

Sulphur content and the hydrogen evolving activity of NiS_x deposits using statistical experimental strategies

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The effect of such electroplating conditions as current density, thiourea (TU) concentration, temperature and pH on the sulphur content of NiS_x deposited electrodes has been systematically studied using fractional factorial design and response surface methodology. Fractional factorial analysis indicates that the main and interaction effects of TU concentration and current density are the key variables influencing sulphur content in a NiS_x deposit. Empirical models for sulphur content and hydrogen evolution overpotential are fitted and plotted, using central composite experimental design, as contour diagrams in order to facilitate comparison with experimental sulphur content trends and hydrogen evolving activity. The results show that, for deposits containing > 12 wt % sulphur content, hydrogen evolving activity increases with increasing sulphur content, while for those possessing < 12 wt % sulphur content, hydrogen evolution overpotential decreases with increasing electroplating current density.

1. Introduction

Hydrogen is an excellent and inexpensive energy carrier due to its nonpolluting and recyclable nature. The electrolysis of alkaline solutions is one way of producing hydrogen and dates from the early 1960s [1]. Traditionally, commercial electrolyzers employ a 28% KOH solution as the electrolyte, mild steel [2] or nickel-plated steel [3, 4] for the cathode, and an oxide-coated titanium electrode (RuO₂, IrO₂, etc.) as the anode. The employment of precious metal/valve metal mixed oxides as anodes has been well researched and dates from Beer's patent [5] on these materials. Potential cathodes can be grouped as either noble metals or nickel based materials such as nickel, nickel alloy (Ni–Zn, Ni–Al, etc.) [6–8], and NiS_x deposits [9–12].

Recently, NiS_x deposits have been considered as potential hydrogen evolving electrocatalytic substitutes for noble metals in alkaline media. In general, a NiS_x deposit can be obtained by electroplating from a Watts bath containing such sulphur sources as potassium thiocyanate (KCNS) [10], thiourea [11], and sodium dithionite [13]. Hine *et al.* [10] reported that the sulphur content of a NiS_x deposit increases with increase in KCNS concentration in the plating bath. Sabela and Paseka [11] reported that the hydrogen evolving activity of a NiS_x deposit is dependent on its sulphur content, typically between 10–20 wt %, which is, in turn, dependent upon the thiourea content of the plating bath. To the present, however, there have been no systematic studies investigating the effects of such electroplating variables as sulphur sources, pH,

current density, and the temperature of plating bath on the sulphur content of a NiS_x deposit. In addition, there is a distinct lack of studies investigating the relationship between the sulphur content of NiS_x deposits and their hydrogen evolving activity. This scarcity of information stimulated the present investigation of the effects of the preparation variables (TU concentration, current density, pH, and temperature) on sulphur content and the hydrogen evolving activity of a NiS_x deposit.

In this study, fractional factorial design [14] was employed in planning the experiments for studying the effects of the preparation variables on the sulphur content of a NiS_x deposit. In order to determine which experimental parameter settings affect sulphur content, the response surface procedure coupled with Central Composite Design [15], was employed in conjunction with additional experiments and regression analysis. Hydrogen overpotentials were subsequently determined and subjected to regression. Ideally, the work will help in 'tailoring' a good NiS_x electrode for hydrogen evolution.

2. Experimental details

2.1. Preparation of NiS_x deposits

Nickel sulphide electrodes were prepared electrolytically using a typical Watts bath, containing mainly NiSO₄ · 6H₂O (250 g dm⁻³), NiCl₂ · 6H₂O (40 g dm⁻³), and H₃BO₃ (35 g dm⁻³). The cathode, consisting of a low carbon 1 cm × 2 cm steel plate, was first cleaned with trichloroethylene, rinsed with distilled water, then acid-cleaned with 30 wt % HCl, and finally rinsed with distilled water. Two electrolytic nickel plates, each

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Table 1. Factors and levels for the 2^{4-1} fractional factorial design

Factors	Levels	
	+	-
A, Temperature ($^{\circ}\text{C}$)	70	40
B, Current density (mA cm^{-2})	40	10
C, TU concentration (g dm^{-3})	100	10
D, pH Value	5	2

possessing a geometric area of about 36 cm^2 , were employed as anodes. The effects of the following parameters on the sulphur content of the NiS_x deposits were investigated: (A) temperature; (B) current density; (C) TU concentration; and (D) pH. Fixed levels of these four parameters are given in Table 1, with the design levels being given in Table 2. The pH of the electroplating solution was adjusted with either NH_4OH or 20 wt % H_2SO_4 .

2.2. Surface morphology and composition of NiS_x deposits

The sulphur content of a NiS_x deposit was determined by BaSO_4 gravimetric chemical analysis [16], while its surface morphology was examined by a Jeol JSM 35 scanning electron microscope (SEM). X-ray diffraction (XRD) measurements were performed in a Rigaku D/MAX-IIIIV X-ray diffractometer using a CuK_α source and a goniometer angular speed of $4^{\circ} (2\theta) \text{ min}^{-1}$.

2.3. Hydrogen overpotential measurements

The hydrogen overpotential of a NiS_x electrode can be stabilized after long-term (about 200 h) cathodic polarization at relatively high current densities (about $500\text{--}800\text{ mA cm}^{-2}$) [11]. In order to improve on hydrogen overpotential reproducibility, the NiS_x electrodes in this study, were accordingly polarized without temperature control for 200 h at a cathodic current density of 700 mA cm^{-2} . The 1 M KOH solution employed for cathodic polarization and overpotential measurements, was preelectrolysed under a cathodic current density of 10 mA cm^{-2} using Ti and IrO_2/Ti electrodes as the cathode and anode, respectively.

Table 2. The design matrix and experimental data from the 2^{4-1} fractional factorial design with the defining relation $I = ABCD$

Run	Factors				Sulphur content /wt %
	A	B	C	D	
1	-	-	-	-	6.50
2	-	-	+	+	16.67
3	-	+	-	+	8.32
4	-	+	+	-	12.46
5	+	-	-	+	7.72
6	+	-	+	-	18.07
7	+	+	-	-	6.22
8	+	+	+	+	13.79

Table 3. Estimates of the effects from the 2^{4-1} fractional factorial design with the defining relation $I = ABCD$

Effects	Estimate
A + BCD	0.4625
*B + ACD	-2.0425
*C + ABD	8.0575
D + ABC	0.8125
AB + CD	-0.8475
AC + BD	0.9025
*BC + AD	-2.2025

After polarization for 200 h, electrode hydrogen overpotentials were measured galvanostatically with a HA-301 potentiostat/galvanostat system (Hokuto Denko Company, Japan). An Ag/AgCl electrode (Argenthal, 3 M KCl, 0.207 V vs. SHE at 25°C) was used as the reference, while a platinum wire was employed as the counter electrode. A Luggin capillary, whose tip was set at a distance of about 1 mm from the surface of the working electrode, was used to minimize errors due to iR drop in the electrolytes. The galvanostatic experiments were carried out at an applied geometric current density of 100 mA cm^{-2} at 25°C , with the potential being measured after 10 min. These values are not iR corrected. The 1 M KOH solution used in studying the hydrogen evolving activity, was degassed before and during the experiments with the purified nitrogen gas (99.9%).

3. Results and discussion

3.1. NiS_x deposit sulphur content

In this study the fractional factorial design method [14] and response surface procedure [15] were first established in order to identify the key variables influencing the sulphur content of a NiS_x deposit. This experimental design allows the influence on each process variable to be observed at a variety of other variable levels, as well as interactions among the variables.

The design factors and levels for the first 2^{4-1} fractional factorial experiments are listed in Table 1 and the results of these experiments are given in Table 2. The level of each variable during a run is indicated in columns 2 to 5, with the sulphur content of NiS_x deposit corresponding to each set of conditions, being shown in column 6. The combination of observations used to estimate the main effect of factor D (pH) is identical to that used to estimate the three-factor interaction effect of factors A (temperature), B (current density), and C (TU concentration); hence, the estimates of factor D and the interaction effect of factors A, B, and C are said to be 'confounded' [14]. Accordingly, the defining relation $I = ABCD$, suggested by Box *et al.* [14], was established in order to identify the relationships between the effects.

Estimates of the experimental variable effects were calculated following the procedure recommended by Box *et al.* [14] and are given in Table 3. Table 3

Table 4. The design matrix and experimental data for the 2⁴⁻¹ fractional factorial design with defining relation I = -ABCD

Run	Factors				Sulphur content /wt %
	A	B	C	D	
1	-	-	-	+	9.47
2	-	-	+	-	17.88
3	-	+	-	-	7.97
4	-	+	+	+	13.14
5	+	-	-	-	7.05
6	+	-	+	+	18.01
7	+	+	-	+	9.27
8	+	+	+	-	11.90

reveals that the effects of TU and current density are confused with the interaction effects of the other three factors ($B + ACD$ and $C + ABD$, respectively), and that the confounded two factor interaction effect of current density and TU concentration and of temperature and pH ($BC + AD$) on sulphur content are significant and require further interpretation. The main/interaction effects of the variables can be individually interpreted, if and only if, the effect of the variable in question is not confused with those of the others.

In order to separate the above confounded effects (see Table 3), alternative 2⁴⁻¹ fractional factorial experiments were performed (see Table 4), from which the main effect of factor D (pH) was found to be identical to the negative value of the ABC interaction effect and the defining relation $I = -ABCD$ was consequently established. The effects of the experimental variables were similarly calculated and are listed in Table 5. Simple addition/subtraction of Tables 3 and 5 yielded unconfounded estimates of all the effects. For example, the unconfounded main effect of factor A is given by $[(A + BCD) + (A - BCD)]/2 = 0.51$, while the corresponding unconfounded BCD interaction is similarly obtained from $[(A + BCD) - (A - BCD)]/2 = -0.0475$.

The estimates, listed in Table 6, obtained by taking the sums and differences of the confounded effects from the individual fractional factorials (Tables 3 and 5), are the same as would be obtained from an analysis of a full 2⁴ design. Current density and TU concentration were found to be the key variables determining the sulphur content of a NiS_x deposit. Factorial design also revealed that the effect of current density depends on the TU concentration and

Table 5. Estimates of the effects from the 2⁴⁻¹ fractional factorial design with the defining relation I = -ABCD

Effects	Estimate
A - BCD	0.5575
*B - ACD	-2.5325
*C - ABD	6.7925
D - ABC	1.2725
AB - CD	0.5875
AC - BD	0.0025
*BC - AD	-2.8925

Table 6. An analysis of the complete set of 16 runs, combining the results of the two fractions with the defining relation I = ABCD and I = -ABCD

Unconfounded effects	Estimate
A	0.5100
*B	-2.2875
*C	7.4250
D	1.0425
AB	-0.1300
AC	0.4525
AD	0.3450
*BC	-2.5475
BD	0.4500
CD	-0.7175
BCD	-0.0475
ACD	0.2450
ABD	0.6325
ABC	-0.2300

vice versa. The sulphur content in a NiS_x deposit, as a function of current density and TU concentration, is given in Fig. 1. An examination of Fig. 1 reveals that the effect of TU concentration on sulphur content is significantly greater at relatively lower current densities (10 mA cm⁻²). Note that a high sulphur content NiS_x deposit can be obtained at low current densities and high TU concentrations.

A comparison of Tables 3 and 5 reveals that although the fractional factorial experimental results are qualitatively the same, the effects of major interest (A, B, C, and D) are complicated by higher order effects. Unconfounded estimates of all the factors can be determined by a simple algebraic calculation. These results are the same as those given by 2⁴ full factorial design and can also be obtained from individual 2⁴⁻¹ fractional factorial designs (Table 3 or Table 5) if the basic assumption of Box *et al.* [14] are employed. These assumptions derive from the fact that higher order interaction effects (three-factor interaction in this study), as well as the interaction effects between the minor variables, are often negligible and can be ignored. If the above assumptions are employed, the fractional factorial design achieves the same unconfounded conclusion as that of 2⁴ full factorial design, but with a substantial reduction in the number of trial runs.

Although the key variables influencing sulphur content in a NiS_x deposit have now been determined, a further verification of these results as well as an investigation of sulphur content dependence on current density and TU concentration were undertaken.

The designed factors and levels for the 11 experiments in a central composite design are listed in Table 7. The sulphur content results, shown in Table 8, were subjected to regression analysis, and generated the following regression equation:

$$S = 10.94 - 1.34i + 2.43tu + 1.24i^2 + 0.86tu^2 - 1.71i \times tu \quad (1)$$

where the i and tu terms, respectively, represent

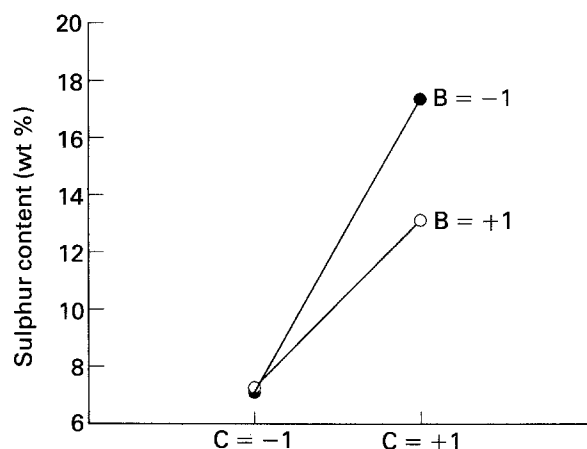
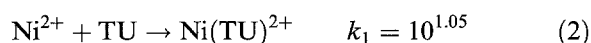


Fig. 1. The interaction effect of current density (B) and TU concentration (C) on sulphur content in a NiS_x deposit. The -1 and $+1B$ terms represent current densities of 10 and 40 mA cm^{-2} . Similarly, the -1 and $+1C$ terms represent TU concentrations of 10 and 100 g dm^{-3} , respectively. Note that the lines representing the effect of factor C for the -1 and $+1$ settings of factor B are not parallel to each other, indicating the existence of an interaction between TU and i .

current density and TU concentration. The multiple correlation coefficient, R^2 , defined as $R^2 = SSR/SST$, where the SSR and SST terms respectively represent the sum of squares of regression and sum of squares of total, gives an indication of regression model fit. Since the value of R^2 (0.95) is close to 1, the regression model is considered to be an accurate representation of the experimental data.

Regression Equation 1 was used in constructing the contour plot for sulphur content against current density and TU concentration shown in Fig. 2. An examination of Fig. 2 reveals that sulphur content increases with increasing TU concentration at relatively low current densities, implying that the Ni and NiS_x electrodepositions are competitive reactions; results substantiated by the X-ray diffraction spectrum of a NiS_x deposit (Fig. 3), which possesses a large background with two major broad peaks corresponding to the Ni 111 ($d = 2.034$) and $\text{Ni}_{2.824}\text{S}_2$ 220 ($d = 1.799$) planes. Assuming that the Ni and NiS_x electrodepositions are competitive reactions, electrodeposited sulphur arises from electroplating of the Ni^{2+} and TU chelates ($\text{Ni}(\text{TU})^{2+}$ and $\text{Ni}(\text{TU})_2^{2+}$ complexes), which form in solution, according to the following reactions [17]



Accordingly, at high TU concentrations, the concentration of the free ion, Ni^{2+} , is relatively low, giving the high sulphur content observed in NiS_x deposits. Figure 2 also reveals that, in regions of high TU concentration, the sulphur content of a NiS_x deposit decreases with increasing current density. This result can be explained in terms of polarization behaviour. At high current density, the Ni-TU complex is more polarized than Ni itself, and consequently, more Ni ions are deposited than Ni-sulphur codeposits.

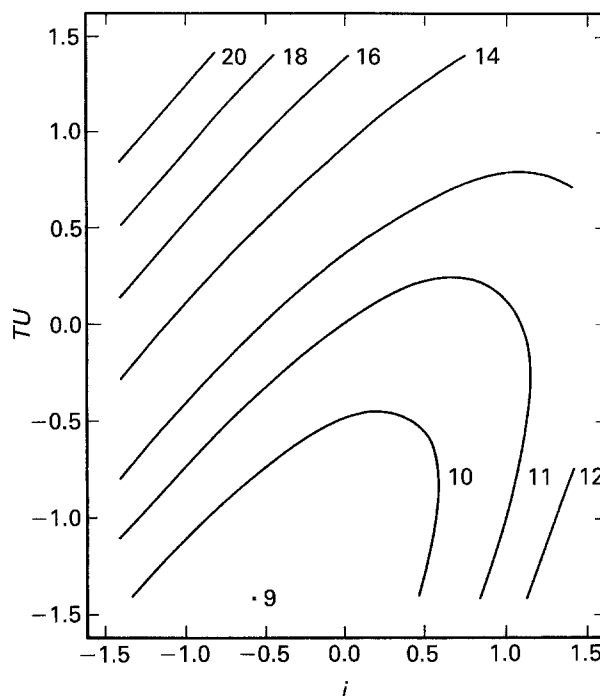


Fig. 2. Constant sulphur content (wt %) contour lines against current density and TU concentration. Note that the symbols of the TU and i coordinates are represented as their corresponding level values (see Table 7).

3.2. Hydrogen evolving activity

In order to appraise the electrolysis performance for practical applications, the NiS_x deposits, after first being cathodically polarized for 200 h, were then polarized at an applied geometric current density of 100 mA cm^{-2} . The overpotential results, listed in the last column of Table 8, were subjected to regression analysis and generated the following regression equation:

$$\eta = 98.00 - 0.47i - 22.01tu - 6.94i^2 + 0.57tu^2 + 12.75i \times tu \quad (4)$$

where the i and tu , as previously, represent current density and TU concentration. The value of R^2 (0.92) is close to 1, the regression model is considered to be an accurate representation of the experimental data.

The dependence of the hydrogen evolving overpotential on current density and TU concentration is shown in Fig. 4. A comparison of Figs 2 and 4 reveals that for deposits containing $> 12 \text{ wt } \%$ sulphur content, hydrogen evolving activity increases with increasing sulphur content, while for those possessing $< 12 \text{ wt } \%$ sulphur content, hydrogen evolving overpotential decreases with increasing electroplating current density. The latter result can be partially explained by the fact that deposits obtained at high current densities are more porous than those obtained at low current densities. The SEM photographs of NiS_x deposits obtained at low TU concentrations, shown in Fig. 5(a) and (c), respectively, reveal that a 'mud-cracked' surface morphology occurs at low current densities (a), while at high

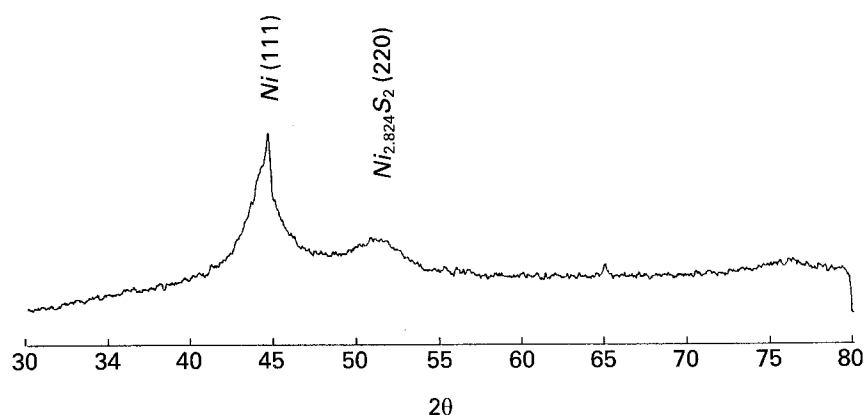
Fig. 3. A X-ray diffraction pattern of a NiS_x deposit.

Table 7. Factors and levels for the central composite design

Levels	Factors	
	i /mA cm ⁻²	TU /g dm ⁻³
$-\sqrt{2}$	4	10
-1	10	23.1
0	25	55
+1	40	86.6
$+\sqrt{2}$	46	100

current densities, the deposited layer becomes more rough and porous (c). The porous layer possesses high surface area and consequently gives high hydrogen evolving activity.

The morphology of deposits obtained at low current densities depends strongly on the TU concentration: a TU concentration of 23.1 g dm⁻³ yields a smooth morphology (Fig. 5a), whereas a TU concentration of 86.6 g dm⁻³ gives a 'cauliflower-like' (Fig. 5b) porous morphology. The latter morphology is responsible for layer porosity, providing a highly active surface area conducive to a high hydrogen evolving activity. Sabela *et al.* [11] showed that the decrease in the hydrogen evolving overpotential after long-term polarization of a NiS_x deposit was associated with the washing-out or reduction of sulphur, resulting in the exposure of a larger active surface area for

Table 8. The design matrix and experimental data from the central composite design for the quadratic form fit

Run	Factors		Sulphur content /wt %	η^* mV
	i	TU		
1	-1	-1	10.51	135
2	-1	1	17.51	66
3	1	-1	11.93	105
4	1	1	12.11	87
5	0	0	11.05	95
6	0	0	11.07	98
7	0	0	10.71	101
8	0	$-\sqrt{2}$	8.33	124
9	0	$\sqrt{2}$	17.02	61
10	$-\sqrt{2}$	0	15.81	73
11	$\sqrt{2}$	0	11.07	82

* Overpotential at 100 mA cm⁻² in 1 N KOH at 25 °C.

hydrogen evolution. Their observations support the present results of an increase in hydrogen evolving activity with an increase in the NiS_x sulphur content.

4. Conclusions

Fractional factorial design has been shown to be a useful tool in reducing the number of trial runs and in reaching the unconfounded result. The experimental results from the response surface method, subjected to regression analysis and plotted as contour diagrams, were extremely useful in studying the effects of the key variables (TU concentration and current density) on sulphur content and the hydrogen evolving activity of a NiS_x deposit. Sulphur content in a NiS_x deposit is predominantly determined by the main/interaction effects of TU concentration and current density. At low current densities and high TU concentrations, a high sulphur content NiS_x deposit

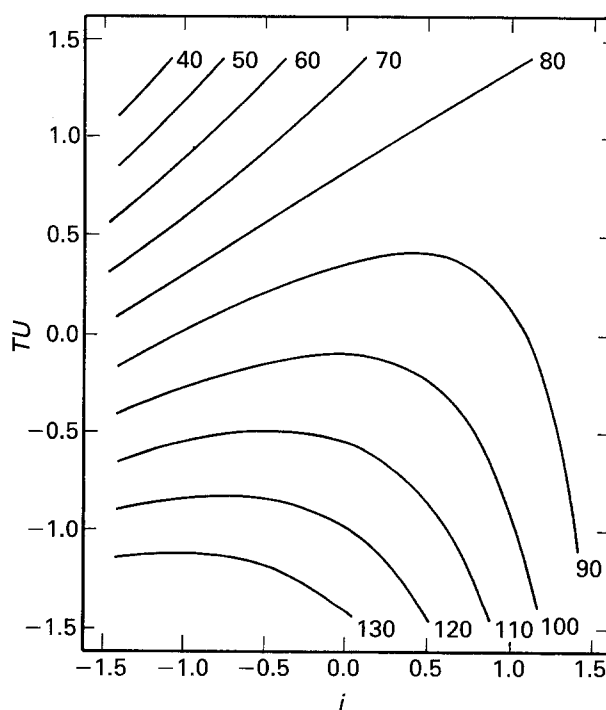


Fig. 4. Constant hydrogen evolving overpotential (mV) contour line against current density and TU concentration. Note that the symbols of the TU and i coordinates are represented as their corresponding level values (see Table 7).

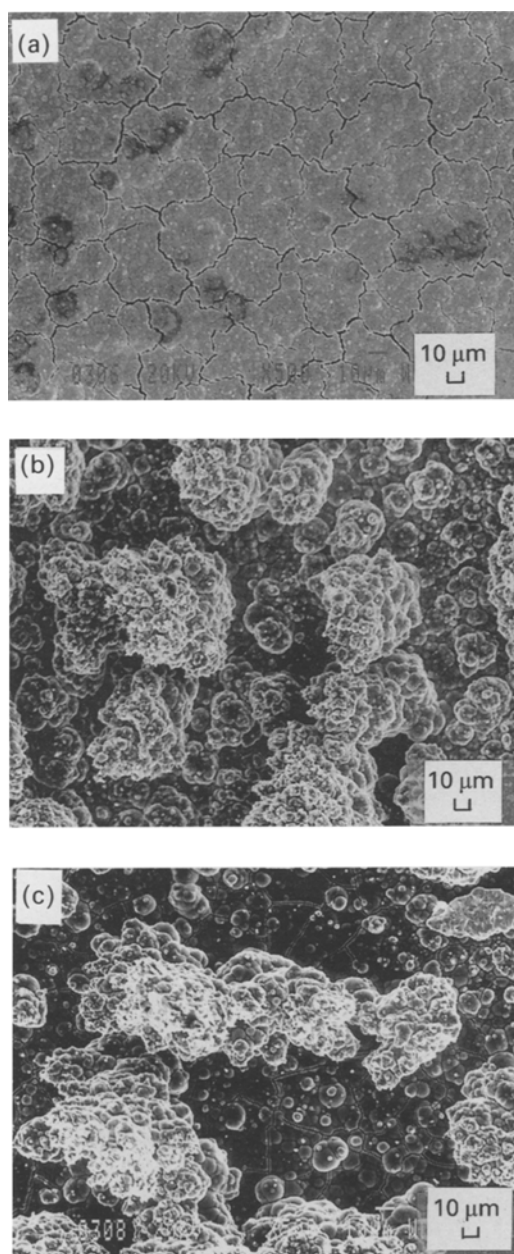


Fig. 5. SEM photographs of NiS_x electrodes resulting from: (a) run 1; (b) run 2; (c) run 3 (see Table 8)

can be obtained, while at high current densities, sulphur content is essentially constant and independent of TU concentration. A NiS_x deposit morphology depends strongly on TU concentration and current density. Long-term cathodic polarization exposes a large active surface area for hydrogen evolution in high sulphur content NiS_x deposits, resulting in a reduction in hydrogen evolving overpotential.

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