

Technical Communication

Electrocatalytic cobalt–molybdenum alloy deposits

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Abstract

Electrodeposition of Mo alloys with iron group metals is of renewed interest. The electrodeposits are used as cathode materials in fuel cells. Electrodeposition of Co–Mo alloy from triammonium citrate bath is described. To get a bright Co–Mo alloy deposit the optimum plating bath conditions are CoSO_4 0.3 M, $(\text{NH}_4)_2\text{MoO}_4$ 0.25 M, triammonium citrate 0.2 M, pH 8, c.d 4 A/dm² at 303 K. Hardness of the alloy deposit increased with molybdenum content and annealing. Increase of Mo content in the alloy favoured electrocatalytic property for hydrogen evolution reaction.

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Keywords: Co–Mo alloy deposit; Electrodeposition; Electrocatalysis and hydrogen evolution reaction

1. Introduction

Electrode materials for water electrolysis with catalytic properties have been studied [1–3]. Many transition metal alloys are characterised as hydrogen electrodes in water electrolysis [4–9] and electrodeposition method is widely used. Whenever metals of the left half of the transition metals in periodic table with empty or less filled d orbitals are alloyed with metals of the right half of the series with more filled d-bands, a maximum in bond strength and stability of the intermetallic alloy phases is expected and also there is a well pronounced synergism in the electrocatalysis.

The formation of Co–Mo deposits by electrodeposition is an induced process [10]. This means that cobalt ions are necessary for the reduction of molybdate species which is incomplete in aqueous solution. Molybdenum alloys have been deposited from acid and alkaline baths. The acid baths are divided into wholly inorganic and those contain organic acids. Usually hydroxyl acids as chelates, pyrophosphates, carbonates are used [11]. In alkaline baths, the presence of free NH_3 is essential. Molybdenum content up to 15% was obtained from sulphate–citrate bath at pH 6.6 [12].

The present communication deals with Co–Mo alloy deposition from an alkaline triammonium citrate bath and the electrocatalytic behaviour of the deposit for hydrogen evolution reaction.

2. Experimental details

The electrodeposition was carried out from an alkaline citrate complex solution. The plating solutions were prepared from Analar grade CoSO_4 , $(\text{NH}_4)_2\text{MoO}_4$, triammonium citrate, ammonia solution and H_2SO_4 using distilled water. Electrodeposition was carried out on a mild steel substrate. The substrates ($5 \times 2 \times 0.025$ cm) were polished with fine grid paper and degreased with trichloroethylene. They were electrocleaned cathodically for 2 min in an alkaline solution composed of 35 gpl NaOH, 25 gpl Na_2CO_3 and 10 gpl trisodium phosphate at 343 K with a current density of 3 A/dm². They were washed in running water and dipped for 5 s in 5% H_2SO_4 solution. Finally thorough washing and drying were done.

For current efficiency measurements, the electrodeposition assembly comprised of platinum as anode and mild steel as cathode ($5 \times 2 \times 0.025$ cm) immersed in a 800 mL solution of 1 l wide mouth glass vessel. The plating solution was agitated and necessary heating was given using a heating cum magnetic stirrer. For current efficiency determination, each specimen was

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weighed before and after plating and the weight of the deposits was found from the difference in weight,

Cathodic current efficiency (%)

$$= \frac{\text{Weight of the metal deposited}}{\text{Theoretical weight obtained from Faraday's laws}} \times 100. \quad (1)$$

The cathodic current efficiency of the alloy is calculated as

$$\text{Cathodic current efficiency (\%)} = \frac{M \times 100}{e_{\text{alloy}} \times Q}, \quad (2)$$

where M is the mass of the alloy deposit, e_{alloy} is the electrochemical equivalent of the alloy and Q is the quantity of electricity passed (A/s). The electrochemical equivalent of the alloy was calculated as

$$e_{\text{alloy}} = \frac{e_{\text{Co}} \times e_{\text{Mo}}}{(e_{\text{Co}} \times f_{\text{Mo}}) + (e_{\text{Mo}} \times f_{\text{Co}})}, \quad (3)$$

where e_{Co} and e_{Mo} are the electrochemical equivalents of the constituent metals, f_{Co} and f_{Mo} are their fractions in the deposits. The density of the alloy was calculated by taking into consideration of the fraction of constituent metals. The electrodeposits were removed chemically by immersing in 1:1 HNO_3 and then the resulting solution containing cobalt and molybdenum were determined using atomic absorption spectroscopy (AAS).

The microhardness of the deposit was measured by an indentation technique using LECO-Hardness meter (Model DM 400). The diamond pyramid indenter was pressed on the deposit under a load of 100 g for 15 s and indentation signal was measured after the load was removed.

Electrochemical measurements were carried out using EG & G—Electrochemical analyzer (Model 6310) at a scan rate of 1 mV s^{-1} to understand the electrocatalytic activity of the Co–Mo alloy deposits in 1 M NaOH for hydrogen evolution reaction using three electrode glass cell. The Co–Mo deposits coated on mild steel specimen of 1 cm^2 area was used as working electrode. The platinum foil and Hg/HgO/OH^- electrode were used as counter and reference electrodes, respectively.

Impedance measurements were also carried out using EG & G—Electrochemical analyzer (Model 6310) for various compositions of Co–Mo alloy electrodeposits in 1 M NaOH solution at 298 K using three electrode cell assembly. The deposits were kept in a solution for 5–10 min to obtain the steady value. The experiments were made in the frequency range of 10 kHz to 100 mHz with a sinusoidal amplitude of 10 mV. Nyquist plots were obtained at a cathodic over potential of 250 mV in the hydrogen evolution region.

3. Results

3.1. Electrodeposition

Co–Mo alloys were electroplated from citrate-molybdate bath. The influence of pH, current density, concentration of $(\text{NH}_4)_2\text{MoO}_4$ ions and temperature on the electrodeposition were studied. The cathodic current efficiency (CCE) and %

Table 1

Effect of cathodic current efficiency on % CCE and % Mo in the alloy deposits

Current density (A dm^{-2})	CCE (%)	% Mo in the alloy deposits
2	14.0	20
3	16.5	30
4	21.0	50
5	20.0	47

Bath composition: CoSO_4 0.3 M, $(\text{NH}_4)_2\text{MoO}_4$ 0.2 M, triammonium citrate 0.2 M and pH 8 at 303 K.

Table 2

Effect of pH on % CCE and % Mo in the alloy deposits

pH	CCE (%)	% Mo in the alloy deposits
6	12.5	22.5
7	15.0	32.5
8	17.0	37.0
9	11.5	27.0

Bath composition: CoSO_4 0.3 M, $(\text{NH}_4)_2\text{MoO}_4$ 0.2 M, triammonium citrate 0.2 M and c.d. 4 A/dm^2 at 303 K.

Table 3

Effect of ammonium molybdate on % CCE and % Mo in the alloy deposits

Conc. of $(\text{NH}_4)_2\text{MoO}_4$ (M)	CCE (%)	% Mo in the alloy deposits
0.05	5.0	10
0.10	10.0	20
0.15	11.5	31
0.20	13.0	38
0.25	20.0	45

Bath composition: CoSO_4 0.3 M, pH 8, c.d. 4 A/dm^2 at 303 K.

Table 4

Effect of temperature on % CCE and % Mo in the alloy deposits

Temperature (K)	CCE (%)	% Mo in the alloy deposits
303	10.5	35
313	21.0	43
323	22.5	48
333	21.0	46

Bath composition: CoSO_4 0.3 M, $(\text{NH}_4)_2\text{MoO}_4$ 0.2 M, triammonium citrate 0.2 M and pH 8.

Mo in the alloy were maximum at 4 A/dm^2 (Table 1). The pH affected both the CCE and % Mo in the alloy. Influence of pH was seen up to a value of 8 and then the pH rise decreased the CCE and % Mo in the alloy (Table 2). The CCE and % Mo in the alloy increased with concentration of ammonium molybdate (Table 3). The CCE and % Mo in the alloy increased with temperature up to 323 K, and then decreased (Table 4).

3.2. Characterisation of the deposit

The cobalt–molybdenum electrodeposits were studied for their hardness values. The 45% Mo alloy had a greater

hardness than cobalt and annealing of this alloy deposit increased the hardness more (Table 5).

The alloy containing molybdenum had good catalytic properties for hydrogen evolution. In the present study, four different molybdenum alloy electrodeposits were chosen to study for their catalytic properties for hydrogen evolution in 1 M NaOH solutions. From the steady open circuit potentials, anodic and cathodic polarisation experiments were carried out (Fig. 1). Anodic Tafel slope was found to be 68 ± 12 mV/decade and cathodic Tafel slope was 128 ± 28 mV/decade. Equilibrium potential for hydrogen evolution reaction (h.e.r) in 1 M NaOH solution was calculated. Extrapolation of linear segment of cathodic polarisation curve was used to calculate $i_{0,H}$. The exchange current density increased with % Mo content in the alloy (Table 6). Fig. 2(a)–(d) present the Nyquist plots for the hydrogen evolution reaction (Table 7). Based on Randles equivalent circuit approach with constant phase element in parallel to R_s , R_{ct} and C_{dl} , double layer capacitance and R_{ct} were

Table 5
Microhardness of the Co, Co–Mo and annealed Co–Mo alloy deposits

Composition of alloy deposits	Microhardness (Kg/mm ²)
Cobalt deposit	95
Co–Mo (45% Mo) alloy deposit	115
Annealed Co–Mo (45% Mo) alloy deposit	147

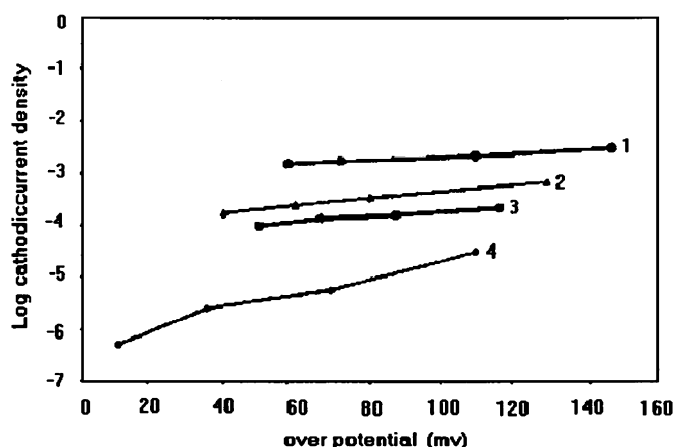


Fig. 1. Potentiodynamic polarisation curves obtained in 1 M NaOH solutions at 303 K for various compositions of Co–Mo alloy deposits: (1) 23% Mo; (2) 37% Mo; (3) 41% Mo; (4) 45% Mo.

Table 6
Tafel slopes and exchange current density for the h.e.r on different composition of alloy deposits at 303 K

% of Mo in the alloy deposits	Tafel slopes (mV/decade)		$i_{0,H}$ (A cm ⁻² × 10 ⁻⁷)
	b_a	b_c	
23	81	146	6.16
37	73	134	49.8
41	69	132	100.0
45	66	103	499.0

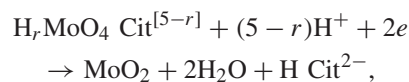
calculated. Charge transfer resistance values decreased while double layer capacitance values increased with Mo content in the electrodeposit.

4. Discussions

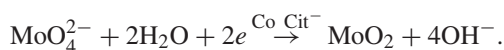
In early 1950's, Case and Krohn [13] reviewed various hypotheses proposed to explain induced codeposition and considered the hypothesis of Meyer [14]. Accordingly a membrane of hydroxide of molybdenum and of the iron group metal is formed on the cathode. The hydroxide of the iron group metal supposedly alters the permeability of the film so that it can be penetrated by molybdate ions. Otherwise only hydrogen would evolve. The discharge of hydrogen is an essential part of the process as this provides a condition for precipitation. Ernst et al. [15,16] proposed an involved explanation of the induced codeposition of Mo. Mo first deposits as an oxide, which in the presence of iron-group metal could be reduced to Mo by hydrogen. The number of unpaired electrons in the iron group metal is also considered as an index of its ability to form a bond with hydrogen and thereby reduce the MoO₂.

An assumption involving the formation of an intermediate with an iron group element is also known [17]. A model assuming the adsorption of an intermediate and the iron group metal ion acts as a catalyst for the molybdate reduction is also suggested [18]. The iron group metal reduction takes place in two steps. The first step generates a monovalent species adsorbed on the surface. The adsorbed species is further reduced to the solid metal. If the adsorbed coverage is low, then the model agreed with earlier concepts.

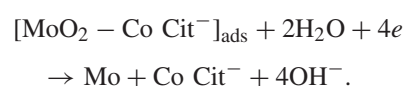
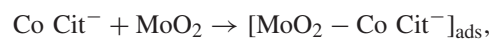
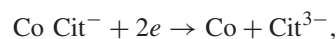
In acidic pH [19], when citrate concentration was doubled compared to cobalt ion concentration, CoCit⁻ complex was predominant at pH 6.6 and fell to 40% at pH 4. HCocit⁻ was the main species. At pH 6.6, the main molybdate species was MoO₄²⁻ and the predominant molybdate species was H_rMoO₄ Cit. The r value increased with lowering of pH [20]



In quasi-neutral sulphate–citrate baths, the formation of molybdenum oxide was favoured in presence of Co Cit⁻ in solution



Both MoO₂ and Co Cit⁻ helped to form Co–Mo alloy through the formation of an adsorbed intermediate [21,22]



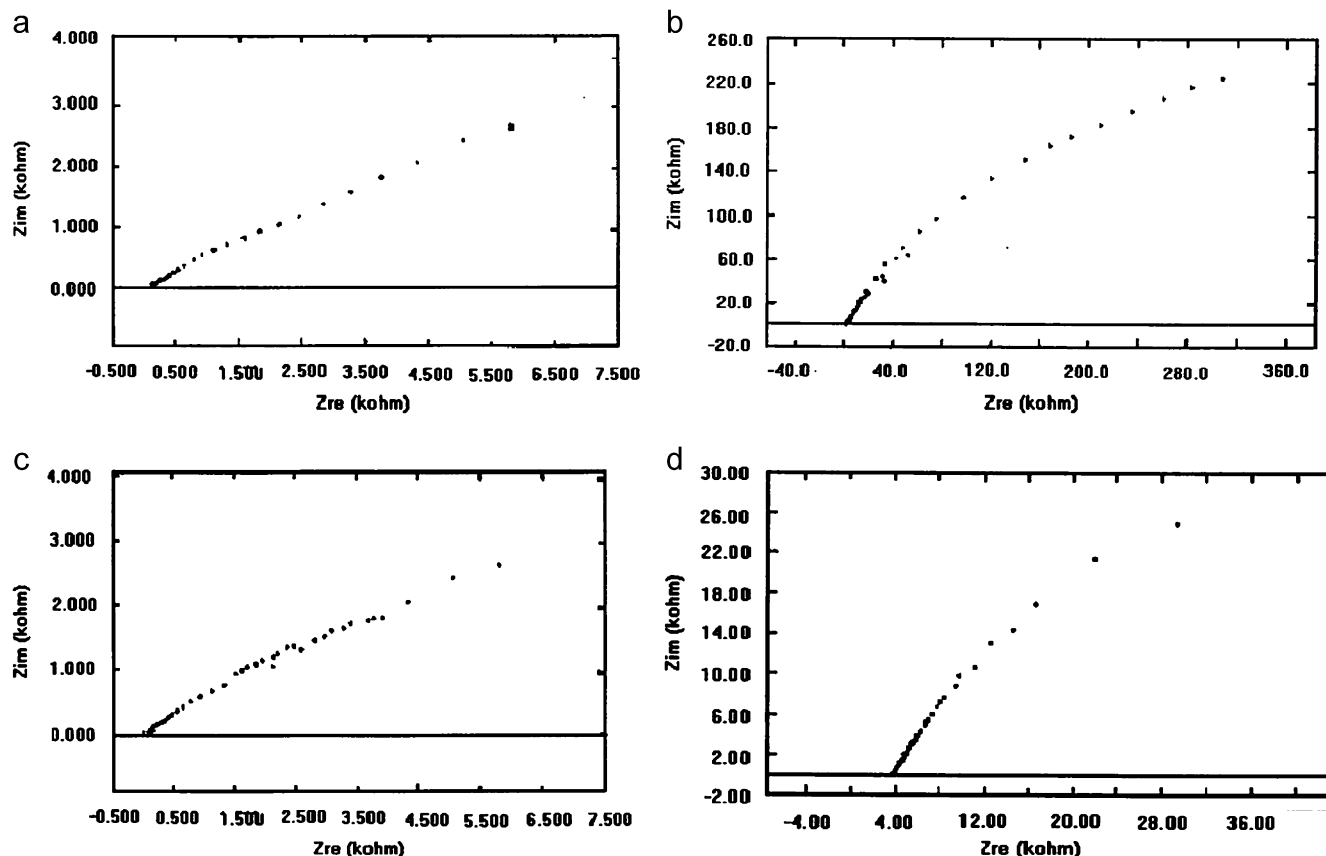


Fig. 2. Nyquist plots obtained in 1 M NaOH solution at 303 K for various compositions of Co–Mo alloy deposits at a cathodic over potential of 250 mV: (a) 23% Mo; (b) 37% Mo; (c) 41% Mo; (d) 45% Mo.

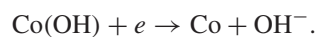
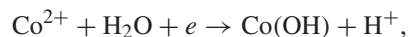
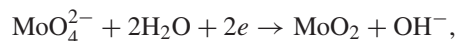
Table 7

Parameters derived from Nyquist plots at a cathodic over potential of 250 mV at 303 K

% of Mo in the alloy deposits	R_{ct} (ohm cm^{-2})	C_{dl} (F cm^{-2})
23	1090	1.4×10^{-3}
37	1085	2.4×10^{-3}
41	559	2.8×10^{-3}
45	123	12×10^{-3}

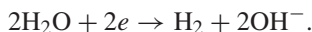
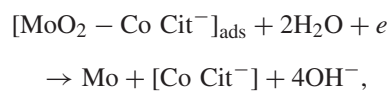
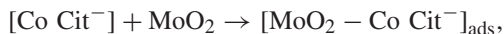
At pH 6.6, cobalt and Mo deposit simultaneously but the presence of a small amount of cobalt is needed to induce the reduction of adsorbed intermediate.

In the present study, in presence of citrate ions, molybdate and cobalt ions form complexes. A low concentration of Co Cit^- was enough to form $[\text{MoO}_2 - \text{Co Cit}^-]_{\text{ads}}$ species



In presence of cobalt nuclei, $[\text{MoO}_2 - \text{Co Cit}^-]$ formation was favoured. When citrate ions and OH^- ions were present the formation of $[\text{Co Cit}^-]$ was hindered. When there was a high concentration of MoO_2 , the formation of $[\text{MoO}_2 - \text{Co Cit}^-]_{\text{ads}}$

species was evident



The evolved hydrogen favoured the reduction of MoO_2 [23,24].

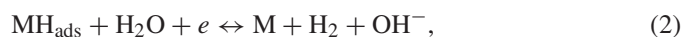
Increase of pH did not favour the formation of more molybdenum alloy. At pH 8, the % Mo in the alloy was maximum and an increase of temperature up to 323 K caused Mo content in the alloy upto 48%, when compared to cobalt–sulphate concentration, molybdate concentrations employed were lower. However the deposits were found to contain upto 45% Mo. This suggests that the alloy formation involved the $[\text{MoO}_2 - \text{Co Cit}^-]_{\text{ads}}$ species which underwent reduction to Mo.

From alkaline solutions at extreme cathodic potentials, the formation of hydrogen helped in the reduction of molybdate ions to low molybdenum oxide. Adsorbed hydrogen atoms reduced the molybdenum oxide to molybdenum metal. Hydrogen took part in the reduction of molybdenum oxide and not in the formation of molybdenum.

4.1. Hydrogen evolution reaction (h.e.r)

Hydrogen evolution reaction in alkaline solutions proceeds via three steps:

1. Electronation of water with adsorption of hydrogen—Volmer reaction.
2. Electrochemical desorption of H₂—Heyrovsky reaction.
3. Chemical desorption—Tafel reaction



where steps (2) and (3) may be alternative or simultaneous.

In the present study, increase of Mo content in the alloy increased the exchange current of hydrogen evolution. Capacitance of the double layer increased with Mo content in the alloy. The adsorbed hydrogen atom and the strength of bonding in the chemisorption appears decisive with surface interaction. A strong bonding would yield a surface species essentially immobile and exhibit high activation energy requirement for further chemical or electrochemical transformation. The adsorption of the H atoms plays a key role in electrocatalysis.

In order to correlate M–H bond energy and exchange current density, various ideas like ‘Volano’ shaped curves were discussed [25,26]. As h.e.r involves the transfer of the electron from an electrode surface (work function) and the density of electrons close to the energy level of metal surface (density of states at E_F) is an important parameter governing electrochemical reaction rates. The electron density of states at E_F may be increased by forming substitution alloys and intermetallic phases to improve the catalytic activity. In this case the lattice parameter and interatomic distance of the Co–Mo alloyed material changes due to the change in the amount of overlap of the electron orbitals of neighbouring atoms. When intermetallic bonding results in reduced lattice parameter, the interatomic distance increased the density of states at E_F and also Mo content in the alloy favoured h.e.r.

5. Conclusions

Bright Co–Mo alloy deposits were obtained from 0.3 M CoSO₄, 0.25 M (NH₄)₂MoO₄, 0.2 M triammonium citrate,

pH 8, at 303 K and 4 A/dm². The alloy deposition in alkaline bath involved the formation of [MoO₂ – Co Cit[−]] adsorbed complex which subsequently reduced to molybdenum. The hardness of the alloy deposit increased with molybdenum content and annealing. From 1 M NaOH solutions, Co–Mo alloy was found to be electrocatalytic for h.e.r and increase of Mo content enhanced catalytic activity.

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