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Influence of plating variables on the electrocatalytic behaviour of Ni-Mn electrocoated cathodes for alkaline water electrolysis

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The electrocatalytic properties of Ni-Mn codeposits as a function of plating parameters is studied in detail. Higher current densities, moderate temperature and baths of neutral pH yield good electrocatalysts.

Key words: Water electrolysis, Ni-Mn coated cathode, electrocatalyst

INTRODUCTION

Nowadays, Ni based coatings prepared by electrodeposition are finding increased use as catalytic cathodes in alkaline water electrolysis [1]. The codeposition of Mn with Ni is bound to exhibit interesting electrocatalytic properties. With this end in view, we have studied the hydrogen evolution characteristics of this system and the findings are reported in this paper.

EXPERIMENTAL

Ni-Mn alloys were electrodeposited from simple sulphate baths in the acidic to neutral ranges. The experimental procedures have already been detailed [2].

RESULTS AND DISCUSSION

Effect of deposition current density

The results of the cathodic polarisation study are given in Tables- IA and IB. The samples fall under the following deposition current density (c.d.) ranges based on their electrocatalytic efficiency - (i) 2 to 10 mA cm^{-2} (low c.d. range) and (ii) 10 to 50 mA cm^{-2} (high c.d. range). The low c.d. ranges at all bath pH levels are not suitable for the preparation of good electrocatalysts. The catalytic activity increases with increase in c.d. in low c.d. ranges for acidic baths and it decreases with increase in c.d. for neutral baths.

High c.d. ranges improve the electrocatalytic activity. At all bath pH levels, electrocatalytic activity increases with increase in c.d. But beyond a limit, characteristic of pH of the bath, further higher c.d.s are not practically feasible as these result in excessively stressed deposits, which get exfoliated. Gelatin addition is found to be useful in preparing good electrocatalysts as moderate c.d.s from baths of neutral pH.

Effect of bath temperature

One of the means of obtaining stable coatings at high c.d. ranges from baths of high pH values is to operate the deposition process at elevated temperature. This practice is bound to be useful. Except at a pH of 2.90 at all other pH values (1.65, 2.23 and 5.12), increase in temperature improves electrocatalytic performance. At highly acidic levels, electrocatalytic activity first decreases and later increases with rise in temperature. For the samples prepared from bath of pH 2.90, the electrocatalytic activity successively decreases with elevation in temperature. Further studies are required to understand the mechanism of the observed phenomenon.

Effect of bath pH

In general, the electrocatalytic activity is found to improve with increase in bath pH. With increase in pH acidic ranges (1.65 to 2.23), there is marked decrease in hydrogen overvoltage (hov). But on increasing the pH to 2.90, there are slight changes only in hov. But on further increase in pH values, the hov gets lowered for specimens obtained at moderate c.d.s.

CONCLUSIONS

The electrocatalytic properties of Ni-Mn system is highly sensitive to deposition parameters. Good electrocatalysts could be obtained by employing high c.d.s and moderately high temperatures. Operation of baths in weakly acidic and neutral ranges yields improved results. In a few cases, addition agents, like gelatin, are found to be useful.

TABLE-I-A and I-B: Effect of electrodeposition parameters on hydrogen evolution

Bath composition: Nickel sulphate 40 gpl
Manganese sulphate 150 gpl
Ammonium sulphate 50 gpl

TABLE-IA:Bath temperature: 307K

pH	Current density ($mA.cm^{-2}$)	Observed voltage* (V)
1.65	3	1.27
	10	1.21
	30	1.18
	70	1.10
2.23	4	1.13
	10	1.08
	30	1.01
2.90	6	1.07
	10	1.05
	30	1.05
	60	1.00
4.00	4	1.00
	10	1.03
5.12	2	1.08
	8	1.06
	30	1.00
	50	0.99
6.46	2	0.97
	10	0.98
	30	0.95
	50	0.95
7.46	2	1.20
	7	1.20
	20	0.98
	(gelatine added)	

*at a polarising c.d. of 600 $mA.cm^{-2}$, versus Hg/HgO/30% KOH

TABLE-IB:

pH	Temp. (K)	Observed voltage* (V)
Current density: 50 $mA.cm^{-2}$		
1.65	318	1.10
	333	1.13
	368	1.02
Current density: 30 $mA.cm^{-2}$		
2.23	307	1.01
	333	1.02
	363	1.01
Current density: 10 $mAcm^{-2}$		
2.90	307	1.05
	328	1.07
	348	1.07
	373	1.08
5.12	323	1.06
	343	1.03
	371	1.01

*at a polarising c.d. of 600 mA cm^{-2}, versus Hg/HgO/30% KOH

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