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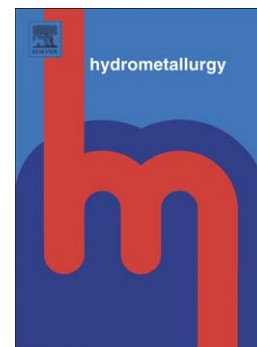
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The effects of thiosulfate ions on the deposition of cobalt and nickel from sulfate solutions

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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 catalysed 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 oxidise residual thiosulfate has been devised based on the results of this study.

Keywords: nickel; cobalt; reduction; thiosulfate; sulfides

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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 (Loglio et al., 2010; Arai et al., 2004). 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; 1978b; 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

2

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 disc (3.5 mm diameter) fabricated from high purity gold rod. The counter electrode was a platinum wire and the reference electrode was a $Hg|Hg_2SO_4$ (saturated K_2SO_4) 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 disc electrode (RDE) was rotated using a drive consisting of an optically controlled unit coupled to a dc motor. Voltammetric experiments were carried out using a Solartron 1285 potentiostat controlled by CorrWare software. Measurements were made at 40 ± 0.1ºC by using a water thermoregulator (Rowe

3

Scientific Pty Ltd). Voltammetry was conducted at a scan rate of 1 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 deionised water.

All electrolyte solutions were prepared from chemicals of analytical grade (sodium sulphate, sodium thiosulfate, cobalt sulphate and nickel sulphate) and high quality water from a Millipore Milli-Q system. All experiments have been performed in 0.1 M Na_2SO_4 solutions and the pH of the electrolyte was adjusted to either 3 or 4 by addition of H_2SO_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 hour in 0.1M solutions of thiosulfate at pH 4. No turbidity was observed during the period of the experiments at concentrations of 0.01M or lower.

4

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 mV s^{-1}) using the gold electrode commenced at the open circuit potential to a negative limit of about -1 V and reversed to a positive limit of about 0.55 V. Fig. 1 summarizes the voltammetric scans in a solution containing 0.1 M Na$_2$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 V respectively. The calculated equilibrium potentials for the reduction of these metal ions under these conditions are

$$Ni^{2+} + 2e = Ni \qquad\qquad E = -0.297 \text{ V} \qquad (1)$$

$$Co^{2+} + 2e = Co \qquad\qquad E = -0.344 \text{ V} \qquad (2)$$

A limiting current is apparent at potentials below about -0.9 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 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 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 sulphate 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 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 oxidised if present as an alloy with cobalt.

Fig. 2 shows cyclic voltammetric scans obtained in 0.1 M Na_2SO_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 V, and reversed to positive potentials of about 0.54 V at 1 mV s^{-1}. In the background solution of 0.1 M Na_2SO_4 and 0.01 M thiosulfate, reduction of protons is responsible for the increase in cathodic current at potentials below about -0.9 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 suggests 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 V suggesting that more than one species is formed during reduction. As

6

could be expected, use of a solution that contains both cobalt and nickel ions results in cathodic currents which are almost double those for the individual metals and the charge associated with the corresponding anodic peak is approximately double.

The subsequent anodic stripping curves show major peaks in the potential region -0.1 to 0.1 V and smaller peaks at more negative and more positive potentials. The presence of thiosulfate results in a large stripping peak for nickel confirming the well-known effect of sulfur in eliminating passivation of this metal. As will be demonstrated below, the major peaks are associated with stripping of the metals while the peaks at higher potentials are due to oxidation of metal sulfides.

The total cathodic and anodic charges obtained by integrating the current in Fig. 2 are summarized in Table 1, which shows that about 28% of the cathodic charge (Q_C) in the case of cobalt can be attributed to the reduction of protons (Q_H). The corresponding amount for nickel is 47% while the fraction in the presence of both metal ions is between that of the individual ions. These figures do not take into account the possible relatively minor effects of deposition and stripping of sulfide species under these conditions. These data mirror industrial practice in which the current efficiency for the electrowinning of cobalt is generally greater than that for nickel.

3.2 Potentiostatic reduction / voltametric stripping
A number of tests were conducted in which the electrode was held potentiostatically at -0.65 V for 5 or 10 minutes in 0.01M cobalt and/or 0.01M nickel containing solutions at pH 4 in the presence or absence of 0.01 M thiosulfate ions. The resulting current/time transients are summarized in Fig. 3. There are several observations to be made from these data.

7

a) The limiting current density for the reduction of either Co(II) or Ni(II) to the metals under these conditions can be estimated from the Levich equation to be 72 A m^{-2} for a diffusion coefficient of 8 x 10^{-6} cm^2 s^{-1}. In the absence of thiosulfate, the initial nucleation and growth transients make way for steady-state currents for nickel and cobalt deposition, which are about 50% of the mass transport controlled rate at this potential. The cobalt deposition rate is slightly higher than that for nickel which is expected given the higher exchange current density for reduction of cobalt(II) ions of 10$^{-6.9}$ A cm-2 compared to 10$^{-8.7}$ for nickel (Vijh and Randin, 1975).

b) The steady-state current for deposition from the solution containing both metal ions is similar to that for the individual ions. This is also apparent in Figure 1 that shows similar cathodic currents at -0.65V.

c) Addition of thiosulfate results in significant increases in cathodic currents in all cases to values which are greater than predicted by the Levich equation for mass transport. Thus, the limiting values of about 85, 95 and 160 A m^{-2} in solutions containing 0.01 M Ni(II), 0.01 M Co(II) and both 0.01 M Ni(II) and 0.01 M Co(II) are observed. The limiting current density for the reduction of either Co(II) or Ni(II) to the metals under these conditions can be estimated from the Levich equation to be 72 A m^{-2} for a diffusion coefficient of 8 x 10^{-6} cm^2 s^{-1}. This observation will be discussed at a later stage.

The anodic stripping voltammograms measured after the above potentiostatic deposition period are shown in Fig. 4. In the absence of thiosulfate, the peak for cobalt at about 0 V is slightly greater than that for nickel at about 0.15 V. Nickel alone in the absence of thiosulfate at pH 4 also gives a well defined anodic stripping peak at 0.12 V. This stripping peak for nickel was not observed at pH 3

8

(Fig. 1) and this has been explained by Sury (1976) in terms of catalysis of anodic dissolution of nickel by hydroxyl ions that minimizes passivation. In the absence of thiosulfate, only one anodic stripping peak was observed in the solution containing both metals for which the maximum current densities and the magnitude of the cathodic and anodic charges (Table 2) as well as the position of the anodic peak were similar to the results for the solution that contain only Co(II) ions. This suggests that when both metal ions are present at pH 4, the rate of deposition of nickel is reduced on the alloy surface compared to a nickel surface.

After 10 minutes potentiostatic reduction in the presence of thiosulfate ions, black deposits were observed on the surface of the electrode in all solutions indicating the formation of metal sulfides. The anodic peaks due to dissolution of the metals are larger with the position of that for nickel displaced negatively by about 50 mV and cobalt by about 15 mV. In addition, smaller peaks are apparent at potentials between about 0.4 and 0.7 V which are due to oxidation of metal sulfides produced during the deposition period. The black deposits were not observed after anodic stripping.

The anodic and cathodic charges calculated from the areas under the peaks are summarized in Table 2. There are several features of these data

a) The charges for deposition and stripping of the metals in the absence of thiosulfate are roughly the sum of those for the individual metals. In the case of all metals, the current efficiency for deposition as reflected in the ratio of the anodic and cathodic charge is greater as expected at pH 4 than pH 3 due to a lower rate of hydrogen evolution at the higher pH value.

b) In the presence of thiosulfate, the ratio of the total anodic to cathodic charge is close to 1 except for cobalt for which the value is greater than 1.

9

c) The anodic charge for stripping of the metals (M) is significantly greater in the presence of thiosulfate than in its absence for all three solutions. This implies that reduction of nickel(II) and cobalt(II) ions to the metallic phase is enhanced in the presence of thiosulfate ions.

d) The anodic charge for oxidation of sulfides (MS) is greater for cobalt than nickel while that for the mixture of metal ions is between that for cobalt and nickel.

The effect of thiosulfate concentration on the potentiostatic reduction of 0.01 M Co(II) and/ or 0.01 M Ni(II) on gold electrodes at -0.65 V for 10 minutes was investigated at additional concentrations of 0.001 to 0.1 M and the potentiostatic current/time transients are shown in Fig. 5 while Fig. 6 shows the subsequent anodic stripping voltammograms. The current transients for a thiosulfate concentration of 0.001M are similar to those observed at a concentration of 0.01M as described above. However, at the highest thiosulfate concentration of 0.1M, the transients for cobalt and the solution containing both metal ions show increasing cathodic currents. For the latter, the current after 10 minutes is twice that at the lower concentrations of thiosulfate and still increasing. At the lowest the thiosulfate concentration very little sulfide is produced as shown in Fig. 6 by the small anodic peaks at potentials above 0.3 V. On the other hand, large amounts of sulfides are produced in addition to the metals at a thiosulfate concentration of 0.1M. Considerably more sulfide is produced in the case of cobalt than nickel.

The relevant charges during cathodic reduction and anodic oxidation for the various thiosulfate concentrations are summarized in Table 3. The amounts of the metals deposited as reflected in the charge associated with the first anodic peak are roughly similar for each metal at all thiosulfate concentrations except for

nickel at 0.1M thiosulfate. However, the extent of sulfide formation increases with increasing thiosulfate concentration particularly for cobalt. The total anodic charge can exceed that for the cathodic reactions by a factor as much as 4.35. There appears to be a linear relationship between the extent of metal sulfide formation and the concentration of thiosulfate with the effect being greatest for cobalt and the solution containing both metal ions.

As suggested by Itabashi (1978a; 1978b; 1980), thiosulfate ions are involved in the reduction of both metal ions forming CoS and NiS. Other possible known metal sulfides for which there is thermodynamic data could also be the products of reduction by reactions such as those given in Table 4. The potentials were calculated using standard potentials (HSC Chemistry Ver 7) modified for solution concentrations using the Nernst equation. The Table also shows the number of electrons involved per mole of metal sulfide produced in each case.

In these and other reactions, the potentials shown are calculated using the bulk solution composition of 0.01M metal ions and 0.01M thiosulfate at pH 4. In addition to the anodic oxidation of the metals (Reactions 1 and 2) oxidation of sulfides are also possible by the reverse of reactions shown in Table 5.

Note that equations (3) through (6) have been written in terms of either the stoichiometric or metal rich sulfides as it is unlikely that the sulfur-rich sulfides would form under these cathodic conditions.

Comparison of the calculated potentials for these possible reactions with both the potentials at which the sulfides form and the anodic stripping peaks shows that formation of CoS, Co_9S_8, NiS and Ni_3S_2 are all possible at a potential of -0.65 V

11

in the presence of thiosulfate ions. Furthermore oxidation of these sulfides to the corresponding metal ions and elemental sulfur is possible at potentials greater than about 0.15 V.

Assuming that the total cathodic charge is due only to reduction of the metal ions to metals and sulfides, one can estimate the cathodic charge associated with sulfide formation and this is compared to the anodic charge for oxidation of the sulfides in the last column in Table 3. Thus, if the sulfide species formed is CoS or NiS (reaction 3 or 5) which are then oxidised by the reverse of reactions 9 or 12, then Q_A/Q_C for MS should be 0.5. This value is reasonably close to those for 0.001M thiosulfate in Table 3. Similarly, if Ni_3S_2 or Co_9S_8 are the only products of reduction then the expected values for Q_A/Q_C are 0.6 and 0.53 respectively. On the basis of this information, it is not possible to definitively assign specific reactions involved in the formation and oxidation of the sulfides. Note that the expected values of Q_A are less than Q_C in all cases whereas the measured values in Table 3 for Q_A are all higher than those for Q_C except at the lowest thiosulfate ion concentration.

3.3 Open-circuit reduction

The higher anodic than cathodic charge in the presence of 0.01 and 0.1M thiosulfate noted above suggests that a non-Faradaic process must be occurring in parallel with cathodic reduction to produce metal sulfides. In order to further investigate this phenomenon, the electrode was held for 2 minutes at -0.65 V at a rotation speed of 500 rpm in order to deposit some metal, after which it was open circuited for 10 minutes followed by a positive-going potential sweep from the open circuit potential. The tests were conducted in solutions of 0.01 M Co(II), 0.01 M Ni(II) or both 0.01 M Co(II) and 0.01 M Ni(II) ions in the absence and

12

presence of 0.1 M $Na_2S_2O_3$. It is apparent from Fig. 7 that the open circuit potentials after cathodic reduction decayed within a few seconds to the expected Co/Co^{2+} and Ni/Ni^{2+} potentials at about -0.3 to -0.2 V respectively and remained at these potentials for the rest of the open circuit period, except for the solution containing 0.01 M Ni(II) ions in the absence of thiosulfate for which the potential increased to about 0.05 V due to passivation under these conditions.

The anodic stripping voltammograms obtained after the above open circuit period are shown in Fig. 8 Comparison with Fig. 4 and Fig. 6 shows that during the period of open circuit, the relative amount of metal sulfides as reflected in the large peaks at the more positive potentials, increased at the expense of the peaks for the stripping of the metals. Thus, metal sulfides can be produced at potentials as positive as -0.25 V. The anodic charge after deposition for only 2 minutes and subsequent 10 minutes open circuit was similar to that obtained after 10 minutes reduction and the ratio of the anodic to cathodic charge increased to 2.27 for nickel, 6.41 for cobalt and 2.93 in the presence of both ions. The presence of at least two peaks for the oxidation of the sulfides suggests that it is unlikely that the simple MS species are the only products of reduction of the metal ions in the presence of thiosulfate.

Fig. 9 compares the anodic stripping sweeps obtained after 10 minutes and 2.5 hours open circuit after deposition of cobalt at -0.65V for 10 minutes. After 10 minutes both cobalt metal and sulfide are present but after 2.5 hours, the open circuit potential increased to -0.05 V as shown in the inset and the subsequent anodic sweep from this potential revealed no peak for the oxidation of metal while the peak for oxidation of sulfide increased substantially with the ratio of anodic to cathodic charges being 9.0.

In the presence of cobalt metal, the following reaction is thermodynamically favourable

$$4Co + S_2O_3^{2-} + 6H^+ = 2CoS + 2Co^{2+} + 3H_2O \qquad \log K = 95 \qquad (13)$$
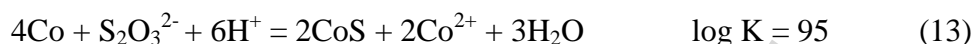
and is partially responsible for the formation of additional cobalt sulfide from the metal under open circuit conditions. However this reaction does not account for the excess anodic charge observed and it is suggested that the following thermodynamically favourable reaction in which cobalt ions are reduced by thiosulfate which is oxidised to tetrathionate also occurs during the open circuit period.

$$2Co^{2+} + 9S_2O_3^{2-} + 6H^+ = 2CoS + 3H_2O + 4S_4O_6^{2-} \qquad \log K = 25 \qquad (14)$$

During the open circuit period, no precipitation of a black sulfide was observed in the solution and it therefore appears that reaction (14) is a very slow homogeneous reaction that is catalysed by the metal/metal sulfide electrode surface. This will account for the excess anodic charge observed after open circuit.

It is possible that similar effects to those observed in this study may apply during the electrowinning of other metals such as zinc. In the presence of reducible sulfur (or selenium and tellurium) species, it is possible to form metal sulfides (or selenides and tellurides) of ions such as cobalt, nickel and copper. These are insoluble in zinc metal and could act as nuclei on which the rate of hydrogen evolution is promoted resulting in reduced current efficiency for the deposition of zinc.

14

4. Practical Implications

In the plant at which the original observations were made, hydrogen peroxide is added in the electrolyte feed tank in order to oxidise any residual thiosulfate in the electrolyte. However, excess peroxide has detrimental effects on cathode current efficiency and control of the pH in the catholyte. The observation that nickel sulfide is formed by reduction of thiosulfate on a nickel surface by the equivalent reactions 13 and 14 can be used as a method of controlling the addition of peroxide to the electrolyte in a nickel refinery. Thus, Fig. 11 shows two nickel sheets exposed for 15 minutes to an actual plant electrolyte. The left sheet was immersed in the electrolyte that contained a low concentration of thiosulfate ions. The black coating is indicative of nickel sulfide. Addition of hydrogen peroxide as an oxidant for thiosulfate results in a solution which does not show the typical black sulfide coating. This method is routinely being applied to control the addition of peroxide in order to minimize cost and also to reduce the presence of excess peroxide in the electrolyte.

5. Conclusions

The following conclusions can be made based on the results of an investigation into the effect of thiosulfate ions on the reduction and oxidation processes of both cobalt and nickel in acidic sulfate solutions.

a) Even in the presence of low concentrations of thiosulfate, metal sulfides are formed in addition to the metals in a cathodic reaction involving reduction of thiosulfate in the presence of these metal ions.

b) Thiosulfate ions are responsible for the formation of black metal sulfides as the products of reduction of nickel and cobalt ions at pH values of 3 or 4.

15

c) The anodic passivity of nickel is prevented in the presence of thiosulfate ions.

d) Chemical reduction of thiosulfate by metallic cobalt and nickel to form metal sulfides has been established. This has been used to control the addition of peroxide to oxidise thiosulfate in a nickel electrowinning plant.

e) Reduction of cobalt ions by thiosulfate catalysed by the metal/metal sulfide surface accounts for the excess anodic charge observed during open circuit of a cobalt metal/sulfide surface in thiosulfate solutions.

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Captions for Tables

Table 1. Cathodic and anodic charges during deposition with thiosulfate

Table 2. Effect of 0.01 M thiosulfate ions on the cathodic and anodic charges during potentiostatic reduction and subsequent anodic stripping

Table 3. Effect of thiosulfate ion concentration on the cathodic and anodic charges during potentiostatic reduction and subsequent anodic oxidation

Table 4. Possible reactions for the formation of metal sulfides during reduction of cobalt and nickel ions in the presence of thiosulfate

Table 5. Possible reactions for the oxidative stripping of metal sulfides formed during reduction of cobalt and nickel ions in the presence of thiosulfate

Captions for Figures

Fig. 1. Voltammetric scans in 0.1 M Na_2SO_4 solutions containing either 0.01 M Co(II) or 0.01 M Ni(II) or 0.01M Co(II) + 0.01M Ni(II) at pH 3

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 Na_2SO_4 at pH 4

Fig. 3. Current-time transients for the reduction of 0.01 M Co(II) and/or 0.01 M Ni(II) at -0.65 V in 0.1M Na_2SO_4 with or without 0.01M $Na_2S_2O_3$ at pH 4

Fig. 4. Anodic stripping voltammograms after potentiostatic reduction at -0.65V for 10 mins in solutions containing 0.01 M Co(II) and/or 0.01 M Ni(II) in 0.1M Na_2SO_4 with or without 0.01M $Na_2S_2O_3$ at pH 4

Fig. 5. Current-time transients for the reduction of 0.01 M Co(II) and/or 0.01 M Ni(II) at -0.65 V in 0.1M Na_2SO_4 with 0.001M or 0.1M $Na_2S_2O_3$ at pH 4

Fig. 6. Anodic stripping voltammograms after potentiostatic reduction at -0.65V for 10 mins in solutions containing 0.01 M Co(II) and/or 0.01 M Ni(II) in 0.1M Na_2SO_4 and 0.001M or 0.1M $Na_2S_2O_3$ at pH 4

Fig. 7. Open circuit potentials after 2 minutes reduction of 0.01 M Co(II) and/or 0.01 M Ni(II) at -0.65 V in 0.1M Na_2SO_4 with or without 0.1M $Na_2S_2O_3$ at pH 4

Fig. 8. Anodic stripping after deposition and open circuit period shown in Fig.7

Fig. 9. Effect of open circuit time on the formation of cobalt sulfides in solution containing 0.01 M Co(II) and 0.1M $Na_2S_2O_3$ at pH 4 after deposition at -0.65V for 10 minutes.

Fig. 10. Photographs of nickel sheet exposed to electrolyte containing thiosulfate ions (left) and after oxidation with peroxide (right).
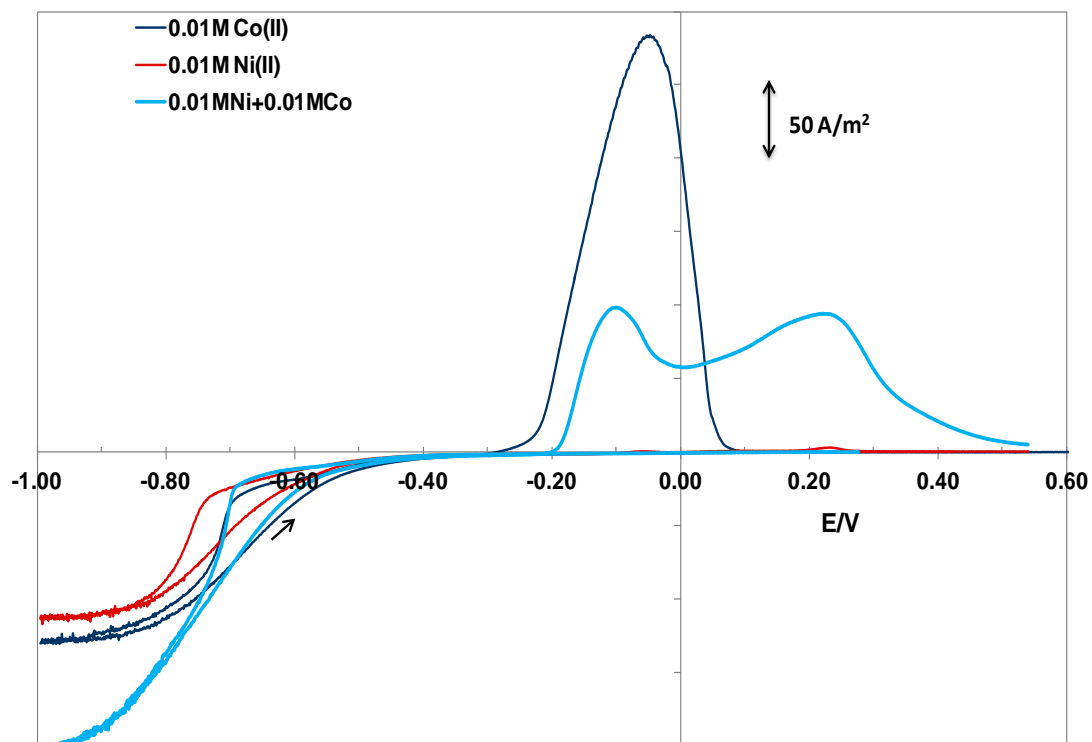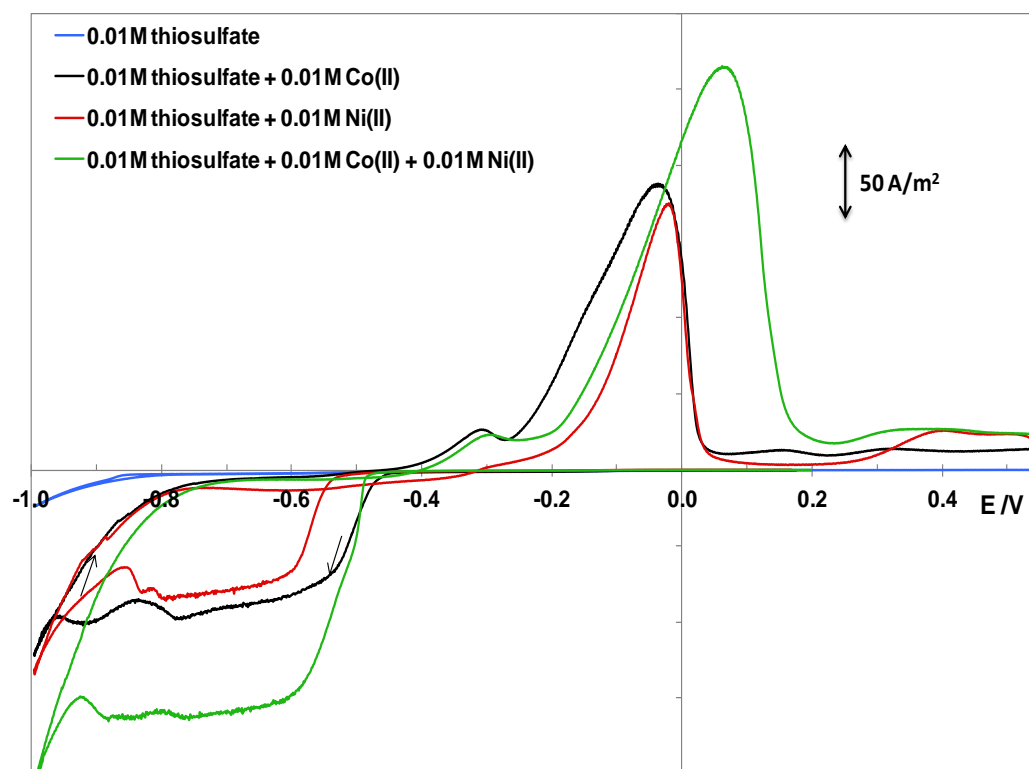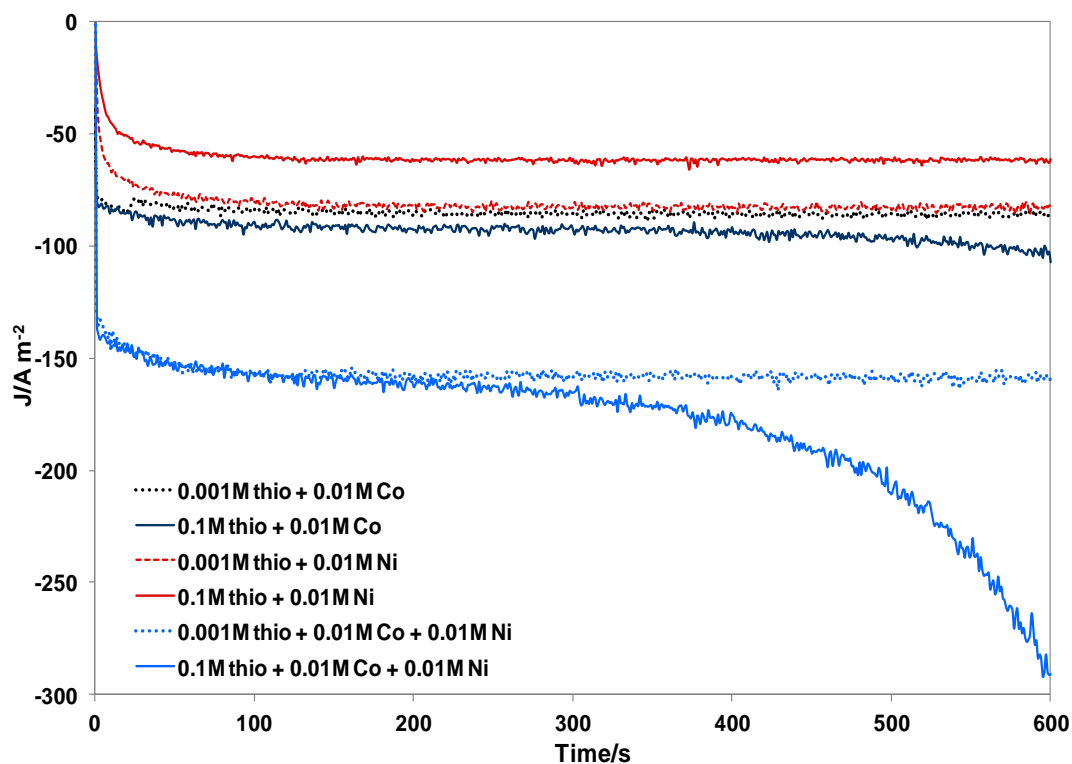
Fig. 1

Fig. 2

Fig. 3

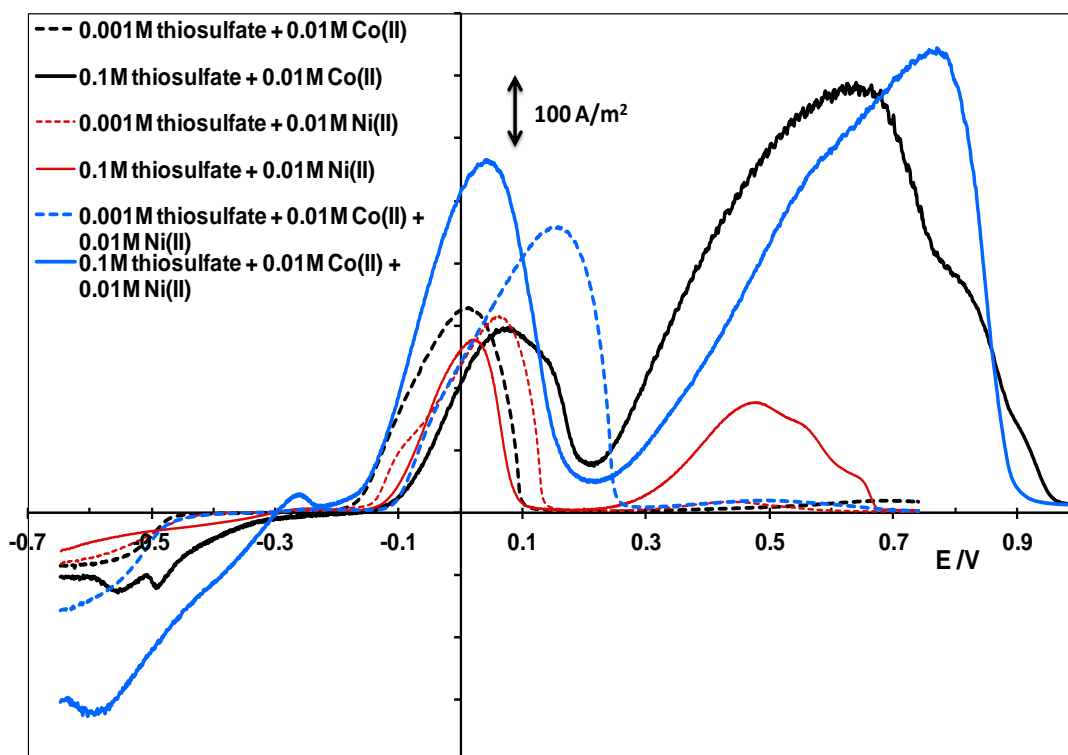Fig. 4
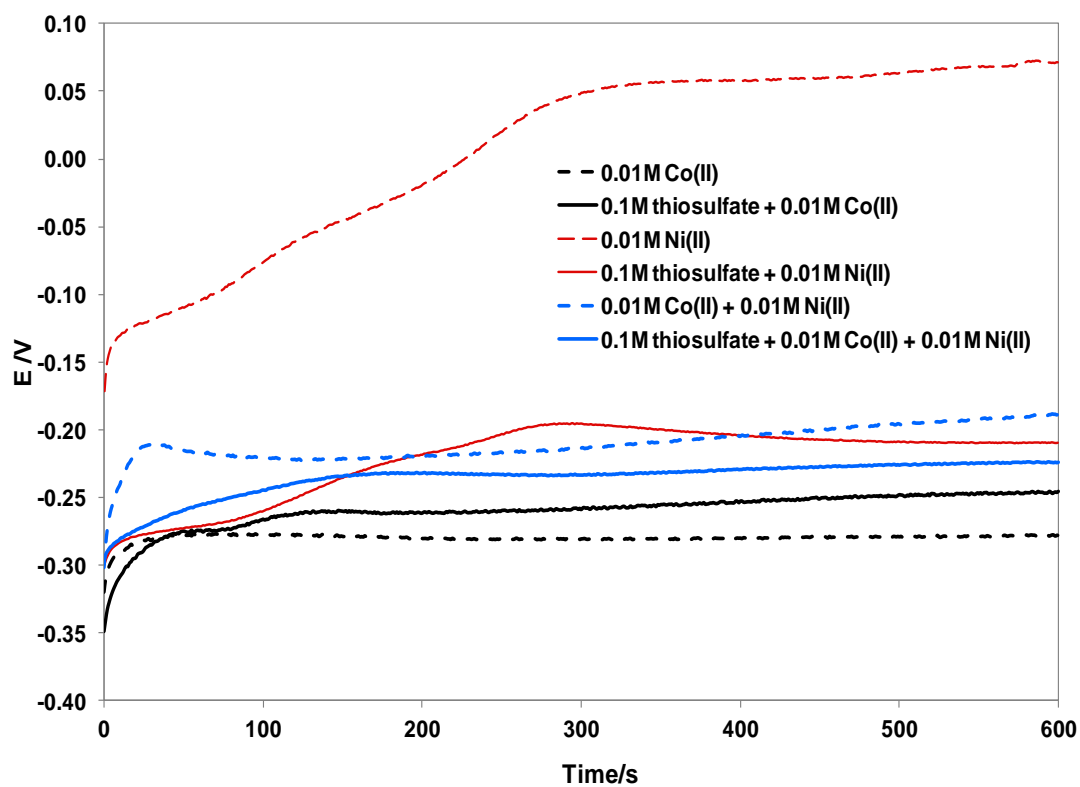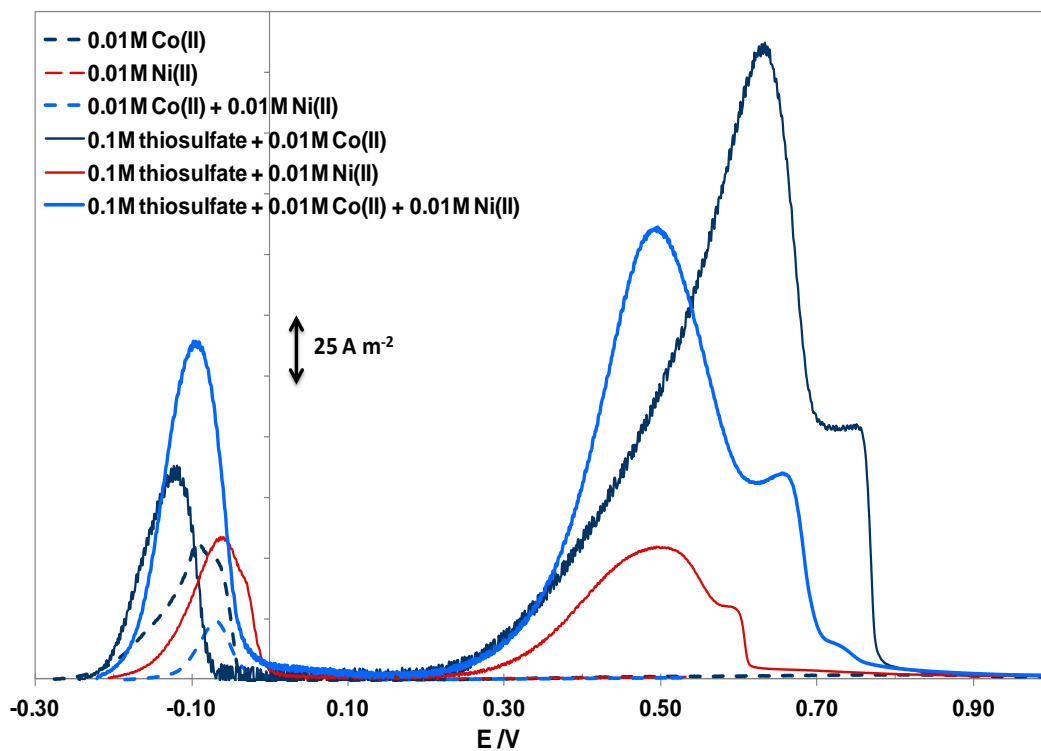
Fig. 5

Fig. 6
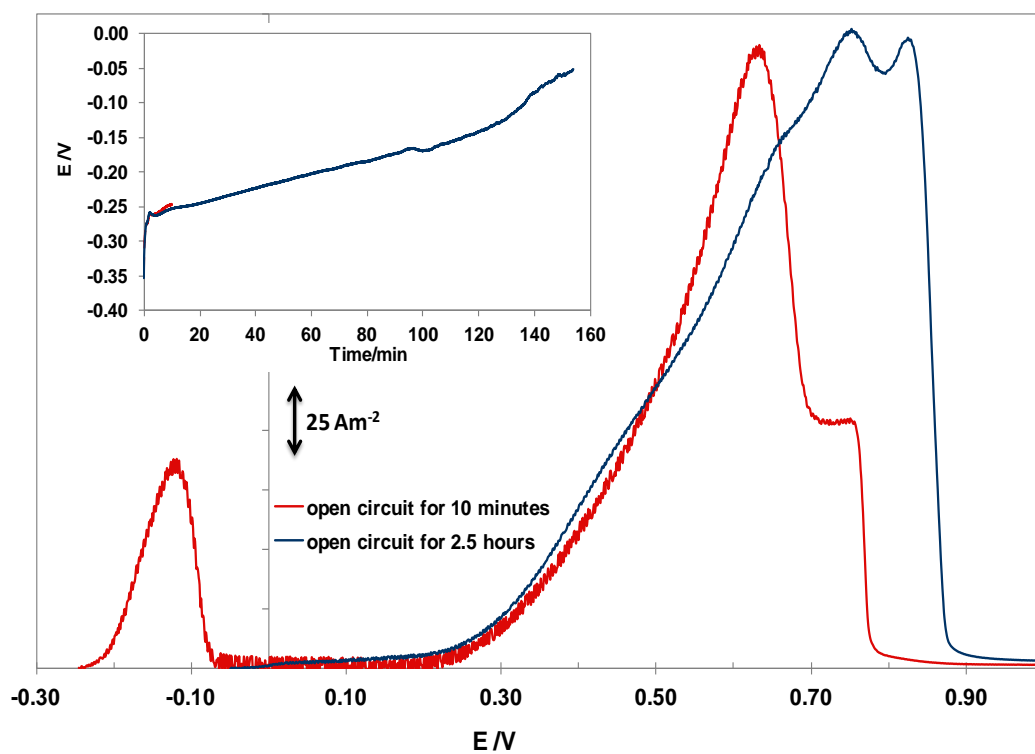
Fig. 7

Fig. 8

Fig. 9

Fig. 10

Table 1 Cathodic and anodic charges during deposition with thiosulfate

Solution	Cathodic charge / C	Anodic charge / C	Q_H Charge / C	Q_A/Q_C
0.01 M thiosulfate	0.036	-	0.036	-
0.01 M thio + 0.01 M Co(II)	0.524	0.377	0.147	0.72
0.01 M thio + 0.01 M Ni(II)	0.466	0.245	0.221	0.53
0.01 M thio + 0.01 M Co(II) + 0.01 M Ni(II)	0.888	0.613	0.275	0.69

Table 2. Effect of 0.01 M thiosulfate ions on the cathodic and anodic charges during potentiostatic reduction and subsequent anodic stripping.

Solution	Cathodic charge C	Anodic charge M C	Anodic charge MS C	$Q_{A(Total)}/Q_C$
0.01 M thiosulfate	0.029	0.0	0.00	0.00
0.01 M Co(II)	0.276	0.239	0.00	0.87
0.01 M Ni(II)	0.231	0.185	0.00	0.80
0.01 M Co(II) + 0.01 M Ni(II)	0.269	0.230	0.00	0.85
0.01 M thio + 0.01 M Co(II)	0.668	0.529	0.236	1.22
0.01 M thio + 0.01 M Ni(II)	0.578	0.461	0.096	0.96
0.01 M thio + 0.01 M Co(II) + 0.01 M Ni(II)	1.145	0.945	0.211	1.01

Table 3. Effect of thiosulfate ion concentration on the cathodic and anodic charges during potentiostatic reduction and subsequent anodic oxidation.

Solution	Cathodic charge C	Anodic charge M C	Anodic charge MS C	$Q_{A(Total)} / Q_C$	Q_A / Q_C MS
0.001 M thio + 0.01 M Co(II)	0.597	0.517	0.046	0.94	0.58
0.01 M thio + 0.01 M Co(II)	0.668	0.529	0.236	1.15	1.70
0.1 M thio + 0.01 M Co(II)	0.776	0.538	2.84	4.35	11.93
0.001 M thio + 0.01 M Ni(II)	0.562	0.494	0.032	0.93	0.47
0.01 M thio + 0.01 M Ni(II)	0.578	0.461	0.096	0.96	0.82
0.1 M thio + 0.01 M Ni(II)	0.435	0.327	0.39	1.65	3.61
0.001 M thio + 0.01 M Co(II) + 0.01 M Ni(II)	1.071	0.970	0.049	0.95	0.49
0.01 M thio + 0.01 M Co(II) + 0.01 M Ni(II)	1.145	0.945	0.211	1.01	1.06
0.1 M thio + 0.01 M Co(II) + 0.01 M Ni(II)	1.614	1.056	2.61	2.27	4.68

Table 4. Possible reactions for the formation of metal sulfides during reduction of cobalt and nickel ions in the presence of thiosulfate.

Reaction	E, V	e/Mol MS	No
$2Co^{2+} + S_2O_3^{2-} + 6H^+ + 8e^- = 2CoS + 3H_2O$	0.126	4	(3)
$9Co^{2+} + 4S_2O_3^{2-} + 24H^+ + 34e^- = Co_9S_8 + 12H_2O$	0.134	34	(4)
$2Ni^{2+} + S_2O_3^{2-} + 6H^+ + 8e^- = 2NiS + 3H_2O$	0.099	4	(5)
$3Ni^{2+} + S_2O_3^{2-} + 6H^+ + 10e^- = Ni_3S_2 + 3H_2O$	0.077	10	(6)

Table 5. Possible reactions for the oxidative stripping of metal sulfides formed during reduction of cobalt and nickel ions in the presence of thiosulfate.

Reaction	E, V	e/Mol MS	No
$8CoS + Co^{2+} + 2e = Co_9S_8$	-0.091	2	(7)
$9Co^{2+} + 8S + 18e = Co_9S_8$	0.137	18	(8)
$Co^{2+} + S + 2e = CoS$	0.158	2	(9)
$2NiS + Ni^{2+} + 2e = Ni_3S_2$	-0.008	2	(10)
$3Ni^{2+} + 2S + 6e = Ni_3S_2$	0.066	6	(11)
$Ni^{2+} + S + 2e = NiS$	0.104	2	(12)

Highlights

Metal sulfides are formed in addition to the metals in a cathodic reaction involving reduction of thiosulfate in the presence of these metal ions.

The presence of thiosulfate ions in the electrolyte is responsible for the formation of black metal sulfides as the products of reduction of nickel and cobalt ions

The anodic passivity of nickel is prevented in the presence of thiosulfate ions.

Chemical reduction of thiosulfate by metallic cobalt and nickel to form metal sulfides has been established.

Reduction of cobalt ions by thiosulfate is catalysed by the metal/metal sulfide surface.