

# Electrocatalytic properties of electrodeposited Ni–Mn–S system in alkaline electrolytes

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Ni–Mn–S was electrodeposited on mild steel from sulphate–thiocyanate baths. The resultant materials were evaluated for electrocatalytic activity towards hydrogen evolution reaction in 30 wt-% KOH. Incorporation of sulphur in Ni–Mn improves the electrocatalytic activity giving a sizeable increase in exchange current density  $j_0$ . In Ni–Mn the hydrogen evolution reaction is through a Volmer–Tafel mechanism whereas in the Ni–Mn–S system follows a Tafel mechanism. The influence of deposition current density (CD) was investigated. Electrocatalytic activity increased with increase in the deposition CD and was maximum in samples deposited at 80 mA cm<sup>-2</sup>.

**Keywords:** Electrodeposition, Co-deposits, Ni–Mn–S, Electrocatalytic activity, Hydrogen evolution

## Introduction

One of the major factors limiting the operational efficiency of alkaline water electrolyzers is the cathode over potential. Among the different materials used, nickel based electrocoatings are generally considered the most suitable ones for concentrated alkaline solutions owing to their low hydrogen over voltages and chemical stability. Previously our earlier studies on Ni–Mo–Fe, Ni–Zn–Fe, Ni–Mn and Ni–Mn–Fe coatings yielded interesting results.<sup>1–6</sup> The presence of sulphur in alkaline electrolytes, lowers the hydrogen over potential.<sup>7,8</sup> Because electrodeposited Ni–Mn coatings showed encouraging electrocatalytic applications,<sup>5</sup> the incorporation of a small amount of sulphur in these, i.e. the Ni–Mn–S ternary system, is likely to exhibit improved hydrogen discharge. The present investigation is therefore devoted to studying the hydrogen evolution reaction (HER) on Ni–Mn–S electrocoated cathodes in highly concentrated alkaline electrolytes, i.e. 30 w/o aqueous solutions at 30°C. The electrode materials were not in their respective state of thermodynamic equilibrium because the cathodes were pre-electrolysed at 500 mA cm<sup>-2</sup> for 30 min prior to measurements. In this paper, the influence of deposition CD on the hydrogen evolution characteristics of Ni–Mn–S co-deposits is reported.

## Experimental

The experimental electrode consisted of a cylindrical mild steel rod with a circular cross-sectional area of 0.33 cm<sup>2</sup>, embedded in 'Araldite', which covered the unwanted areas. Ni–Mn–S alloys were electrodeposited on this substrate from sulphate baths after the usual cleaning treatments. A bagged graphite rod was used as

the insoluble anode. The bath composition used consisted of NiSO<sub>4</sub> 6H<sub>2</sub>O 40 g dm<sup>-3</sup>, MnSO<sub>4</sub> H<sub>2</sub>O 150 g dm<sup>-3</sup>, (NH<sub>4</sub>)CNS 10 g dm<sup>-3</sup> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 50 g dm<sup>-3</sup>.

Ammonium sulphate functioned as additive in the bath. A constant cathodic current, ranging from 10 to 100 mA cm<sup>-2</sup> was applied. All the coatings were grown to the same thickness. After deposition, the samples were removed from the bath, rinsed well with distilled water and immersed in 30 wt-% KOH at 30°C. The cell used for the electrochemical measurements is described in detail elsewhere.<sup>2–4</sup> The temperature was maintained constant at 30°C. Non-purified 30 wt-% KOH solutions were employed.

After immersion of the electrode in alkaline solution, a constant cathodic current of 500 mA cm<sup>-2</sup> was applied for 30 min, until the variation of hydrogen over-potential with time was less than 1 mV min<sup>-1</sup>. The current density was then varied galvanostatically from 500 to 1 mA cm<sup>-2</sup> and the corresponding Tafel slope  $b$ , exchange current density  $j_0$  and the hydrogen over voltage at a current density of 250 mA cm<sup>-2</sup> ( $\eta_{250}$ ) were determined. The polarization experiments were done with 'Aplab' high precision DC electronic power supply.

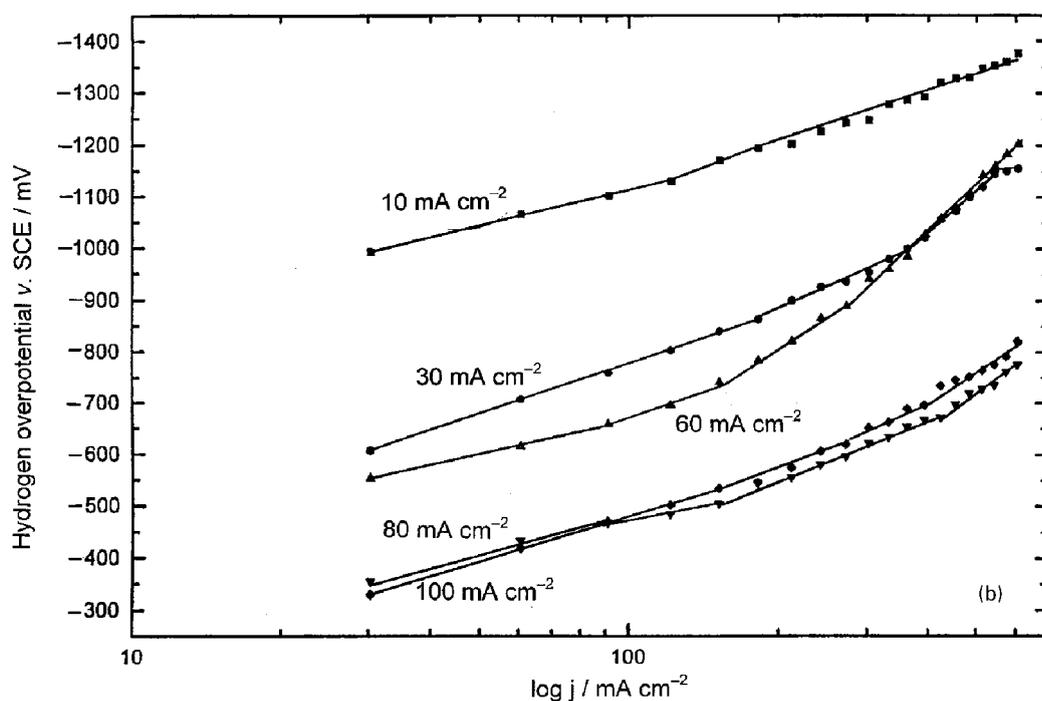
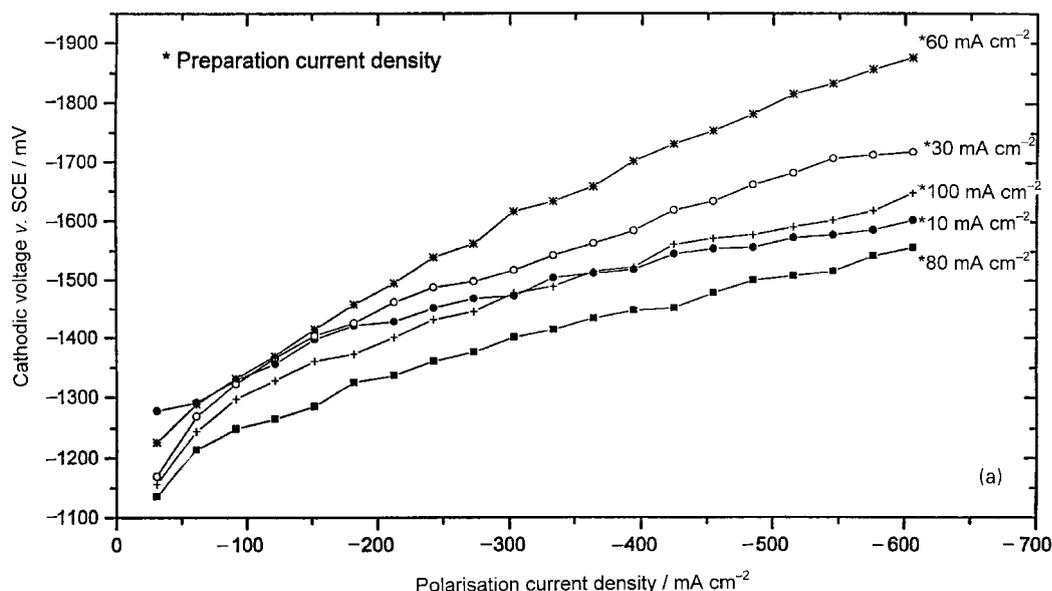
## Results and discussion

The results of cathodic polarisation experiments for Ni–Mn–S samples are shown in Fig. 1. The hydrogen evolution characteristics for the deposits studied are shown in Table 1.

An examination of Fig. 1 indicates the influence of deposition CD on the electrocatalytic behaviour. The sample deposited at 10 mA cm<sup>-2</sup> has an inferior electrocatalytic activity with a  $\eta_{H_2}$  (250) of -1233.7 mV. The sample displays a low exchange CD of 0.022 mA cm<sup>-2</sup>. The high  $b$  value of 236.18 mV revealed that the hydrogen evolution occurs by the Tafel mechanism. For this analysis, the values of  $b$  given in the work of Choquette *et al.*<sup>9</sup> for the different HER mechanism are

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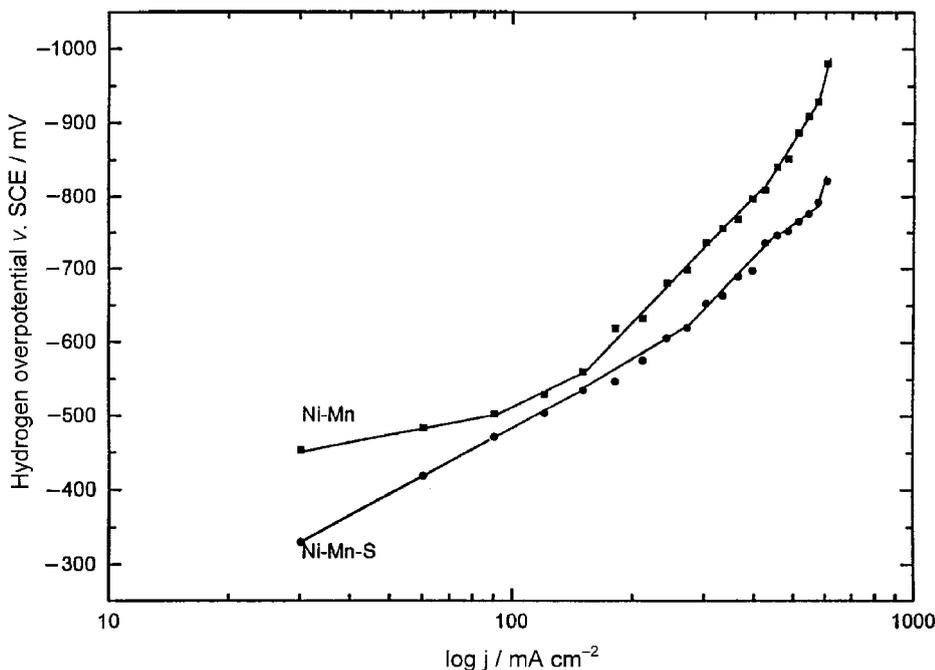
1 a, b Hydrogen evolution characteristics of Ni-Mn-S co-deposits

taken as the reference (values of the Tafel slope *b* up to 66 mV per decade indicate the Heyrovsky-Volmer mechanism; values in the neighbourhood of 118 mV per decade indicate a Tafel-Volmer mechanism and above 200 mV per decade they indicate the Tafel mechanism). There is a marked improvement in

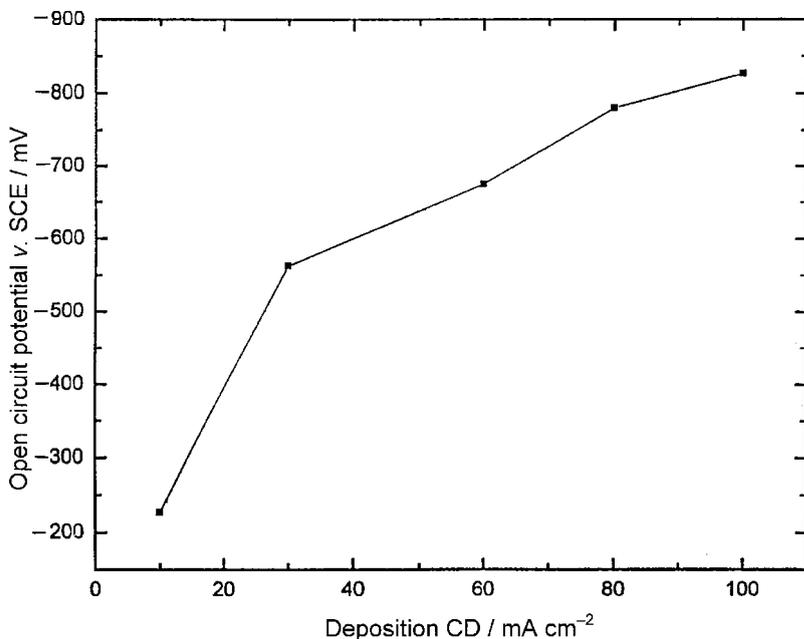
electrocatalytic activity on increasing the preparation CD to 30 mA cm<sup>-2</sup>. The improvement in hydrogen evolution is shown by a hundredfold increase in *j*<sub>0</sub>. The occurrence of the Tafel mechanism is revealed by the large *b* value of about 333.98 mV. Further increase in deposition CD to 60 mA cm<sup>-2</sup> brings down the  $\eta_{H_2}$  (250) marginally by about 66 mV. Hydrogen evolution reaction proceeds through a Volmer-Tafel mechanism. Further increase in deposition CD to 80 mA cm<sup>-2</sup> results in excellent electrocatalytic deposits. The deposit shows a low  $\eta_{H_2}$  (250) of -581.49 mV. This increase in electrocatalytic activity corresponds to an increase in *j*<sub>0</sub> to 9.9 mA cm<sup>-2</sup>. Further increase in deposition CD up to 80 mA cm<sup>-2</sup> and decreases thereafter. This improvement with respect to deposition CD is partially due to

Table 1 Hydrogen evolution characteristics of Ni-Mn-S coatings

Deposition CD/mA cm <sup>-2</sup>	<i>j</i> <sub>0</sub> /mA cm <sup>-2</sup>	<i>b</i> /mV dec <sup>-1</sup>	$\eta_{250}$ /mV
10	0.022	236.18	-1233.7
30	2.266	333.98	-932.04
60	1.977	248.62	-866.37
80	9.90	211.32	-581.49
100	15.24	342.26	-602.21



2 Comparison of hydrogen evolution characteristics of Ni-Mn and Ni-Mn-S co-deposits



3 Influence of deposition current density on open circuit potential of Ni-Mn-S in 30 w/o KOH

increase in surface area (because of reduced crystal size) as evident from increasing  $j_0$  values.

In order to find the effect of sulphur incorporation in Ni-Mn system, the electrocatalytic behaviour was

Table 2 Comparison of hydrogen evolution mechanisms on Ni-Mn and Ni-Mn-S coatings

System	Deposition CD/ $\text{mA cm}^{-2}$	$j_0/\text{mA cm}^{-2}$	$b/\text{mV dec}^{-1}$	$\eta_{250}/\text{mV}$
Ni-Mn	80	0.96	137.02	-680.37
Ni-Mn-S	80	16.87	291.47	-610.68

compared between the best sample identified from polarisation experiments (samples deposited at  $80 \text{ mA cm}^{-2}$ ) and the corresponding Ni-Mn co-deposit without sulphur inclusion. The results of polarisation experiments are shown in Fig. 2 and Table 2. It can easily be seen that there is significant improvement in hydrogen evolution characteristics because of sulphur inclusion. An analysis of the parameters of the electrochemical kinetics, brings out the difference in hydrogen evolution reaction mechanism between Ni-Mn and Ni-Mn-S co-deposits. As seen from the first Tafel slope parameters, the exchange CD  $j_0$  is

very much higher in Ni-Mn-S co-deposit. Tafel slope values indicate that for Ni-Mn the hydrogen evolution reaction is through the Tafel-Volmer mechanism whereas on the Ni-Mn-S co-deposit it exhibits Tafel behaviour.

The variations in open circuit potentials of the Ni-Mn-S samples with increase in deposition CD are shown in Fig. 3. It can be seen that the open circuit potential increases with deposition CD. This observation is attributed to the increased manganese content with deposition CD.

## Conclusions

Electrodeposited Ni-Mn-S system appears to be a promising candidate for alkaline water electrolysis. The hydrogen discharge on incorporation of sulphur in Ni-Mn is enhanced, manifest in a sizeable increase in exchange current density  $j_0$ . The maximum efficiency can be obtained by employing optimum deposition current density for the electrocatalytic surface coating.

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