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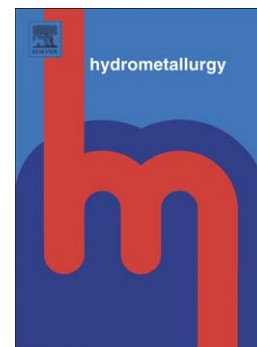
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Anna D'Aloya, Aleksandar N. Nikoloski

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An electrochemical investigation of the formation of CoS_x and its effect on the anodic dissolution of iron in ammoniacal-carbonate solutions

Anna D'Aloya and Aleksandar N. Nikoloski*

Parker Centre, Murdoch University, South Street, Murdoch, WA 6150, Perth, Australia

Abstract

It has been found that the co-presence of cobalt (II) and thiosulfate ions in ammoniacal-carbonate solutions promotes the passivation of iron, under conditions in which it would otherwise continue to dissolve anodically. Electrochemical experiments have shown a relationship between the immersion time required for passivation and the formation of a solid species on the iron surface, which is thought to be implicated in the mechanism of passivation, whilst not being itself the protective species. Based on a combination of electrochemical, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and grazing incidence X-ray diffraction (GIXRD) characterisation techniques, said species has been identified as CoS_x , resulting from the interaction of cobalt (II) and thiosulfate ions. It is thought to form as a product of the cathodic reactions taking place on the iron surface during its active dissolution.

These findings are particularly relevant to the Caron process, in which ammoniacal-carbonate solutions containing dissolved cobalt and thiosulfate ions are used to leach nickel and cobalt from pre-reduced laterite ores rich in metallic iron. Both the loss of cobalt into the CoS_x layer and the passivation of iron and of its alloys with nickel and cobalt, are potential contributing factors to the low cobalt and nickel recoveries, which are typical of the Caron process. This study provides a better understanding of the conditions under which the CoS_x layer forms and promotes the passivation of iron, and may therefore provide useful information to help minimise the effect this may have on the extraction efficiency of the process. In particular, at the cobalt and thiosulfate ion concentrations usually encountered at a Caron plant, the passivation of iron was found to be prevented by maintaining a high enough concentration of ammonia.

1. Introduction

The electrochemical behaviour of metallic iron in ammoniacal solutions has been studied by several researchers over the years due to its relevance to hydrometallurgical systems. In particular, the leaching stage of the Caron process employs ammonia-ammonium carbonate solutions to extract nickel and cobalt from pre-reduced laterite ores. During the pre-treatment step of the process, the ore is roasted under reducing conditions in order to convert the nickel and cobalt, present as oxides and silicates, to the metallic state. This also results in the reduction of a significant amount of iron, which tends to form alloys with the nickel and cobalt. Therefore, despite it being an unwanted metal in the feed, the dissolution of iron and its alloys is necessary in order to liberate the nickel and cobalt contents. Most of the iron dissolution occurs during the first stage of the leaching, under oxygen-free conditions. In the subsequent leaching stages, which take place under aerated conditions, the dissolved iron precipitates mainly as ferric hydroxide, whereas metallic iron is thought to passivate. This is supported by measurements conducted at the QNi Caron plant in Yabulu, Australia (Nicol et al., 2004; Nikoloski et al., 2003). Although iron rejection is necessary at this stage of the process, the passivation of iron has been identified as one of the possible factors behind its relatively poor extraction efficiency, as suggested by several investigations into the active-passive behaviour of iron in ammoniacal-carbonate solutions (Jandova and Pedlik, 1991; Kho et al., 1992; Kim et al., 1991; Lee et al., 1985; Nicol et al., 2004; Nikoloski and Nicol, 2006; Nikoloski et al., 2003; Osseo-Asare, 1983). It is therefore important to gain a better understanding of the factors and conditions that affect the anodic behaviour of iron, in order to have better control over it and therefore improve the overall efficiency of the process. Although the passivation of iron induced by polarisation has been consistently reported in many studies (Jandova and Pedlik, 1991; Kho et al., 1992; Kim et al., 1991; Lee et al., 1985; Nicol et al., 2004; Nikoloski and

* Corresponding author. Tel.: + 61 8 9360 2835; fax: + 61 8 9360 6343.

E-mail address: A.Nikoloski@murdoch.edu.au (A. N. Nikoloski).

Nicol, 2006; Nikoloski et al., 2003), only a few of these have documented it taking place as a spontaneous process. Under open circuit conditions, iron has generally been found to remain in active dissolution, except in heavily aerated or oxygenated solutions (Nikoloski et al., 2003). Under normal conditions of aeration, or in de-oxygenated solutions, the spontaneous passivation of iron has only been observed under very specific conditions. In particular, iron and its alloys with nickel or cobalt have been found to passivate during short periods of immersion in ammoniacal-carbonate solutions containing copper (II) ions (D'Aloya and Nikoloski, 2012) or in the presence of nickel, cobalt and thiosulfate ions (Nicol et al., 2004; Nikoloski et al., 2003). Iron powder was also found to passivate after 3 days of immersion in ammoniacal-carbonate solutions containing cobalt ions at a significantly lower ammonia concentration than employed in the Caron process (Kasherininov, 1960).

The passivation of iron, iron-nickel and iron-cobalt alloys in solutions containing nickel, cobalt and thiosulfate ions, prepared specifically to simulate typical Caron leach solutions, is of significant industrial relevance due to its potential effect on the extraction efficiency of the process (Nicol et al., 2004; Nikoloski and Nicol, 2006; Nikoloski et al., 2003). Following the passivation of iron in these solutions, a surface layer containing cobalt, nickel and sulfur was also observed, and thought to contribute to further losses of nickel and cobalt from the leach solution by precipitation into such layer (Nikoloski et al., 2003). More importantly, the layer appears to be somehow implicated in the passivation process, by a mechanism which is not fully understood and is subject of ongoing investigation.

2. Experimental details

The electrochemical study was carried out using a 6310 EG&G Princeton Applied Research potentiostat connected to a three electrode cell. The working electrode consisted of a 99.98% polycrystalline iron rotating disk electrode (RDE), the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). The latter was connected to the cell via a Luggin capillary containing the cell solution, which was positioned with its tip a few millimetres from the working electrode, in order to minimise the solution iR drop. No other form of iR correction was applied to the measurements, and all potentials reported have been converted to the standard hydrogen electrode (SHE) scale. The cell was jacketed and connected to a thermostat-controlled water bath set to 45°C in order to simulate the Caron process conditions. The results reported generally refer to experiments that were not conducted under de-oxygenated conditions, unless it is clearly stated in the figure caption. For those experiments which were carried out under de-oxygenated conditions, nitrogen was sparged through the solution prior to the measurement. In order to minimise the loss of ammonia, the nitrogen line was passed through a bubbler containing an ammoniacal carbonate solution of approximately the same composition prior to reaching the cell solution. Additionally, a rotating paraffin oil seal was employed to prevent oxygen from entering the cell and to allow the nitrogen sparge to be stopped during the measurements. Immediately prior to immersion, the working electrode surface was polished with 1200 grit silicon carbide paper wetted with ammonia-ammonium bicarbonate solution, and its rotation speed was kept at 500 rpm for all experiments.

The variables investigated during this study were the concentrations of ammonia, ammonium bicarbonate, cobalt (II) ions, thiosulfate ions, and the duration of the immersion of the iron RDE in the cell solutions. These were prepared using de-ionised water and AR grade reagents, with $[\text{NH}_3]_{\text{T}}$ referring to the total concentration of ammonia species, initially added as aqueous ammonia or ammonium bicarbonate, and $[\text{CO}_2]_{\text{T}}$ to the total concentration of species originating from the bicarbonate ions. The molar ratio between $[\text{NH}_3]_{\text{T}} : [\text{CO}_2]_{\text{T}}$ was always 5:1, except for experiments reported in section 3.3 in which they were studied as independent variables. The cobalt (II) ions were added as cobalt sulfate, and the thiosulfate as its sodium salt.

Microscope images and elemental analyses were obtained using a Philips XL20 scanning electron microscope (SEM) combined with an Oxford Link ISIS 5175 energy dispersive X-ray spectroscopy (EDX) detector. The grazing incidence X-ray diffraction (GIXRD) study was conducted using an Empyrean diffractometer system.

3. Results and discussion

3.1 The anodic dissolution of iron in the presence of dissolved cobalt

The presence of cobalt ions in ammoniacal-carbonate solutions, at concentrations similar to those encountered in the Caron process, was not found to promote the spontaneous passivation of iron in the range of concentrations studied. This is in contrast to the behaviour observed in the presence of copper ions, which under the same conditions were found to promote passivation even at concentrations of an order of magnitude lower (D'Aloya and Nikoloski, 2012). During a 3 hour immersion of an iron RDE in de-oxygenated 12 mM $[\text{Co(II)}]$, 5M $[\text{NH}_3]_{\text{T}}$ and 1M $[\text{CO}_2]_{\text{T}}$, the

measured OCP remained in the -0.7 V to -0.6 V potential region, indicating active dissolution of the iron. SEM observation of the iron surface following immersion revealed a high density of pits, with a small amount of cobalt being detected by the EDX analysis. A similar OCP behaviour was observed at half the $[\text{NH}_3]_{\text{T}}$ and $[\text{CO}_2]_{\text{T}}$, with a precipitate (Figure 1) also being observed on the pitted iron surface. This was thought to consist mainly of iron corrosion products, with the cobalt being present either in its metallic state, due to cementation, or within the iron hydroxides and carbonates, due to adsorption or co-precipitation. The morphology of the precipitate was found to vary depending on whether the solution had been sparged with nitrogen or not. This variation is more likely to be due to the loss of ammonia during sparging than to the presence of oxygen in solution. The precipitate was not visible at the higher $[\text{NH}_3]_{\text{T}}$ and $[\text{CO}_2]_{\text{T}}$, due to the formation of soluble complexes being favoured.

Figure 1. SEM image of the iron surface following 3 hours of immersion in de-oxygenated 2.5 M $[\text{NH}_3]_{\text{T}}$, 0.5 M $[\text{CO}_2]_{\text{T}}$, and 12 mM $[\text{Co(II)}]$ solution.

Cyclic voltammetric measurements showed an anodic response typical of the behaviour of iron in ammoniacal-carbonate solutions. As the potential was scanned in the positive direction from the OCP of around -0.7 V, the anodic current increased steadily, followed by a sudden drop denoting potentiodynamic passivation of the electrode, and significantly reduced anodic currents thereafter (Figure 2). The anodic peak current density and the corresponding passivation potential were found both to decrease for increasing immersion times.

Small cathodic currents were also observed following reversal of the scan, possibly due to the reduction of cobalt complexes, and these currents became larger at longer immersion times. As the applied potential was further decreased below -0.4 V, reactivation of the dissolution of iron was observed.

Figure 2. Cyclic voltammetry of the iron RDE following different times of immersion in de-oxygenated 12 mM $[\text{Co(II)}]$, 5 M $[\text{NH}_3]_{\text{T}}$ and 1M $[\text{CO}_2]_{\text{T}}$ solutions.

3.2 The passivation of iron induced by cobalt and thiosulfate ions

The presence of metastable thiosulfate ions in ammoniacal-carbonate solutions was found to significantly enhance the dissolution of iron, with the anodic currents measured during linear polarisation reaching values an order of magnitude higher than in their absence. However, the presence of both cobalt and thiosulfate ions was also found to promote passivation. For this system, following an initial stage of active dissolution the OCP of the iron RDE was found to undergo a steep transition to values above 0 V. The co-occurrence of such potential increase with the passivation of iron has been shown in a previous study in which the iron dissolution rate was also monitored by measuring changes in the iron concentration in solution (Nikoloski et al., 2003). In de-oxygenated solutions containing 22 mM $[\text{S}_2\text{O}_3^{2-}]$, 5M $[\text{NH}_3]_{\text{T}}$ and 1M $[\text{CO}_2]_{\text{T}}$, and no cobalt (II) ions, the OCP of iron remained just above -0.7 V for over 3 hours, in the same region as in solutions containing cobalt (II) but no thiosulfate ions. When both cobalt and thiosulfate ions were present, the OCP of iron during the active dissolution stage was found to be approximately 0.1V higher than in solutions containing either ion separately.

The timing of the OCP transition in solutions containing both cobalt and thiosulfate ions at 5M $[\text{NH}_3]_{\text{T}}$ and 1M $[\text{CO}_2]_{\text{T}}$ showed little reproducibility, attributed mainly to the difficulty in controlling the ammonia concentration accurately, in particular when nitrogen sparging was employed. Therefore, since passivation was found to take place regardless of whether the solution had been sparged with nitrogen or not, experiments in which it was important to have a more accurate control of $[\text{NH}_3]$ were conducted in solutions that had not been de-oxygenated.

At half the $[\text{NH}_3]_{\text{T}}$ and $[\text{CO}_2]_{\text{T}}$, with the same $[\text{Co(II)}]$ and $[\text{S}_2\text{O}_3^{2-}]$, passivation took place consistently after approximately $\frac{1}{2}$ hour of immersion, while at half the $[\text{Co(II)}]$ and $[\text{S}_2\text{O}_3^{2-}]$, it took place after about 1 hour (Figure 3). It should be noted that under the same conditions but in the absence of thiosulfate, spontaneous passivation was not observed within 2.5 hours, even at a cobalt concentration as high as 36 mM. It is however not to be excluded that even in the absence of thiosulfate ions, spontaneous passivation may still take place at high enough cobalt concentrations, lower ammonia concentrations or at significantly longer periods of immersion than those encountered in practice, as observed by Kasherininov (Kasherininov, 1960). Nevertheless, the fact that passivation was observed at significantly lower cobalt concentrations and shorter immersion times when both species were present, indicates the participation of a different mechanism, likely to involve an interaction between cobalt and thiosulfate, or a species derived from it.

Figure 3. OCP the iron RDE in 2.5 M $[\text{NH}_3]_{\text{T}}$, 0.5 M $[\text{CO}_2]_{\text{T}}$ solutions containing a) 36 mM $[\text{Co(II)}]$; b) 6 mM $[\text{Co(II)}]$ + 11 mM $[\text{S}_2\text{O}_3^{2-}]$; c) 12 mM $[\text{Co(II)}]$ + 22 mM $[\text{S}_2\text{O}_3^{2-}]$.

3.3 The effect of $[\text{NH}_3]$ and $[\text{CO}_2]$ on passivation time

The effect of $[\text{NH}_3]_{\text{T}}$ on the immersion time required for passivation to occur was investigated both at a constant $[\text{CO}_2]_{\text{T}}$ and at a constant $[\text{NH}_3]_{\text{T}} : [\text{CO}_2]_{\text{T}}$ molar ratio of 5:1. As can be seen in Tables 1 and 2, increasing the initial amount of ammonia added to the solution whilst maintaining a constant amount of ammonium bicarbonate (Table 1), or increasing the initial amounts of both reagents at a constant molar ratio between them (Table 2), was found to significantly delay passivation. On the other hand, varying the amount of ammonium bicarbonate at a constant initial concentration of ammonia was not found to have any significant effect on the passivation time.

In contrast with the behaviour of iron observed in the presence of copper amines (D'Aloya and Nikoloski, 2012), where increasing the ammonium bicarbonate concentration at a constant $[\text{NH}_3]_{\text{T}}$ was found to delay passivation, in the presence of cobalt and thiosulfate ions the opposite trend was observed. (Table 3). The fact that in the current work passivation took place sooner as the ammonium bicarbonate concentration was increased can be attributed to the decrease in $\text{NH}_3/\text{NH}_4^+$ ratio and hence the pH. Whereas in solutions containing copper (II) ions, increasing the pH appeared to promote passivation, in the current work it appears to inhibit passivation, as can also be seen by comparing the passivation times at 5 M $[\text{NH}_3]_{\text{T}}$ and different $[\text{CO}_2]_{\text{T}}$ (Tables 1 and 2). However, since the effect of pH cannot be studied as an independent variable to $[\text{NH}_3]$, it cannot be ascertained whether the observed delay in passivation is due to an increase in metal complexation by the ammonia ligands or whether the increase in hydroxyl ion concentration also plays a role.

Table 1. Immersion time required for passivation of the iron RDE at different $[\text{NH}_3]_{\text{T}}$, 2 M $[\text{CO}_2]_{\text{T}}$, 12 mM $[\text{Co(II)}]$ and 22 mM $[\text{S}_2\text{O}_3^{2-}]$.

Table 2. Immersion time required for passivation of the iron RDE at different $[\text{NH}_3]_{\text{T}}$, 12 mM $[\text{Co(II)}]$, 22 mM $[\text{S}_2\text{O}_3^{2-}]$, and a constant molar ratio of $[\text{NH}_3]_{\text{T}} : [\text{CO}_2]_{\text{T}} = 5 : 1$.

Table 3. Immersion time required for passivation of the iron RDE at different $[\text{NH}_3]_{\text{T}} : [\text{CO}_2]_{\text{T}}$ molar ratios, 6 M $[\text{NH}_3]_{\text{T}}$, 12 mM $[\text{Co(II)}]$ and 22 mM $[\text{S}_2\text{O}_3^{2-}]$.

3.4 Linear and cyclic voltammetry studies of iron in the $\text{NH}_3\text{-CO}_2\text{-Co(II)-S}_2\text{O}_3^{2-}$ system

Linear polarisation measurements conducted in the de-oxygenated $\text{NH}_3\text{-CO}_2\text{-Co(II)-S}_2\text{O}_3^{2-}$ system, following different times of immersion, resulted in the progressive reduction of the iron oxidation peak current density, suggesting a gradual coverage of the iron surface by species thought to hinder the dissolution process (Figure 4). Following longer immersion times, several other anodic processes also began to appear at more positive potentials. These are thought to correspond to the oxidation of the solid species formed on the iron surface during its anodic dissolution. These can be seen more clearly in Figure 5, which shows a cyclic voltammetric measurement taken following 2 hours of immersion at 24 mM $[\text{Co(II)}]$ and 44 mM $[\text{S}_2\text{O}_3^{2-}]$. The resulting iron oxidation peak (A) was found to be significantly reduced, and followed by a slight inflection in current. A second significant increase in current density began as the potential was scanned in the positive direction above -0.3 V, with a slight inflection followed by peaks at approximately -0.1 V (B), 0 V (C) and +0.1 V (D). As the potential was further scanned above +0.2 V, again the anodic current increased steadily, reaching its maximum as the potential approached +0.4 V (E), and then dropping to significantly lower values thereafter.

Upon reversal of the scan, no significant current was observed until the potential reached values below -0.1 V, with a cathodic peak (F) being observed at a potential slightly more negative than -0.3 V. As the potential approached -0.4 V, the reactivation of the dissolution of iron took place (A^1), resulting in a peak current density over 3 times larger than that observed during the anodic scan (A). This is possibly due to the fact that the species hindering the iron dissolution during the anodic scan were oxidised as the anodic scan proceeded to more positive potentials, and therefore no longer inhibiting the oxidation of the RDE surface during the cathodic scan. On the other hand, the thin oxide layer which caused passivation of the iron surface continued to shield it until the applied potential became negative enough for its reduction to take place, allowing re-activation of the dissolution of iron.

Figure 4. Linear polarisation of the iron RDE following different times of immersion in de-oxygenated solutions containing 12 mM [Co(II)], 22 mM [S₂O₃²⁻], 5 M [NH₃]_T and 1M[CO₂]_T.

Figure 5. Cyclic voltammetry of the iron RDE following 2 hours of immersion in 24 mM [Co(II)], 44 mM [S₂O₃²⁻], 5 M [NH₃]_T and 1 M [CO₂]_T.

In order to compare the voltammetric response just before and a few minutes after passivation, measurements were also taken at a slightly lower [NH₃]_T of 4 M, at which the OCP transition was consistently observed after approximately 2 hours of immersion (Figure 6). Prior to passivation, the iron oxidation peak (A) was found to be reduced in size, followed by a broad anodic feature with three ill-defined peaks thought to correspond to peaks B, C and D in Figure 5. Neither of these anodic processes was observed after passivation, as the species involved were only present at the iron surface during its active dissolution, and are likely to have either lost electrical contact or to have been oxidised during the OCP transition.

On the other hand, peak E was observed both before and after passivation, reaching a lower maximum current density at a less positive potential in the latter case. In both cases, reversal of the scan resulted in a cathodic process thought to correspond to that labelled F in Figure 5, although this time it did not reach a clear maximum before the reactivation of iron prevailed (A¹).

Figure 6. Cyclic voltammetry measurements taken a few minutes before (OCP = -0.54 V) and a few minutes after (OCP = 0.05 V) passivation of the iron RDE in 4 M [NH₃]_T, 0.8 M [CO₂]_T, 12 mM [Co(II)] and 22 mM [S₂O₃²⁻].

3.4.1 Surface changes during active dissolution at 5 M [NH₃]_T

In order to further investigate the surface species formed on iron during its active dissolution, a study was conducted following longer periods of active dissolution at 5 M [NH₃]_T, 1 M [CO₂]_T. As can be seen in Figure 7, a cyclic voltammetric measurement taken after 8.5 hours of immersion, during which the OCP remained within the active dissolution region resulted in the almost complete suppression of peak A. At potentials more positive than -0.4 V, a broad anodic feature began to increase, with the appearance of ill-defined peaks thought to correspond to B, D and E. Upon reversal of the scan, an anodic current density of about 2 mA/cm² was maintained until the applied potential approached -0.2 V. As the potential was further scanned in the negative direction, a cathodic feature peaked at around -0.4 V, followed by a small anodic current peaking around -0.5 V, due to the anodic dissolution of iron (A¹). A cyclic voltammetry measurement reversed prior to reaching the potential region of peak E, taken after 4 hours of immersion, is also shown in Figure 7. The anodic scan resulted in peaks A, B and D, whereas following reversal of the applied potential, a cathodic current starting around 0 V resulted in peak G. No obvious reactivation of the anodic dissolution of iron was observed, probably due to the fact that the species hindering the dissolution of iron was still present at the RDE surface, following its reduction resulting in peak G.

Figure 7. Cyclic voltammetry of the iron RDE in 5 M [NH₃]_T, 1 M [CO₂]_T, 22 mM [S₂O₃²⁻], 12 mM [Co(II)] following 8.5 h immersion (solid line); following 4 h immersion, potential reversed at +0.24 V (dotted line).

SEM images taken after 16 hours of active dissolution revealed the presence of a thick layer (Figure 8), which based on EDX analyses was thought to consist mainly of iron hydroxides, oxides or carbonates, with small amounts of cobalt and sulphur present. Although it was found to suppress the dissolution of iron, this layer did not promote the passivation of iron, as consistent with the OCP remaining in the active dissolution region over the long immersion period during which it formed.

Figure 8. SEM images of the surface layer formed on the iron RDE following 16 hours active dissolution in 5 M [NH₃]_T, 1 M [CO₂]_T, 22 mM [S₂O₃²⁻], 12 mM [Co(II)].

3.4.2 Surface changes leading to passivation at 2.5 M [NH₃]_T

At half the $[\text{NH}_3]_{\text{T}}$, cyclic voltammetric measurements conducted at different immersion times prior to passivation, resulted in the intermediate peaks B, C and D being significantly reduced or absent (Figure 9). The progressive decrease in anodic current density at peak A and simultaneous increase at peak E became evident at shorter immersion times, indicating that the progressive suppression of the anodic dissolution of iron and simultaneous increase in surface coverage by the species being oxidised at E took place faster at lower $[\text{NH}_3]_{\text{T}}$. The shape of the anodic peak was also found to change progressively, with a steep drop in current typical of a passivation phenomenon being observed when the measurement was taken immediately prior to the OCP transition. The increased height of peak E and shorter delay to passivation are consistent with a surface species other than the iron corrosion products observed at higher $[\text{NH}_3]_{\text{T}}$, which unlike the latter appears to promote passivation.

Figure 9. Cyclic voltammetry of the iron RDE in 2.5 M $[\text{NH}_3]_{\text{T}}$, 0.5 $[\text{CO}_2]_{\text{T}}$, 22 mM $[\text{S}_2\text{O}_3^{2-}]$, 12 mM $[\text{Co(II)}]$ at the immersion times shown on the chart.

3.5 The effect of $[\text{Co(II)}]$ and $[\text{S}_2\text{O}_3^{2-}]$

The immersion time required for passivation to take place was found to depend both on $[\text{Co(II)}]$ and to a lesser extent on $[\text{S}_2\text{O}_3^{2-}]$, as shown in Figure 10. The slight shoulder in the OCP transition from the active to the passive potential region, visible around -0.15 V (Figure 3), became more evident for decreasing $[\text{Co(II)}]$ concentrations. Cyclic voltammetric measurements conducted following passivation showed an increase in the current density at peak E for increasing $[\text{Co(II)}]$ (Figure 11). Correlation between the height of peak E and the corresponding time required for passivation in the same solutions (Figure 10) confirmed that shorter delays to passivation are reflected by higher anodic current densities at peak E. Both of these quantities became less sensitive to $[\text{Co(II)}]$ as it was increased above 9 mM. On the other hand, measurements conducted at a fixed $[\text{Co(II)}]$ of 12 mM showed that by increasing $[\text{S}_2\text{O}_3^{2-}]$ between 8 and 22 mM, the increase in anodic current density at peak E was only slight, as was the decrease in passivation time (Figure 10).

Figure 10. The dependence of the time required for passivation of the iron RDE on $[\text{Co(II)}]$ (solid triangles) at 22 mM $[\text{S}_2\text{O}_3^{2-}]$, and on $[\text{S}_2\text{O}_3^{2-}]$ (outline circles) at 12 mM $[\text{Co(II)}]$, 2.5 M $[\text{NH}_3]_{\text{T}}$ and 0.5 $[\text{CO}_2]_{\text{T}}$.

Figure 11. Cyclic voltammetry of the iron RDE in 2.5 M $[\text{NH}_3]_{\text{T}}$, 22 mM $[\text{S}_2\text{O}_3^{2-}]$, and $[\text{Co(II)}] = 3$ mM (dotted line); 6 mM (dashed line); 12 mM (solid line).

From these results it appears that the dissolved cobalt plays an important role in the formation of the species being oxidised at peak E, which is thought to consist of a CoS_x layer deposited cathodically during the anodic dissolution of the iron. Based on the OCP and cyclic voltammetry results, there is strong evidence to suggest that formation of such layer is likely to be implicated in the mechanism of passivation of iron.

3.6 Study of the CoS_x layer formed on iron

SEM/EDX investigation of the iron RDE surface following immersion and passivation in ammoniacal carbonate solutions containing cobalt and thiosulfate ions, revealed the presence of a cracked surface layer containing up to 10 atomic percent (at.%) Co and 20 at.% S (Figure 12). This layer is thought to contain the species responsible for peak E and is therefore likely to be implicated in the mechanism of passivation. Depending on the experimental conditions, different thicknesses of the layer were observed, with varying cobalt and sulfur contents, usually present at an approximate 1:2 ratio. Layers formed at a lower $[\text{NH}_3]_{\text{T}}$ appeared to be thinner, almost indistinguishable from the iron surface.

Figure 12. SEM image of the iron RDE following immersion in de-oxygenated ammoniacal-carbonate solution containing 12 mM $[\text{Co(II)}]$ and 22 mM $[\text{S}_2\text{O}_3^{2-}]$.

The layer was also analysed by Grazing Incidence X-Ray Diffraction (GIXRD), and found to be amorphous. Addition of a few drops of concentrated hydrochloric acid to the surface of the iron RDE resulted in the distinctive smell of hydrogen sulfide gas, therefore indicating the presence of sulfide ions. Based on these observations it

appears possible that the surface species responsible for the anodic peak (E) and implicated in the mechanism of passivation, is a cobalt sulfide or polysulfide.

In order to confirm that the species responsible for peak E was not significantly affected by removal of the RDE from the solution, following passivation in a solution containing 2.5 M $[\text{NH}_3]_{\text{T}}$, 0.5 $[\text{CO}_2]_{\text{T}}$, 12 mM $[\text{Co(II)}]$ and 22 mM $[\text{S}_2\text{O}_3^{2-}]$, the electrode was taken out, rinsed with de-ionised water and allowed to dry. Following SEM/EDX analysis, which confirmed the presence of approximately 3 at% cobalt and 7 at% sulfur, the electrode was re-immersed in a barren solution of the same $[\text{NH}_3]_{\text{T}}$ and $[\text{CO}_2]_{\text{T}}$, in which it had an OCP of around 0.15 V, in the same region as in the previous solution (Figure 13). Linear polarisation in the positive direction resulted in the anodic peak E, which was found to decrease the longer the electrode was left in the solution prior to the measurement (Figure 14). Following the linear polarisation scan, the OCP was found to drop within 15 minutes from an initial value of 0.3 V to values just below 0 V, and to continue to decrease slowly thereafter (Figure 13). SEM/EDX analysis of the RDE surface following the linear polarisation and OCP measurements revealed the presence of approximately 1at.% cobalt and 2 at.% sulphur. Reaction with concentrated hydrochloric acid confirmed that a sulfide or polysulfide species was still present on the iron surface. When an analogous set of measurements was conducted after re-immersion of the RDE in the same solution in which it had passivated, the observed behaviour was similar, except for the OCP measured after linear polarisation, which was found to relax back to the same region in which it was prior to the polarisation.

Figure 13. OCP of the passive iron RDE in 2.5 M $[\text{NH}_3]_{\text{T}}$, 0.5 M $[\text{CO}_2]_{\text{T}}$: a) upon re-immersion; b) following linear polarisation to 0.742 V.

Figure 14. Linear polarisation of the passive iron RDE in barren 2.5 M $[\text{NH}_3]_{\text{T}}$ and 0.5 M $[\text{CO}_2]_{\text{T}}$: a) upon re-immersion; b) 10 minutes after re-immersion.

In order to further investigate the cathodic processes taking place during immersion of the iron RDE separately from the response due to the iron species, a set of experiments was conducted in an iron-free system, using an inert graphite RDE. Scanning the potential in the cathodic direction resulted in a current response likely to be due to the simultaneous reduction of the various cobalt ammine and thiosulfate species present in solution. Nevertheless, it was possible to distinguish at least two diffusion limited cathodic processes (Figure 15), the first in the 0.1 V to -0.7 V potential region, and the second at potentials more negative than -0.7 V. The latter was attributed to the deposition of metallic cobalt, which overall can be described by the following half-reaction:



Assuming that most of the cobalt was present in solution as the cobaltous pentammine complex, by applying the Nernst equation (2) to half-reaction 1 it is possible to estimate the potential region below which it is thermodynamically feasible:

$$E = E^\circ - 0.0137 \ln \left[\frac{a_{\text{NH}_3}^5}{a_{[\text{Co}(\text{NH}_3)_5]^{2+}}} \right] \quad (2)$$

In the ammonia activity range of 1 to 2.5, the equilibrium potential of half-reaction 1 was found to be between -0.51 V and -0.57 V, therefore confirming that the deposition of metallic cobalt is a feasible process likely to be contributing to the cathodic currents observed below -0.7 V. This was confirmed upon reversal of the scan by the appearance of an anodic peak (H) around -0.4 V, which was assigned to the oxidation of metallic cobalt, by comparison with measurements conducted in the absence of thiosulfate ions. This was followed by a small shoulder and prevailing cathodic currents up to potentials above 0 V. As the potential was further scanned in the positive direction, an anodic current increased at around 0.1 V, as previously observed in the iron RDE. Following a slight shoulder around 0.2 V, an anodic current peak was observed just above 0.4 V and assigned to the same process responsible for peak E observed on the iron RDE (Figure 15).

Figure 15. Cyclic voltammetry of the graphite RDE (solid line) and of the iron RDE following passivation (dotted line) in 2.5 M $[\text{NH}_3]_{\text{T}}$, 0.5 M $[\text{CO}_2]_{\text{T}}$, 12 mM $[\text{Co(II)}]$ and 22 mM $[\text{S}_2\text{O}_3^{2-}]$.

Comparison of the cathodic currents obtained in solutions containing both cobalt and thiosulfate ions, with those obtained in solutions containing either ion separately (Figure 16) indicated that the overpotential for the deposition of metallic cobalt was significantly reduced in the presence of thiosulfate ions. In solutions containing only cobalt (II) ions, the deposition of metallic cobalt took place at potentials more negative than 0.9 V (Figure 16, b). Although the corresponding cathodic currents could not be distinguished from those due to the evolution of hydrogen, this was confirmed by stripping the metallic cobalt anodically. Measurements conducted in solutions containing only thiosulfate ions suggested the possible occurrence of a reductive process as the potential was scanned cathodically down to the hydrogen evolution region (Figure 16, a), whereas no significant anodic current was observed upon reversal of the scan.

Figure 16. Linear polarisation of the graphite RDE in 2.5 M [NH₃]_T, 0.5 M [CO₂]_T, 12 mM [Co(II)] and 22 mM [S₂O₃²⁻] (solid line); dotted lines: a) without Co(II); b) without S₂O₃²⁻.

The graphite RDE was also polarised for 30 minutes at -0.52 V, the potential corresponding to the OCP of iron during its active dissolution in the same solution. This resulted in some cobalt and sulfur being detected by EDX analysis of the graphite surface, and reaction with concentrated hydrochloric acid indicated the presence of sulfide or polysulfide ions. Cyclic voltammetry measurements conducted following the potentiostatic polarisation at both 2.5 M and 5 M [NH₃]_T resulted in multiple anodic peaks in the 0 V to 0.6 V region (Figures 17 and 18) and a cathodic peak around -0.5 V (I). Second and subsequent cycles resulted in peak E being observed, with a small shoulder around 0.2 V as previously observed (Figure 15). Peak E was also observed when the electrode was taken out following the potentiostatic polarisation and then re-immersed in a barren solution, as shown in Figure 17. These results confirm that at the potential corresponding to the anodic dissolution of iron, a CoS_x species deposits onto the iron surface, as proven by the presence of peak E, resulting from its oxidation.

Figure 17. Cyclic voltammetry of the graphite RDE in 2.5 M [NH₃]_T, 0.5 M [CO₂]_T, 12 mM [Co(II)] and 22 mM [S₂O₃²⁻], following potentiostatic polarisation for 30 minutes at -0.52 V (solid line); second cycle, measured after 30 minutes (dashed line); following potentiostatic polarisation for 30 minutes at -0.52 V, and re-immersion in barren 2.5 M [NH₃]_T and 0.5 M [CO₂]_T solution (dotted line).

Figure 18. Cyclic voltammetry of the graphite RDE in 5 M [NH₃]_T, 1 M [CO₂]_T, 12 mM [Co(II)] and 22 mM [S₂O₃²⁻] following potentiostatic polarisation for 2 hours at -0.6 V (solid line); second cycle, taken immediately after (dashed line).

Two possible mechanisms have been suggested in the past for the reduction of thiosulfate ions during the first leaching stage of the Caron process (Queneau and Weir, 1986). One is the reduction to sulphide by metallic iron as it is dissolved oxidatively to form a ferrous ammine. The other is the disproportionation to sulfide and sulfate according to reaction 3, supported by plant measurements which indicated a decrease in dissolved cobalt and sulfur, and a simultaneous increase in sulfate ions.



The formation of the CoS_x both on the cathodically polarised graphite electrode and on iron may possibly take place via similar reactions, albeit with less well-defined stoichiometry and oxidation states of both the cobalt and the sulfur.

4. Conclusions

The present study has shown that during the anodic dissolution of iron in ammoniacal-carbonate solutions containing both cobalt (II) and thiosulfate ions, a CoS_x species forms on the iron surface. The presence of such species was confirmed by a combination of SEM/EDX, GIXRD and electrochemical characterisation methods. Linear polarisation and cyclic voltammetry measurements indicated that the CoS_x species undergoes an oxidative process which results in a distinctive current peak in the 0.3 V to 0.5 V potential region.

Formation of the CoS_x species on the dissolving iron surface is thought to be implicated in the mechanism of passivation of iron, as suggested by the relationship between the height of its oxidation peak and the immersion time required for passivation. The results of this study are particularly relevant to the leaching stage of Caron process

which takes place in ammoniacal solutions containing both cobalt and thiosulfate ions. The formation of the CoS_x species during the leach may therefore have a negative effect on the efficiency of the Caron process, not only by causing the loss of dissolved cobalt from the leach solution, as it precipitates into the layer itself. It also has the potential to prevent further dissolution of the metal values, by promoting the passivation of iron and its alloys with nickel and cobalt. The findings described in this study provide a better understanding of the conditions which promote the passivation of iron, which at the cobalt and thiosulfate ion concentrations typically encountered at a Caron plant, can be prevented by maintaining a high enough concentration of ammonia ($> 4\text{M}$).

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Table 1

[NH₃]	[CO₂]_T	[NH₃]_T	Time to passivation
1 M	2 M	3 M	20 min
2 M	"	4 M	35 min
3 M	"	5 M	1.5 h
4 M	"	6 M	> 6 h

Table 2

[NH₃]	[CO₂]_T	[NH₃]_T	Time to passivation
0.8 M	0.2 M	1 M	10 min
1.6 M	0.4 M	2 M	20 min
2.4 M	0.6 M	3 M	40 min
3.2 M	0.8 M	4 M	2 – 2.5 h
4.0 M	1.0 M	5 M	> 6 h

Table 3

[NH ₃]	[CO ₂] _r	[NH ₃] _r	Time to passivation
4 M	2 M	6 M	> 5 h
3 M	3 M	"	~1 h
2 M	4 M	"	< 1 h

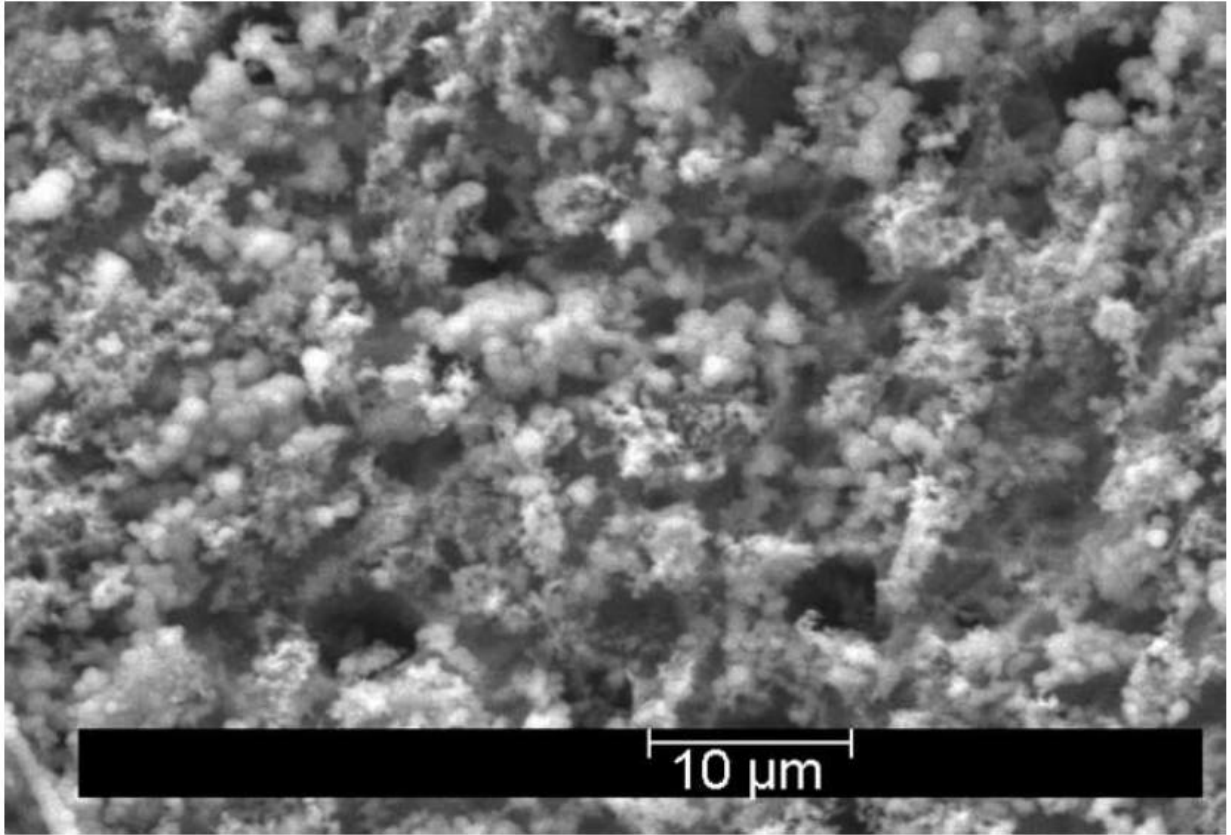


Fig. 1

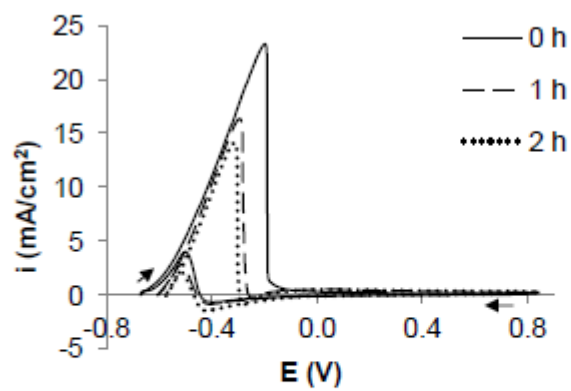


Fig. 2

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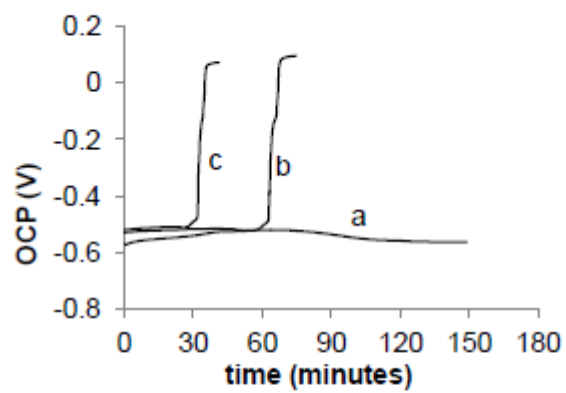


Fig. 3

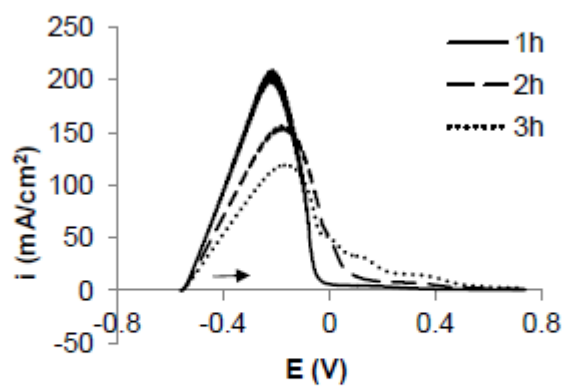


Fig. 4

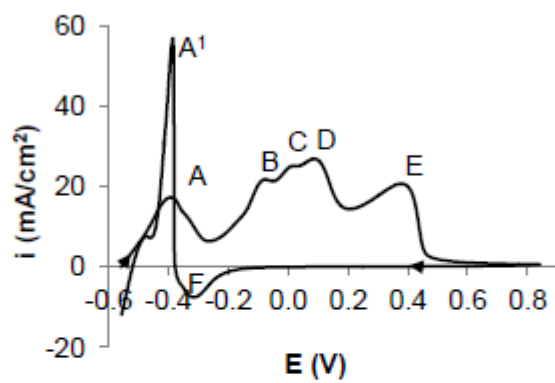


Fig. 5

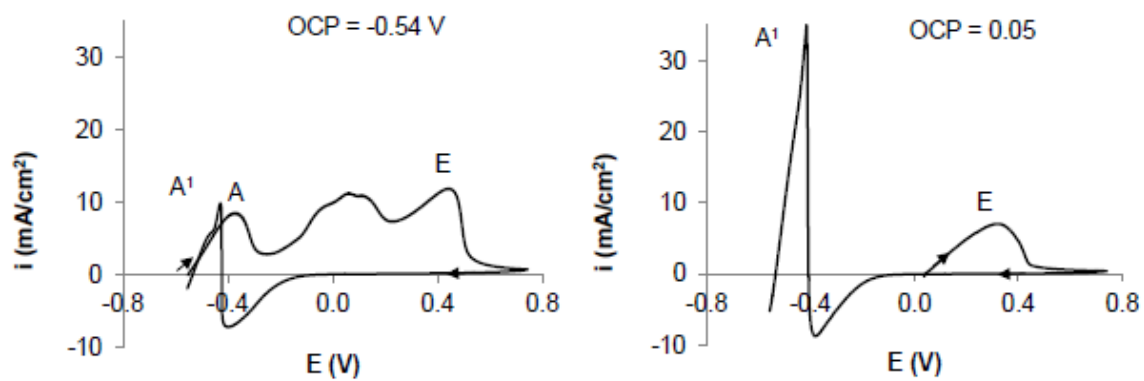


Fig. 6

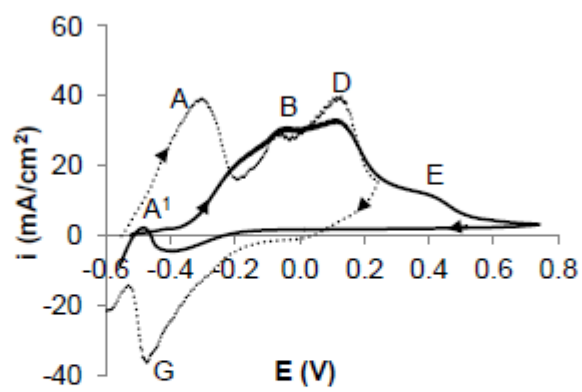


Fig. 7

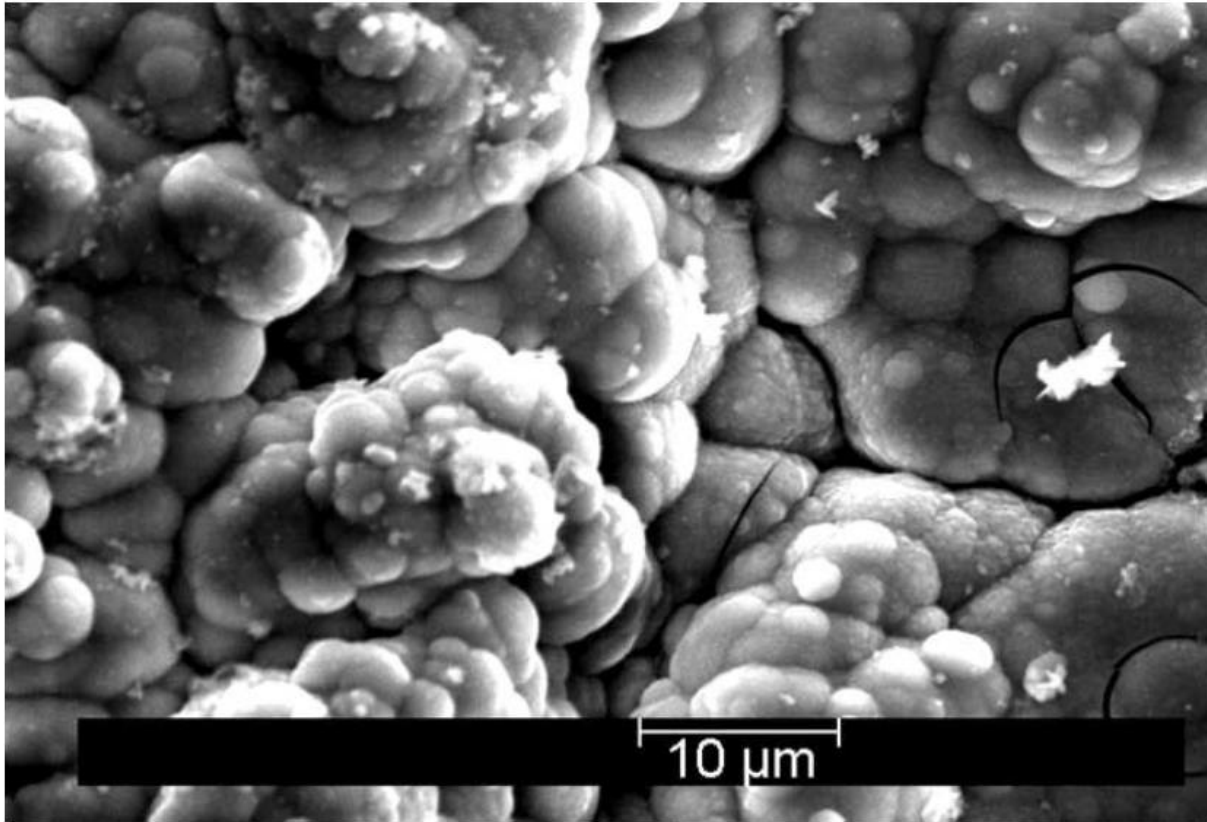


Fig. 8

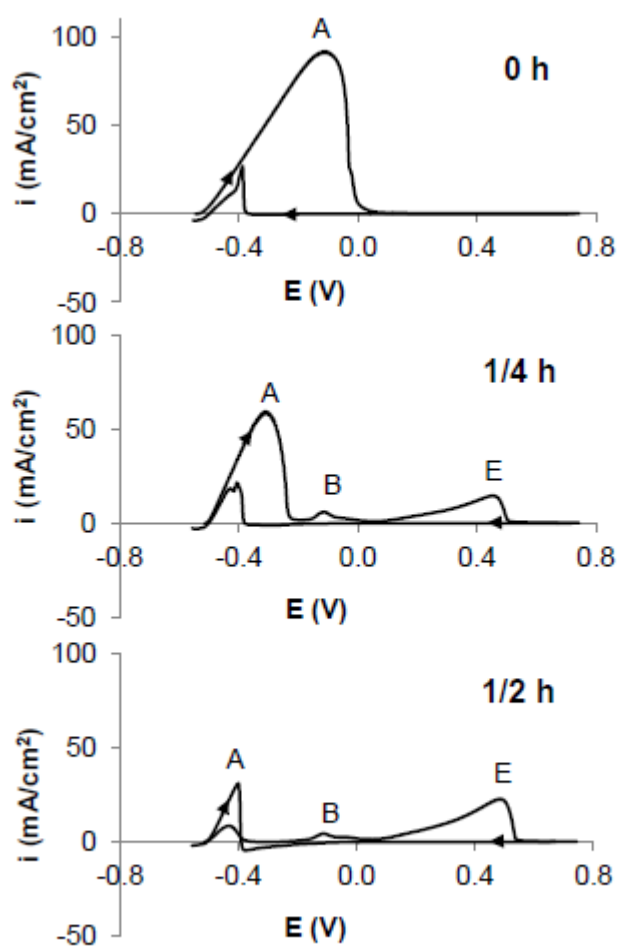


Fig. 9

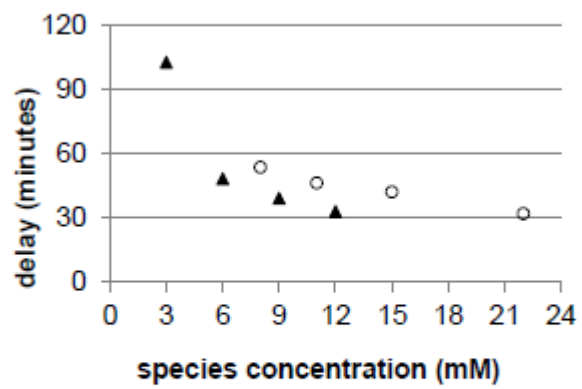


Fig. 10

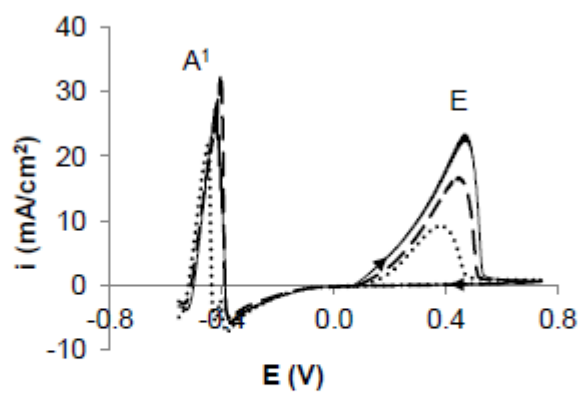


Fig. 11

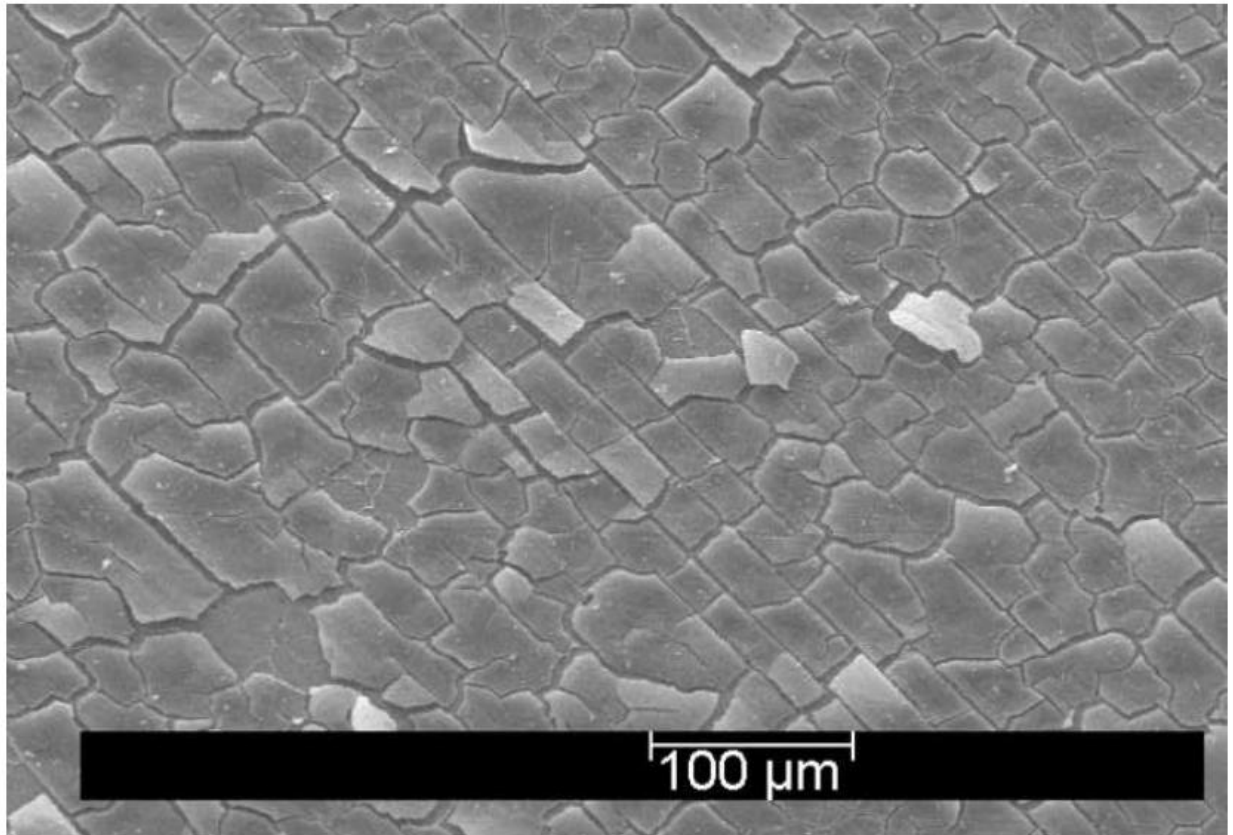


Fig. 12

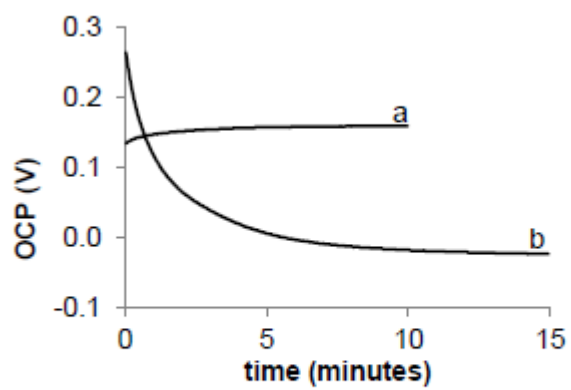


Fig. 13

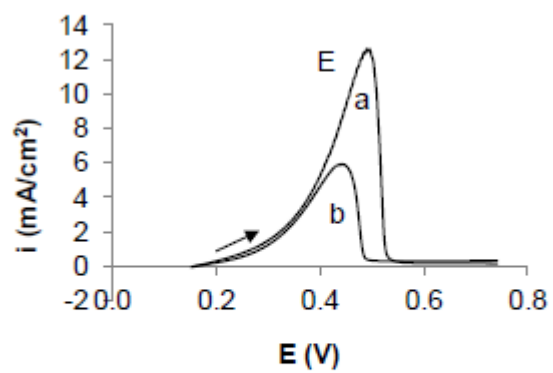


Fig. 14

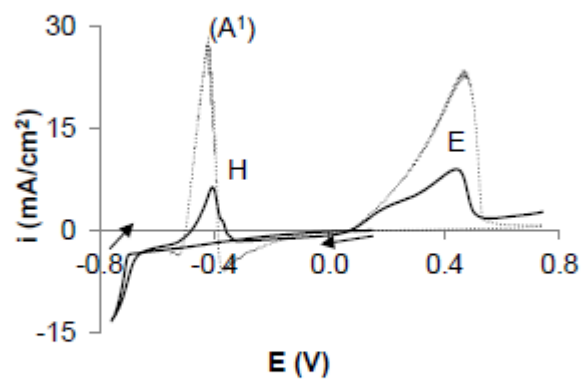


Fig. 15

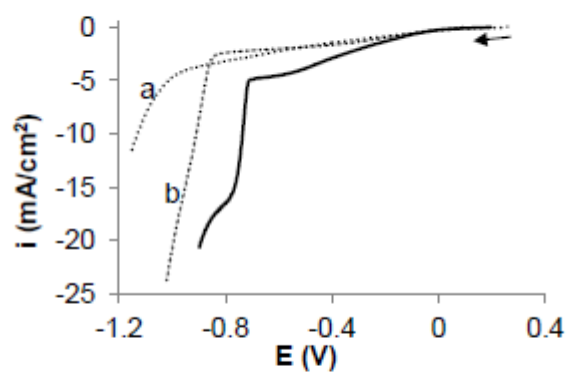


Fig. 16

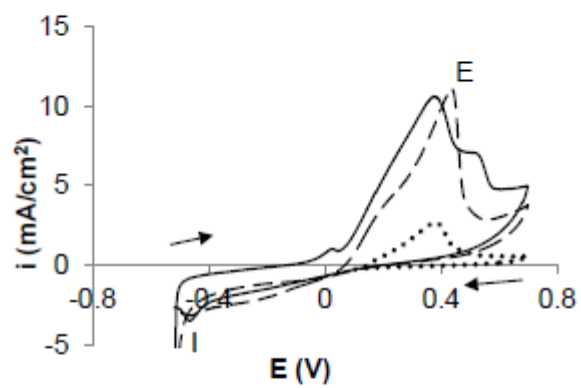


Fig. 17

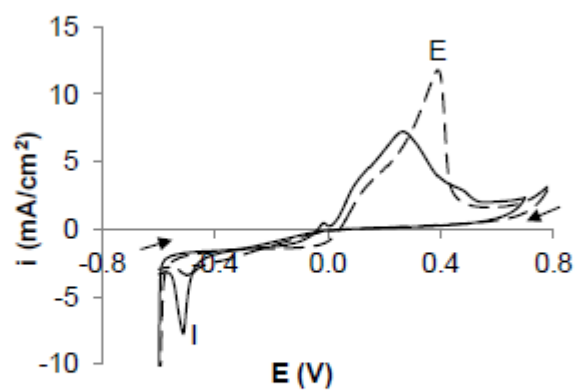


Fig. 18

Highlights

- Fe passivation in aqueous $\text{NH}_3/\text{NH}_4\text{HCO}_3$ with Co(II) occurs only if $\text{S}_2\text{O}_3^{2-}$ also present
- The co-presence of Co(II) and $\text{S}_2\text{O}_3^{2-}$ results in the formation of CoS_x
- Passivation occurs faster at higher $[\text{Co(II)}]$ and lower $[\text{NH}_3]$

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