The

presence of WO₃ in the deposit enhances the relative oxidation rate and catalytic activity compared to platinum for methanol oxidation in both H₂SO₄ and KOH media at normal working temperatures. Heat treatment of the co-deposit resulted in new phases. The WO₃-Pt co-deposits are very stable with good corrosion resistance in both H₂SO₄ and KOH media. Retardation of the methanol oxidation with platinum by reaction intermediates is reduced considerably using WO₃-Pt.

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