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Electrodeposition of lead-cobalt composite coatings electrocatalytic for oxygen evolution and the properties of composite coated anodes for copper electrowinning

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Abstract
Metal-matrix composite coatings of lead-cobalt (Pb-Co) and lead-cobalt oxide (Pb-Co$_3$O$_4$) were electrodeposited onto the surface of a conventional PbCaSn anode in an effort to develop an improved anode for use in base metal electrowinning. The developed coated anodes were examined in terms of their electrochemical and physical stability over several days of polarisation for the evolution of oxygen under typical copper electrowinning conditions. Results from scanning electron microscopy have shown that fresh Pb-Co and Pb-Co$_3$O$_4$ composite coated anodes have rougher surface than conventional (uncoated) PbCaSn anodes but the apparent differences in surface area become insignificant after several days of polarisation under typical copper electrowinning conditions. The Tafel slope on the Pb-Co anode was 92 mV dec$^{-1}$ and on the Pb-Co$_3$O$_4$ it was 90 mV dec$^{-1}$, which is significantly less than the 122 mV dec$^{-1}$ measured on the conventional PbCaSn anodes. The composite anodes exhibited consistently lower oxygen evolution potentials than the conventional type and the potential remained relatively stable throughout the polarisation period. The reduction in the operating anode potential can be attributed to the presence of cobalt in the surface layer while the decrease in the Tafel slope shows that this reduction can be related to a change in the mechanism of the oxygen evolution reaction. Corrosion rates estimated from 16 h tests showed that the composite coated anodes are more stable than the conventional type during short periods of operation. It was also observed that for the Pb-Co coated anode, both the rate of corrosion and the overpotential for the oxygen evolution reaction can be further reduced by the addition of organic additives such as thiourea.

Keywords: electrowinning, overpotential, anode, lead, cobalt, thiourea, corrosion

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1 INTRODUCTION

Lead based anodes have been used in the electrowinning of base metals for more than a century due to their low cost and availability. However, the conventional types of lead based anodes, such as PbCaSn, operate at relatively high oxygen overpotential, which results in significant energy consumption, and suffer from corrosion which takes place at a slow rate during the electrowinning process. It is reported that 20-25% of the overall cell energy consumption in tankhouses using conventional lead based anodes is attributed to oxygen evolution overpotential (Schmachtel et al., 2008). On the other hand, the slow corrosion is adding to the cost of anode replacement but, also, leads to contamination of the cathodes with lead from the corrosion product which lowers the quality of the produced cathodes.

The development of anodes that can evolve oxygen from acidic sulphate solutions at lower overpotential than on the conventional lead based anode has a long history in the hydrometallurgical research field. This was revisited in the present study, with particular attention given to the low cost options, such as the addition of cobalt. Some of the earliest references relating to the effect of cobalt go back to 1938 when Ray and his co-workers reported on testwork evaluating the effect that cobalt in the electrolyte had on the performance of lead anodes used for copper electrowinning. They reported that cobalt, even at relatively low concentrations of 20-70 mg dm$^{-3}$, can aid the evolution of oxygen, lower the potential of anode and decrease the corrosion rate of anode (Ray et al., 1938). Similarly, in 1941, Koenig and his co-workers investigated the effect of different impurities on the anode potential and observed that 20 mg dm$^{-3}$ cobalt in the electrolyte decreased the anodic potential by almost 110 mV. These two groups of researchers related the observed effects to an unspecified process occurring in preference of the conversion of lead to lead dioxide when cobalt ions are present in the electrolyte. The conclusion was that to keep the anode potential low, one needed to maintain the cobalt concentration by continuous addition of cobalt ions to the electrolyte (Koenig et al., 1941). Tsuruoka (1958) followed a similar approach to study the effect of cobalt ions in a typical zinc electrowinning system and also observed a reduction in lead dissolution when cobalt ions were present in the electrolyte. Even with a small amount of cobalt present (50–200 mg dm$^{-3}$), the performance of the anodes was improved, albeit with negative consequences on the cathodic process. An early attempt at interpreting the mechanism of the observed effect of cobalt was offered by Koch (1958), who noted that cobalt affects the oxygen evolution reaction when the anode potential reaches the potential suitable for the oxidation of Co$^{2+}$ to Co$^{3+}$ ($\sim$1.83V/NHE). As observed by Koch, the
reduction in oxygen overpotential could be related to an increased concentration of cobalt at the anode surface.

Research on developing methods to produce catalytically active composite coated anodes which can operate as anodes to generate oxygen at a low overpotential and maintain good resistance to corrosion continues (Musiani and Guerriero, 1998; Bertoncello et al., 1999; Bertoncello et al., 2000; Hrussanova et al., 2001, 2002, 2004a and 2004b; Cattarini et al., 2001; Velichenko et al., 2002, 2008, 2009a and 2009b). Prengaman and Siegmund (2007) filed a patent on the addition of cobalt to PbCaSn anodes as an alloy, to improve the efficiency of oxygen evolution at the anodes with decreasing the corrosion of anodes. A subsequent paper (Prengaman and Ellis, 2010) addressed the new lead anodes alloyed with cobalt and reported that they behave similar to conventional PbCaSn anodes operating in the presence of cobalt ions in electrolyte. Some of the published work relating to the effect of cobalt and behaviour of the anode in the presence of cobalt has been reviewed by Ivanov et al. (2000a, 2000b). An updated literature review on the influence of cobalt in solution on the performance of lead based anodes in copper electrowinning was provided by Nikoloski and Nicol (2008), followed by a separate review focusing on the direct addition of cobalt to the lead surface layer (Nikoloski and Nicol, 2010). These papers outline the effects of cobalt addition, either to the electrolyte or to the surface layer of the anode and show that in either case the main benefits involve i) reduced energy consumption due to depolarised oxygen evolution reaction and ii) reduced anode corrosion resulting in less PbO$_2$ produced and lower contamination of cathodes. In addition, by decreasing the anode potential one can change the rate of other reactions which take place on the anode surface such as the oxidation of manganese and chromium.

This paper presents the results of a study which aims to extend the previous work and utilise some of the benefits of cobalt by introducing it directly into the surface layer of the anode, thus avoiding the need to continuously add cobalt ions to the electrolyte. Several attempts to produce composite anodes containing lead with cobalt have been considered in the past. Composite anodes have been prepared by mechanical alloying, metal-ceramics, electrical arc, cementation and pulse plating techniques (Forsen et al., 1992, Kiryakov and Stender, 1951, Yoshida, 1953 and Rashkov et al., 1999). In this study, the composite anode preparation process considered the formation of a surface composite coating by simultaneous cathodic electrodeposition of lead and cobalt metal or cobalt oxide, onto a lead substrate. There appears to be no prior information on the formation of lead with cobalt composite coatings produced in this way. Therefore, the goal was to i) develop new methods for preparation of composite coated anodes which can offer improved performance in base metal
electrowinning than the conventional PbCaSn, and ii) characterise their performance in terms of operating potential and stability.

2 EXPERIMENTAL METHODS AND MATERIALS

The composite coatings were electrodeposited onto a resin-sheathed PbCaSn electrode with a diameter of 5.00 mm, using a standard three-electrode electrochemical set-up, in which Pt wire was used as an anode and mercury mercurous sulphate (MSE) electrode as a reference. The potentials are reported in the normal hydrogen electrode (NHE) scale. The ohmic drop between the reference and working electrode was not compensated. The material for the PbCaSn electrode that was served as a substrate for the coatings was supplied by Consolidated Alloys Pty and had the composition Pb-Ca(0.75%)-Sn(1.50%)-Al(0.005%). The substrate was subjected to a cleaning pre-treatment ahead of the electrodeposition in order to obtain an adherent coating.

2.1 Pre-treatment of the PbCaSn substrate

The PbCaSn substrate was pre-treated by degreasing and etching. The pre-treatment steps involved i) cleaning the surface with SiC sand paper, 600 and 1200 grits; ii) cathodic degreasing at a current density of 500 A m\(^{-2}\) for 5 minutes in a solution containing 40 g dm\(^{-3}\) Na\(_3\)PO\(_4\). 12 H\(_2\)O at 40°C; iii) anodic etching at a current density of 500 A m\(^{-2}\) for 2 h in boiling 10% oxalic acid; and iv) rinsing with distilled water before proceeding to the electrodeposition step. The etching and coating of the electrodes were conducted under constant current density.

2.2 Deposition of Pb-Co and Pb-Co\(_3\)O\(_4\) composite coatings

Two different types of composite coatings were produced and tested, one type involving lead and cobalt ions reduced on a cathode to form Pb-Co composite coating, and another type involving lead ions reduced on a cathode with Co\(_3\)O\(_4\) solid particles (suspended in the bath) incorporated to form Pb-Co\(_3\)O\(_4\) composite coating. The cathodic electrodeposition processes can be described by reactions 1, 2 (for the type one coating) and 3 (for the type two coating). Upon subsequent application as anodes, the surface of the coatings was converted to metal oxide but, for simplicity, in this paper the two types of composite coated anodes will consistently be referred to as Pb-Co and Pb-Co\(_3\)O\(_4\). More than one coated anode of each type was prepared and tested to develop the methods.

\[ \text{Pb}^{2+} + 2\epsilon^- = \text{Pb} \]  
(Reaction 1)
\[
\begin{align*}
\text{Co}^{2+} + 2e^- &= \text{Co} & \text{(Reaction 2)} \\
\text{Pb}^{2+} + \text{Co}_3\text{O}_4 + 2e^- &= \text{Pb-Co}_3\text{O}_4 & \text{(Reaction 3)}
\end{align*}
\]

The **Pb-Co composite coatings** were electrodeposited cathodically from a nitrate electrolyte containing 100 g dm\(^{-3}\) \(\text{NH}_2\text{SO}_3\text{NH}_4\), 0.3 M \(\text{Pb(NO}_3)_2\) and 0.7 M \(\text{Co(NO}_3)_2\). The pH of the solution was adjusted to 2.8 at the start and no buffer solution was used to maintain the solution pH. Using the equipment described above, three different Pb-Co composite coated anodes were prepared, under the conditions detailed in Table 1. The first Pb-Co coatings was deposited at a current density of 200 A m\(^{-2}\) and fixed temperature of 25°C over a period of two hours. It was found that the surface roughness due to dendritic growth is dependent on current density, and a second Pb-Co coating was produced with a lower current density of 100 A m\(^{-2}\). The Pb-Co composite coated anodes prepared at 200 and 100 A m\(^{-2}\) without a levelling additive showed reasonable cobalt content (3 and 1 at. % respectively) but also a highly dendritic surface structure. To minimise the formation of dendrites further, a third Pb-Co based coating was produced. In this test 50 mg dm\(^{-3}\) thiourea was added, resulting in a smoother Pb-Co (0.5%) coating. It was observed that the addition of an additive such as thiourea can significantly affect surface roughness due to dendritic growth.

**Table 1. Conditions for the preparation of composite coated anodes**

The **Pb-Co\(_3\)O\(_4\)** composite coatings were electrodeposited using a sulphamate bath containing 60 g dm\(^{-3}\) Co (as \(\text{Co}_3\text{O}_4\)), 150 g dm\(^{-3}\) lead sulphamate, 100 g dm\(^{-3}\) \(\text{NH}_2\text{SO}_3\text{NH}_4\), 1 g dm\(^{-3}\) \(\text{O-toluidine}\) and 0.2 g dm\(^{-3}\) glue. Considering that \(\text{Co}_3\text{O}_4\) is more stable in mildly acidic solutions (Musiani and Guerriero, 1998), the pH of this deposition bath was adjusted to 5. In all of the Pb-Co\(_3\)O\(_4\) electrodeposition experiments, the temperature was also maintained at 25°C and current density was 200 A m\(^{-2}\). Two almost identical Pb-Co\(_3\)O\(_4\) composite coated anodes were produced as detailed in Table 1, containing much higher surface concentration cobalt (approximately 27.5 at. %).

Analytical Reagents (AR) grade chemicals and deionised water were used to prepare the electrolytes. The pre-treatment and deposition were carried out in a double-walled glass cell, connected to a water bath to maintain a constant temperature. A plastic lid was used to support the anode, cathode and reference electrode. The data was monitored and recorded on a computer running LabVIEW\textsuperscript{®} 7.1 software. The power supply in all experiments was an EG&G Princeton Applied Research
Potentiostat (model 173). The working electrode was positioned in a vertical plane in order to minimise the attachment of gas bubbles onto the surface.

2.3 Physical characterisation

In each case, immediately after the electrodeposition, the coated electrode (anode) was removed from the cell, rinsed with deionised water and dried in air. The coated anode surface was then observed using a scanning electron microscope (SEM), Philips XL20, which was equipped with an energy dispersive X-ray spectroscopy (EDS) detector, Oxford Link ISIS 5175.

2.4 Electrochemical characterisation

Each composite coated electrode was tested for i) stability when used as anode under typical copper electrowinning conditions, ii) oxygen evolution potential, and iii) corrosion rate. Tafel plot and cyclic voltametric measurements were also performed to examine the electrochemical characteristics of the coated anodes. The anode potential, exhibited under typical copper electrowinning conditions, was one of the key performance indicators for the new composite coated anodes. Two sets of operating performance tests were conducted. Short-term tests for a period of 16 h were used to evaluate the adequacy of the developed coated anode for further work, followed by longer tests maintained for a period of 168 h. The operating performance of the composite coated anodes was tested in an electrolyte containing 180 g dm\(^{-3}\) H\(_2\)SO\(_4\) under a constant current density of 300 A m\(^{-2}\), in the presence and in the absence of additives. The temperature of the cell was maintained at 40°C ±2°C by circulating water from a thermostated water bath. The electrolyte was agitated using a magnetic stirrer. During the test period, samples of the electrolyte were taken to determine the amount of cobalt released from the coating. The samples were analysed with an Atomic Absorption Spectrophotometer (AAS), GBC 933 PLUS.

Cyclic voltammetry was used to determine the overpotential for the oxygen evolution reaction on the composite coated anodes. Once the polarisation period in the coating bath was completed, the fresh coated anodes were immediately removed from the bath, rinsed with deionised (DI) water, dried with a stream of air and immersed into the 180 g dm\(^{-3}\) H\(_2\)SO\(_4\) electrolyte. To minimise the chance of galvanic reactions affecting the performance of the fresh coatings, the cyclic voltammograms were commenced within 7 seconds of the coated anodes being replaced into the testing electrolyte. The potential of the working electrode (coated anode) was cycled from the open circuit potential observed on freshly prepared coated anode to a vertex at 2 V and reversed to -1 V, at a scan rate of 2
mV Sec\(^{-1}\). The overpotential for the oxygen evolution reaction is reported as the difference between the potential at which the oxygen evolution reaction becomes apparent and the calculated standard reduction potential for this reaction, which under the conditions involving 180 g dm\(^{-3}\) H\(_2\)SO\(_4\) and 40 °C is 1.236 V. The corrosion rate of the coated anodes was estimated using potentiodynamic sweep measurements recorded right after the 16 h operating performance tests, from the magnitude of the area under the peak for the reduction of PbO\(_2\) to PbSO\(_4\). The potential of each coated electrode was scanned from the operating potential at 300 A m\(^{-2}\) to -1 V and the corrosion rate calculated from the charge involved in the reduction of PbO\(_2\) to PbSO\(_4\) and the total polarisation time during the operating period.

3 RESULTS AND DISCUSSION
3.1 SEM measurements of surface morphology

SEM images of the composite coated anodes before and after 168 h anodisation in 180 g dm\(^{-3}\) H\(_2\)SO\(_4\) are shown in Figure 1. For comparison, images of the conventional PbCaSn anode are also shown. The images “a” and “b” show that the freshly deposited composite coatings have a relatively rough surface compared to the conventional PbCaSn anode “c” abraded with 600 and 1200 grit sand papers. Also, the surface of the Pb-Co\(_3\)O\(_4\) coated anode is slightly more compact and fine-grained than the Pb-Co(3%). In this context there seems to be consistency with earlier reports by other researchers (Musiani and Guerriero, 1998, Cattarin et al., 2001, Hrussanova et al., 2001) which observed that incorporation of cobalt species into the surface layer of lead based anodes increases the roughness of the anode. Naked eye observation showed that the Pb-Co\(_3\)O\(_4\) composite coating displays a spongy structure whereas the Pb-Co surface appears dendritic. The cobalt content in the coating was higher when using suspended Co\(_3\)O\(_4\) particles in the electrolyte ranging from 0.5 to 3 atomic percent (at. %) in the Pb-Co coating to 27-28 at. % in the Pb-Co\(_3\)O\(_4\) composite coatings. Specifications of the different composite coatings produced are summarised in Table 1.

Figure 1, also shows that the surface of the PbCaSn anode (image “f”) undergoes significant roughening during the period of electrolysis and becomes relatively similar to the surface of the used composite coated anodes Pb-Co (image “d”) and Pb-Co\(_3\)O\(_4\) (image “e”). Hence, the initial variation in actual surface area between the conventional (uncoated) anode and the composite coated anodes is no longer evident.
This suggests that roughness is probably a factor that would contribute to reduction of the anode potential on the composite coated anodes at the start of the anodisation, but this is not expected to play a significant role in the later stages of the polarisation tests. Therefore, in accordance with the description by Guerrini and Tsaratti (2006) on the factors that influence electrocatalysis, the other factors that can explain the apparent lower potential would likely be related to the catalytic activity of the composite coated anodes and the effect of the cobalt. To evaluate this possibility, the catalytic activity of the composite coated anodes was tested using Tafel slope measurements.

3.2 Tafel plot measurements of catalytic activity

Tafel plot measurements were conducted next to evaluate the likelihood of a catalytic effect playing a role in the evolution of the oxygen at lower overpotential. A lower Tafel slope can confirm whether the depolarisation of the composite coated anode is due to enhancement of the catalytic activity or geometric extension of the surface. The results of these measurements are illustrated in Figure 2. The measurements were recorded in the potential range relevant for the oxygen evolution reaction which varied from one anode to another.

*Figure 2. Tafel plots for oxygen evolution on composite coated anodes and PbCaSn anode*

Tafel slopes related to Pb-Co and Pb-Co$_3$O$_4$ coated anodes were 92 and 90 mV dec$^{-1}$ respectively, which is significantly less than the 122 mV dec$^{-1}$ that was recorded for the PbCaSn anode. Values for Tafel slope for oxygen evolution on the Pb-Co$_3$O$_4$ composite coated anode prepared in a sulphamate solution at 100 A m$^{-2}$ reported by Musiani and Guerriero (1998) ranged between 80-85 mV dec$^{-1}$. The decreased Tafel slopes observed on the composite coated anodes confirm that the depolarisation of these anodes is due to increased catalytic activity for oxygen evolution. These results also show that the overpotential for oxygen evolution is lower on the composite coated anodes. Table 2 summarises the observed oxygen overpotential values and Tafel slopes.

*Table 2. Kinetics parameters of composite coated anodes*
3.3 Cyclic Voltammetry measurements of chemical reactions

The cyclic voltammograms in Figure 3 show the polarisation response of the freshly prepared Pb-Co(3%) and Pb-Co$_3$O$_4$ composite coated anodes, and conventional PbCaSn, in 180g dm$^{-3}$ H$_2$SO$_4$.

*Figure 3. Cyclic voltammograms on Pb-Co and Pb-Co$_3$O$_4$ coated anodes and the PbCaSn anode*

It is apparent from these results that with the increase in potential from the open circuit potential (OCP), the PbCaSn surface converts initially to lead sulphate (peak A) followed by oxidation to lead dioxide. Following the formation of the conductive lead dioxide, oxygen gas was observed to evolve simultaneously which is indicated by the rapid increase in the current density (peak B). Upon reversing the potential, the reduction of PbO$_2$ to PbSO$_4$ (peak C) takes place at approximately 1.55V, followed by reduction of PbSO$_4$ to Pb (peak D) at more negative potentials.

In the case of the composite coated anodes, peak A was absent. This might be related to passivation of the surface by lead sulphate formed in a chemical process coupling lead oxidation and cobalt catalysed hydrogen reduction, hence, the electrochemical formation of lead sulphate is no longer apparent (Musiani et al., 1999). After this, the coated anodes remain passive until oxygen evolution starts (peak B). Peak B, shown more clearly in Figure 4, can be used to compare the potential at which oxygen evolution begins on the different anodes.

*Figure 4. Oxygen evolution potential of composite coated anodes and PbCaSn anode*

It is evident that oxygen is evolved at less positive potential on both of the composite coated anodes. These results are in agreement with previous observations reported by Musiani and Guerriero (1998) which show higher overpotential for the evolution of oxygen on pure PbO$_2$ compared with the cobalt doped composite anodes. In the reverse sweep, the reduction peak is observed at around 1.55V. In comparing the magnitude of this peak it is apparent that the current associated with this process was significantly greater for the Pb-Co composite coated anode. As mentioned above, the cyclic voltammetry technique allows the approximate amount of lead dioxide formed on the surface of the anode to be quantified from the reduction charge. Peak C is shown more clearly in Figure 5.
The height of peak C observed with the PbCaSn anode is almost twice as high as for the Pb-Co\(_3\)O\(_4\) coated anode but much lower than for the Pb-Co coated anode. This suggests that the formation of PbO\(_2\) has reduced in the presence of Co\(_3\)O\(_4\) particles compared to the conventional PbCaSn anode but it has increased for the Pb-Co composite coated anode which had a much greater amount of lead dioxide formed during the anodic scan. Considering that all of the anodes were polarised to the same final potential of 2 V the Pb-Co composite coated anode had reached much higher current density compared with the PbCaSn and Pb-Co\(_3\)O\(_4\) anode. Therefore, the greater corrosion of the Pb-Co composite coated anode can be related to the fact that in the anodic sweep this anode passed a higher current which would have contributed to the increased oxidation of the surface. This would not be expected to occur however, under a controlled current density operation.

### 3.4 Service life studies

Figure 6 shows the operating potential of the Pb-Co(3%) composite coated anode used as anode under typical copper electrowinning conditions involving 180 g dm\(^{-3}\) H\(_2\)SO\(_4\) at 40°C and current density of 300 A m\(^{-2}\) on the anode, over a period of 16 h. The results are compared with the anode potential measured on a conventional PbCaSn anode in the presence and in the absence of cobalt ions in the electrolyte. The results show significantly lower (~300 mV) anode potential on the Pb-Co(3%) composite coated anode.

This could in part be attributed to the large “real” surface area due to the rough surface. The geometric surface area of the produced Pb-Co (3%) composite coated anode was 19.63 mm\(^2\); however, the real surface area was significantly higher due to the dendritic structure. The results from the longer (168 h) test showed that the Pb-Co (3%) composite coated anode loses some of its roughness during the operation and cobalt ions enter the electrolyte. It is probable that some of the dendrites break off and decompose in the absence of the anodic protection. During longer-lasting tests, the amount of cobalt gradually builds up which confirms that the surface coating is slowly decomposing. A similar phenomenon has been observed by Rashkov and his co-workers (1999). These authors prepared Pb-Co (0.5-6%) composite coated anodes by using a pulse plating technique and measured the amount of cobalt entering the electrolyte over time during anodic polarisation.
increasing amount of cobalt in the electrolyte was related to the formation of an oxide layer during anodisation, whereby the conversion of the intermediate lead sulphate product to lead dioxide causes parts of the surface layer to separate from the coated anode and enter the solution.

The concentration of cobalt in the electrolyte was observed to increase rapidly at first and continued to do so gradually during the first 100 hours of polarisation of the Pb-Co (3%) composite coated anode but it reached a point thereafter where the change in concentration with time was relatively small. The result showed that the maximum concentration of cobalt in the electrolyte was reached at 168 hours of polarisation and measured approximately 2 mg dm$^{-3}$. To evaluate the effect of the released cobalt on the behaviour of the conventional PbCaSn anode, the test was repeated in an electrolyte containing 2 mg dm$^{-3}$ of cobalt and the result is shown in Figure 6. It is apparent that even with the 2 mg dm$^{-3}$ cobalt present in the electrolyte, the conventional anode operates at a significantly higher potential (~200 mV) than the Pb-Co(3%) anode. This supports the idea that even though cobalt when present in the solution has a catalytic effect on the oxygen evolution reaction, placing cobalt directly into the surface coating of the anode has a much greater beneficial effect.

Nevertheless, the presence of cobalt changes the lead oxide surface giving it a rougher structure, which obviously results in larger real surface area and therefore lower actual current density. In an effort to investigate this aspect further, a Pb-Co (1%) composite coated anode was prepared using a lower current density of 100 A m$^{-2}$ which reduced the extent of dendrite formation. This coated anode when tested in the sulphate electrolyte showed approximately 150 mV reduction of anodic potential versus the conventional PbCaSn; however, the surface structure still appeared somewhat dendritic. Another attempt to produce a Pb-Co coating with smooth surface involved the addition to the electrodeposition bath of thiourea (TU) at concentration of 50 mg dm$^{-3}$. According to the theory of diffusion-controlled processes for electrodeposition (Kanani, 2004), the TU which is often used as a levelling aid in the electroplating industry could be expected to adsorb preferentially onto the raised areas of the electrode surface, thereby locally increasing the resistance to current flow and hindering the cathodic deposition process, which can be expected to reduce the extent of dendrite formation on the surface and edges of the electrode. The composite coating produced in the deposition bath containing TU confirmed this expectation. Although only 0.5% of cobalt was present in the composite coating of this anode, the coated anode operated at a potential of 1.95 V which is approximately 100 mV lower that the conventional PbCaSn anode. Figure 7 compares the anodic potential of all the Pb-Co composite coated anodes produced and the conventional (uncoated)
PbCaSn anode. It is apparent from this figure that the depolarisation of an anode is strongly related to the concentration of cobalt in the surface coating.

Figure 7. Potential-time curves obtained on Pb-Co composite coated anodes

On the other hand, when the composite coating was prepared by introducing lead along with cobalt oxide, the composite coating contained up to 28% cobalt. As shown in Figure 8, during anodic polarisation of this Pb-Co$_3$O$_4$ composite coated anode, the potential stabilised at 1.96 V, which is a depolarisation of approximately 100 mV. The concentration of cobalt ions in the electrolyte increased to 2 mg dm$^{-3}$ in the first 20 minutes and then gradually reached 5 mg dm$^{-3}$ by the end of the 168 h test (see Figure 10). This suggests that a portion of the cobalt oxide was released from the surface, which may explain the gradual raise of the potential. EDS data of the coated anode surface after the electrolysis confirmed the loss of cobalt from the surface on qualitative basis. The fact that during the anodic polarisation of the Pb-Co$_3$O$_4$ composite coated anode more cobalt was released to the electrolyte can be attributed to the spongy structure of this coating and relatively larger amount of cobalt incorporated into the coating of this composite coated anode.

Figure 8. Potential-time curves on Pb-Co$_3$O$_4$ coated anode in the presence and absence of TU

3.5 Corrosion rate and influence of the organic additives

Organic additives are often used in copper and zinc electrowinning for different reasons, including to lessen the extent of cathode re-dissolution and to form smooth deposits. Ivanov (2004) and Ivanov and Stefanov (2002) tested the effect of hydroxyethylated- butyne-2-diol-1,4 and a mixture of ethoxy acetic alcohol and triethyl- benzyl- ammonium chloride organic additives on the quality of a zinc deposit. It was reported that up to 2% increase in current efficiency could be achieved in the presence of organic additives in comparison with the current efficiency obtained in the absence of inhibitors. TU has also been used in copper electrowinning as a levelling agent to inhibit the crystallisation and dendrite growth on the surface of the cathode (Muresan et al., 2000), and in the current work as a levelling agent for the preparation of the electrodeposited composite coatings. In addition, the effect of TU was also tested as an additive in the stage where the Pb-Co$_3$O$_4$ composite coated anode was used under typical copper electrowinning conditions to see if it could improve the performance of this anode.
Figure 8 also shows the effect of 10 mg dm$^{-3}$ TU on the performance of the Pb-Co$_3$O$_4$ coated anode. It became apparent that the coated anode operated at a potential lower than observed in the absence of this additive. The TU addition also appears to have delayed the decomposition of the composite coating by several hours. The overpotential for the oxygen evolution reaction was 704 mV after 16 h of operation in an electrolyte containing 10 mg dm$^{-3}$ TU, which is roughly 30 mV less than in the absence of TU; although, after 168 h, the difference was no longer apparent and the overpotential became 644 mV in both electrolytes.

In addition, the effect of TU on the stability of the composite coating was also apparent from the lead dioxide reduction peaks recorded as part of the cyclic voltammograms. Tests were conducted using a fresh Pb-Co$_3$O$_4$ coated anode and one operated for 16 hours in the 180 g dm$^{-3}$ H$_2$SO$_4$ at 300 A m$^{-2}$, in the presence and in absence of 10 mg dm$^{-3}$ TU. The results given in Figure 9 show that in the presence of TU, the cathodic peaks related to the reduction of lead dioxide to lead sulphate are lower, both on the fresh composite coated anode and after 16 h of anodic polarisation.

![Figure 9. Reduction sweep of a Pb-Co$_3$O$_4$ coated anode a) fresh and b) after 16 h of anodic polarisation; dashed lines showing the effect of TU](image)

The release of cobalt from the Pb-Co$_3$O$_4$ coating into the electrolyte was also monitored during the 168 h tests. Information regarding the effect of TU on the stability of the coating can also be deducted from these tests. The results, given in Figure 10, show that the concentration of cobalt reaches a plateau at 60-70 h and remains relatively constant for the rest of the tests. However, the concentration of cobalt in the electrolyte containing TU (2.5 mg dm$^{-3}$) is approximately half the amount released in the electrolyte where TU was not added. This data is in agreement with the results in Figures 8 and 9, which showed that TU improves the performance and stability of the Pb-Co$_3$O$_4$ coated anode. This data might further suggest that the addition of TU slows the formation of lead dioxide on the surface of the composite coated anode, resulting in reduced rate of corrosion of the Pb-Co$_3$O$_4$ coated anodes operated in a sulphuric acid electrolyte.

![Figure 10. Cobalt release during anodic polarization of Pb-Co$_3$O$_4$ coated anode](image)
Figure 11 corresponds to the section of the cyclic voltammograms where the current associated with reduction of the corrosion product formed during 16 h anodic polarisation is observed. The data was generated using potentiodynamic polarisation of each coated anode scanned from the operating potential reached after a period of 16 h at 300 A m\(^{-2}\) to -1 V, at a scan rate of 2 mV Sec\(^{-1}\). For comparison, results generated in the same way using the conventional PbCaSn anode in the absence and presence of varied concentration of cobalt ions in the solution are also shown. The charge consumed to reduce the corrosion product (lead dioxide) formed during the polarisation period can be calculated and used to estimate the corrosion rate for each coated anode.

Figure 11. Cathodic peaks for the reduction of PbO\(_2\) in the presence and absence of cobalt and TU

Evidently, a decrease in the extent of the formation of PbO\(_2\) can be observed for all the lead-cobalt composite coated anodes and for the PbCaSn anode anodised in electrolytes containing cobalt ions. Addition of cobalt ions as small as 2 mg dm\(^{-3}\) reduced the rate of corrosion significantly. Adding more cobalt (150 mg dm\(^{-3}\)) further decreased the corrosion rate. The data for the composite coated anodes, Pb-Co(0.5%) and Pb-Co\(_3\)O\(_4\) (with and without TU present) show that the extent of lead dioxide formation on the surface of the PbCaSn anode is greater than on the composite anodes when cobalt is not added to the electrolyte, however, the addition of even 2 mg dm\(^{-3}\) Co compensates for this difference. Further addition of cobalt ions to the electrolyte granted the PbCaSn anode better stability than that displayed by the composite coated anodes.

The size of the peak related to the conversion of PbO\(_2\) to PbSO\(_4\) on the Pb-Co\(_3\)O\(_4\) coated anode was smaller than on the Pb-Co coated anode, suggesting greater stability, whilst further improvement in the stability of the Pb-Co\(_3\)O\(_4\) coated anode could be observed in the presence of 10 mg dm\(^{-3}\) TU. Another interesting feature in Figure 11 is a shift of approximately 0.5 V in the reduction peak for the composite anodes, which might be related to a greater reactivity of the lead dioxide formed on these composite coated anodes. The estimated corrosion rates of the tested coated anodes are summarised in Figure 12. The corrosion rate of the conventional PbCaSn anode, after a 16 h period of polarisation in 180 g dm\(^{-3}\) H\(_2\)SO\(_4\) in the absence of cobalt, was 7.03 g kA\(^{-1}\) h\(^{-1}\), reducing to 4.3 and 0.5 g kA\(^{-1}\) h\(^{-1}\) in solutions containing 2 and 150 mg dm\(^{-3}\) of cobalt respectively. The corrosion rates of Pb-Co and Pb-Co\(_3\)O\(_4\) coated anodes in 180 g dm\(^{-3}\) H\(_2\)SO\(_4\) were 4.7 and 3.5 g kA\(^{-1}\) h\(^{-1}\) respectively. Addition of 10 mg dm\(^{-3}\) thiourea to the electrolyte further decreased corrosion rates of Pb-Co\(_3\)O\(_4\) coated anode to 2 g kA\(^{-1}\) h\(^{-1}\).
This data confirm the earlier indications that the addition of TU slows the rate of corrosion of the Pb-Co\textsubscript{3}O\textsubscript{4} coated anodes. The effect of TU on the Pb-Co coated anodes was not tested and it is possible that it will have a similar effect. However, the concentration of TU was not optimised in these tests and the effect of variation in the TU concentration needs to be established. This is especially relevant considering some observations which suggest that although the addition of TU to a system can have the effect of reducing the corrosion rate, depending on the added amount it may also increase the rate of corrosion (Stankovic and Vukovic, 1996).

4 CONCLUSIONS

This study focused on the development of catalytic active composite coated anodes containing lead and cobalt. A review of developments in anode technology identified several promising options for further investigation. Methods were developed to produce, and evaluate the performance of, new type of anodes. The anodes were produced by cathodic electrodeposition of composite lead-cobalt coatings on the surface of conventional PbCaSn anodes followed by conversion to the oxide form.

The composite coated anodes were characterised by increased surface roughness, which contributed to decrease in the anode potential. Galvanostatic oxidation experiments at 300 A m\textsuperscript{-2} followed by negative potential sweeps of the anode surface have shown that the composite coated anodes generate oxygen at significantly lower overpotential than the conventional (uncoated) PbCaSn type anode and suffer less PbO\textsubscript{2} formation. Nevertheless, the Pb-Co and Pb-Co\textsubscript{3}O\textsubscript{4} coated anodes were characterised by Tafel slopes of 92 and 90 mV dec\textsuperscript{-1}, respectively, whereas the Tafel slopes for the PbCaSn anode was 122 mV dec\textsuperscript{-1}. The change in the Tafel slopes show that the oxygen evolution mechanism is changed and the depolarisation is mostly likely primarily due to a catalytic effect.

The possible benefits of incorporation of Co in lead alloys are well described, however, the challenge is to produce long lasting coatings. Result of the present study regarding Pb-Co and Pb-Co\textsubscript{3}O\textsubscript{4} coated anodes showed promising stability when anodised for 168 h in 180 g dm\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4} at 40°C. The degradation of the composite coated anodes was determined by measuring the formation of lead dioxide. The estimated corrosion rate after a 16 h of polarisation was 7.03 g kA\textsuperscript{-1} h\textsuperscript{-1} for conventional PbCaSn, dropping to 4.3 and 0.5 g kA\textsuperscript{-1} h\textsuperscript{-1}, respectively when 2 and 150 mg dm\textsuperscript{-3} cobalt was added.
Pb-Co and Pb-Co$_3$O$_4$ coated anodes anodised in 180 g dm$^{-3}$ H$_2$SO$_4$ showed 4.7 and 3.5 g kA$^{-1}$ h$^{-1}$, while addition of 10 mg dm$^{-3}$ TU to the electrolyte further decreased corrosion rates of Pb-Co$_3$O$_4$ to 2 g kA$^{-1}$ h$^{-1}$.

5 ACKNOWLEDGMENTS

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6 REFERENCES


Table 1. Conditions for the preparation of composite electrodes

<table>
<thead>
<tr>
<th>Composite coated anode</th>
<th>Co, at. %</th>
<th>C.D., A m$^{-2}$</th>
<th>Additive, mg dm$^{-3}$</th>
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<tr>
<td>Pb-Co</td>
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<tr>
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<td>100</td>
<td>No</td>
</tr>
<tr>
<td>Pb-Co</td>
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<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Pb-Co$_3$O$_4$</td>
<td>27 &amp; 28</td>
<td>200</td>
<td>No</td>
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Table 2. Kinetics parameters of composite electrodes

<table>
<thead>
<tr>
<th>Composite coated anode</th>
<th>Co at. %</th>
<th>$\eta$, mV after 16 h</th>
<th>$\eta$, mV after 168 h</th>
<th>Tafel slope, mV dec$^{-1}$</th>
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<tr>
<td>Pb-Co</td>
<td>3</td>
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<td>717</td>
<td>--</td>
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<td>Pb-Co</td>
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<td>635</td>
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<td>PbCaSn</td>
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<td>834</td>
<td>804</td>
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</tr>
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</table>
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10
Figure 11
Figure 12
Highlights

- Alternative anodes for evolution of oxygen at significantly lower overpotential than conventional ones were produced by cathodic electrodeposition of composite lead-cobalt coatings.

- Tafel slopes of 92 and 90 mV dec\(^{-1}\) were observed with Pb-Co and Pb-Co\(_3\)O\(_4\), respectively, versus 122 mV dec\(^{-1}\) with a conventional PbCaSn electrode.

- The composite anodes show promising stability when anodised for 7 days in 180 g dm\(^{-3}\) H\(_2\)SO\(_4\) at 40°C.