Short communication

Preparation and characterization of Co–W alloys as anode materials for methanol fuel cells

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Abstract

Co–W alloys are developed by an electroplating technique using a bath solution which contains triammonium citrate (TAC) and dimethyl sulfoxide (DMSO) under suitable plating conditions. The alloys are characterized by polarization studies in order to determine their prospects as effective anode materials for methanol fuel cells in both acidic and alkaline media. Scanning electron microscopic and X-ray diffraction analysis shows that the coatings are partially amorphous. The alloys exhibit low overvoltage even on prolonged electrolysis, and have good corrosion resistance in acidic and alkaline media. Electrochemical parameters for methanol oxidation depend on the heat treatment, deposition potential and microstructure of the deposit. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

It has been widely suggested that the methanol fuel cell is an ideal power source for electric vehicles. Unfortunately, however, methanol oxidation at the anode is not facile on many electrode materials under ambient conditions. Platinum-group metals supported on active carbon have been examined as anode materials for oxidation of methanol in acidic and alkaline media [1,2]. A recent review on the subject is noteworthy [3]. Electro-oxidation of methanol is a complex process which involves several intermediates. These, in turn, depend on factors such as the nature of the electrode surface, the methanol concentration, and the nature and concentration of the supporting electrolyte [4,5]. In recent years, an electrochemical method for preparation of the electrode materials for fuel cell applications has gained prominence [6]. The successful development of electrode materials for fuel cell technology involves solving problems such as the poor stability of electrode materials, surface contamination of solution components, and decrease in electrocatalytic activity after few cycles.

Cobalt forms hard alloys with tungsten that are free from surface contamination and exhibit good corrosion resistance towards acidic and alkaline media [7,8]. Co–W alloys are effective cathode materials for alkaline water electrolysis [9]. The present communication reports the electrochemical preparation and characterization of Co–W alloys as anode materials for methanol oxidation in both acidic and alkaline media.

2. Experimental

The solutions were prepared using AR grade chemicals and double-distilled water. Experiments were carried out using a conventional three-compartment glass cell of 250 ml capacity. Co–W alloys were electroplated potentiostatically on suitably pre-treated copper foils [10] (2 cm × 5 cm, 0.3 mm thick) at 323 K in a plating bath solution at pH 8.0. The solution was stirred. A scanning potentiostat (EG 2G 362A PAR, USA) was used as a current source. Calomel and Hg/HgO electrodes were used as reference electrodes during plating and anodic polarization, respectively. In both the cases, a platinum foil (area: 4 cm^2) was used as the auxiliary electrode. The alloys were stripped in 1:4 HNO$_3$ solution and the compositions were determined by means of atomic absorption spectroscopy (Perkin-Elmer 1000). The alloys obtained under optimum experimental conditions were subjected to scanning electron microscopy (SEM, JEOL JSM 840-A) and X-ray diffraction analysis (Siemen D 5005, Cu Kα radiation).

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3. Results and discussion

In a slightly alkaline solution (pH 8.0), suitable organic compounds (individually and in combinations) were selected to complex Co and W ions in the plating bath solution. Among these organic compounds, only triammonium citrate (TAC) was found to be a good complexing agent for Co^{2+} ions. Dimethyl sulfoxide (DMSO) was also used as a reducing agent, which facilitated the co-deposition of W.

It is known that the solution components in the plating bath solution and the experimental conditions play a decisive role in deciding the quality and functional properties of the coatings [11]. Accordingly, detailed studies have been made to understand the influence of these variables on the electroplating of Co–W alloys. The composition of the bath solution and the plating conditions were optimised to provide good quality Co–W alloys. The bath solution containing 65 wt.% Co gives a Co–W alloy with 90 wt.% Co in the deposit at a deposition potential −600 mV. The composition of Co in the alloy is found to decrease by increasing the deposition potential from −600 to 800 mV (Table 1).

The surface features of the coated alloys deposited at −600 mV with W content <10 wt.% have been examined by SEM. The surface appears to be partly crystalline and partly amorphous with a nodular structure (Fig. 1A) A surface with greater grain refinement is observed (Fig. 1B) by depositing alloy at −800 mV. A smooth surface feature develops (Fig. 1C) on the application of heat treatment.

Recent XRD results [12] (Table 2) indicate the presence of multilayers in the deposits. It is known that Co–W alloy consists of a basic tetrahedral unit, which forms clusters as a dense aggregate and does not exhibit crystal symmetry under normal conditions. This accounts for the induced co-deposition of W during Co–W alloy plating, which results in a greater proportion of the amorphous state.

Alloys of sufficient thickness (> 20μm) with different compositions were prepared and used as anode materials for methanol oxidation. Sulfuric acid and potassium hydroxide are used extensively as electrolyte solutions in methanol fuel cell technology [13]. In the present investigation, methanol was oxidized in an electrochemical cell which contained 0.5 M H_2SO_4/3 M KOH electrolyte with a Co–W (<10 wt.% W) alloy as the anode.

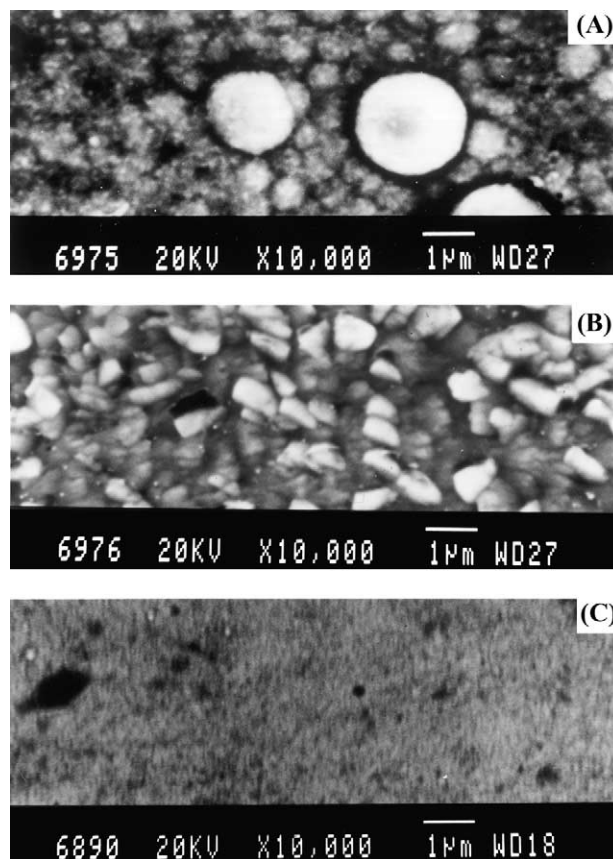Polarization curves for the methanol oxidation reaction (MOR) on Co–W alloy as plated (at −600 mV) and with heat

Fig. 1. Electron micrographs of Co–W alloys deposited at: (A) −600 mV; (B) 800 mV; (C) −600 mV (heat treated).

treatment (at 698 K under N_2 atmosphere for 5 h) in 0.5 M H_2SO_4 medium are shown in Fig. 2. Methanol is oxidized with a current density up to 100 mA cm^{-2}. A sufficient low overpotential (measure of catalytic activity) is observed. The polarization parameters were evaluated from Tafel diagrams and are listed in Table 3. The heat treated samples perform as better anode materials with low overpotentials for methanol oxidation.

The results obtained from polarization during methanol oxidation in 3 M KOH at 323 K using a Co–W alloy (<10 wt.% W), without and with heat treatment as the anode are presented in Fig. 3. Compared with a 0.5 M H_2SO_4 medium, the as plated Co–W alloys are not so effective as

Table 1
Bath composition and operating conditions

Bath composition (mol dm^{-3})	Operating conditions
$CoSO_4 \cdot 7H_2O$ (0.10)	E_{dep} −600 mV
$Na_2WO_4 \cdot 2H_2O$ (0.02)	−800 mV
$(NH_4)_3C_6H_5O_7$ (0.10)	pH = 8.0
$(CH_3)_2SO$ (0.05)	Pt foil anode
$Na_2SO_4 \cdot 10H_2O$ (0.3)	Cu foil cathode
NaCl (0.2)	Temperature = 323 K
H_3BO_3 (0.05)	Time = 60 min, agitation

Table 2
XRD data obtained[a] on Co–W alloys (<10 wt.% W)

2θ	As deposited			After heat treatment		
	d (nm)	Phase		2θ	d (nm)	Phase
47.78	2.2120	Co_3W (200)		47.77	2.2117	Co_3W (220)
58.96	1.8797	Co_3W (102)		51.36	2.0663	Co_3W (002)
89.08	1.2798	Co_3W (220)		54.52	1.9567	Co_3W (201)
				70.26	1.5562	CO_7W (216)
				88.76	1.2060	Co_3W (220)

[a] Cu Kα radiation.
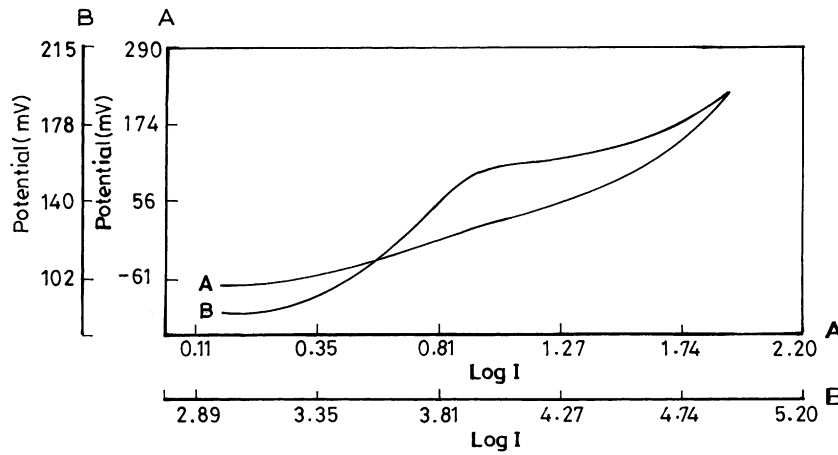
Fig. 2. Tafel plots for Co–W alloy (<10 wt.% W, deposited at −600 mV) in 0.5 M H$_2$SO$_4$ at 323 K: A, without heat treatment; B, with heat treatment.

Table 3
Electrochemical parameters for methanol oxidation on Co–W alloys (<10 wt.% W) at 323 K

Medium	Open-circuit potential (mV vs. SCE)	i_{corr} (μA cm^{-2})	b_a (mV decade^{-1})	$\eta_{100\,mA\,cm^{-2}}$ (mV)	Plating conditions
3 M CH$_3$OH + 0.5 M H$_2$SO$_4$	−150	65	112	368	E_{dep} = −600 mV
3 M CH$_3$OH + 0.5 M H$_2$SO$_4$	74	25	66	118	E_{dep} = −600 mV heat treated
3 M CH$_3$OH + 3 M KOH	−870	20	78	1440	E_{dep} = −800 mV
3 M CH$_3$OH + 3 M KOH	−918	18	70	390	E_{dep}=−800 mV heat treated

anodes in 3 M KOH medium. After heat treatment, however, the alloys show an improvement in catalytic activity. The catalytic activity is found to decrease on increasing the W content in the alloy (deposited at −800 mV), which is attributed to the change in microstructure of the deposit [14]. The surface feature did not change much even after prolonged polarization.

The alloys exhibit better corrosion resistance (Table 3) even in highly corrosive media such as H$_2$SO$_4$ and KOH. Prolonged tests were conducted for up to 100 h using alloys (25 cm^2) in both 3 M KOH and 0.5 M H$_2$SO$_4$ at 323 K and a current density of 100 mA cm^{-2}. The anode is quite stable with a steady potential ±10 mV (Fig. 4).

Electro-oxidation of methanol is retarded by the strong adsorption of reaction intermediates (CO, formaldehyde, formic acid, etc.) on the electrode surface [15]. During cyclic voltammetric investigation of acidic zinc sulfate in the presence of formaldehyde, a characteristic peak is noticed on the platinum electrode [16]. This experimental approach was used to identify the presence of formaldehyde (if any) as an intermediate in the present system. A H$_2$SO$_4$–methanol mixture was electrolyzed for 2 h at 100 mA cm^{-2} using a Co–W alloy as the anode. The resulting reaction mixture was mixed with zinc sulfate solution and cyclic voltammetric experiments were conducted on a platinum electrode. Cyclic voltammograms obtained with a reference
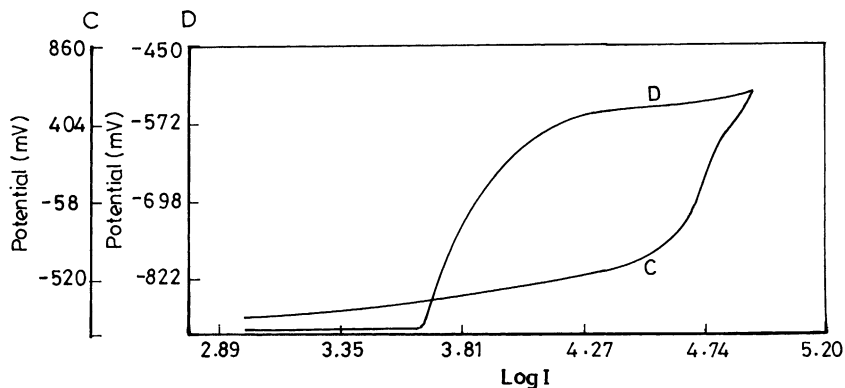

Fig. 3. Tafel plots for Co–W alloy (deposited at −800 mV) in 3 M KOH at 323 K: C, without heat treatment; D, with heat treatment.
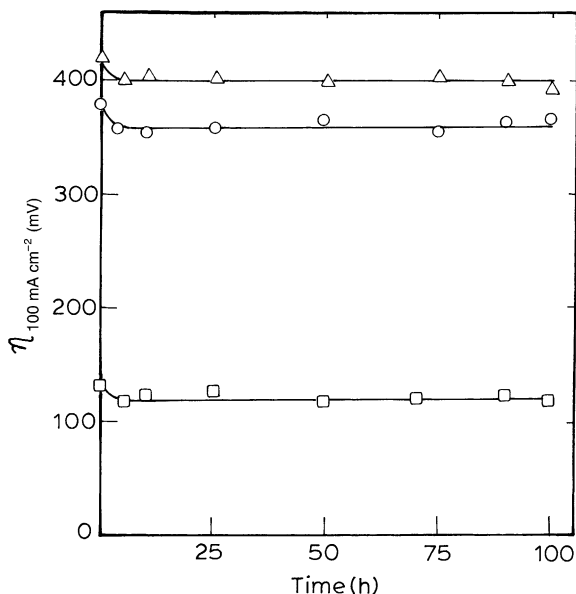
Fig. 4. Variation of overpotential (η, at 100 mA cm^{-2}) with time on Co–W alloy, in acidic and alkaline media at 323 K: ($\bigcirc$), deposited at -600 mV without heat treatment in 0.5 M H$_2$SO$_4$; ($\square$), deposited at -600 mV with heat treatment in 0.5 M H$_2$SO$_4$; ($\triangle$), deposited at -800 mV with heat treatment in 3 M KOH.
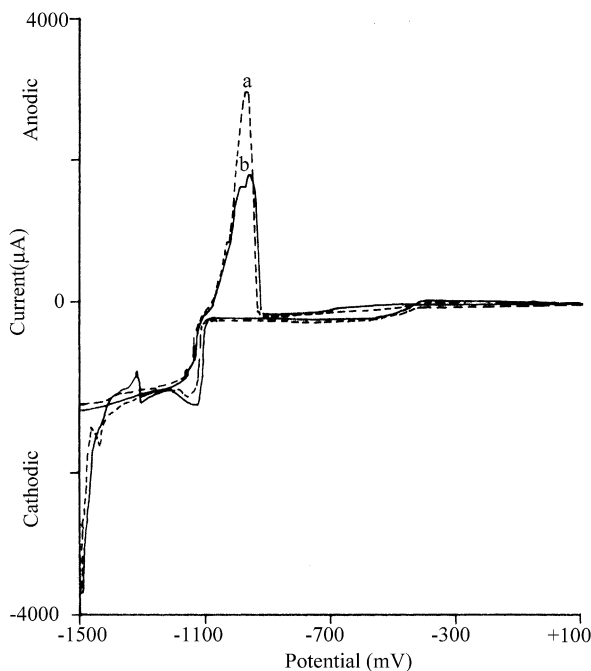

Fig. 5. Cyclic voltammograms obtained in zinc plating bath solution (2×10^{-2} M ZnSO$_4$ + 1×10^{-2} M Na$_2$SO$_4$) at scan rate 10 mV s^{-1}, temperature 298 K, pH 3.0: (a) with formaldehyde; (b) with reaction mixture (methanol and sulfuric acid).

solution of formaldehyde and in the presence of the oxidation mixture are almost identical (Fig. 5). This demonstrates the participation of formaldehyde as an intermediate during electro-oxidation of methanol on Co–W alloy anodes.

4. Conclusion

Electroplating conditions are optimized to obtain Co–W alloys of good quality. The alloys are characterized as effective anode materials for methanol oxidation in H$_2$SO$_4$ and KOH. The coatings are partially amorphous and exhibit good corrosion resistance towards H$_2$SO$_4$ and KOH. Heat treatment increases the catalytic activity of the alloy.

Acknowledgements

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