



## Recovery of activated nickel from residues for electroforming applications

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### Abstract

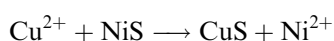
An electrochemical approach was made to recover the nickel from plating wastes in the form of activated nickel by incorporating additives such as thiourea, sodium metabisulfite and sodium thiosulfate in the electrolyte. The anodic behaviour of the nickel produced was studied for its suitability in a Watts nickel and chloride free sulfate baths. It was found that the activated nickel produced with sodium metabisulfite and thiourea additives performs similarly to commercially available activated nickel anodes.

### 1. Introduction

Very few countries produce primary nickel by exploiting sulfide or lateritic ore bodies and many are totally dependent on the import of nickel and its compounds. This dependence is motivating a drive to exploit secondary sources of the metal. For example, secondary nickel can be obtained from a number of sources, including spent nickel oxide catalyst, the bleed solution of a copper electrorefining cell, sludge produced during the pickling of stainless steel and scrap metal. The buildings or nodules generated in the nickel plating and electroforming process is another secondary source. During plating, these nodules usually grow at the contact points and also at the edges and corners of the job being plated. Accumulated in tonnage quantities these nodules can conveniently be processed for the production of nickel or its pure salts. Further, these plating wastes are relatively clean compared to other secondary sources.

Activated nickel is a special form of refinery nickel developed for use in nickel plating solutions. This activated nickel incorporates a small but important amount of sulphur which gives a high degree of electrochemical activity making the material most suitable for use, where titanium anode baskets are employed [1–4]. Activated nickel dissolves more smoothly than nonactivated nickel.

An interesting property of the nickel sulfide residue from activated nickel is its reaction with copper ions contaminating the plating solution. Although nickel sulfide is very insoluble, copper sulfide is even less soluble and the following reaction occurs:



The solubility products of nickel and copper sulfide at 18 °C are  $1.4 \times 10^{-24}$  and  $8.5 \times 10^{-45}$ , respectively [5].

In this work the authors have studied the development of activated nickel anodes from a secondary source such as nodules using additives such as thiourea, sodium metabisulfite and sodium thiosulfate in the electrolyte. Hull cell experiments, electroforming of foils and anodic polarization of the activated nickel anodes were carried out and compared with commercially available activated nickel.

### 2. Experimental details

The nickel nodules obtained from an electroplating unit could be conveniently grouped into four fractions small lumps, bunches of nodules, nickel-coated copper wires and foils and dust. Small and discrete lumps were found to be advantageous because they were easily handled. The other major fraction of the material is in the form of bunches with cluster-like formations of nodules at the centre. These materials were used as anodes. Table 1 shows the bath composition and operating conditions of Watts and chloride free sulfate bath.

#### 2.1. Hull cell studies

A 267 ml Hull cell made of PVC was used for studying the effect of additives on the deposit characteristics at various current densities [6]. Brass panels of size 100 mm × 75 mm were mechanically polished and degreased. These panels were alkaline cleaned, acid dipped and are used as cathodes. Electrolytic nickel was used as anode. A current was applied, from the

Table 1. Bath composition and operating conditions

Composition	Watts bath	Chloride free sulfate bath
Nickel sulfate	250 g l <sup>-1</sup>	250 g l <sup>-1</sup>
Nickel chloride	40 g l <sup>-1</sup>	—
Boric acid	40 g l <sup>-1</sup>	40 g l <sup>-1</sup>
pH	3.0–4.5	3.0–4.5
Temperature	40–50 °C	40–50 °C
Current density	3–7 A dm <sup>-2</sup>	3–7 A dm <sup>-2</sup>

regulated supply, at 3 A for a duration of 5 min. Hull cell patterns were recorded.

## 2.2. Electroforming of activated nickel foils

The electroforming of the activated nickel was carried out on a stainless steel mandrel of size 200 mm × 125 mm to a thickness of 150 μm from the Watts bath at 45–50 °C at anode current densities of 3–7 A dm<sup>-2</sup> using different additives such as sodium metabisulfite, thiourea and sodium thiosulfate [7]. The anodes were made from residues for electroforming applications. After deposition foils were removed from the mandrel and used for polarization measurements.

## 2.3. Anodic polarization studies

Electroformed activated nickel strips of 1 cm<sup>2</sup> area were mounted on a special holder and cleaned electrochemically. Anodic polarization measurements were carried out in a single compartment cell by potentiodynamic method in a Watts bath and chloride free sulfate nickel electrolytes using a BAS-100 A electrochemical analyser. Platinum foil of 1 cm<sup>2</sup> area was used as the cathode.

Sweep rate of 1 mV s<sup>-1</sup> was used and the potentials were measured with respect to a saturated calomel electrode [8]. Anodic polarization characteristics of the activated nickel anodes were compared with those of an activated nickel anode available in the market.

## 3. Results and discussion

### 3.1. Hull cell studies and electroforming of activated nickel foils

Figure 1 gives the code for recording Hull cell pattern. Figure 2(a), (b) show the Hull cell pattern obtained from the plain bath and with saccharin and sodium lauryl sulfate. It was found that in the former case the bright deposit region is completely narrow and deposits are stressed. Hence, for further studies 0.2 g l<sup>-1</sup> of saccharin and 0.2 g l<sup>-1</sup> of sodium lauryl sulfate were added to reduce the stress in the Watts bath.

Figure 3 shows the Hull cell patterns obtained with different concentrations of sodium metabisulfite. It was found that the brightening region is widened from 1.8 to 2.4 A dm<sup>-2</sup> with an increase in additive concentration.

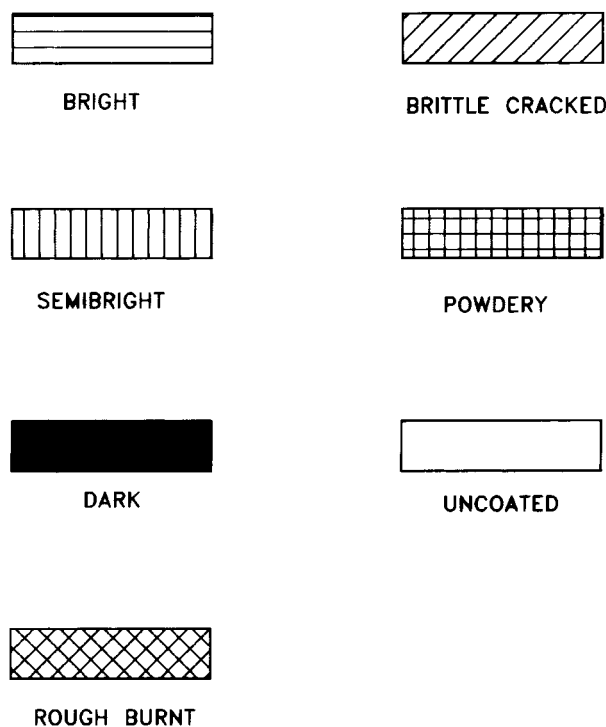


Fig. 1. Codes for recording the Hull cell pattern.

A current density of 1.8 A dm<sup>-2</sup> was fixed for the electroforming of the activated nickel at a concentration range from 0.5 to 2 g l<sup>-1</sup>. Higher additions produced highly brittle nickel foil. It is seen from Figure 4 that the deposit is bright when the concentration range of thiourea is from 0.01 to 0.03 g l<sup>-1</sup>. At higher than 0.03 g l<sup>-1</sup> concentration the deposit is semibright. At 6 A dm<sup>-2</sup> the deposit is semibright in the whole concentration region. Thus, this current density was fixed for obtaining electroformed foil even though the deposit was semibright. The deposit obtained with higher concentrations of thiourea (> 0.15 g l<sup>-1</sup>) was highly cracked.

The Hull cell patterns obtained using additions of sodium thiosulfate is shown in Figure 5. It was found that as the concentration was increased from 0.01 to 0.04 g l<sup>-1</sup> the bright deposit range increased from 4.5 to

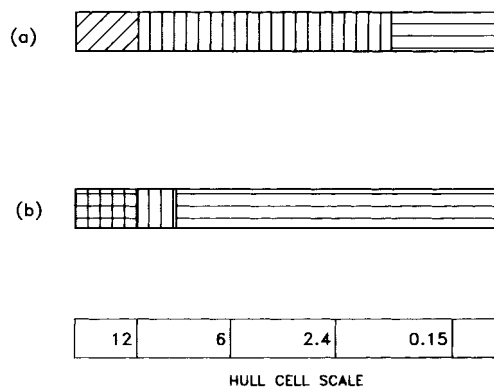


Fig. 2. Appearance of Hull cell test plates in a Watts bath (a) In a plain Watts bath, (b) a Watts bath containing 0.2 g l<sup>-1</sup> sodium lauryl sulfate and 0.2 g l<sup>-1</sup> saccharin.

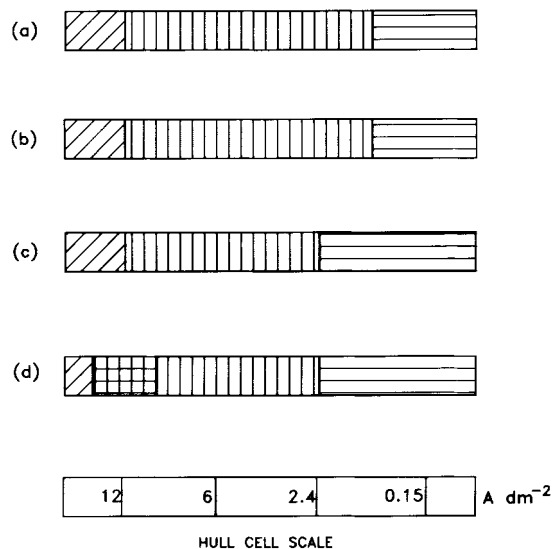


Fig. 3. Appearance of Hull cell plates in Watts bath with different concentrations of sodium metabisulfite: (a) 0.5, (b) 0.9, (c) 1.59 and (d) 2.0 g l<sup>-1</sup>.

12 A dm<sup>-2</sup>. Thus, a current density of 4.5 A dm<sup>-2</sup> was fixed for obtaining good electroformed foil at all concentration ranges. The deposit obtained from the above conditions was good and stress free.

### 3.2. Anodic polarization studies in Watt's bath

The anodic polarization of electrolytic nickel and commercial activated nickel carried out in a Watts bath showed dissolution potentials of +200 and -200 mV, respectively, with respect to the saturated calomel

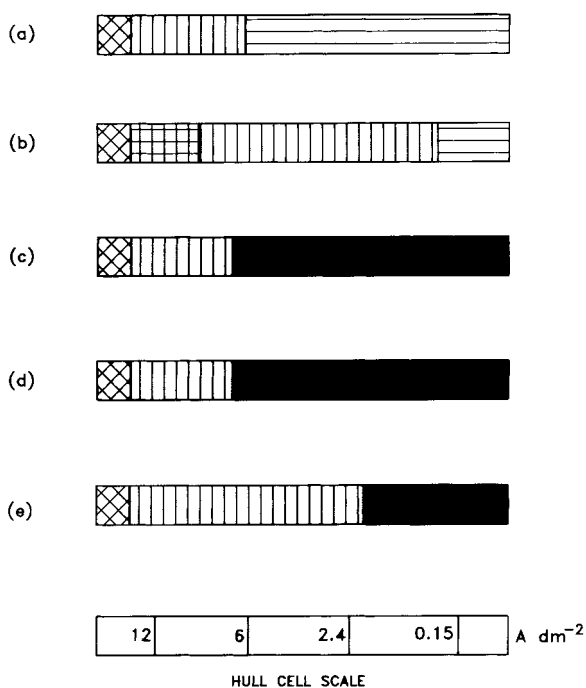


Fig. 4. Appearance of Hull cell plates in a Watts bath with different concentrations of thiourea: (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.10 and (e) 0.15 g l<sup>-1</sup>.

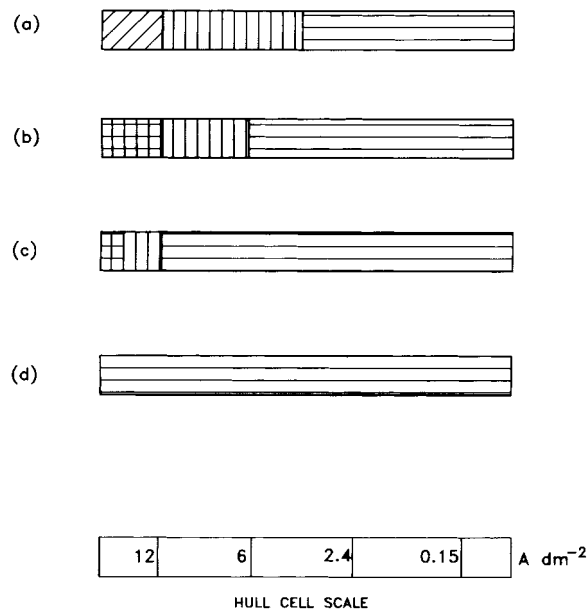


Fig. 5. Appearance of Hull cell plates in a Watts bath with different concentrations of sodium thiosulfate: (a) 0.01, (b) 0.02, (c) 0.03 and (d) 0.04 g l<sup>-1</sup>.

electrode. It is evident that the performance of activated nickel is by far superior compared to electrolytic nickel. Its dissolution potential is lowered by 400 mV and at this lower voltage it is active throughout the current density range, say, up to 10 A dm<sup>-2</sup> studied.

The results for anode polarization of the activated nickel electrode prepared from the Watts bath, using different amounts of sodium metabisulfite, are presented in Table 2 and Figure 6. As the concentration is increased, the dissolution potential becomes lower and beyond a concentration of 1 g l<sup>-1</sup> it starts increasing. It was found that the addition of 1 g l<sup>-1</sup> sodium metabisulfite results in activated nickel electrodes having a minimum dissolution potential of -0.25 V. This activated nickel electrode has about 50 mV lower dissolution potential compared to the commercially available activated nickel anode. It is further noted that the electrode is active throughout the current densities studied. Results of polarization of the activated nickel electrodes prepared from the Watts bath using different amounts of thiourea are presented in Table 3 and Figure 7. As the concentration is increased, the dissolution potential is lowered, and beyond a concentration

Table 2. Anodic polarization studies in a Watts bath using different concentrations of sodium metabisulfite

Concentration of sodium metabisulfite /g l <sup>-1</sup>	Dissolution potential /V vs SCE
0.5	-0.175
1.0	-0.250
1.5	-0.185
2.0	-0.140

System: activated nickel prepared using sodium metabisulfite

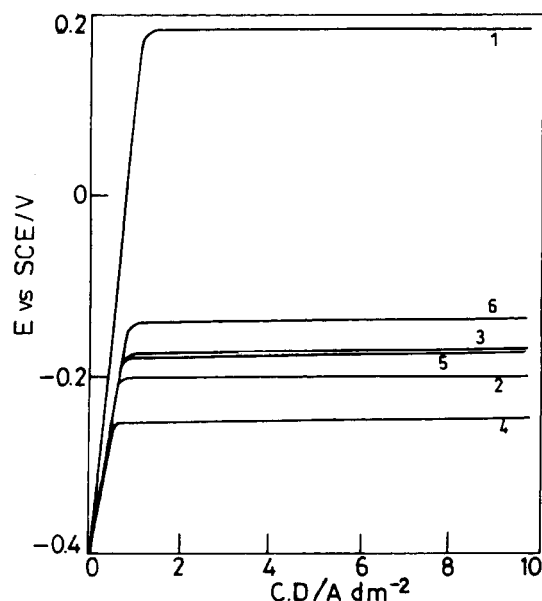


Fig. 6. Anodic polarization of activated nickel electrodes prepared using different concentrations of sodium metabisulfite in a Watts bath. Key: (1) electrolytic nickel, (2) activated nickel, (3) 0.5, (4) 1.0, (5) 1.5 and (6) 2.0 g l<sup>-1</sup>.

of 0.1 g l<sup>-1</sup> it increases. It was found that the addition of 0.1 g l<sup>-1</sup> thiourea results in activated nickel electrodes which have a minimum dissolution potential of -0.22 V. As in the earlier case the electrode is active throughout the current densities studied.

Results of polarization of the activated nickel electrode prepared from the Watts bath using different amounts of sodium thiosulfate are presented in Table 4 and Figure 8. As the concentration is increased, the dissolution potential is lowered and beyond a concentration of 0.02 g l<sup>-1</sup> it increases. At a concentration of 0.02 g l<sup>-1</sup> thiourea, the resultant activated nickel electrodes have a minimum dissolution potential of 0.165 V. This activated nickel electrode has about 35 mV higher dissolution potential compared to the commercial activated nickel sample. There is energy saving when compared with the use of electrolytic nickel. However, its performance is not impressive when compared with commercial activated nickel.

Of the three additives tried the use of sodium metabisulfite at a concentration of 1 g l<sup>-1</sup> would be the best followed by thiourea at a concentration of 0.1 g l<sup>-1</sup>.

Table 3. Anodic polarization studies in a Watts bath using different concentrations of thiourea

Concentration of thiourea /g l <sup>-1</sup>	Dissolution potential /V vs SCE
0.01	-0.160
0.03	-0.180
0.05	-0.185
0.10	-0.220
0.15	-0.210

System: activated nickel prepared using thiourea

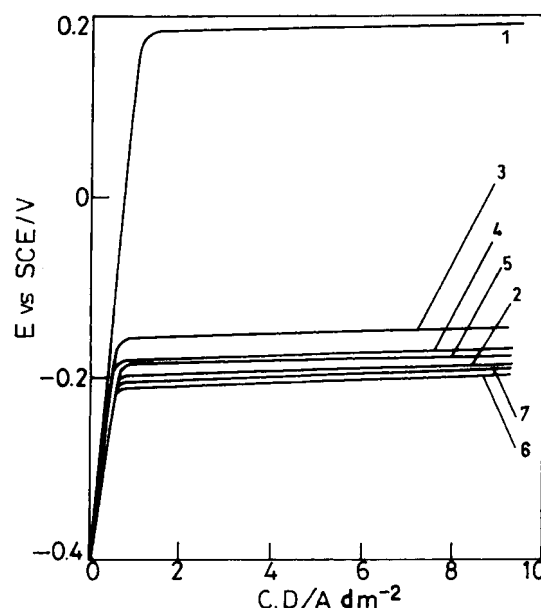


Fig. 7. Anodic polarization of activated nickel electrodes prepared using different concentrations of thiourea in a Watts bath. Key: (1) electrolytic nickel, (2) activated nickel, (3) 0.01, (4) 0.03, (5) 0.05, (6) 0.10 and (7) 0.15 g l<sup>-1</sup>.

### 3.3. Anodic polarization studies in chloride free bath

The data obtained in anodic polarization studies of activated nickel and commercial nickel carried out in chloride free baths are given in Table 5. It is evident that the performance of the activated nickel is by far superior compared to the electrolytic nickel. For electrolytic nickel the active current range is only up to 1.75 A dm<sup>-2</sup> and for activated nickel it has been extended upto 7.5 A dm<sup>-2</sup>.

Table 6 and Figure 9 show the polarisation behaviour of activated nickel produced using sodium metabisulfite additions. With an increase in sodium metabisulfite concentration from 0.5 to 1 g l<sup>-1</sup> the active current range increases from 8.4 to 9.9 A dm<sup>-2</sup>. Further increase in the concentration beyond 1 g l<sup>-1</sup> decreases the active current range. Thus it was found that 1 g l<sup>-1</sup> addition is the best for producing an active nickel anode.

Table 7 and Figure 10 show the results for polarization behaviour obtained in the presence of thiourea addition. With increase in concentration from 0.01 to 0.05 g l<sup>-1</sup> of thiourea there is no change in the active

Table 4. Anodic polarization studies in a Watts bath with different concentrations of sodium thiosulfate

Concentration of sodium thiosulfate /g l <sup>-1</sup>	Dissolution potential /V vs SCE
0.01	-0.080
0.02	-0.165
0.03	-0.135
0.04	-0.085

System: activated nickel prepared using sodium thiosulfate

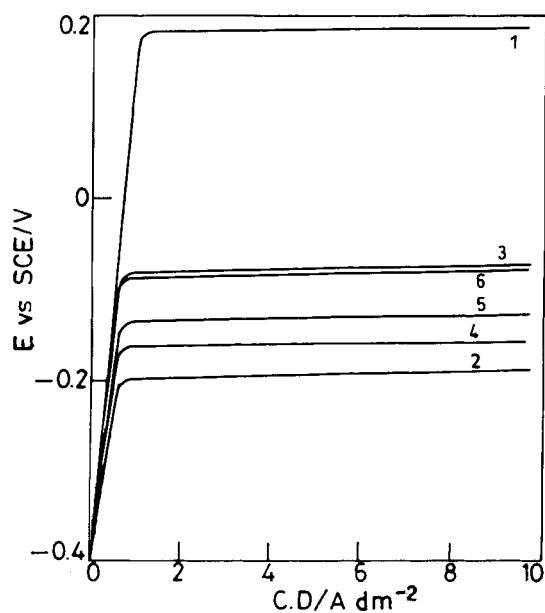


Fig. 8. Anodic polarization of activated nickel electrodes prepared using different concentrations of sodium thiosulfate in a Watts bath. Key: (1) electrolytic nickel, (2) activated nickel, (3) 0.01, (4) 0.02, (5) 0.03 and (6) 0.04 g l<sup>-1</sup>.

current and it remains constant at 10 A dm<sup>-2</sup>. Further increase in concentration resulted in decrease in the active current range. Hence, 0.01 g l<sup>-1</sup> was chosen as the best for obtaining activated nickel.

The polarization behaviour of activated nickel anodes prepared by the addition of sodium thiosulfate in chloride free bath is shown in Table 8 and Figure 11. As in the case of metabisulfite, sodium thiosulfate also enhances the active current with increase in concentration. However, an increase in the concentration beyond

Table 5. Values of  $E_{crit}$  and active current density range obtained in anodic polarization studies in chloride free bath

System	* $E_{crit}$ /V vs SCE	Active current density range /A dm <sup>-2</sup>
Electrolytic nickel	+1.38	1.75
Activated nickel	-0.05	7.50

\* Critical anodic potentials at which the passivity starts

Table 6. Values of  $E_{crit}$  and active current density range obtained in anodic polarization studies in chloride free bath with different concentrations of sodium metabisulfite

Concentration of sodium metabisulfite /g l <sup>-1</sup>	$E_{crit}$ /V vs SCE	Active current density /A dm <sup>-2</sup>
0.5	-0.07	8.4
1.0	+0.50	9.9
1.5	+0.14	6.9
2.0	-0.15	5.9

System: activated nickel prepared using sodium metabisulfite

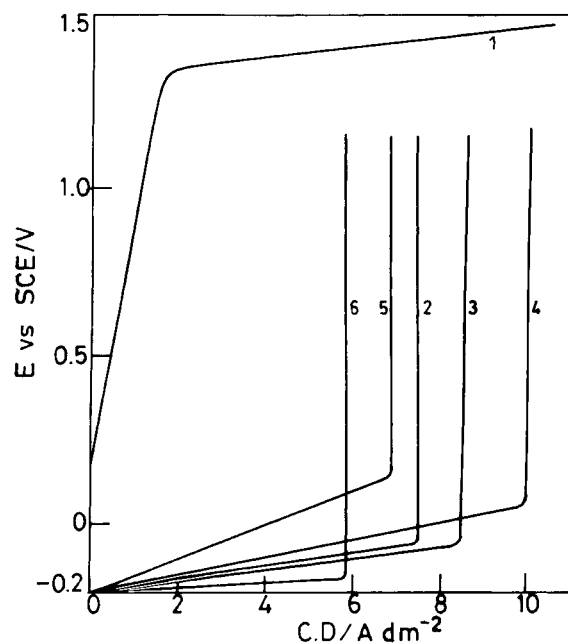


Fig. 9. Anodic polarization of activated nickel electrodes prepared using different concentrations of sodium metabisulfite in chloride free bath. Key: (1) electrolytic nickel, (2) activated nickel, (3) 0.50, (4) 1.00, (5) 1.50 and (6) 2.00 g l<sup>-1</sup>.

0.02 g l<sup>-1</sup> decreases the active current range. Hence, 0.02 g l<sup>-1</sup> was selected as an optimum concentration for obtaining activated nickel.

#### 4. Conclusions

The bath composition and operating conditions for producing activated nickel anodes using sodium metabisulfite 1 g l<sup>-1</sup> or thiourea 0.1 g l<sup>-1</sup> are given in Table 9.

The influence of the different additives on the performance of an activated nickel anode in chloride free bath follows the following sequence, based on active current density: sodium thiosulfate > thiourea > sodium metabisulfite. The trend is exactly reversed in the Watts nickel electrolyte.

Table 7. Values of  $E_{crit}$  and active current density range obtained in anodic polarization studies in chloride free bath with different concentrations of thiourea

Concentration of thiourea /g l <sup>-1</sup>	$E_{crit}$ /V vs SCE	Active current density /A dm <sup>-2</sup>
0.01	+0.10	10.0
0.03	+0.30	10.0
0.05	+0.06	10.0
0.10	-0.03	9.80
0.15	-0.10	6.40

System: activated nickel prepared using thiourea

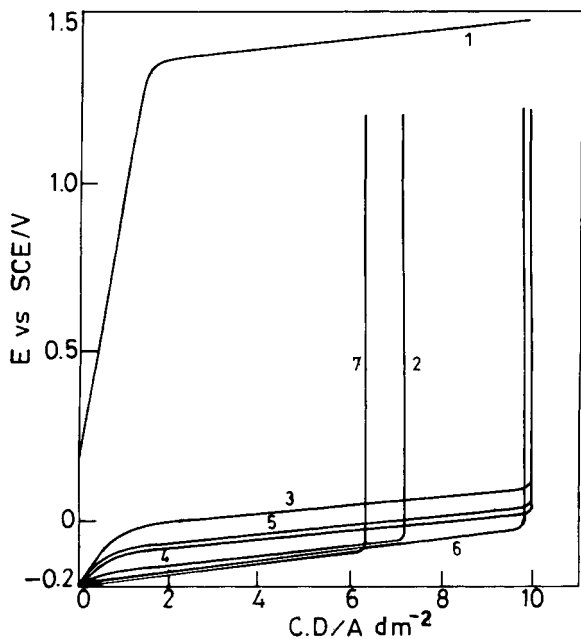


Fig. 10. Anodic polarization of activated nickel electrodes prepared using different concentrations of thiourea in chloride free bath. Key: (1) electrolytic nickel, (2) activated nickel, (3) 0.01, (4) 0.03, (5) 0.25, (6) 0.10 and (7) 0.15 g l<sup>-1</sup>.

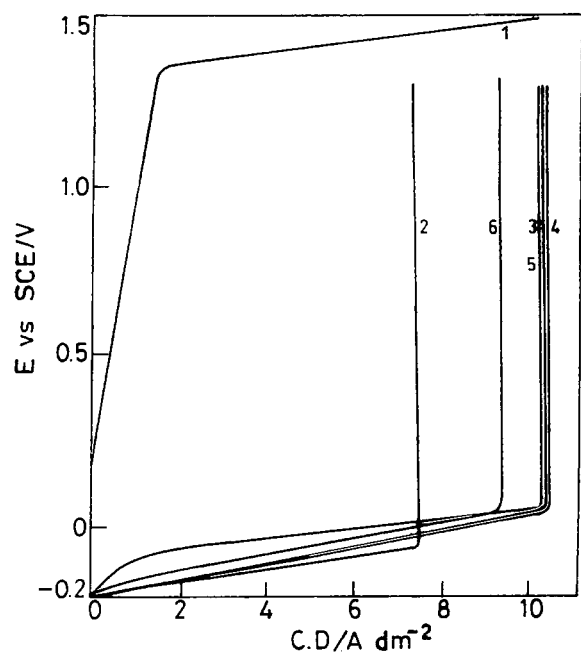


Fig. 11. Anodic polarization of activated nickel electrodes prepared using different concentrations of sodium thiosulfate in chloride free bath. Key: (1) electrolytic nickel, (2) activated nickel, (3) 0.01, (4) 0.02, (5) 0.03 and (6) 0.04 g l<sup>-1</sup>.

Table 8. Values of  $E_{crit}$  and active current density range obtained in an anodic polarization studies in chloride free bath with different concentrations of sodium thiosulfate

Concentration of sodium thiosulfate /g l <sup>-1</sup>	$E_{crit}$ /V vs SCE	Active current density /A dm <sup>-2</sup>
0.01	0.02	10.3
0.02	0.03	10.4
0.03	0.02	10.3
0.04	0.08	9.40

System: activated nickel prepared using sodium thiosulfate

Table 9. Bath composition and operation conditions for producing activated nickel anode

Nickel sulfate	250 g l <sup>-1</sup>
Nickel chloride	40 g l <sup>-1</sup>
Boric acid	40 g l <sup>-1</sup>
Sodium lauryl sulfate	0.2 g l <sup>-1</sup>
Saccharin	0.2 g l <sup>-1</sup>
Anode	nickel wastes from plating
pH	3.0-4.5
Current density	3-7 A dm <sup>-2</sup>
Temperature	40-50 °C

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