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ALTERNATIVE LOW-COST COMPOSITE COATED ANODES FOR BASE METAL ELECTROWINNING

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Abstract
Metal matrix and metal oxide matrix composite coatings containing lead and cobalt were electrodeposited onto PbCaSn and Ti substrates in an effort to develop an improved yet low-cost anode for base metal electrowinning. The anodes were tested under typical copper electrowinning conditions to study their polarisation behaviour. Lead balance method was used to calculate the corrosion rates of composite coated anodes and compare this with the corrosion rate of a conventional uncoated PbCaSn anode. The results show that incorporation of cobalt into the surface of lead has the effect of reducing the anode potential and corrosion rate during 7-day tests. Some of the new anodes showed much better performance than PbCaSn in 168 hour tests.

Keywords: Electrowinning, Overpotential, Anode, Cobalt, Corrosion

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 type of lead based anodes, such as PbCaSn, operate with 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 [1]. 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 the conventional lead based anode has a long history in the hydrometallurgical research field [2,3,4,5,6,7,8,9,10,11,12,13,14]. Most of the developments rely on the addition to the surfaces of costly catalytic ingredients. This topic was expanded further in the present study, with particular attention given to low cost options, such as the addition of cobalt to the surface of an electrode.

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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. [15, 16]. 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 [17], followed by a separate review focusing on the direct addition of cobalt to the lead surface layer [18]. 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 PbO₂ 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.

PbO₂ is one of the most common surfaces for oxygen evolution in sulphuric acid solutions and it is well known for its chemical stability. Recent results show that compositing PbO₂ with cobalt oxides could lead to production of electrocatalytic anode material. In coated anodes containing a PbO₂ layer deposited on top of an inert substrate, titanium is the most widely used substrate [19] due to its corrosion resistance [20]. Generally, substrates are chosen for good mechanical and chemical stability and are frequently pre-treated either by polishing, chemical or electrochemical methods [21] to clean the surface before coating. In the case of lead-titanium anodes, titanium usually stabilizes the lead, preventing it from spalling and passivation [22]. Beer in the 1960s [23] proposed that titanium can be used as a substrate in industrial applications to produce dimensionally stable anodes (DSAs). Such anodes are usually used in the evolution of chlorine or oxygen [24]. Titanium’s resistance to corrosion is due to the formation of a very stable passive TiO₂ layer on the surface of the metal. However, the gradual thickening of this oxide layer can also lead to deactivation of the DSA anodes. The method by which the anode coating is applied and how the substrate is prepared, determine the subsequent stability and electrochemical properties of the coated anode. The most widely investigated Ti-based anode for oxygen evolution has an IrO₂ coating. The service life of this anode is reported to be around 20 times longer than another common type of anode which has a RuO₂ coating [25]. On the other hand, IrO₂ is more expensive than RuO₂ and its electrocatalytic activity is slightly lower [26]. As anodes with a PbO₂ coating possess high electrical conductivity, good electrochemical and chemical stability against corrosion and are relatively inexpensive, researchers have long considered using lead dioxide as a surface layer on a Ti substrate, with the lead dioxide sometimes doped with other metal oxides such as ZrO₂, TiO₂, Ta₂O₅, CoOₓ, Co₃O₄, RuO₂ and others [2,4,9,12,13,14,27,28].

This paper presents the results of a study which aimed to utilise the observed benefits of cobalt in the system without the need to continuously add cobalt ions to the electrolyte. The performance of the developed anodes was considered in terms of anode potential, stability in copper electrowinning condition and corrosion resistance.

2 EXPERIMENTAL METHODS AND MATERIALS

One way to utilise the benefits of cobalt on the anodic process is by introducing the cobalt directly into the surface of the anode. In the present study, this was examined through electrodeposition of composite coatings of lead and cobalt alloy, or lead and cobalt oxide, onto PbCaSn or Ti substrates. Metal matrix composite coatings were prepared using resin-sheathed PbCaSn substrate. The material for the PbCaSn electrode was supplied by Consolidated Alloys
Pty and had a composition of Pb-Ca (0.75%)-Sn (1.50%)-Al (0.005%). Metal oxide matrix composite coatings were acquired using Ti substrates which were covered by heat shrink tubes around the edges. The substrate material for the coated titanium anodes was Ti Grade 2 supplied by Titanium International. In every experiment, a fresh produced composite anode with a diameter of 5.00 mm has been used. All experiments were carried out using a standard three-electrode electrochemical system, with Pt wire used as counter electrode (cathode) and a mercury mercurous sulphate (MSE) reference electrode. All of the potentials in this paper are reported in the normal hydrogen electrode (NHE) scale. The ohmic drop between the reference and working electrode (tested anode) was not compensated. Substrate electrodes were subjected to a surface pre-treatment ahead of the electrodeposition in order to obtain an adherent coating. In each experiment, a glass cell with a plastic lid was used to hold the anode, the cathode and the reference electrode. The temperature was kept constant during the experiments by using a thermostated water bath. The generated data was recorded on a computer using LabVIEW® 7.1 software. Potentiostat EG&G Princeton Applied Research, model 173, was used in all experiments. The tested anode was positioned in a vertical plane in order to minimise the attachment of gas bubbles onto the surface. In each case, immediately after the electrodeposition, the composite anode was removed from the cell, rinsed with deionised water and dried in air. Operating performance tests were then carried out to investigate the oxygen evolution potential and service life of the composite coated anodes. Corrosion rates of composite anodes were also estimated via lead balance method and compared with that of conventional PbCaSn anode.

2.1. Pre-treatment of the Substrates

Pre-treatment of PbCaSn substrate 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 hours in boiling 10% oxalic acid; and iv) rinsing with distilled water before proceeding to the electrodeposition step. Pre conditioning of Ti substrate was consisted of wet polishing the substrate with 600 and 1200 SiC papers followed by 10 minutes of cleaning in an ultrasonic bath containing DI water. Subsequently, the Ti electrodes were etched in boiling 10% oxalic acid for 2 h.

2.2. Preparation of Composite Coated Anodes

Four different composite coated anodes were prepared and tested. A Pb-Co composite coating was electrodeposited onto PbCaSn substrate from a nitrate bath containing 100 g dm\(^{-3}\) NH\(_2\)SO\(_3\)NH\(_4\), 0.3 M Pb (NO\(_3\))\(_2\), 0.7 M Co (NO\(_3\))\(_2\) and 50 mg dm\(^{-3}\) thiourea. The initial pH of the coating bath was 2.8 and no buffer solution was used to maintain this pH. Pb-Co coating was deposited cathodically at a current density of 100 A m\(^{-2}\) over a period of two hours at 25 °C, using the equipment described above. Cathodic electrodeposition of the PbCaSn based Pb-Co\(_3\)O\(_4\) composite coating was conducted using a sulphamate bath containing 60 g dm\(^{-3}\) Co (as Co\(_3\)O\(_4\) solid particles<10 µ supplied by Sigma Aldrich), 150 g dm\(^{-3}\) lead sulphamate, 100 g dm\(^{-3}\) NH\(_2\)SO\(_3\)NH\(_4\), 1 g dm\(^{-3}\) O-toluidine and 0.2 g dm\(^{-3}\) glue. The pH of this deposition bath was adjusted to 5. In all of the Pb-Co\(_3\)O\(_4\) electrodeposition experiments the temperature was 25 °C and current density was 200 A m\(^{-2}\).

Ti based PbO\(_2\)-Co\(_3\), composite coated anode was produced by 2 h anodic deposition from a 0.5 M lead sulphamate + 0.5 M cobalt nitrate bath at pH 1.6. The coating was applied potentiostatically at 1.75 V at 25 °C.
Ti based PbO₂-Co₃O₄ composite coated anode on was produced using an electrolyte containing 0.13 M lead acetate and 0.9 M lead nitrate with 5% w/v Co₃O₄ solid particles. The bath pH was 4.4. The electrodeposition temperature was 25 °C and the anodic electrodeposition was carried out potentiostatically at 1.75 V for 2 h.

A SnO₂-Sb₂O₃ interlayer was deposited onto the Ti prior to the electrodeposition in each test using Ti substrate. To apply the SnO₂-Sb₂O₃ interlayer, the pre-treated Ti substrate was dipped into a precursor solution for 5 minutes then oven dried at 110 °C for 15 min. The precursor solution was prepared by dissolving 20 g SnCl₄ . 5 H₂O, 2 g SbCl₃ and 13.2 mL HCl into 100 mL isopropanol. This procedure was repeated 3 times. Then, the electrode was annealed in a muffle furnace at 500 °C for 1 h. Fresh precursor solution was used for each treatment.

2.3. Potential of Anode and Service Life Studies

The performance of the composite anodes was evaluated in two sets of operating performance tests. Short term tests were run for a period of 16 h and they indicated the suitability of the developed anodes for further testwork. This was followed by longer term tests which were maintained for a period of 168 h.

The operating performance of the composite anodes was tested in an electrolyte containing 180 g L⁻¹ H₂SO₄ under a constant current density of 300 A m⁻². The electrolysing cell was maintained at 40±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 into the electrolyte. The samples were analysed using Atomic Absorption Spectrophotometer (AAS) model GBC 933 PLUS.

2.4. Corrosion Rate Measurements

The corrosion study was carried out using plate anodes with dimensions as shown in Figure 1. The corrosion rates of composite electrodes were estimated using lead balance method. In this method the total amount of lead migrated from the surface of the composite electrodes into the solution, collected as cell mud and deposited on the surface of cathodes determine the corrosion rate of each composite electrode.

<table>
<thead>
<tr>
<th>Label</th>
<th>Size, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>130</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>70</td>
</tr>
<tr>
<td>D</td>
<td>60</td>
</tr>
<tr>
<td>E</td>
<td>60</td>
</tr>
</tbody>
</table>

*Figure 1 Schematic of anodes used for corrosion tests*

Anodic corrosion of each composite electrode anodised for 168 h in 180 g L⁻¹ H₂SO₄ was calculated using equation 1.

\[
\text{Corrosion rate (g m}^{-2}\text{h}^{-1}) = \frac{m.w + C.V}{S.t}
\]
Where m is lead concentration in slime and w is total anode slime mass, C is concentration of lead in the electrolyte, V is electrolyte volume, S is apparent working surface area and t is the elapsed electrolysis time [29]. The information pertinent to the tested anodes is given in Table 1.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Thickness, mm</th>
<th>Dimensions, mm²</th>
<th>Submerged area, mm²</th>
<th>Current, A</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCaSn</td>
<td>2</td>
<td>60×39</td>
<td>4950</td>
<td>2.29</td>
</tr>
<tr>
<td>PbCaSn-Pb-Co</td>
<td>2</td>
<td>60×63</td>
<td>7930</td>
<td>2.09</td>
</tr>
<tr>
<td>PbCaSn-Pb-Co₃O₄</td>
<td>2</td>
<td>60×45</td>
<td>5700</td>
<td>1.70</td>
</tr>
<tr>
<td>Ti-SnO₂-Sb₂O₃-PbO₂-CoO₅</td>
<td>1</td>
<td>60×45</td>
<td>5550</td>
<td>1.67</td>
</tr>
<tr>
<td>Ti-SnO₂-Sb₂O₃-PbO₂-Co₃O₄</td>
<td>1</td>
<td>60×45</td>
<td>5550</td>
<td>1.67</td>
</tr>
</tbody>
</table>

3 RESULT AND DISCUSSION

3.1 Potential of Anode and Service Life Studies

Freshly prepared composite coated anodes were subjected to galvanostatic polarisation tests in 180 g L⁻¹ H₂SO₄ solution at 300 A m⁻² and 40 °C. For comparison, conventional PbCaSn electrode was anodised in the same condition and results were compared in Figure 2. Figure 2-a shows that incorporation of cobalt into the surface coating of the composite anodes resulted in reduced anode potential relative to PbCaSn. Reduction of almost 200 mV was recorded for the PbCaSn-Pb-Co composite anode during 16 h anodisation. The PbCaSn-Pb-Co₃O₄ composite anode started with much lower potential, and although this difference faded away within the first 2 h of anodisation, the potential becomes stable at 1.96 V which was approximately 100 mV lower than PbCaSn. The increase in potential could be related to separation of parts of the coating from the surface. This would mean that portions of the surface occupied by cobalt oxide species were released to the electrolyte. Indeed, it was evident from the result of AAS analysis of samples taken from the electrolyte during the anodisation that the cobalt dissolution rate from the PbCaSn-Pb-Co₃O₄ composite coated anode during anodisation was 0.031 µg cm⁻³ h which is greater than that of PbCaSn-Pb-Co composite coating which was 0.012 µg cm⁻³ h.

Similarly, significant depolarisations were observed with the Ti based composite coated anodes. Figure 2-a shows much lower initial potential for Ti-SnO₂-Sb₂O₃-PbO₂-CoO₅ composite coated anode compared to PbCaSn. During the first few hours of operation, the oxygen evolution reaction was strongly depolarised on the surface of this anode, probably due to a higher surface area, but after 9 h of polarisation the potential increased and became approximately 50 mV higher than that of PbCaSn. This surface coating was not stable and flaked off during the testing, which appeared to be the main reason for the observed deterioration of performance. The loss of part or all of the coating places titanium in direct contact with the electrolyte, leading to passivation through formation of TiO₂, which was evidenced by the ascending anode potential. The best performing anode in this round of testing was the Ti-SnO₂-Sb₂O₃-PbO₂-Co₃O₄ composite coated anode. This anode operated a very low potential of approximately 1.7 V, indicative of depolarisation of approximately 400 mV versus PbCaSn and showed great stability.
Analyses of the electrolytes revealed that the loss of cobalt from two Ti based composite coated anodes took place at a rate of \(0.014 \, \mu g \, cm^{-3} \, h\) for the Ti-SnO\(_2\)-Sb\(_2\)O\(_3\)-PbO\(_2\)-CoO\(_x\) anode and \(0.037 \, \mu g \, cm^{-3} \, h\) for the Ti-SnO\(_2\)-Sb\(_2\)O\(_3\)-PbO\(_2\)-Co\(_3\)O\(_4\).

Figure 2 Potential-time transient of composite anodes and PbCaSn over a) short and b) long term electrolysis
Longer term tests (168 h) were carried out under the same condition. It can be seen from Figure 2-b, that the PbCaSn-Pb-Co, PbCaSn-Pb-Co\textsubscript{3}O\textsubscript{4} and Ti-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3}-PbO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4} composite anodes operated at a lower potential than that of PbCaSn and remained stable over the entire anodisation period. A longer term test was not performed with the Ti-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3}-PbO\textsubscript{2}-CoO\textsubscript{x} composite coated anode because of the gradual degradation observed in the short term test. Details on the kinetic parameters pertinent to these composite anodes can be found in authors recent papers [30, 31].

3.2. Corrosion Rate Measurements

After electrolysis in 180 g dm\textsuperscript{-3}H\textsubscript{2}SO\textsubscript{4} for 168 h, each cathode was examined for lead deposition. There was no evidence of lead deposition on the cathodes in any of the tests using composite anodes, whereas in the test using PbCaSn anode significant amount of lead was deposited on the cathodes. The cathodes were rinsed with deionised water and any scale carefully removed from the surface and weighted. In addition, all electrolytes and anode slimes were measured and analysed using AAS to determine the mass of lead present there. The results are given in Table 2.

### Table 2 Lead in electrolyte, slime and cathodes after electrolysis and calculated corrosion rates

<table>
<thead>
<tr>
<th>Anode</th>
<th>Pb in electrolyte, mg L\textsuperscript{-1}</th>
<th>Slime mass, g</th>
<th>Pb in slime, g kg\textsuperscript{-1}</th>
<th>Pb on cathodes, g</th>
<th>Corrosion rate, g m\textsuperscript{2} h\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCaSn-Pb-Co</td>
<td>2.2</td>
<td>7.6</td>
<td>450</td>
<td>--</td>
<td>2.6</td>
</tr>
<tr>
<td>PbCaSn-Pb-Co\textsubscript{3}O\textsubscript{4}</td>
<td>2.1</td>
<td>0.3</td>
<td>460</td>
<td>--</td>
<td>2.7</td>
</tr>
<tr>
<td>Ti-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3}-PbO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4}</td>
<td>0.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.004</td>
</tr>
<tr>
<td>Ti-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3}-PbO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4}</td>
<td>1.5</td>
<td>0.3</td>
<td>290</td>
<td>--</td>
<td>0.1</td>
</tr>
<tr>
<td>PbCaSn</td>
<td>0.6</td>
<td>--</td>
<td>--</td>
<td>5.6</td>
<td>6.7</td>
</tr>
</tbody>
</table>

The data in Table 2 shows that the rate of lead loss from the anodes and resultant incorporation of lead into cathodes can be expected to decrease with the use of the composite coated anodes. It is evident from Table 2 that, the corrosion rate of the PbCaSn anode of 6.7 g m\textsuperscript{2} h\textsuperscript{-1} was more than twice higher than the rates of corrosion of the PbCaSn-Pb-Co\textsubscript{3}O\textsubscript{4} or PbCaSn-Pb-Co composite coated anode. Moreover, the composite coated anodes produces onto a Ti substrate, showed the very low corrosion rates of 0.1 g m\textsuperscript{2} h\textsuperscript{-1} for Ti-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3}-PbO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4} and 0.004 g m\textsuperscript{2} h\textsuperscript{-1} for the Ti-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3}-PbO\textsubscript{2}-CoO\textsubscript{x} anode.

## 4 CONCLUSIONS

- Four alternative anodes consisting of composite coatings including (i) PbCaSn-Pb-Co, (ii) PbCaSn-Pb-Co\textsubscript{3}O\textsubscript{4}, (ii) Ti-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3}-PbO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4} and (iv) Ti-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3}-PbO\textsubscript{2}-CoO\textsubscript{x} were prepared and tested. The performance of the composite anodes was evaluated in terms of the stability, oxygen evolution potential and corrosion rate under typical copper electrowinning conditions and compared to conventional PbCaSn anode.
- The results have shown that incorporation of cobalt into the surface coating of the composite anodes results in reduced anode potential during operation. The depolarisation ranged from approximately 100 and 200 mV versus PbCaSn for the PbCaSn-Pb-Co and PbCaSn-Pb-Co\textsubscript{3}O\textsubscript{4} respectively, to roughly 400 mV for the Ti-SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3}-PbO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4} anode. The best performing alternative anode showed very good stability, operating at a very low potential of approximately 1.7 V over 168 hours.
Corrosion rate measurements have shown significantly lower corrosion rate for the metal oxide matrix composite anodes Ti-SnO$_2$-Sb$_2$O$_3$-PbO$_2$-CoO$_x$ (0.004 g m$^{-2}$ h$^{-1}$) and Ti-SnO$_2$-Sb$_2$O$_3$-PbO$_2$-Co$_3$O$_4$ (0.1 g m$^{-2}$ h$^{-1}$), than the corrosion rates observed for the metal matrix composite electrodes Pb-Co (2.6 g m$^{-2}$ h$^{-1}$) and Pb-Co$_3$O$_4$ (2.7 g m$^{-2}$ h$^{-1}$) over 168 hours. These results were in every case significantly lower than the corrosion rate recorded for the conventional PbCaSn anode (6.7 g m$^{-2}$ h$^{-1}$) under the same conditions.

The benefits of incorporating cobalt into the electrode base are now well defined.

5 ACKNOWLEDGMENT

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6 REFERENCES


