ELECTROCATALYSTS BASED ON Ni-Mo-Fe COMPOSITE CATHODE AND HYDRATED NICKEL OXIDE ANODE FOR ALKALINE WATER ELECTROLYSIS

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Ni-Mo-Fe composite surface coatings obtained through electrodeposition on mild steel has exhibited very good electrocatalytic activity for the hydrogen evolution reaction (h.e.r.) in alkaline medium. Similarly hydrated nickel oxide coating obtained on stainless steel has exhibited very good electrocatalytic activity for the oxygen evolution reaction (o.e.r.) in alkaline medium. The cell voltage-current density relationship obtained by employing these catalytic electrodes in a laboratory size, monopolar unit alkaline water electrolytic cell showed 1.8 V at 300 mA.cm^{-2} in 6 M KOH at 303 K. A Brief discussion on the salient features of the preparation, characterization and test results obtained in these experiments are presented.

Keywords: Electrocatalysts, water electrolysis, composite cathode

INTRODUCTION

Several transition metals based composite materials are widely investigated for their electrocatalytic applications in alkaline water electrolyzer/fuel cells [1-10]. In our efforts to find out electrocatalysts suitable for both h.e.r. and o.e.r. in alkaline medium in order to replace the state of art cathodes and anodes, several binary and ternary composite surface coatings [11-12] based on Ni, Mo, W, Co, Cu, Fe and Cr obtained through electrolytic codeposition on mild steel substrates. are assessed for their electroctalytic activity as cathodes for the h.e.r. in 6 M KOH. Similarly, hydrated nickel oxide coated on stainless steel strips through anodic deposition is assessed [13] for its electrocatalytic activity as anode for the o.e.r. in 6 M KOH. In this paper, the electrocatalytic activities exhibited by Ni-Mo-Fe paper, the electrocatalytic activities exhibited by Ni-Mo-Fe cathode and $Ni_3O_2(OH)_4 . xH_2O$ anode for alkaline water electrolytic processes are brought out through systematic investigations.

EXPERIMENTAL

Electrodes

Mild steel and stainless steel foils were sized into 20 cm by 5 cm rectangular strips. They were masked with epoxy for edge effects and used as catalyst supports. The optimum deposition conditions employed for obtaining a uniform and adherent coating are presented in Tables I and II. The electrodes thus obtained by electrodeposition were subjected to further detailed characterization.

ZEM experiments

The surface microstructures of the coatings were investigated with scanning electron microscope (SEM, JEOL, JSM 35 CF). The chemical composition of the Ni-Mo-Fe coating was

TABLE I: Bath characteristics employed for the electrolytic codeposition of Ni-Mo-Fe on mild steel cathode

Parameters	Values
$NiSO_46H_2O$	85 gpl
$Na_2MoO_42H_2O$	10 gpl
$K_3C_6H_5O_7H_2O$	60 gpl
$FeSO_4H_2O$	10 gpl
Na_2CO_3	Excess
pH	10
Temperature	301 K
Current density	10 mA.cm^{-2}
Anodes employed	Graphite
Duration	90 min
Agitation	250 rpm
Colour of the coating	Dull grey

TABLE II: Bath characteristics employed for the electrolytic deposition of $Ni_3O_2(OH)_4$ x H_2O on stainless steel anode

Parameters	Values
$NiSO_4$ $6H_2O$	1 M
Aq. NH_3OH	Stoichiometric amount to obtain nickel tetramine complex
pH	8.25
Temperature	303 K
Current density	15 mA.cm^{-2}
Cathodes employed	Platinum foil
Duration	5 min
Colour of the coating	Black

obtained through electron probe microanalysis (EPMA) technique.

Electrochemical half-cell polarization experiments

The Ni-Mo-Fe coated cathodes and the hydrated nickel oxide anodes were designed for testing with exposed geometric area of 8.0 cm^2. The polarization experiments were carried out in a three compartment cell under galvanostatic steady state conditions. The counter electrodes were two stainless steel screens contained in nylo bags. Hg/HgO, OH$^-$ was the reference electrode. The electrolyte was prepared from AnalaR KOH pellets and was pre-electrolyzed. The working test electrodes were invariably pre-polarized at 1 mA.cm^{-2} for 30 min at room temperature. The open circuit potential was measured after 60 min at equilibrium conditions. The galvanostatic steady state potential were measured as a function of applied current densities. The IR compensation was done by interruptor method. The IR corrected potential values were used for the construction of Tafel plots. The electrochemical parameters were obatined from these curves.
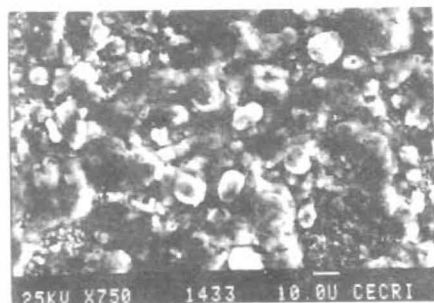

Fig. 1: SEM picture of the Ni-Mo-Fe coating on mild steel just after deposition
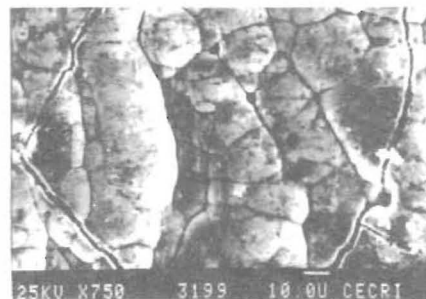

Fig. 2: SEM picture of the hydrated nickel oxide coating on stainless steel just after deposition

The long term evaluation of the test electrodes was done by periodically replenishing the water lost by evaporation and electrolysis at 3 kA.m^{-2} and at 353 K for about 1000 h of operation.

RESULTS AND DISCUSSION

Physicochemical characteristics

The coatings of Ni-Mo-Fe on mild steel substrates were extremely smooth and strongly adherent. The thickness of the coating ranged from 3.9 to 4.1 μm. The weight of the coating ranged from 3.4 to 3.6 mg.cm^{-2}. The SEM picture of the Ni-Mo-Fe coating on mild steel just after deposition is shown in Fig. 1. This shows fine grains and evidence for stress. The feasibility of co-deposition of metals like Mo, W, Co, Fe, Zn and Cr along with Ni is well established [14-17] although Mo cannot be deposited as such from aqueous solutions [18]. The chemical composition of the Ni-Mo-Fe coatings was found to be 70% Ni, 15% Mo and the rest Fe by gram atomic weight.

The hydrated nickel oxide coatings were pale black in colour initially just after deposition. The SEM picture of this coating on stainless steel just after deposition is shown in Fig. 2.

TABLE III: The reversible open circuit potential values of Ni-Mo-Fe cathode

Coating	Potential/mV against Hg/HgO, OH$^-$ (6 M)	Temperature K
	-957	303
	-941	318
Ni-Mo-Fe	-924	333
	-912	353

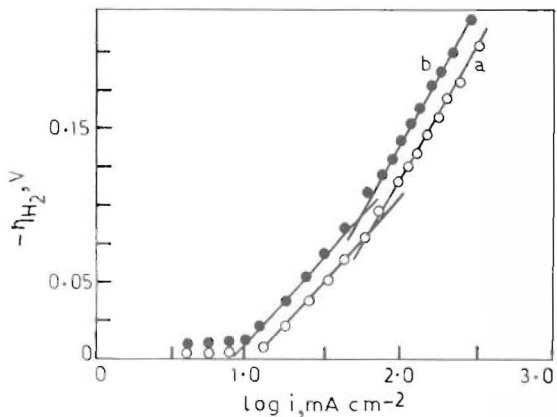Fig. 3: *Tafel plots for the hydrogen evolution reaction on Ni-Mo-Fe ternary electrodeposits (a) at 353 K (b) at 303 K in 6 M KOH*

Fig. 4: *Time variation effect of the cathode potential at 300 mA.cm^{-2} and at 353 K in 6 M KOH*

Electrochemical characteristics

The reversible open-circuit potential values measured on Ni-Mo-Fe cathode are presented in Table III as a function of temperature. It becomes evident that the influence of temperature on these values is very significant. This suggests that the adsorption of hydrogen formed during the pre-cathodization step on the cathode surface is influenced significantly by the temperature, resulting in a negative temperature coefficient of the open-circuit values.

The Tafel plots for the h.e.r. obtained on the Ni-Mo-Fe ternary codeposit cathode is shown in Fig. 3. It was noted that dual Tafel slopes exist. The apparent values of Tafel slopes and the equilibrium exchange current density were derived from these. Arrhenius plots were made both at low and high polarization conditions, (figures not shown), to calculate the apparent energy of activation values. The kinetic parameters for the h.e.r. on Ni-Mo-Fe and mild steel cathodes are presented in Table IV. It becomes evident that the cathode contribution to the electrolyzer voltage can be reduced by 0.3 V under typical industrial conditions by
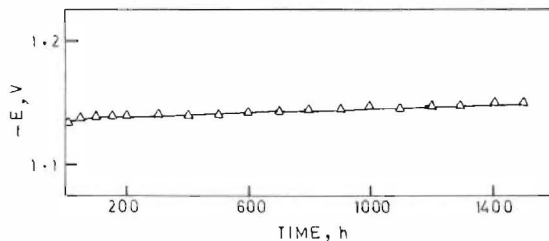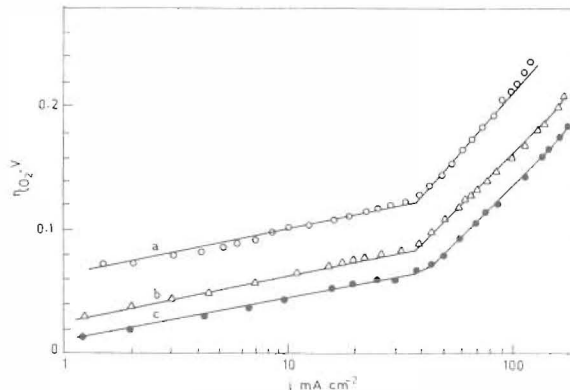

Fig. 5: *Tafel lines obtained ob hydrated nickel oxide anode in 6 M KOH (a) at 301 K (b) at 333 K (c) at 353 K*

employing the codeposit cathode in the place of the state of the art and the conventional mild steel cathode. The time variation effect of the cathode potential for the Ni-Mo-Fe co-deposit on continuous operation in 6 M KOH at a constant current density of 300 mA.cm^{-2} and 353 K is shown in Fig. 4. The results of accelerated life tests carried out on the Ni-Mo-Fe cathode indicated that the variation in the cathode potential is 35 mV over a period of 60 days at

TABLE IV: Kinetic parameters for hydrogen evolution reaction on Ni-Mo-Fe and mild steel cathodes in 6 M KOH

Codeposit	Temp (K)	b (mV.dec^{-1})		$10^3 i_0$ (A.cm^{-2})		$-\eta H_2$ (mV)	E_{act} (kJ mol^{-1})	
		at i < 50 mA.cm^{-2}	at i > 50 mA.cm^{-2}	at i < 50 mA.cm^{-2}	at i > 50 mA.cm^{-2}	at 300 mA.cm^{-2}	at low η	at high η
Ni-Mo-Fe	303	112	105	9.22	16.61	203	—	—
Ni-Mo-Fe	333	115	108	10.04	18.03	193	—	—
Ni-Mo-Fe	353	120	110	10.48	18.95	187	4.78	4.308
Mild steel	353	135	125	—	—	540	59.80	68.100

TABLE V: Electrochemical parameters for oxygen evolution on hydrated nickel oxide anode

Electrocatalyst material	Temp (K)	b (V.dec^{-1})		i_0 (A.cm^{-2})		Oxygen overpotential (V)	
		Low C.D.	High C.D.	Low C.D.	High C.D.	at 3 kA.m^{-2}	at 6 kA.m^{-2}
	301	0.040	0.220	9.6×10^{-8}	10^{-4}	0.60	0.85
Hydrated	333	0.040	0.184	5.6×10^{-6}	10^{-4}	0.39	0.51
nickel oxide	353	0.037	0.180	4.5×10^{-4}	10^{-3}	0.27	0.35

600 mA.cm^{-2} and 353 K. The steady cathode potential value of -1.13 V at 300 mA.cm^{-2} and at 353 K over a period of 1400 h indicates that the stability of Ni-Mo-Fe is reasonably good to employ this in industrial electrolytic cells.

The behaviour of hydrated nickel oxide anode under steady state conditions in 6 *M* KOH is shown in Fig. 5. The electrochemical parameters for the o.e.r. are presented in Table V. There exists dual Tafel slopes depending upon the operating current density and not upon the operating temperature. At low current densities (i 0.5 kA.m^{-2}), the Tafel slope ranges from 0.04 to 0.06 V.dec^{-1} and at high current densities (i = 0.5 to 1.5 kA.m^{-2}), the Tafel slope is from 0.180 to 0.20 V.dec^{-1}. The o.e.r. is therefore controlled by the contributing influences of mass transfer and the non-uniform current distribution in the porous electrode structure. The apparent exchange current density values ranged from 10^{-4} to 10^{-3} A cm^{-2} as a function of operation temperature. The oxygen overpotential was 0.27 V at 3 kA.m^{-2} and 353 K. This value compares well with that of many reported electrocatalyst systems [19] and is better than that of smooth Ni sheet anode (0.375 V at 3 kA.m^{-2} and at 373 K in 10 *M* KOH) [20].

A laboratory size exploratory unit alkaline water electrolytic cell was assembled with the Ni-Mo-Fe cathode and hydrated nickel oxide anode and operated in 6 *M* KOH. The typical polarization curves obtained after IR correction are shown in Fig. 6. For the purpose of comparison, the polarization curve obtained with the mild steel cathode and nickel coated mild steel anode, which is also in industrial use by convention, obtained under identical conditions, is also included.

It is brought out that at 300 mA.cm^{-2} and 353 K, a laboratory size unit, monopolar, tank type alkaline water electrolytic cell works at 1.8 V with these electrocatalytic electrodes (15 cm by 10 cm size) whereas the conventional cell works at 2.3 V. In terms of electrical power in an industry engaged in the electrochemical production of pure hydrogen for various end uses, with 50 tank type electrolytic cells connected in series, a minimum energy saving of 36% is possible.
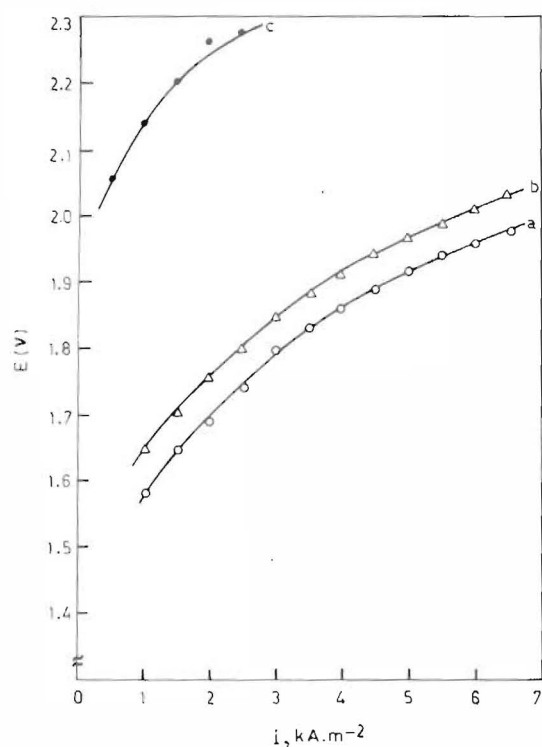

Fig. 6: Current density versus unit cell voltage plot for the electrolysis of water (a) and (c) at 353 K, (b) at 333 K. For curves (a) and (b): Cathode is Ni-Mo-Fe and anode is hydrated nickel oxide. For curve (c): Cathode is mild steel and anode is nickel plated mild steel

CONCLUSION

It has been shown in that Ni-Mo-Fe cathode and hydrated nickel oxide anode offer good electrocatalytic activities in alkaline water electrolysis. A laboratory size unit cell which worked at 1.8 V, 300 mA.cm^{-2} and 353 K was demonstrated whereas the conventional cell worked at 2.3 V. The energy

saving could be more significant if the present data are compared with data available from industry namely, 2.2 to 2.5 V at 50 to 100 mA.cm^{-2} and at 313 K in 25% NaOH [21].

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