



# The effects of thiosulfate ions on the deposition of cobalt and nickel from sulfate solutions



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## ABSTRACT

A detailed electrochemical study of the effects of thiosulfate ions on the reduction of nickel(II) and cobalt(II) ions in sulfate solutions in the pH range 3 to 4 has been undertaken. Even in the presence of small amounts of thiosulfate, metal sulfides are formed in addition to the metals in a reaction involving reduction of thiosulfate in the presence of these metal ions. In addition, chemical reduction of thiosulfate by metallic cobalt and nickel to form metal sulfides has been established. Reduction of cobalt ions by thiosulfate catalyzed by the metal and/or metal sulfide surface accounts for the excess anodic charge observed during open circuit contact of cobalt metal and/or cobalt sulfide with thiosulfate solutions. It has been shown that thiosulfate is responsible for the formation of black cathodic films of the metal sulfides periodically observed during electrowinning of these metals. A simple method for the control of the peroxide addition to the electrolyte in order to oxidize residual thiosulfate has been devised based on the results of this study.

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## 1. Introduction

A major goal in the electrowinning and refining of metals is the production of high quality and purity cathode metals. In several nickel/cobalt electrowinning operations, one of the ongoing issues is the occasional occurrence of black deposits on the nickel and, particularly, the cobalt cathodes. It is suspected that these coatings are nickel and cobalt sulfides (Arai et al., 2004; Loglio et al., 2010). Inclusion of sulfides during electrowinning must originate from reducible sulfur species (other than sulfate) such as dithionate ( $S_2O_6^{2-}$ ), sulfite ( $SO_3^{2-}$ ), tetrathionate ( $S_4O_6^{2-}$ ) or thiosulfate ( $S_2O_3^{2-}$ ) ions in the electrolyte as the source of sulfur.

The electrochemical behavior of cobalt(II) and nickel(II) ions in sulfate solutions containing thiosulfate ions has attracted little attention. The mechanism for the reduction of nickel(II) and cobalt(II) in solutions containing thiosulfate at mercury electrodes has been studied by Itabashi (1978a,b, 1980). The author proposed without experimental verification that metal sulfides, MS (M is either cobalt or nickel), are produced during the process of the electroreduction of the metal ions, through a sequence of reactions involving reduction of the metal–thiosulfate complex.

The inclusion of sulfides in these metals has been claimed to be responsible for the initiation of crevice corrosion, stress corrosion cracking and corrosion fatigue (Sury, 1976). The effect of sulfur inclusions on the anodic reactivity of nickel has been well documented (Di Bari and Petrocelli, 1965) and this is applied commercially in nickel used as

anodes in the nickel electroplating industry. Thus, as little as 0.01% sulfur in the metal increases the current density at which anodic passivation occurs by some two orders of magnitude. In a similar study (Arai et al., 2004) the effect of colloidal sulfur, produced by acid decomposition of thiosulfate ions, on the anodic properties of nickel deposits was investigated and it was established that the anodic passivation typical of pure nickel could be avoided if the metal contained sulfur. It was also noted that cathodic deposition of nickel from a typical Watt's bath was enhanced in the presence of colloidal sulfur.

The formation of nickel sulfides during the leaching of pre-reduced laterite ores has been established (Nikoloski and Nicol, 2010) as being due to the reduction of nickel (and cobalt) ions on the surface of metallic iron in the presence of thiosulfate ions.

In this paper the effects of thiosulfate ions on the reduction and anodic stripping of both cobalt and nickel ions in sulfate solutions are reported.

## 2. Experimental procedure

The electrochemical studies were performed using a conventional three-electrode system. The working electrode was a rotating gold disk (3.5 mm diameter) fabricated from high purity gold rod. The counter electrode was a platinum wire and the reference electrode was a Hg|Hg<sub>2</sub>SO<sub>4</sub> (saturated K<sub>2</sub>SO<sub>4</sub>) electrode (MSE, E = +0.645 V versus SHE) which was connected to the main cell by a Luggin capillary passing through a screw fitting in the base of the cell. All potentials are reported with respect to the standard hydrogen electrode (SHE).

The rotating disk electrode (RDE) was rotated using a drive consisting of an optically controlled unit coupled to a dc motor. Voltammetric

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experiments were carried out using a Solartron 1285 potentiostat controlled by CorrWare software. Measurements were made at  $40 \pm 0.1$  °C by using a water thermoregulator (Rowe Scientific Pty Ltd). Voltammetry was conducted at a scan rate of  $1 \text{ mV s}^{-1}$  and electrode rotation speed of 500 rpm. Prior to all tests, the exposed surface of the working electrode was wet-polished using 1200 silicon carbide paper and rinsed with deionized water.

All electrolyte solutions were prepared from chemicals of analytical grade (sodium sulfate, sodium thiosulfate, cobalt sulfate and nickel sulfate) and high quality water from a Millipore Milli-Q system. All experiments have been performed in 0.1 M  $\text{Na}_2\text{SO}_4$  solutions and the pH of the electrolyte was adjusted to either 3 or 4 by addition of  $\text{H}_2\text{SO}_4$ . Throughout the experiments, the electrolyte was purged with high purity nitrogen to remove oxygen from the system. All the tests were conducted in 50 mL of electrolyte and fresh solutions were prepared for each experiment.

### 3. Results and discussion

The effects of various concentrations of thiosulfate on the deposition of both cobalt and nickel ions on the gold electrode in sulfate solutions were investigated using voltammetry and potentiostatic reduction followed by anodic stripping of the reduced species. Although thiosulfate is not thermodynamically stable in acidic solutions, the rate of the disproportionation reaction to form elemental sulfur and tetrathionate ions is slow in dilute solutions at pH values above about 3. During the experiments described, a milky white precipitate was only observed after about 1 h in 0.1 M solutions of thiosulfate at pH 4. No turbidity was observed during the period of the experiments at concentrations of 0.01 M or lower.

#### 3.1. Cyclic voltammetry

The effect of thiosulfate ions on the deposition of both cobalt and nickel was first monitored by cyclic voltammetry. The scans ( $1 \text{ mV s}^{-1}$ ) using the gold electrode commenced at the open circuit potential to a negative limit of about  $-1 \text{ V}$  and reversed to a positive limit of about  $0.55 \text{ V}$ . Fig. 1 summarizes the voltammetric scans in a solution containing 0.1 M  $\text{Na}_2\text{SO}_4$  with either 0.01 M Co(II) or 0.01 M Ni(II) ions at pH 3.

As the potential is swept in a negative direction, the reduction of both Co(II) and Ni(II) ions commences at potentials of about  $-0.69$  and  $-0.74 \text{ V}$  respectively. The calculated equilibrium potentials for the reduction of these metal ions under these conditions are

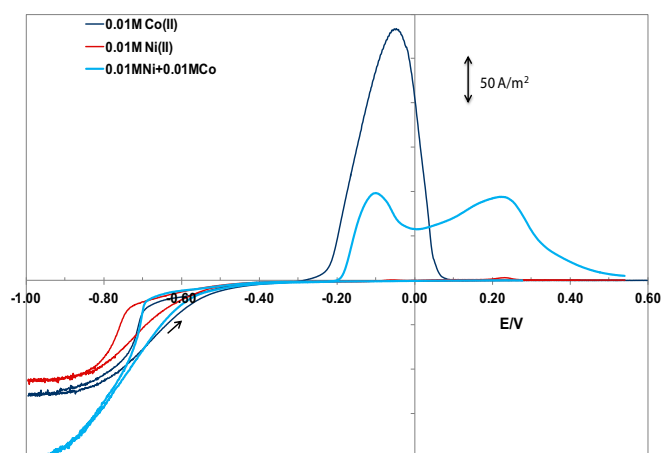


Fig. 1. Voltammetric scans in 0.1 M  $\text{Na}_2\text{SO}_4$  solutions containing either 0.01 M Co(II) or 0.01 M Ni(II) or 0.01 M Co(II) + 0.01 M Ni(II) at pH 3.



A limiting current is apparent at potentials below about  $-0.9 \text{ V}$  for both metals. The limiting current density for the reduction of nickel or cobalt under these conditions can be estimated from the Levich equation to be about  $70 \text{ A m}^{-2}$ . The difference between the calculated and observed values is probably due to simultaneous mass transport controlled reduction of protons in the pH 3 solution. The positive hysteresis in the positive-going scan confirms that nucleation of these metals on the gold surface is relatively slow compared to growth. For solutions containing cobalt, a broad anodic stripping peak is observed at about  $-0.05 \text{ V}$  due to the oxidation of Co(0) to Co(II) ions.

The ratio of the measured anodic to the cathodic charge is 0.61 for cobalt deposition and dissolution that confirms the simultaneous reduction of protons during cathodic deposition of cobalt. Nickel is known (Sury, 1976) to be readily passivated in sulfate solutions at low pH values and resists oxidative dissolution in the absence of a catalyst. A very small anodic peak due to the oxidation of Ni(0) to Ni(II) ions was observed at more positive potentials of about  $0.22 \text{ V}$ . Simultaneous deposition of both metals results in cathodic currents that are twice as large and a broad anodic stripping peak consisting of two overlapping peaks is evident. Thus, nickel can be anodically oxidized if present as an alloy with cobalt.

Fig. 2 shows cyclic voltammetric scans obtained in 0.1 M  $\text{Na}_2\text{SO}_4$  solutions containing 0.01 M thiosulfate ions in the absence and presence of 0.01 M Co(II), or 0.01 M Ni(II) or both 0.01 M Co(II) and 0.01 M Ni(II) ions. All solutions were adjusted to pH 4 to reduce the rate of disproportionation of thiosulfate ions and no colloidal sulfur was visible during the period of each experiment. The scan was started from the open circuit potential to negative potentials of about  $-1.0 \text{ V}$ , and reversed to positive potentials of about  $0.54 \text{ V}$  at  $1 \text{ mV s}^{-1}$ . In the background solution of 0.1 M  $\text{Na}_2\text{SO}_4$  and 0.01 M thiosulfate, reduction of protons is responsible for the increase in cathodic current at potentials below about  $-0.9 \text{ V}$ . Thiosulfate appears to be electrochemically inert in the potential region of interest under these conditions.

Both cobalt(II) and nickel(II) in thiosulfate solutions are reduced at more positive potentials than observed in the absence of thiosulfate. The current plateaus are approximately the same in magnitude as those in the absence of thiosulfate. The relatively low cathodic currents on the reverse positive-going scan suggest that a species formed at the most negative potentials inhibits further reduction of both Co(II) and Ni(II). Additional small peaks are visible at potentials below about  $-0.75 \text{ V}$  suggesting that more than one species is formed during reduction. As could be expected, use of a solution that contains both cobalt and nickel ions results in cathodic currents which are almost double

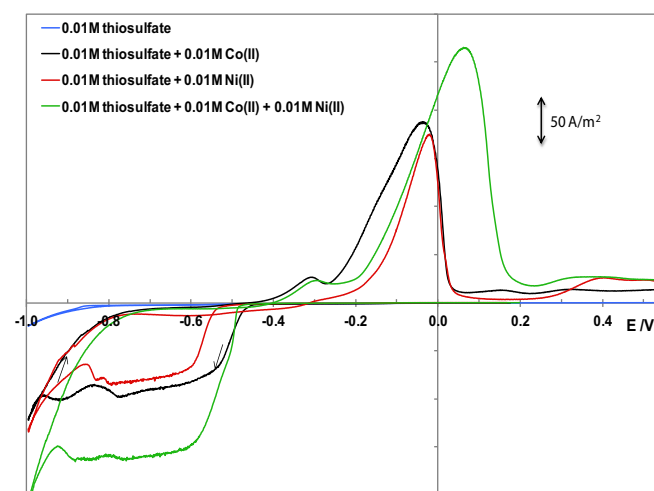


Fig. 2. Effect of thiosulfate on voltammetry in solutions containing 0.01 M Co(II) or 0.01 M Ni(II) or 0.01 M Co(II) + 0.01 M Ni(II) and 0.1 M  $\text{Na}_2\text{SO}_4$  at pH 4.

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