THE ROLE OF MANGANESE IN THE
ELECTROWINNING OF COPPER AND ZINC

THIS THESIS IS PRESENTED FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY OF MURDOCH UNIVERSITY, WESTERN AUSTRALIA

BY

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I declare that this thesis is my own account of my research and contains as its main content work that has not previously been submitted for a degree or examination at any tertiary education institution.

Venny Tjandrawan

October 2010
Manganese ions are often encountered as impurities in the electrolyte used in the electrowinning of copper and zinc. The effects of manganese ions in the electrolyte on the anodic behaviour of lead alloy anodes used in the electrowinning of copper and zinc have not previously been definitively established. Potentiostatic and galvanostatic oxidation of rotating disc electrodes of Pb-Ag and Pb-Ca-Sn anodes has been used to investigate the anodic behaviour of these anodes and the oxidation reactions of manganese ions in sulphuric acid solutions. The electrochemical measurements were complemented by chemical analyses of the oxidised manganese species formed during the oxidation process, which allow for the determination of the partial charge involved in oxidation of lead and manganese as well as for oxygen evolution.

The oxidation of manganese on these anodes was found to be dependent on the formation of lead dioxide at potentials above about 1.7 V and is also accompanied by oxidation of the lead and evolution of oxygen at potentials above about 2.0 V. It will be demonstrated that the amount of manganese oxidized increases with increasing oxidation potential, concentration of manganese ions, time of oxidation and the silver content of the alloy.

The presence of manganese in the electrolyte decreases the rate of formation of lead dioxide and reduces the fraction of the charge associated with oxygen evolution. It will also be shown that both cobalt and manganese ions have an effect on reducing the rate of
corrosion of the anodes and thereby the incorporation of lead on the cathodes. Higher
centrations of manganese ions and lower oxidation potentials favour the production of
manganese(III) species which can form a MnOOH intermediate layer, while permanganate
is produced under the opposite conditions. Manganese dioxide produced by chemical
precipitation reactions involving manganic and permanganate ions, was also formed in the
bulk electrolyte and on the walls of the cell.

Mechanisms for the oxidation of manganese ions on these lead alloy anodes are presented
together with recommendations for optimization of the additions of manganese to zinc
circuits and minimization of permanganate formation in copper tankhouse electrolytes.
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My deepest thanks are devoted to my loving and caring husband Matthew Supranata, my beloved family and my friends at Perth Indonesian Church who are always by my side, encourage me, accept my mistakes, and make me feel proud whenever I have tried my best.

Finally, I would like to thank everybody who was important to the successful realization of this thesis and would like to express my apology to those whom I could not mention personally.
DEDICATION

This thesis is lovingly dedicated to:

The glory of my Lord Jesus Christ

My forever hope, strength, love and source of inspiration.

For from him and through him and to him are all things.
To him be the glory forever! Amen.

Romans 11:36
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Chapter 1

INTRODUCTION

Over the past several decades, electrowinning has become the preferred method for the final recovery of metals such as copper, zinc, nickel, manganese and cobalt. Nearly 20% of the world production of copper and more than 85% of the world’s zinc are produced by means of an electrowinning process preceded by leaching and solution purification steps. The electrowinning stage is typically the most energy intensive part of this process and involves the highest component of the operating costs. The cost of electrical energy for electrowinning can constitute up to 80% of the total energy cost of recovering metals from concentrates (M.J. Nicol, personal communication, March 30, 2010). Furthermore, electrowinning is also the most crucial stage in the process in relation to the quality of the final product. Given the current economic circumstances and uncertainties about the future costs and availability of energy, it is important that further studies of the electrowinning process to be conducted with the goal of reducing energy consumption and maximizing capital intensity without compromising the product quality.

In electrowinning, the most significant contribution to the overall energy consumption is directly connected to the processes at the anodes, where the current oxidizes water and produces oxygen gas. This process requires significant overvoltage and the contribution of the anodic potential to the overall cell voltage is between 50 and 70% in zinc electrowinning and is also a significant fraction for copper. The electrical energy
consumed in the world-wide electrowinning of copper and zinc is currently in excess of 6000 GWh/annum (M.J. Nicol, personal communication, March 30, 2010). Even a small saving of 10% would not only save the cost of energy but also significantly reduce the carbon footprint of the industry.

In addition, the main consequence of the oxygen evolution reaction on the anode is corrosion of the lead-based anodes which are universally used in such operations. Initially, a non-conducting layer of lead sulfate is formed on the anode surface, followed by the formation of lead(II) hydrated oxides and finally a conducting lead dioxide layer that aids in oxygen evolution. As corrosion of the substrate continues, an internal stress develops and cracking of the protective inner layer may occur. The evolved oxygen causes flaking of the corrosion product from the anode. Dissolved lead ions and suspended lead dioxide and sulfate particles contaminate the electrodeposited copper and zinc. The increasingly tight specifications for lead in both copper and zinc cathodes have highlighted the importance of minimizing and controlling the corrosion of the anodes. The use of a diaphragm in the electrowinning of nickel and cobalt assists in minimizing this problem with these metals.

Despite the high operating potentials and susceptibility to corrosion, lead-based alloys still dominate the base metal electrowinning operations. As pure lead is mechanically weak, lead must be alloyed in order to improve its mechanical and corrosion properties. Common lead alloys include lead-calcium-tin (Pb-Ca-Sn anodes) which are used in the electrowinning of copper and nickel, and lead-silver (Pb-Ag anodes) used in the production of zinc. Significant research and development is required in order to improve the performance of these alloys in terms of reduced overpotentials and corrosion rates, both of
which are susceptible to the presence of certain other metal ions in the electrolytes. Thus, manganese is added to zinc electrolytes and cobalt to copper electrolytes. In particular, manganese may be present in the copper and zinc electrolytes as an impurity and manganese ions are often added to zinc electrolytes in order to reduce the operating potential and minimize corrosion of the anodes. However, there is also evidence that the presence of low concentrations of manganese ions may increase the corrosion of anodes in copper tankhouses. The mechanisms involved in these apparent conflicting effects are not well understood. Thus an understanding of the role of manganese in the anode reactions on lead alloy anodes could assist in the optimization of the electrowinning processes for both copper and zinc with possible application to the electrowinning of nickel.

In addition to the major reaction of oxygen evolution, manganese ions may also be oxidized at the lead alloy anodes, thus generating either soluble species such as Mn$^{3+}$ and MnO$_4^-$ ions or insoluble oxides such as MnO$_2$ and possibly MnOOH. The formation of layers of these oxides on the lead anode surface may assist in minimizing disintegration of the anode and also modify the kinetics of the oxygen evolution reaction. However, excessive amounts of MnO$_2$ scale have a tendency to break away from the anode causing increased corrosion of the underlying lead anode. Moreover, the anodes must be cleaned periodically to remove the deposit which may otherwise cause short-circuiting between the anode and the cathode and increasing the energy consumption. The concentration of manganese(II) ions in industrial zinc electrolytes is generally controlled between 1 and 10 g L$^{-1}$.

In processes which involve solvent extraction as in the copper heap leach process and in one zinc operation, the concentration of manganese in the electrolyte is typically
maintained at low levels between 1 and 250 mg L\(^{-1}\). The problem of manganese in the electrolyte in such circuits is mainly associated with a decrease in the kinetics of solvent extraction and capacity of the solvent due to oxidation of the reagents by the higher oxidation states of manganese generated at the anode.

The kinetics involved in the oxidation of manganese ions on lead alloy anodes have not been experimentally well characterized and therefore the mechanisms are not understood. The research in this project is aimed at improving the understanding of the role of manganese on the performance of Pb-Ag and Pb-Ca-Sn anodes used in the electrowinning of zinc and copper respectively. This also includes an investigation into the fundamental electrochemistry of the oxidation of manganese on these two selected lead alloys, and their behaviour with respect to the oxygen evolution reaction. This will hopefully assist in optimizing the additions of manganese to zinc circuits while reducing the impact of manganese ion incursions in the electrowinning of copper.
Chapter 2

LITERATURE REVIEW

2.1 Electrowinning of Copper

About 20% of the world’s primary copper is produced by hydrometallurgical processing, which generally involves heap leaching, solvent extraction and electrowinning as indicated in Figure 2.1. The copper minerals most commonly treated this way are so-called oxides such as carbonates, hydroxy-silicates, oxides and sulphates; and secondary copper sulphide minerals, such as chalcocite and covellite (Davenport et al. 2002).

The leaching process is accomplished with dilute sulphuric acid (1 to 10 g L\(^{-1}\)) to dissolve copper and other chemically amenable ore constituents such as iron and manganese. Oxide copper minerals are leached quickly without oxidation, but leaching of secondary sulphide minerals normally requires an oxidant such as bacterially generated ferric ions. The dissolved copper (1 to 6 g L\(^{-1}\)) from the leach solution is then extracted into an organic extractant, usually a mixture of an aldoxime and ketoxime dissolved in petroleum distillate, in a process called solvent extraction. Subsequently, the loaded copper is stripped from the organic extractant into a strong sulphuric acid solution (150 to 180 g L\(^{-1}\)) producing a relatively pure and concentrated copper electrolyte suitable for electrowinning.
Figure 2.1 Hydrometallurgical process for recovery of copper by heap leaching

- **Heap leaching**
  - Ore 'heap'
  - $\text{H}_2\text{SO}_4$ (10 g L$^{-1}$), Cu (1-6 g L$^{-1}$)
  - Make up $\text{H}_2\text{SO}_4$
  - $\text{H}_2\text{SO}_4$ leach solution, recycle from solvent extraction

- **Solvent extraction**
  - Advanced electrolyte
  - $\text{H}_2\text{SO}_4$ (180 g L$^{-1}$), Cu (40-50 g L$^{-1}$)

- **Electrowinning**
  - Cathode copper

- **Spent Electrolyte**
  - $\text{H}_2\text{SO}_4$ (10 g L$^{-1}$), Cu (0.3 g L$^{-1}$)

- **Raffinate**
In electrowinning, the copper rich solution (40 to 50 g L\(^{-1}\)) is filtered to remove entrained organics, heated, and then passed through a series of polymer concrete electrolytic cells, where the pure metallic copper is produced at the cathodes (reaction 2.1) and gaseous oxygen at the anodes (reaction 2.2).

\[
\begin{align*}
\text{Cu}^{2+} + 2e^- &\rightarrow \text{Cu}^0 & E^0 &= 0.34 \text{ V} \quad (2.1) \\
\text{H}_2\text{O} &\rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- & E^0 &= 1.23 \text{ V} \quad (2.2)
\end{align*}
\]

The cathodes are either copper starter sheets or stainless steel sheets. The stainless steel sheets are preferred because they deliver a product of higher purity, give fewer short circuits and require less maintenance (Addison et al. 1999). The most widely used anodes are rolled Pb-Ca-Sn alloys. The anodes and the cathodes are interleaved and separated by several polymer spacer knobs in the anodes in order to minimize short circuits between the anodes and cathodes.

The copper is stripped from the cathodes about every seven days, and the stainless steel mother blanks are returned to the electrolytic cell for further electrolysis. Electrowinning takes place at a cell voltage of approximately 2 V and a current density of 280–340 A m\(^{-2}\). The details of a typical operation for the electrowinning of copper are summarized in Table 2.1.

The cathodic current efficiency during the electrowinning of copper is generally about 90 to 95%. The decrease in the current efficiency is mainly caused by the oxidation and reduction of iron in solution and to a lesser extent the reduction of dissolved oxygen and the anode/cathode short circuits. Although the presence of iron is detrimental in relation to cathode current efficiency, about 1.0 to 2.0 g L\(^{-1}\) of iron in the electrolyte has been claimed.
to have beneficial effects in lowering the solution potential and smoothing the cathode surface.

Table 2.1 Typical operating parameters for electrowinning of copper

<table>
<thead>
<tr>
<th>Annual copper production, tonnes</th>
<th>151000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathodes</td>
<td>Stainless steel sheets</td>
</tr>
<tr>
<td>Copper cathode impurities, mg L(^{-1})</td>
<td>Pb (&lt;3), S (&lt;8), Fe (&lt;0.8), Mn (&lt;0.5), Co (&lt;0.8), Ni (&lt;0.8), Zn (&lt;1), Sn (&lt;0.2)</td>
</tr>
<tr>
<td>Anodes</td>
<td>Rolled Pb-0.08%Ca-1.5%Sn-0.02%Al plates</td>
</tr>
<tr>
<td>Anodes life, years</td>
<td>5</td>
</tr>
<tr>
<td>Anodes/cathodes per cell</td>
<td>61/60</td>
</tr>
<tr>
<td>Total anodes</td>
<td>29280</td>
</tr>
<tr>
<td>Current Density, A m(^{-2})</td>
<td>290</td>
</tr>
<tr>
<td>Anode-cathode voltage, V</td>
<td>1.9-2.0</td>
</tr>
<tr>
<td>Cathode current Efficiency, %</td>
<td>92</td>
</tr>
<tr>
<td>Energy Consumption, MWh t(^{-1}) cathode</td>
<td>1.8-1.9</td>
</tr>
<tr>
<td>Cu, g L(^{-1})</td>
<td>40-50</td>
</tr>
<tr>
<td>H(_2)SO(_4), g L(^{-1})</td>
<td>180</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>40-50</td>
</tr>
<tr>
<td>Fe(^{2+}), g L(^{-1})</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe(^{3+}), g L(^{-1})</td>
<td>1.2</td>
</tr>
<tr>
<td>Mn(^{2+}), mg L(^{-1})</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Co(^{2+}), mg L(^{-1})</td>
<td>150</td>
</tr>
<tr>
<td>Cl(^{-}), mg L(^{-1})</td>
<td>18</td>
</tr>
<tr>
<td>Guar gum, g t(^{-1})</td>
<td>200</td>
</tr>
</tbody>
</table>
Aside from iron, the most undesirable metallic impurity in the continuous process of solvent extraction and electrowinning of copper is manganese. Manganese(II) itself has minimal effects on the process of solvent extraction. In the electrowinning stage, the Mn$^{2+}$ ions may be oxidised to Mn$^{3+}$, MnO$_4^-$, MnOOH and MnO$_2$ both on the anode and in the electrolyte. Problems can arise when these high valence manganese ions are returned to the solvent extraction circuit in which a decrease in the kinetics and loading capacity of the organic extractant as a result of oxidation can often be observed (Miller, Readett & Hutchinson 1997). Therefore, the prevention or minimisation of the oxidation of manganese ions at the anode during the electrowinning stage is critical.

Cobalt sulphate is normally added to provide about 150 mg L$^{-1}$ Co$^{2+}$ in the electrolyte to reduce both the corrosion rate and oxygen overpotential of the Pb-Ca-Sn anodes. The addition of cobalt ions also reduces the rate of electrolytic production of manganese dioxide (Ravindran, Heerman & Van Simaeys 1975) which in turn can minimize the contamination of the cathodes with lead and extend the life of the anodes.

Chloride ions are either naturally present in the electrolyte or added as hydrochloric acid to promote dense, fine grain, low impurity copper deposits on the cathode, but the concentration should be maintained below about 30 mg L$^{-1}$ (Davenport et al. 2002). At higher concentrations, chlorine gas will be evolved at the anodes and pitting of the stainless steel cathodes is observed. Small quantities of an organic additive such as guar gum are also added as smoothing agents to form a dense copper deposit without nodular growth.
2.1.1 Lead Anode Materials Used in the Electrowinning of Copper

The classical anode used in copper electrowinning is lead alloyed with 6-10% antimony (Pb-Sb anode) (Ettel 1972; Gendron, Ettel & Abe 1975). Antimony in lead alloys offers advantages of improved mechanical properties, uniform grain structures, and ease in conventional casting (Hrussanova, Mirkova & Dobrev 2002). However, the inadequate electrochemical and corrosion properties are a disadvantage of Pb-Sb anodes. Reduction in the antimony content of the alloys decreases the mechanical properties markedly. On the other hand, increasing the concentration of antimony increases the corrosion rate (Prengaman 1997). The overvoltage for oxygen evolution is similar to that of pure lead anodes (Chen, Guo & Klaus 1997).

New alloys of lead with calcium and/or strontium were developed to replace the conventional Pb-Sb anodes (Hood et al. 1975; Prengaman 1984). The addition of calcium or strontium to the lead improves the hardness. However, the quantities in the alloys must be carefully controlled to produce a fine-grained structure with minimal alloy segregation (Hrussanova, Mirkova & Dobrev 2002).

The Pb-Ca-Sn anodes are the most widely used anodes in the electrowinning of copper. Tin is normally added to improve both the conductivity of the anodic film and the mechanical properties. Addition of calcium with tin produces an anode with a high mechanical strength to prevent distortion, warping and short circuits during electrolysis (Prengaman & Siegmund 2007). Tin also reacts with calcium to form fine uniform Sn$_3$Ca particles within the grain structure, preventing corrosion from penetrating into the anode and improving the stability of the anode (Prengaman & Siegmund, 1999). The optimum
calcium content is between 0.05 and 0.08%, while the concentration of tin in the alloy should be between 1.0 to 2.2% (Prengaman & Siegmund 2007).

A recent variation of the Pb-Ca-Sn alloys by Prengaman and Siegmund (2007) involves the addition of cobalt (0.005-0.040%), aluminium (0.001-0.008%) and silver (0.002 to 0.080%). The alloying of cobalt to the anode reduces the need for adding cobalt to the electrowinning circuit. Aluminium is added as an anti-drossing agent to prevent the oxidation of calcium. The addition of silver to the alloys reduces anode corrosion, maintains the mechanical properties and reduces creep and structural changes in the alloy at elevated temperatures (Prengaman & Siegmund 2007). Silver also enhances the oxygen evolution rates and decreases the overvoltage of the oxygen evolution reaction (Zhong et al. 1999).

The techniques used in the manufacture of anodes for electrowinning have changed over the years in order to provide a more corrosion resistant and hence longer lasting anode. Rolled anodes are preferable to cast anodes due to their superior performance since the rolling process has been shown to produce a more uniform cross section and grain structure and also less porosity and lower corrosion rates (Prengaman 1984). The production of cast anodes results in an oriented, dendritic grain structure and the formation of numerous holes or voids in the anode surface that can initiate internal corrosion in localized areas. Therefore, the anode sheets are generally rolled to the desired thickness from a cast billet to break up the original cast grain structure to produce a smoother surface with less corrosion and easier removal of the PbO₂-MnO₂ scale (Prengaman & Siegmund, 1999). The rolling process is normally performed at elevated temperatures to produce a fine uniform grain structure both at the surface and throughout the rolled sheet. It has been
shown that the corrosion behavior improved with increasing rolling temperature (Stelter, Bombach & Saltykov 2006).

2.2 Electrowinning of Zinc

The production of zinc from zinc sulphide concentrates is predominantly conducted through the roast-leach-electrowinning process (Figure 2.2), which was first used in 1916 by Anaconda and Cominco. A concentrate of the zinc sulphide ore, in which sphalerite (ZnS) is the predominant component, is first roasted in a fluidized bed furnace (900-1000 °C) forming zinc oxide. The zinc oxide is then fed into the leaching tanks together with sulfuric acid solution in the spent electrolyte from electrowinning. During leaching, careful manipulation of temperature and pH encourages the precipitation of ferric hydroxide which acts as a metal ion collector and partially removes arsenic, antimony and germanium (Bond 1999).

A subsequent purification step is carried out by zinc dust precipitation in two or three stages, in which the leached solution is mixed with a fine dust of metallic zinc which caused the reductive precipitation of the metal ions electropositive to zinc, while the zinc metal is oxidized. The purified zinc solution is then circulated through the electrowinning plant, where zinc deposits on aluminium cathodes, oxygen is produced at the lead silver anodes and acid is regenerated for recycle to leaching. The overall reaction is given by reaction 2.3.

\[
\text{ZnSO}_4 + \text{H}_2\text{O} \rightarrow \text{Zn} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{SO}_4
\]  

(2.3)
A major operating consideration in the electrowinning of zinc is the purity of the electrolyte. The presence of impurity metal ions can have significant impacts in terms of both the cathodic current efficiency and the quality of the electro-deposited zinc. The former is reduced due to catalysis of the competing reaction of hydrogen evolution on the cathode. The impurity metal ions have been classified with respect to their deleterious effect on zinc deposition as follows Ge > Sb > Ni > Co > Bi > Cu > As > Sn > Fe (Cachet, Rerolle & Wiart 1999). Typical operating data for the electrowinning of zinc is summarized in Table 2.2.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual zinc production, tonnes</td>
<td>315000</td>
</tr>
<tr>
<td>Cathodes</td>
<td>Aluminium sheets</td>
</tr>
<tr>
<td>Anodes</td>
<td>Sandblasted Pb-0.75%Ag plates</td>
</tr>
<tr>
<td>Anodes life, years</td>
<td>3.5</td>
</tr>
<tr>
<td>Anodes/cathodes per cell</td>
<td>51/50</td>
</tr>
<tr>
<td>Current Density, A m$^{-2}$</td>
<td>471</td>
</tr>
<tr>
<td>Anode-cathode voltage, V</td>
<td>3.3</td>
</tr>
<tr>
<td>Cathode current Efficiency, %</td>
<td>92</td>
</tr>
<tr>
<td>Energy Consumption, MWh t$^{-1}$ cathode</td>
<td>2.95</td>
</tr>
<tr>
<td>Zn, g L$^{-1}$</td>
<td>50-65</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$, g L$^{-1}$</td>
<td>150-165</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>30-40</td>
</tr>
<tr>
<td>Ca, g L$^{-1}$</td>
<td>0.43</td>
</tr>
<tr>
<td>Mn, g L$^{-1}$</td>
<td>2.5</td>
</tr>
<tr>
<td>Mg, g L$^{-1}$</td>
<td>3.2</td>
</tr>
<tr>
<td>Na, g L$^{-1}$</td>
<td>8</td>
</tr>
<tr>
<td>Fe, mg L$^{-1}$</td>
<td>1502</td>
</tr>
<tr>
<td>Cl$^{-}$, mg L$^{-1}$</td>
<td>200</td>
</tr>
<tr>
<td>F$^{-}$, mg L$^{-1}$</td>
<td>21</td>
</tr>
<tr>
<td>Glue, g t$^{-1}$</td>
<td>20-25</td>
</tr>
<tr>
<td>SrCO$_3$, g t$^{-1}$</td>
<td>700</td>
</tr>
<tr>
<td>Na$_2$SiO$_3$, g t$^{-1}$</td>
<td>75</td>
</tr>
<tr>
<td>Licorice, g t$^{-1}$</td>
<td>60-80</td>
</tr>
</tbody>
</table>
Additional manganese ion is often introduced to the zinc sulphate electrolyte if not present in the ore to maintain a concentration of between 2 and 10 g/L. The presence of manganese assists in reducing the corrosion of anodes and minimizing the contamination of the zinc cathodes by co-deposited lead.

### 2.2.1 Lead Anode Materials Used in the Electrowinning of Zinc

The electrolytic production of zinc is normally operated at a higher (than copper) current density of about 500 A m$^{-2}$. The Pb-Ca-Sn anodes are not suitable for use at this high current as it will lead to high energy consumption (Stelter, Bombach & Saltykov 2006). Tin cannot be used as an alloying element because it will dissolve into the electrolyte and reduce the cathode current efficiency in addition to contaminating the cathode zinc (Prengaman & Morgan 2001). Instead, lead alloys containing 0.45 to 1% silver (Pb-Ag anode) have been used for many years. Silver is alloyed with the lead anode to reduce the rate of corrosion and improve the conductivity of the anode. In addition, the addition of silver also lowers the oxygen evolution overpotential by approximately 120 mV compared to pure lead (Stelter, Bombach & Saltykov 2006). A small amount of silver oxide may be formed on the surface of the anode in addition to the lead oxides. However, the poor mechanical properties are the disadvantage of Pb-Ag anodes in that they are relatively weak and bend quite easily when struck by cathode sheets as they are removed or inserted to the cells. Therefore, calcium to the extent of 0.05 to 0.08% is sometimes added to the alloys to improve the mechanical properties (Prengaman & Morgan 2001).
Due to the high cost of silver metal, other alloying elements have been investigated in an effort to reduce or replace the silver. Thus, cobalt has been found to be a potential additive in lead alloys as it can improve the stability of a lead anode. However, Pb-Co anodes have not to-date been used in any industrial application because of the difficulties in producing suitable Pb-Co alloys (Rashkov et al. 1999). The addition of cobalt ions to the electrolyte in zinc electrowinning is not advantageous, since it will adversely affect the current efficiency (Yu & O’Keefe 2002, Petrova et al. 1999).

The formation of a dense adherent protective layer of PbO$_2$/MnO$_2$ on the surface of the anode is normally a very slow process. It can take from three to six months for the surface anode to be fully established (Ramachandran et al. 1980). A number of different surface pretreatment methods for Pb-Ag and Pb-Ag-Ca alloy anodes have been developed to accelerate its formation, such as chemical oxidation in a KMnO$_4$-H$_2$SO$_4$ electrolyte at 70°C (Gonzalez 2001), KF electrochemical pretreatment (Newnham 1992), sandblasting (Rodrigues, Garbers & Meyer 2001) and shot-peening (Jin et al. 2003). All of the methods aim to roughen the anode surface to enhance the generation of a hard adherent corrosion layer in a relatively short time.

The permanganate chemical method, however, is sensitive to the rate of cooling after the pretreatment process, which, if too rapid, can cause cracking and curling of the anodic layer. The electrochemical preconditioning process in fluoride containing solutions provides an extra resistance to corrosion due to the formation of the lead difluoride layer between the lead substrate and the lead dioxide coating. Abrasive blasting and peening are carried out with relative coarse silica sand, glass beads or steel at high pressures above 500 kPa. The adherent oxide layer forms soon after installation and remains intact for at least
two months allowing a stable PbO$_2$-MnO$_2$ layer to form underneath. Sandblasting is currently the most common preconditioning method since peening with steel shot or glass beads can result in a significant deformation of the surface of lead anode and actual warping of the entire anode if not carried out carefully (Tuffrey 2004).

2.3 Electrochemical Behaviour of Lead Alloys in Sulphate Solutions

Due to the extensive use of lead in battery applications and as the preferred anode in base metal electrowinning processes from sulphate solutions, significant efforts have been made by many researchers to understand the electrochemistry of lead and its corrosion mechanism. The electrochemical studies involved various techniques such as potential-pH equilibrium diagrams, potentiostatic or galvanostatic oxidation, linear sweep or cyclic voltammetry, electrochemical impedance spectroscopy and X-ray diffraction analysis.

2.3.1 Potential-pH Diagram for the Lead-Water-Sulphate System

Metallic lead can be dissolved by acid oxidizing solutions with the formation of divalent plumbous ions Pb$^{2+}$. More powerful oxidation can result in conversion of divalent plumbous ions into brown quadrivalent lead dioxide PbO$_2$. In the absence of passivating substances such as carbonates, an oxidizing action can cause lead to corrode, except at high electrode potentials where PbO$_2$ is stable (Pourbaix 1974).
Figure 2.3 shows the potential-pH diagram of lead in sulphuric acid solutions (Guo 1992). This diagram includes the basic lead sulphates PbO.PbSO₄, 3PbO.PbSO₄.H₂O and the tetragonal oxide, PbO (PbO₄). When a lead electrode is immersed in sulphuric acid solution and polarized anodically to potentials in the area of stability of PbO₂, two main reactions occur on the electrode, which are the evolution of oxygen (shown as the dotted line) and the oxidation of PbSO₄ to PbO₂. The oxidation of water to oxygen is theoretically possible at 1.23 V, but oxygen production is only observed at potentials several tenths of a volt more positive than the equilibrium potential for the PbO₂/ PbSO₄ couple (Lander 1956). Therefore the oxidation of lead sulphate to lead dioxide and the evolution of oxygen gas require significant overpotentials. It has been suggested that the oxygen evolution reaction occurs at the anodic layer – solution interface and that its rate is affected by the quantity of PbO₂ on the electrode surface (Zhong et al. 1999).

It has also been observed that two forms of lead dioxide are formed with the rhombic (α-form) being stable at lower potentials than the tetragonal (β-form). Thus, Astakhov, Vaisberg and Kabanov (1964) have established that α-PbO₂ forms more dense deposits, composed of large and closely packed crystals. The β-PbO₂ deposits are less compact being composed of poorly bonded, fine, needle shaped crystals. On the basis of X-ray diffraction analyses, Sharpe (1975) reported that β-PbO₂ resides primarily in the outer portion of the film and α-PbO₂ exists in the inner portion of the film closer to the metal together with PbO₄. Ivanov et al. (2000) stated that α-PbO₂ is formed through an intermediate complex with hydroxyl ions, while β-PbO₂ is formed through an intermediate complex containing sulfate ions. Thus, on this basis, α-PbO₂ can be obtained only in alkaline or neutral media and β-PbO₂ only by oxidizing PbSO₄ in acidic media. α-PbO₂ is believed to be formed in a
localized high pH environment that is protected from the bulk acid by a PbSO₄ layer highly permeable to H₂SO₄ (Sharpe 1975).

![Potential-pH diagram for Pb-H₂O-SO₄ system](image)

Figure 2.3 Potential-pH diagram for Pb-H₂O-SO₄ system

### 2.3.2 Cyclic Voltammetry of Lead in Sulphate Solutions

Numerous studies have been made to characterize the reactions taking place on lead using potentiodynamic methods such as cyclic voltammetry (G. Cifuentes, L. Cifuentes & Crisostomo 1998; Mahato 1979; Sharpe 1975; Yamamoto et al. 1992). Figure 2.4 shows a typical cyclic voltammogram for a lead electrode in sulphuric acid solution with the following features:
(a) During the forward sweep, oxidation of metallic lead to lead(II) sulphate occurs in peak a.

\[ \text{Pb}(s) + \text{SO}_4^{2-}_{\text{aq}} \rightarrow \text{PbSO}_4(s) + 2e^- \]  

(2.4)

(b) The lead surface is passivated by the lead(II) sulphate film in the potential region from 0 V to about 2 V.

(c) Formation of lead(IV) dioxide by oxidation of lead(II) sulfate as shown in the following reactions which occur at potentials above about 2 V:

\[ \text{PbO} + \text{H}_2\text{O} \rightarrow \alpha-\text{PbO}_2 + 2\text{H}^+ + 2e^- \]  

(2.5)

\[ \text{PbSO}_4 + 2\text{H}_2\text{O} \rightarrow \beta-\text{PbO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2e^- \]  

(2.6)

The anodic oxidation to PbO₂ coincides with the simultaneous evolution of oxygen gas.

(d) During the reverse sweep, reduction of lead(IV) dioxide to lead(II) sulphate and non-stoichiometric basic-sulphates occurs in peak c, which is the reverse of reactions (2.5) and (2.6).

(e) Reduction of lead(II) sulphate and non-stoichiometric basic-sulphates occurs in peaks d and e.

\[ \text{PbO} + 2\text{H}^+ \rightarrow \text{Pb} + \text{H}_2\text{O} + 2e^- \]  

(2.7)

\[ \text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-} \]  

(2.8)

(f) At more negative potentials, hydrogen gas evolution occurs.

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \]  

(2.9)
2.3.3 Mechanism of the Electrochemical Oxidation of Lead

As a result of analysis of the anodic layer on lead and the thermodynamic considerations (Figures 2.3 and 2.4), three main potential regions have been identified as follows:

- From -0.325 to 0.245 V (versus SHE) the fresh anode surface is initially covered with a non-conducting layer of PbSO$_4$ crystals.
- From 0.245 to 1.65 V, the formation of tetragonal PbO (PbO$_t$) occurs together with thickening of a basic PbSO$_4$ film. PbO$_t$ has a very low electronic conductivity.
Above 1.65 V, the anodic layer contains $\alpha$- and $\beta$-PbO$_2$, PbO$_t$ and hydrated (gel) zones donated as PbO(OH)$_2$.

When lead is placed in sulphuric acid, a layer of PbSO$_4$ forms spontaneously, the mechanism of which was first advanced by Pavlov (1978). He suggested that the formation of the PbSO$_4$ layer is controlled by solid state diffusion of Pb$^{2+}$ and SO$_4^{2-}$ ions through the intergranular pores of the layer. During the growth, the layer acts simultaneously as a permselective membrane for Pb$^{2+}$ ions and as a blocking membrane for the access of SO$_4^{2-}$ ions to the interfacial region. As a consequence, the anodic current passing through the electrode makes protons in the anodic film move towards the electrolyte and OH$^-$ ions migrate towards the lead surface. The migration of these ions leads to an increase in pH and production of basic lead sulphates and PbO$_t$ between the PbSO$_4$ sublayer and the metal (Guo 1992).

With increasing anodic polarization, PbSO$_4$ is then transformed to a conductive layer of PbO$_2$. Codaro and Vilche (1997) suggested that the formation of PbO$_2$ proceeds through reactions 2.5 and 2.6 above. The $\alpha$-PbO$_2$ is formed from the oxidation of PbO.xPbO$_2$ or basic lead sulphate according to a two-dimensional nucleation and growth mechanism. The $\beta$-PbO$_2$ is formed from the oxidation of PbSO$_4$ in the outer layer. This final solid phase change is followed by oxygen evolution and the corrosion increases rapidly with increasing potential (Dawson 1979).

Pavlov and Dinev (1980) further suggested that the surface layers formed by oxidation of lead electrodes in sulfuric acid solutions also contain non-stoichiometric lead oxides PbO$_n$ (1<n<2). At the Pb/PbO interface, Pb is oxidised to PbO$_v^{2+}$ (reaction 2.10) where PbO$_v^{2+}$ is
a PbO molecule containing an $O_2$ vacancy ($O_v^{2+}$). Under the action of the electric field, the $O_2$ vacancy migrates into the oxide layer and reaches the oxide/solution interface where it reacts with water (reaction 2.11). The $H^+$ ions migrate through the PbSO$_4$ membrane into the bulk of the solution.

(Pb/PbO interface) \[ \text{Pb} \rightarrow \text{PbO}_v^{2+} + 2 \text{e}^- \] (2.10)

(PbO/PbSO$_4$/electrolyte interface) \[ \text{PbO}_v^{2+} + \text{H}_2\text{O} \rightarrow \text{PbO} + 2 \text{H}^+ \] (2.11)

PbO is then oxidised at the PbO/electrolyte interface via solid phase reactions to nonstoichiometric PbOn without a change of its crystal structure (reaction 2.12)

\[
k \text{PbO} + (m/2) \text{H}_2\text{O} = k \text{PbO}_n + m \text{H}^+ + m \text{e}^- \] (2.12)

in which, $n = (k + (m/2))/k$, (1 < $n$ < 2).

The value of $n$ is potential dependent and progressively increases closer to the oxide/solution interface. With increasing $n$, the electronic conductivity also rises. After passage of a critical charge, $n$ reaches critical value $\approx 1.4$ at which point nucleation of the new phase, $\alpha$-PbO$_2$, commences in the pores of the PbSO$_4$ membrane. When this phase reaches the acid solution interface, the oxidation of PbSO$_4$ crystals to $\beta$-PbO$_2$ begins in the outer portion of the film upon oxidation above 1.685 V and $\alpha$-PbO$_2$ exists along with PbO$_t$ in the inner portion of the film closer to the metal (Mahato 1979).
2.3.4 Mechanism of Oxygen Evolution on Lead

The production of a conducting PbO₂ layer from the insulating PbSO₄ film permits the evolution of oxygen on the lead alloy/oxide layer surface. Several mechanisms of the electrochemical processes that proceed during the oxygen evolution reaction (OER) on or in the PbO₂ layer in acidic solution have been proposed.

The first mechanism ignores the direct involvement of the PbO₂ layer in the kinetics of the OER (Bockris 1956; Codaro & Vilche 1997). The PbO₂ surface is considered as an inert electrode on which the mechanism of the OER is likely to be similar to that occurring on noble metals such as Pt and Ir. The rate limiting reaction has been suggested to be the primary discharge of H₂O molecules (reaction 2.13).

\[
\begin{align*}
H₂O &= OH_{ads} + H^+ + e^- & (2.13) \\
OH_{ads} &= O_{ads} + H^+ + e^- & (2.14) \\
2O_{ads} &= O₂ & (2.15)
\end{align*}
\]

Codaro and Vilche (1997) also suggested that β-PbO₂ is a better catalyst for the OER than α-PbO₂. The β-PbO₂ layer is considered as being constituted by small cylindrical crystals surrounded by PbSO₄ crystals, so that the OER starts on the β-PbO₂/PbSO₄ surface, and at high positive potentials and/or long oxidation times it continues on the β-PbO₂ layer.

A second mechanism involves the PbO₂ layer in the kinetics of the OER. In a first step, water is decomposed forming an intermediate unstable oxide. This oxide is then transformed into a stable species accompanied by oxygen evolution as shown in the following reactions.
H₂O + MOₙ → MOₓ⁺₁ + 2H⁺ + 2e⁻ \hspace{5em} (2.16)  
2MOₓ⁺₁ → 2MOₓ + O₂ \hspace{5em} (2.17)

Kabanov and his co-workers (1964) hypothesized that anodic corrosion of lead in sulphuric acid solution occurs by means of the diffusion of oxygen to the lead through the layer of lead dioxide and lead oxide. They carried out an anodic polarization of one face of a pure lead membrane and measured the potential on the opposite, unpolarized face. They observed that the potential on the polarized side increased and exceeded the equilibrium potential for the PbO₂/PbSO₄/H₂SO₄ system. On the other hand, the potential on the opposite side of the membrane also increased as a result of the penetration of atomic oxygen through the membrane.

Pavlov and Monahov (1996) later proposed a rather complex mechanism involving the formation of a hydrated lead dioxide layer. They established two potential regions in which oxygen evolution is observed on the PbO₂ electrode,

- Passive Potential Region (PPR). In the potential region from 1.645 to 1.945 V, the anodic current density is small and the anodic layer formed contains more β-PbO₂ than α-PbO₂.
- Active Potential Region (APR). Upon further oxidation from 1.945 to 2.245 V, extensive oxygen evolution is observed and α-PbO₂ is the predominant phase in the anodic layer.

They suggested that the PbO₂/electrolyte interface is hydrated, forming a gel-like PbO(OH)₂ phase. The crystalline and the gel components are in equilibrium and it was
suggested that the OER proceeds in the layer located in the gel near its interface with the crystal layer.

\[
PbO_2 + H_2O = PbO(OH)_2
\]

(2.18)
crystal layer hydrated (gel) layer

The anodic layer comprises of Pb/PbO\textsubscript{n} reaction layer/PbO\textsubscript{2} crystal layer/PbO(OH)\textsubscript{2} gel layer/electrolyte. Near the metal surface, n is low but increases to reach that of stoichiometric PbO\textsubscript{2} at a certain distance from the metal. The rate of the OER depends on the electronic conductivity of the anodic layer, which is determined by the stoichiometry of the PbO\textsubscript{2} which in turn depends on the potential of the electrode and on the alloying additives in the alloy.

Pavlov and Monahov (1996) further suggested that the OER reaction occurs in two consecutive electrochemical reactions. The first which proceeds at potentials above 1.645 V, leads to the formation of OH radicals while the second takes place at potentials above 1.945 V. Both reactions are localised in active centers in the hydrated PbO(OH)\textsubscript{2} layer (denoted Pb\textsuperscript{*}O(OH)\textsubscript{2}). At potentials below 1.945 V, the products of the first reaction block these active centers resulting in low current densities. At potentials above 1.945 V, the second reaction proceeds, as a result of which O\textsubscript{2} is evolved due to the oxidation of the OH radicals and the consequent unblocking of the active centers. After formation of the anodic film, 99.2% of the charge is utilised for the OER, 0.67% for production of PbO\textsubscript{2} and 0.13% for other reactions (Ivanov et al. 2000). Thus, the oxide layer continues to slowly grow with increasing time of anodization.
Generally, the corrosion rates increased with increasing temperature and current density. Increased temperature leads to depolarization of the OER reaction, as well as to formation of greater amounts of both the compact and less dense PbO₂ layers (Hrussanova et al. 2004). The spalling of this anodic layer due to internal stresses occurs more frequently at higher temperatures.

The increase in corrosion rate with increasing current density can be attributed in part to the increased rate of oxygen evolution which inhibits the formation of a dense anode layer.

2.3.5 Electrochemical Behaviour of Lead-Calcium-Tin Alloys

Prengaman and Siegmund (1999) studied the influence of calcium and tin in the wrought Pb-Ca-Sn alloys and found that tin reacts with calcium to form fine uniform Sn₃Ca particles within the grain structure which imparts strength to the anode. In addition, tin prevents the formation of PbO₁ at the lead anode/PbO₂ corrosion product interface by the formation of SnO₂-doped PbO₂ according to the following suggested reactions

\[
\begin{align*}
2\text{PbO} + \text{Sn} & \rightarrow \text{SnO.PbO} + \text{Pb} \\
\text{SnO.PbO} + \text{O}_2 & \rightarrow \text{SnO}_2\text{.PbO}_2
\end{align*}
\]

in which tin reduces PbO to form PbO and SnO. This SnO is soluble in PbO and upon further oxidation forms SnO₂-doped PbO₂, which is much more conductive and much less reactive than pure PbO₂.
2.3.6 Electrochemical Behaviour of Lead-Silver Alloys

The addition of silver to the lead has been shown to reduce the rate of anode corrosion and the amount of lead codeposited and occluded in the cathode during zinc electrowinning. It is believed that the presence of silver enables an alternate pathway for the evolution of oxygen, which results in a decreased overpotential for oxygen evolution (Cole & O’Keefe 1981).

Cachet, Rerrole and Wiart (1996) studied the kinetics of the OER on Pb-Ag anodes in acidic solutions containing some manganese ions by utilising electrochemical impedance spectroscopy (EIS). They found that the presence of silver and Mn$^{2+}$ ions decreased the extent of anodic polarisation. The effect of Ag is more pronounced with increasing Ag content up to 0.5%. However, the rate of growth of the PbSO$_4$ layers is independent of the silver content. The oxide layer has the structure of $\beta$-PbO$_2$ in the potential region 1.915 to 1.995 V. In manganese containing electrolytes, this feature persisted above 1.995 V. They proposed that the secondary reactions occurring on the Pb-Ag electrode are as follows in the absence and presence of manganese ions

\[
\begin{align*}
\text{In H}_2\text{SO}_4 \text{ solution} & \quad \text{Ag} & \rightarrow & \text{Ag}^+_\text{surf} + e^- & \rightarrow & \text{AgSO}_4^{-\text{ad}} \\
\text{In H}_2\text{SO}_4/\text{MnSO}_4 & \quad \text{Ag} & \rightarrow & \text{Ag}^+_\text{surf} + e^- & \rightarrow & \text{AgMnO}_4^{-\text{ad}}
\end{align*}
\]

(2.21) (2.22)

The presence of AgSO$_4^{-\text{ad}}$ or AgMnO$_4^{-\text{ad}}$ is thought to inhibit oxygen evolution, but oxidation of these species to form AgO (reaction 2.23) results in a more active catalytic surface for the OER than on PbO$_2$ (Ivanov et al. 2000; McGinnity 2008). The amount of AgO increases with increasing Ag content in the alloy.
In the presence of manganese, silver also exhibits a strong catalytic effect on the OER. However this catalytic effect requires that it be in an intimate contact with the anode (McGinnity 2008).

Studies carried out with silver added as Ag$^+$ ions, rather than via dissolution of silver from the anode, also showed a decrease in the overpotential of the OER but did not affect the corrosion rate of pure lead (Pavlov & Rogachev 1986). It is thought that the effect of the Ag$^+$ ions is limited only to the oxide-solution interface. When silver is alloyed in the metal, silver is oxidized together with lead and the oxidized silver is incorporated in the oxide as a solid solution thereby influencing the mobility of O atoms in the oxide and the phase composition of the anodic layer.

Pavlov and Rogachev (1986) suggested that silver enhances the formation of $\beta$-PbO$_2$ at the oxide-solution interface and also in the zone close to the metal. During the oxidation of tet-

PbO$_n$ silver creates suitable conditions for formation of the crystal lattice for $\beta$-PbO$_2$.

Monahov, Pavlov and Petrov (2000) further revealed that silver decreases the activation energy for the OER and probably increases the number of active centres in the gel zone of the PbO$_2$ layer. This effect appears to increase with increasing silver content in the alloy. However, there is no clear evidence in the literature that the extent of the gel zones on the PbO$_2$ particles affects the oxygen evolution overvoltage.
2.4 Electrochemical Behaviour of Manganese Ions in Sulphate Solutions

Manganese metal can easily be dissolved by acid or neutral oxidizing solutions with the formation of the pale pink manganous Mn$^{2+}$ ion. As shown in the equilibrium potential-pH diagram of the Mn-H$_2$SO$_4$-H$_2$O system (Figure 2.5) (Kelsall et al. 2000), oxidation of manganous ions can, depending on the pH and Eh, produce a number of higher oxidation states with the formation of solid oxides Mn$_3$O$_4$, MnOOH and MnO$_2$. Under more strongly oxidizing conditions, species such as Mn$^{3+}$ ions in very acidic solution, MnO$_4^{2-}$ ions in very basic solution or MnO$_4^{-}$ ions over a wide range of pH can be produced.

Figure 2.5 Potential-pH diagram for Mn-H$_2$O-H$_2$SO$_4$ system
The oxidation of Mn(II) to Mn(III) (reaction 2.24) is generally complicated by the limited stability of the Mn$^{3+}$ ion except in strongly acidic solutions. Disproportionation results in the formation of manganese dioxide as shown in reaction 2.25.

\[
\begin{align*}
\text{Mn}^{2+} &= \text{Mn}^{3+} + e^- \\
E^0 &= 1.509 \text{ V} \quad (2.24) \\
2\text{Mn}^{3+} + 2\text{H}_2\text{O} &= \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+ \\
(2.25)
\end{align*}
\]

Solutions of Mn(III) can be prepared by adding permanganate solution to a solution containing a large excess of Mn(II) in strong sulphuric acid solutions according to reaction 2.26.

\[
\text{MnO}_4^- + 4\text{Mn}^{2+} + 8\text{H}^+ = 5\text{Mn}^{3+} + 4\text{H}_2\text{O} \quad (2.26)
\]

When the concentration of Mn$^{3+}$ ion is relatively high, the addition of more permanganate results in the oxidation of Mn$^{3+}$ to Mn$^{4+}$ (reaction 2.27).

\[
\text{MnO}_4^- + 3\text{Mn}^{3+} + 8\text{H}^+ = 4\text{Mn}^{4+} + 4\text{H}_2\text{O} \quad (2.27)
\]

Mn$^{4+}$ is not stable in the solution and will react with water to form Mn(OH)$_4$ which dehydrates easily to yield solid MnO$_2$ (Kao & Weibel 1992).

\[
\begin{align*}
\text{Mn}^{4+} + 4\text{H}_2\text{O} &\rightarrow \text{Mn(OH)}_4 + 4\text{H}^+ \\
(2.28) \\
\text{Mn(OH)}_4 &\rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} \\
(2.29)
\end{align*}
\]

The stability of the Mn(III) produced is dependent upon the acidity, the ratio of the concentrations of Mn(II) to Mn(III) and the ability of SO$_4^{2-}$ ion to complex with Mn$^{3+}$ ion (Morrow & Perlman, 1973). Selim and Lingane (1959) demonstrated that stable solutions of Mn(III) were formed in 4.6 - 7.2 M H$_2$SO$_4$ in the presence of ten-fold excess of Mn(II),
while Kalra and Gosh (1966) suggested that a much higher Mn(II)/Mn(III) ratio of about 25 or greater in 4.5 M H$_2$SO$_4$ solution is required to stabilize Mn(III) in solution.

The permanganate ion is itself intrinsically unstable in that it will decompose slowly to MnO$_2$ evolving O$_2$ according to the following reaction (Pourbaix 1974).

$$4\text{MnO}_4^- + 4\text{H}^+ \rightarrow 4\text{MnO}_2 + 3\text{O}_2 + 2\text{H}_2\text{O}$$  \hspace{1cm} (2.30)

In summary, manganese can be present as either ions of Mn(II), Mn(III), Mn(VII) and possibly also Mn(IV) in strongly acidic solutions.

It is apparent that a number of manganese species can be oxidized to form deposits on the surface of an electrode, with MnO$_2$ as the predominant product. However, the detailed mechanisms of the anodic oxidation of Mn(II) ions and the deposition of MnO$_2$ are still unresolved particularly on lead alloy anodes. However, there is some information on the mechanism of the deposition of electrolytic manganese dioxide (EMD) on other anode surfaces.

2.4.1 Electrochemical oxidation of Manganese(II) Ions on Inert Electrodes

The formation of EMD (generally regarded as γ-MnO$_2$) by anodic oxidation of manganese sulphate solutions is an industrial process and has been studied using inert anode substrates such as platinum, titanium, gold, and carbon or graphite fibre materials in dilute sulfuric acid (20 to 70 g L$^{-1}$) at current densities of 20 to 120 A m$^{-2}$ and high temperatures (80 to 98 °C) (Duarte, Pilla & Mayer 2003; Kao & Weibel 1992). Several mechanisms have been
proposed for the oxidation of Mn$^{2+}$ and the deposition of MnO$_2$ on inert electrodes in sulphuric acid solution using different techniques. The overall reaction is given by reaction 2.31.

$$\text{Mn}^{2+}_{(aq)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{MnO}_2(s) + 4\text{H}^{+}_{(aq)} + 2\text{e}^- \quad E^0 = 1.228 \text{ V} \quad (2.31)$$

Most researchers agree that this reaction does not occur in a single step since the oxidation state of manganese increases from +2 to +4. The initial step of Mn$^{2+}$ oxidation can be either a one-electron oxidation to Mn$^{3+}$ or a two-electron oxidation to Mn$^{4+}$. Kao and Weibel (1992) carried out rotating ring-disc experiments on platinum/platinum electrodes and found that the initial oxidation product was soluble in the solution and slowly formed a MnO$_2$ deposit. Therefore they suggested that Mn$^{3+}$ ions could be the initial oxidation product (reaction 2.24) because Mn$^{4+}$ ions are not stable in the solution as shown in reactions 2.28 and 2.29.

Nijjer, Thonstad and Haarberg (2000), Kao and Weibel (1992) suggested that the oxidation of Mn$^{2+}$ to form MnO$_2$ on a platinum anode occurs by an electrochemical-chemical-electrochemical (ECE) mechanism involving a Mn(III) intermediate as shown in scheme 1. In this case, Mn$^{3+}$ ions rapidly hydrolyze to form a solid Mn(III) oxide, such as MnOOH which is subsequently oxidized to MnO$_2$. Diffusion of Mn$^{2+}$ ion in the deposited oxide was found to control the rate of growth of MnO$_2$ (Kao & Weibel 1992).

**Scheme 1 (ECE Mechanism of the MnO$_2$ Deposition)**

- Mn$^{2+} \rightarrow$ Mn$^{3+} + \text{e}^-$
- Mn$^{3+} + 2\text{H}_2\text{O} \rightarrow \text{MnOOH} + 3\text{H}^{+}$
- MnOOH $\rightarrow$ MnO$_2 + \text{H}^{+} + \text{e}^-$
At low Mn$^{2+}$ concentrations parts of the electrode surface may still be active for oxidation of Mn$^{2+}$ to Mn$^{3+}$ because of the reduced coverage of the insulating intermediate MnOOH. At high Mn$^{2+}$ concentrations the rate of formation of MnOOH is high and the high surface coverage will deactivate the electrode against further oxidation of Mn$^{2+}$. High temperatures, low acidity and increased mass transport enhance the rate of oxidation of Mn$^{2+}$ to MnO$_2$ (Nijjer, Thonstad & Haarberg 2000).

According to Selim and Lingane (1959), the Mn$^{3+}$ ions are unstable at low acid concentrations and will disproportionate to Mn$^{2+}$ and Mn$^{4+}$ ions. The formal disproportionation constant varies from 10$^{-3}$ in 4 M H$_2$SO$_4$ to 10$^{-4}$ in 7 M H$_2$SO$_4$ at 25 ºC. Rodrigues, Munichandraiah and Shukla (1998) suggested that the deposition of MnO$_2$ occurs by a more complex mechanism involving the formation of hydroxyl radicals as shown in Scheme 2.

This conclusion was based in part on observations that the cyclic voltammetric peak current for the deposition of MnO$_2$ is proportional to the square root of the Mn$^{2+}$ ion concentration in the electrolyte and independent of acidity. However, this evidence cannot be used to derive such a complex mechanism.
Clarke, Browning and Donne (2006) investigated the effect of the concentrations of Mn(II) and sulphuric acid on the deposition of MnO$_2$ on platinum and observed that the increase in peak current for oxidation of Mn$^{2+}$ was not proportional to the increase in Mn(II) concentration. This result has been interpreted in terms of a decrease in the substrate catalytic activity as a result of manganese dioxide deposition. When the deposited manganese dioxide delaminated from the substrate, the current increased as a result of exposure to the more catalytic platinum surface. From the effect of acidity, they suggested that MnOOH is the initial precipitated species in dilute acid (< 1.0 M) as shown in scheme 1. In more concentrated acid electrolytes, the adsorbed Mn$^{3+}$ ion is more stable towards hydrolysis, and so is able to undergo subsequent oxidation or disproportionation to form MnO$_2$ as shown in scheme 2. This was justified in terms of the expected lifetime of the Mn(III) intermediate at various acid concentrations as obtained from rotating disc electrode (RDE) and rotating ring disc electrode (RRDE) voltammetry. Furthermore, they also suggested that the rate of oxidation is activation and not mass transport controlled. However, the extent to which mass transport contributed to the rate of oxidation was found to increase as both temperature and acid concentration increased, reflecting the catalytic nature of the electrode surface and the extent to which the Mn(III) intermediate is soluble.

An alternative mechanism has been suggested in terms of which, Mn$^{2+}$ ions may also be oxidised directly to MnO$_4^-$ at high oxidation potentials which then react with the Mn$^{2+}$ ions in the electrolyte to form Mn$^{4+}$ (Pajunen, Aaroma & Forsen 2003). The Mn$^{4+}$ ions hydrolyse and form dispersed MnO$_2$ in the bulk of the solution.
Scheme 3 (Mechanism of the MnO₂ Deposition at Higher Potentials)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺ + 4 H₂O → MnO₄⁻ + 8 H⁺ + 5e⁻</td>
<td>(2.31)</td>
</tr>
<tr>
<td>2 MnO₄⁻ + 3 Mn²⁺ + 16 H⁺ → 5 Mn⁴⁺ + 8 H₂O</td>
<td></td>
</tr>
<tr>
<td>Mn⁴⁺ + 2 H₂O = MnO₂ + 4 H⁺</td>
<td></td>
</tr>
</tbody>
</table>

2.4.2 Electrochemical Oxidation of Manganese(II) Ions on Lead Anodes

Manganese ions are electrochemically active at lead or lead alloy anodes and may precipitate manganese oxide after PbO₂ is formed on the anode and before extensive evolution of oxygen occurs. It has been shown that the electrochemical deposition of manganese on the anode may act favorably to minimize disintegration of the anode scale by decreasing the amount of lead oxidized to PbO₂ anodes (Yu & O’Keefe 2002).

The mechanism of MnO₂ deposition on lead anodes appears to be different from that on ‘inert’ electrodes. Thus PbO₂ electrodes seem to have significant catalytic properties for the oxidation of Mn²⁺ to MnO₄⁻, but not for the oxidation of Mn²⁺ to Mn³⁺ (Zhang & Park 1994). Cheng et al. (2000) also suggested that there was no evidence for the presence of Mn⁴⁺ in the electrolyte during oxidation of Mn²⁺ on a PbO₂ anode.

Kelsall et al. (2000) suggested that anodic oxidation of Mn²⁺ ions on Pb/PbO₂ anode operating at potentials above 1.8 V with a current density of 500 A/m² involves reaction 2.32 coupled to the homogeneous electron transfer reaction 2.26.

\[
\text{Mn}^{2+} + 4\text{H}_2\text{O} = \text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^-  \quad (2.32)
\]
As mentioned above, manganese(III) ions are unstable except in very concentrated acid solutions and disproportionate by the reaction (2.25) to form MnO₂.

The MnO₂ deposited on the anode and formed by disproportionation in solution were both reported to be γ-MnO₂ which is a solid solution of MnO₂ and a lower oxidation state manganese oxide containing hydroxyl ions and water. The general formula has been proposed as MnOₙ(2-n)H₂O, which is MnO₂ for n = 2, and MnOOH for n = 1.5.

Comninellis and Petitpierre (1991) reported that Ag(I) is a very effective catalyst for the oxidation of Mn²⁺ to MnO₄⁻ in sulphuric acid solution by way of Ag(II) as an intermediate at anodic potentials below 1.945 V,

\[
5\text{Ag(I)} = 5\text{Ag(II)} + 5e^- 
\]  \hspace{1cm} (2.33)

\[
\text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Ag(II)} \rightarrow \text{MnO}_4^- + 5\text{Ag(I)} + 8\text{H}^+ 
\]  \hspace{1cm} (2.34)

Above 1.945 V, AgO is deposited at the anode and the current efficiency for formation of permanganate decreases due to the simultaneous evolution of oxygen.

\[
5\text{Ag(I)} + 5\text{H}_2\text{O} = 5\text{AgO} + 10\text{H}^+ + 5e^- 
\]  \hspace{1cm} (2.35)

\[
\text{Mn}^{2+} + 5\text{H}_2\text{O} + 5\text{AgO} \rightarrow \text{MnO}_4^- + 5\text{Ag(I)} + 10\text{H}^+ 
\]  \hspace{1cm} (2.36)

Yu and O’Keefe (2002) also suggested that the formation of MnO₂ occurs via disproportionation of Mn³⁺ (reaction 2.25) or the hydrolysed form

\[
2\text{MnOH}^{2+} = \text{Mn}^{2+} + \text{MnO}_2 + 2\text{H}^+ 
\]  \hspace{1cm} (2.37)

They suggested that the MnO₂ formed could catalyse the disproportionation of Mn³⁺. They found that MnO₂ not only deposited on the PbO₂ surface but extensive deposition of MnO₂
also occurred on the insulating material surrounding the anode. They confirmed that Mn\(^{3+}\) could be produced from Mn\(^{2+}\) oxidation (reaction 2.24), the reaction between Mn\(^{2+}\) and MnO\(_4^-\) (reaction 2.26) and/or the oxidation of Mn\(^{2+}\) by PbO\(_2\) (reaction 2.38).

\[
2\text{Mn}^{2+} + \text{PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ \rightarrow 2\text{Mn}^{3+} + \text{PbSO}_4 + 2\text{H}_2\text{O} \quad (2.38)
\]

They found that a high Mn\(^{2+}\) concentration and low electrode potential favour the formation of Mn\(^{3+}\) and MnO\(_2\) while the formation of MnO\(_4^-\) is enhanced at higher potentials. The precipitation of MnO\(_2\) was observed on the walls and bottom of the cell, indicating that reaction (2.26) might occur in the bulk electrolyte followed by reaction (2.25) which when combined could give the overall reaction

\[
3\text{Mn}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+ \quad (2.39)
\]

The MnO\(_2\) formed on PbCaSn anode has been characterised by Ipinza et al. (2003) as a double layer consisting of a thick external layer of non-adhering and easily removable scale and a thin internal layer which adheres relatively well to the surface of the electrode. They suggested that MnO\(_2\) slimes were composed of

- Hexagonal \(\varepsilon\)-MnO\(_2\) as a non-adhering layer produced by oxidation on the PbO\(_2\) surface as an amorphous structure which slowly crystallises in contact with the electrolyte; and
- Tetragonal \(\beta\)-MnO\(_2\) which is produced by a chemical precipitation reaction at the electrode-electrolyte interface which may be catalysed by PbO\(_2\) active sites. The precipitation starts as a result of formation of MnO\(_4^-\) as suggested by Yu and O’Keefe (2002).
More recently, Ipinza et al. (2007) suggested that the formation of $\varepsilon$-MnO$_2$ on the anode occurs through the oxidation of MnOOH to the MnO$_4^-$ ion followed by reaction with Mn$^{2+}$ ions as shown in scheme 4.

They stated that amorphous MnOOH, which is semi-conducting, is the dominant product on the lead anode in the presence of ferrous ion or at potentials less than that required for MnO$_4^-$ formation. The decrease in anode overpotential of about 100 mV is also attributed to the presence of this MnOOH layer.

Yu and O’Keefe (2002) suggested that as the MnO$_2$ layers build up and increase in thickness they may become less conductive and more inert for the OER. By the use of scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), it has been shown that an inert PbSO$_4$ layer is formed between the MnO$_2$ and the conductive PbO$_2$ layers. Therefore, the dislodged manganese dioxide flakes contribute to the loss of lead from the anode. The Pb$^{2+}$ ions in the solution may be co-precipitated with manganese dioxide slimes and hence may be removed from the electrolyte (Fukushima 1962). The formation of manganese scale on the anode increases with an increase in manganese concentration, however, the protective effect of manganese scale does not increase in proportion to the manganese ion concentration.
The rate of formation of manganese dioxide is more significant on Pb-Ag anodes than on Pb-Ca-Sn anodes, with a thicker layer forming on the former material. The presence of cobalt (II) ions in the electrolyte also enhances the rate of formation of MnO$_2$ on Pb-Ca-Sn anodes, although the oxide that forms is denser and less powdery. It has been suggested that there are possible catalytic effects of the Ag(I/II) and Co(II/III) couples on the oxidation of manganese ions (Yu & O’Keefe 2002; Cachet, Rerolle & Wiart 1999).

2.5 Electrochemical Oxidation of Cobalt(II) Ions on Lead

The strong beneficial effects of cobalt in lowering both the oxygen overvoltage and the corrosion rate of lead alloy anodes have been well established. However, the exact mechanism by which cobalt acts on the oxidation process has not been resolved. It is apparent that the anodic film formed on lead alloy anodes in the presence of cobalt ions is more adherent, thin and compact. Therefore, there is a reduced tendency for the oxide scales to become dislodged. This provides another significant benefit in reducing the extent of lead contamination of the cathodes.

Krivolapova and Kabanov (1953) proposed that cobalt decreases the oxidation of lead by the adsorption of Co$^{3+}$ ions or CoO$_2$ in the pores of the lead oxide, possibly forming a dense blocking film. This assumption was based in part on observations that the color of the Pb-Sb anodes was pale red in the presence of cobalt ions.

Yu and O’Keefe (2002) reported that the effect of cobalt is only observed at potentials above 1.8 V where the oxygen evolution was enhanced significantly. The effect is more pronounced with increasing cobalt concentration (Gendron, Ettel & Abe 1975). Koch
(1959) also stated that the beneficial effect of cobalt in reducing the corrosion of lead is effective at potentials above 1.83 V where Co\(^{2+}\) ions are oxidized to Co\(^{3+}\) ions (reaction 2.40).

In agreement with Koch (1959), Ramachandran et al. (1996) reported that when oxygen was evolved in the presence of cobalt, very much less PbO\(_2\) was formed on the lead anode. They suggested that oxygen evolution occurs more readily in the presence of cobalt ions and therefore once a conducting PbO\(_2\) layer is formed a greater fraction of the current may be used for the oxygen evolution in preference to the oxidation of PbSO\(_4\). Koch (1959) postulated that cobalt ions supply an alternative pathway for the OER by means of the following reactions.

\[
\begin{align*}
\text{Co}^{2+}_{(aq)} & \rightarrow \text{Co}^{3+}_{(aq)} + e^- \quad E^0 = 1.83 \text{ V} \quad (2.40) \\
\text{Co}^{3+}_{(aq)} + \text{OH}^- & \rightarrow \text{CoOH}^{2+}_{(aq)} \quad (2.41) \\
2\text{CoOH}^{2+}_{(aq)} & \rightarrow 2\text{Co}^{2+}_{(aq)} + \text{H}_2\text{O} + \text{O} \quad (2.42) \\
\text{O} + \text{O} & \rightarrow \text{O}_2 \quad (2.43)
\end{align*}
\]

The oxidation of Co\(^{2+}\) ions is likely to be catalyzed by the PbO\(_2\) surface and the resulting Co\(^{3+}\) ions are adsorbed on the surface and undergo reduction by oxidation of water.

In a similar mechanism, it was suggested by Antonov and Stepanenko (1972) that the catalytic effect of cobalt on the OER is due to the following continuous process that takes place on the anode:

\[
\begin{align*}
4 \text{Co}^{3+}_{(ads)} + 2 \text{H}_2\text{O} & = 4 \text{Co}^{2+}_{(ads)} + 4 \text{H}^+ + \text{O}_2 \quad (2.44) \\
\text{Co}^{2+}_{(ads)} & = \text{Co}^{3+}_{(ads)} + e^- \quad (2.45)
\end{align*}
\]
They assumed that the Co$^{2+}$ or Co$^{3+}$ ions in the solution are adsorbed on the active areas of the lead anodic surface. The unstable oxidized cobalt inside the protective layer then oxidizes water, which reaction is catalytically accelerated in the presence of PbO$_2$. It is suggested that this circular catalytic process is responsible for the lower potential at the anode. This hypothesis was later supported by Gendron, Ettel and Abe (1975) who also observed a reduction in the anode potential by about 100 mV during the polarization of a Pb-Sb anode at 300 A m$^{-2}$ in the presence of 3 g L$^{-1}$ cobalt. The absence of any significant amount of cobalt on the surface of the aged anodes confirms the instability of the oxidized cobalt compounds.

More recently, an alternative mechanism was suggested by Nguyen and Atrens (2009) who did not support the cobalt film mechanism. They postulated that cobalt ions hinder the oxidation of lead by the formation of a more protective corrosion product. By the use of X-ray diffraction (XRD) and X-ray photon electron spectroscopy (XPS) techniques, they revealed that the surface anodic film in the presence of cobalt ions was thin and compact and there are no crystalline compounds of cobalt. They suggested that cobalt increases the imperviousness of the $\alpha$-PbO$_2$ layer in hindering both the oxidation of metallic lead to $\alpha$-PbO$_2$ and the oxidation of PbSO$_4$ to $\beta$-PbO$_2$. Danilov, Velichenko and Nishcheryakova (1992) explained that cobalt ions increase the amount of labile oxygen containing species and decrease the number of adsorbed hydroxyl species that are strongly bound to the anode surface. As a result, the formation of lead oxides is inhibited.
2.6 Scope of the Present Research

The aim of this project is to develop a fundamental understanding of the role of manganese ions in the corrosion and electrocatalytic behaviour of selected lead alloys in the electrowinning of zinc and copper. In order to achieve this objective, an investigation has been conducted into the oxidation of both lead as an anode material and manganese as ions on lead alloy anodes, in particular Pb-Ag and Pb-Ca-Sn anodes, in sulphuric acid solutions containing manganese ions.

The electrochemical study was to be performed using rotating disc electrodes involving potentiostatic and galvanostatic oxidation followed by negative potential sweeps at various manganese concentrations, oxidation potentials, times of oxidation and silver alloy concentrations. The electrochemical measurements were complemented by chemical analyses of the oxidised manganese species formed during the oxidation process, which allow for the determination of the partial charge involved in oxidation of lead and manganese as well as for oxygen evolution.

The results of this study will assist in deriving a mechanism for the oxidation of manganese ions on these lead alloy anodes and in the understanding of the role of manganese in the electrowinning processes for both copper and zinc.
Chapter 3

EXPERIMENTAL

Several electrochemical and analytical techniques have been selected to investigate the role of manganese ions in the electrolytic behaviour of Pb-Ag and Pb-Ca-Sn anodes. These techniques include: (1) potentiostatic or (2) galvanostatic electrolysis followed by (3) linear potential sweep voltammetry, (4) UV-visible spectroscopy and (5) potentiometric titration for analysis of the manganese species. This chapter describes these techniques and their procedures.

3.1 Electrochemical Measurements

The study of the kinetics of electrochemical reactions involves measurements of the rate or currents as a function of the potential. A three electrode system is generally utilised for the electrochemical measurements, involving a working electrode, a reference electrode and a counter electrode. The counter electrode is used to make an electrical connection to the electrolyte so that a current can be applied to the working electrode. The reference electrode has a stable and well-known electrode potential which is used as a reference which enables the working electrode potential to be established.
3.1.1 Equipment, Electrodes and Electrochemical Cell

The electrochemical studies were performed using a conventional three-electrode system. An outline of the cell is shown in Figure 3.1. A modified Metrohm glass cell covered with a detachable lid was used as a reaction vessel. The working electrode was a rotating disc fabricated from commercial pure lead or lead alloys (Table 3.1). The reference electrode was a Hg|Hg$_2$SO$_4$ (saturated K$_2$SO$_4$) electrode (SSE, $E = +0.645$ V versus SHE) which was joined to the main cell by a Luggin capillary passing through a screw fitting in the base of the cell. The tip of the Luggin capillary was placed ~0.5 cm below the surface of the working electrode. The counter electrode was a platinum wire housed in a glass tube which was separated from the bulk solution by a glass frit. All potentials are reported with respect to the standard hydrogen electrode (SHE).

![Figure 3.1 Schematic diagram of the electrochemical cell](image)
Figure 3.2 Schematic diagram of the complete electrochemical set up. (a) Labview system, (b) potentiostat/ galvanostat, (c) rotating rig controller, (d) rotating rig, (e) electrochemical cell, (f) water bath
The complete electrochemical set up is schematically shown in Figure 3.2. The rotating disc electrode (RDE) was rotated using a drive consisting of an optically controlled unit coupled to a dc motor. The electrodes were rotated at 500 rpm in all tests. Voltammetric experiments were carried out using a Princeton Applied Research Model 173 Potentiostat/ Galvanostat and Model 376 Logarithmic Current Converter together with an EG&G PARC Model 175 Universal Programmer. Analogue data from the potentiostat were collected using a National Instrument data acquisition board controlled by Labview software. The temperature of the electrolyte was maintained at 40±0.1ºC by using a water thermoregulator (Rowe Scientific Pty Ltd).

3.1.2 Anode Materials

Table 3.1 summarizes the compositions of the anodes used in the rotating disc electrode experiments. The anode pieces were cut into cylindrical rods and bonded to a brass screw using silver conductive epoxy resin. Following this, the electrode was embedded in an epoxy resin (Araldite LC191) to insulate the body of the electrode, leaving only a disc of known area exposed to the solution. Prior to all tests, the exposed surface of working electrodes was wet-polished using 800 then 1200 silicon carbide papers and rinsed with deionised water.
Table 3.1 Anodes used in rotating disc electrode experiment

<table>
<thead>
<tr>
<th>Anode</th>
<th>Composition</th>
<th>Process</th>
<th>Diameter (mm)</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Pb</td>
<td>99.99% Pb</td>
<td>Rolled</td>
<td>4.2</td>
<td>Consolidated Alloys</td>
</tr>
<tr>
<td>Pb-Ag</td>
<td>Pb-0.25%Ag</td>
<td>Rolled</td>
<td>5.0</td>
<td>RSR Corporation</td>
</tr>
<tr>
<td>Pb-Ag</td>
<td>Pb-0.42%Ag</td>
<td>Rolled</td>
<td>5.0</td>
<td>Hudson Bay</td>
</tr>
<tr>
<td>Pb-Ag</td>
<td>Pb-0.75%Ag</td>
<td>Cast</td>
<td>5.0</td>
<td>Consolidated Alloys</td>
</tr>
<tr>
<td>Pb-Ag</td>
<td>Pb-1.0%Ag</td>
<td>Rolled</td>
<td>5.0</td>
<td>RSR Corporation</td>
</tr>
<tr>
<td>Pb-Ag</td>
<td>Pb-2.0%Ag</td>
<td>Rolled</td>
<td>5.0</td>
<td>RSR Corporation</td>
</tr>
<tr>
<td>Pb-Ca-Sn</td>
<td>Pb-0.08%Ca-1.3%Sn-0.01%Al</td>
<td>Rolled</td>
<td>5.0</td>
<td>Consolidated Alloys</td>
</tr>
</tbody>
</table>

3.1.3 Electrolyte Composition

All electrolyte solutions were prepared from chemicals of analytical grade and high quality water from a Millipore Milli-Q distilled water as shown in Table 3.2. The experiments were carried out in sulphuric acid solutions containing only manganese ions, unless otherwise specified.

Table 3.2 Chemicals used for the electrolyte solutions

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Supplier</th>
<th>Grade</th>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphuric acid</td>
<td>Merck</td>
<td>AR (98%)</td>
<td>H2SO4</td>
</tr>
<tr>
<td>Manganese Sulphate</td>
<td>Chem-Supply</td>
<td>AR</td>
<td>MnSO4.4H2O</td>
</tr>
<tr>
<td>Cobalt Sulphate</td>
<td>Univar</td>
<td>AR</td>
<td>CoSO4.7H2O</td>
</tr>
<tr>
<td>Phosphoric acid (ortho)</td>
<td>Rowe Scientific</td>
<td>AR (85%)</td>
<td>H3PO4</td>
</tr>
<tr>
<td>Ferrous Sulphate</td>
<td>Chem-Supply</td>
<td>AR</td>
<td>FeSO4.7H2O</td>
</tr>
</tbody>
</table>

Four different concentrations of sulphuric acid (50, 100, 150 and 200 g L⁻¹) were used in the preliminary testwork to examine the effect of acidity on the anodic behaviour of the Pb-0.42%Ag anode. A sulphuric acid solution of concentration 150 g L⁻¹ was then used as the base electrolyte for subsequent experiments.
The role of manganese ions was investigated by adding 0.1, 1, 5 or 10 g L\(^{-1}\) Mn\(^{2+}\) ions to the base electrolyte. The tests were initially conducted in 100 mL of electrolyte and then in 200 mL of electrolyte as required for the longer experiments.

Cobalt ion (150 mg L\(^{-1}\)) was also added for the galvanostatic electrolysis of the Pb-Ca-Sn anode to study its effects on the oxidation of both lead and manganese. The tests were conducted in the base electrolyte containing either 0.1 or 1 g L\(^{-1}\) Mn\(^{2+}\) ions.

Phosphoric acid can be used to complex the manganic Mn\(^{3+}\) ion and hence reduce its disproportionation to MnO\(_2\) (Velayutham, Noel & Chidambaram 1993). Various concentrations of phosphoric acid (1.78, 17.83 and 35.66 g L\(^{-1}\)) were added to the base electrolyte containing 1 g L\(^{-1}\) Mn\(^{2+}\) ion for the galvanostatic electrolysis of the Pb-0.75%Ag anode.

Cyclic voltammetry in solution containing ferrous ion (10 g L\(^{-1}\)) was performed to study the electrochemical oxidation of iron(II) ions in comparison with manganese(II) ions on both Pb-0.42%Ag and Pb-Ca-Sn anodes.

### 3.1.4 Electrochemical Test Methods

3.1.4.1 Potentiostatic Electrolysis

This electrochemical measuring technique is applied to determine the kinetics and mechanism of electrode reactions based on the control of the electrode potential. Hence a constant potential was applied and the variation of current was observed as a function of time.
After immersion in the electrolyte, the lead alloy anodes were potentiostatically anodized for a specific time (15 minutes to 48 hours) at various potentials (1.50 to 2.05 V), at a rotation speed of 500 rpm. This was followed by a potential sweep in a negative direction from the set potential at a rate of 1 mV s\(^{-1}\) and analysis of the solutions for determination of the partial charge involved in oxidation of lead and manganese. The charge involved in the evolution of oxygen was obtained by difference from the total charge passed during the anodization process. An overview of the different parameters used in the potentiostatic electrolysis is given in Table 3.3.

Table 3.3 Parameters in the potentiostatic electrolysis measurements

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Working Electrode</th>
<th>([\text{H}_2\text{SO}_4]) g L(^{-1})</th>
<th>([\text{Mn}^{2+}]) g L(^{-1})</th>
<th>Time (hours)</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid concentration</td>
<td>Pb-0.42%Ag</td>
<td>50, 100, 150, 200</td>
<td>-</td>
<td>2</td>
<td>1.8, 1.9, 2.0</td>
</tr>
<tr>
<td>Time of oxidation in the absence</td>
<td>Pb-0.42%Ag</td>
<td>150</td>
<td>-</td>
<td>0.25, 0.5, 1, 2, 5, 24, 48</td>
<td>1.8, 2.0</td>
</tr>
<tr>
<td>of manganese</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applied constant potential</td>
<td>Pb-0.42%Ag</td>
<td>150</td>
<td>5</td>
<td>2</td>
<td>1.5, 1.6, 1.7, 1.8, 1.85, 1.9, 1.95, 2.0</td>
</tr>
<tr>
<td>Manganese concentration</td>
<td>Pb-0.42%Ag</td>
<td>150</td>
<td>0.1, 1, 5, 10</td>
<td>2</td>
<td>1.8, 1.85, 1.9, 1.95, 2.0</td>
</tr>
<tr>
<td>Time of oxidation in the presence</td>
<td>Pb-0.42%Ag</td>
<td>150</td>
<td>0.1, 1, 5, 10</td>
<td>0.25, 0.5, 1, 2, 5, 24, 48</td>
<td>1.95, 2.0, 2.05</td>
</tr>
<tr>
<td>of manganese</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Working electrode</td>
<td>Pb-0.42%Ag, Pb-Ca-Sn</td>
<td>150</td>
<td>0.1, 1</td>
<td>0.25, 2, 24</td>
<td>1.7, 1.8, 1.9, 2.0</td>
</tr>
<tr>
<td>Silver alloy concentration</td>
<td>Pure Pb, Pb-(0.25, 0.42, 0.75, 1.0 &amp; 2.0%)Ag</td>
<td>150</td>
<td>5</td>
<td>24</td>
<td>2.0</td>
</tr>
</tbody>
</table>
3.1.4.2 Galvanostatic Electrolysis

The rate of the electrochemical reaction by the galvanostatic method was measured by applying a constant current to an electrode and the variation of the resultant potential was observed as a function of time.

The lead alloy anodes were oxidized at either 300 (typical of copper electrowinning) or 500 (typical of zinc electrowinning) A m\(^{-2}\) in the electrolyte for 24 hours at a rotation speed of 500 rpm, followed by a potential sweep in a negative direction at a rate of 1 mV s\(^{-1}\). This technique was employed to determine the effect of alloying elements as well as that of manganese and manganese-cobalt ions on oxygen overvoltage during polarization of the Pb-Ag and Pb-Ca-Sn anodes. The sulphuric acid concentration was 150 g L\(^{-1}\) and the temperature was held constant at 40\(^\circ\)C for all experiments. Table 3.4 gives an overview of the different parameters used in the galvanostatic experiments.

Table 3.4 Parameters in the galvanostatic electrolysis measurements

<table>
<thead>
<tr>
<th>Working Electrode</th>
<th>Current Density A m(^{-2})</th>
<th>[Mn(^{2+})] g L(^{-1})</th>
<th>[Co(^{2+})] g L(^{-1})</th>
<th>[H(_3)PO(_4)] g L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Pb</td>
<td>500</td>
<td>0, 1, 5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb-0.75%Ag</td>
<td>500</td>
<td>0, 0.1, 1, 5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb-0.75%Ag</td>
<td>500</td>
<td>1</td>
<td>-</td>
<td>1.78, 17.83, 35.66</td>
</tr>
<tr>
<td>Pb-Ca-Sn</td>
<td>500</td>
<td>0, 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb-Ca-Sn</td>
<td>300</td>
<td>0, 0.1, 1, 5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb-Ca-Sn</td>
<td>300</td>
<td>-</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>Pb-Ca-Sn</td>
<td>300</td>
<td>0.1, 1</td>
<td>0.15</td>
<td>-</td>
</tr>
</tbody>
</table>

3.1.4.3 Linear Sweep Voltammetry

Linear sweep voltammetry is a potentiodynamic method in which the current at the working electrode is measured while the potential applied to the working electrode is
varied linearly in time. The scan rate of the potential sweep has units of volts per unit time. The anodic or cathodic processes of species are typically shown as peaks in the current signal at the potential at which the species is oxidized or reduced.

All voltammograms in this work were initiated from the rest potential established after potentiostatic or galvanostatic polarization of the lead alloy anodes as mentioned above. The potential was swept in the negative direction at 1 mV s\(^{-1}\) and stopped at -0.9 V.

3.1.4.4 Cyclic Voltammetry

Cyclic voltammetry is an extension of linear sweep voltammetry in which the voltage is swept between two switching potentials in alternate anodic and cathodic directions. The potential can be cycled for several cycles before the experiment is ended at the final potential. This technique has been widely used for studying the phase composition of oxide layers as well as the kinetic parameters of the reactions at lead alloy anodes in sulphate solution. In these experiments, the cyclic polarization curves are obtained initially from the open circuit potential to the potential region of oxygen evolution and then reversed in the negative direction to the potential region of hydrogen evolution.

3.1.4.5 Rotating Disc Electrode

The rotating disc electrode is a valuable tool in electrochemistry for the study of electrochemical reactions under conditions of controlled mass transport. It is generally used as a working electrode which consists of a cylindrical metal rod (or other electrode material) embedded in a larger cylindrical non-conductive resin or polymer that can be rotated at a controlled variable speed. As the electrode rotates, it creates convective
flow perpendicular to the electrode which transforms into radial flow out from the surface of the electrode. Providing the rotation speed is kept within the limits of laminar flow then the rate of mass transport can be calculated from the Levich equation, which can be written in terms of a limiting current density as follows

\[
i_L = (0.620) n F A D^{2/3} w^{1/2} v^{-1/6} C
\]

in which \(i_L\) is the limiting current density; \(n\) is the number of electrons transferred in the electrochemical reaction; \(F\) is the Faraday constant; \(A\) is the electrode area; \(D\) is the diffusion coefficient of the electroactive species; \(w\) is the angular rotation rate of the electrode; \(v\) is the kinematic viscosity; and \(C\) is the concentration of the electroactive species. According to the Levich equation, the current observed at a rotating disc electrode increases linearly with the square root of the rotation rate and the concentration of the electroactive species.

3.2 Analytical Measurements

3.2.1 Visible Spectroscopy

Visible spectroscopy was used to identify the high-oxidation state manganese species in solution, namely manganic (Mn\(^{3+}\)) and permanganate (MnO\(_4^–\)) ions. The visible absorption spectrum of Mn\(^{3+}\) ions has a broad absorbance maximum at 482 nm, while MnO\(_4^–\) ion gives maxima at 488, 506, 524, 544 and 565 nm (Cheng et al. 2000). At the end of each test, samples of the electrolyte were filtered (membrane pore size 0.45 µm) and transferred to a Unicam 1.0 cm Optical Path Length Quartz Glass cell for immediate spectral analysis. An Agilent 8453 UV-Visible Spectrophotometer was used to scan from 900 to 350 nm at a rate of 600 nm/min.
The results of the absorbance measurements showed that in all cases only Mn$^{3+}$ ions and no MnO$_4^-$ ion was present.

### 3.2.2 Potentiometric Titrations

At the end of each experiment involving potentiostatic oxidation and subsequent linear cathodic sweep voltammetry, the concentrations of the manganic ion as well as any precipitated MnO$_2$ solid were determined by first reacting the solution and solids with excess ferrous ammonium sulphate and then back titrating with standard potassium dichromate solution.

#### 3.2.2.1 Reagents

All solutions were prepared from chemicals of analytical grade and deionised water. Solutions of ferrous ammonium sulphate ((NH$_4$)$_2$(SO$_4$)$_2$.6H$_2$O) of concentrations 0.01 and 0.05 M were prepared by dissolving the required amount in 0.1 M sulphuric acid. A solution of potassium dichromate (K$_2$Cr$_2$O$_7$) of 0.01 M was used as the titrant.

#### 3.2.2.2 Apparatus

A Radiometer-Copenhagen ETS822 end-point autotitration which comprises of ABU80 autoburette, TTT80 titrator, TTA80 titration assembly, PHM82 standard pH meter equipped with a combined platinum ring electrode in 3 M KCl (Metrohm 6.0451.100) was used.
3.2.2.2 Procedure

The concentration of the ferrous ammonium sulphate solutions were determined by titrating 25 mL aliquots with 0.01 M potassium dichromate (reaction 3.1) to an end-point potential of 599 mV.

\[ \text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O} \]  

(3.1)

0.01M ferrous solutions were used for analysis of the Mn\(^{3+}\) ions and MnO\(_2\) solids after electrolysis periods of less than 24 hours, while the higher ferrous concentration (0.05 M) was required for analysis of the greater amounts of manganese oxidized after longer periods.

The concentration of the manganic ion was determined by reacting 25 mL of the filtered electrolyte with 25 mL of excess ferrous ammonium sulphate. The amount of MnO\(_2\) was determined by dissolving the MnO\(_2\) solids that were precipitated on the wall of the cell, in the bulk of the solution and on the rotating disc electrode in 25 mL of the stirred ferrous solution. The unreacted ferrous ion was then back titrated with potassium dichromate. The amounts of Mn\(^{3+}\) and MnO\(_2\) were calculated from the amount of ferrous ions consumed according to the following equations.

\[ \text{Mn}^{3+} + \text{Fe}^{2+} = \text{Mn}^{2+} + \text{Fe}^{3+} \]  

(3.2)

\[ \text{MnO}_2 + 2\text{Fe}^{2+} = \text{Mn}^{2+} + 2\text{Fe}^{3+} \]  

(3.3)
Chapter 4

RESULTS AND DISCUSSION

4.1 Potentiostatic Oxidation of Lead-Silver Anodes in Sulphuric Acid

4.1.1 Effect of Varying Sulphuric Acid Concentration

The first part of this study involved an investigation of the behaviour of the Pb-0.42%Ag alloy as an anode in sulphuric acid solution. The experiments were performed in 100 mL of a solution containing various H$_2$SO$_4$ concentrations, i.e. 50, 100, 150 and 200 g L$^{-1}$. Three potentiostatic oxidation tests, i.e. at 1.8, 1.9 and 2.0 V, were carried out with each acid concentration for 2 hours followed by a potential sweep in the negative direction. The measurements were performed at 40°C with a rotation speed of the disc electrode of 500 rpm. A total of 12 tests have been performed and results are presented in Table 4.1 and Figures 4.1 and 4.2.
Figure 4.1 Current-time transients during oxidation of Pb-0.42%Ag anodes at various sulphuric acid concentrations
The cumulative charge ($Q_T$) passed during oxidation for 2 hours under each condition was obtained from the current-time curves in Figure 4.1. It is apparent from the current densities measured and the total charge passed that the rate of oxidation increased substantially as the potential was increased to 2.0 V. Oxygen evolution was more readily visually observed at 2.0 V. The charge passed during oxidation at all potentials decreased with increasing acidity as shown in Table 4.1. The current-time curves exhibit current maxima in the initial stages of oxidation at 1.8 and 1.9 V which also varied with the acidity.

Table 4.1 Effect of acid concentration on the charge fraction for Pb oxidation and O₂ evolution

<table>
<thead>
<tr>
<th>[H₂SO₄] / g.L⁻¹</th>
<th>Total Charge, $Q_T$ / Coulomb</th>
<th>Charge Fraction for Pb Oxidation, $Q_{Pb}/Q_T$</th>
<th>Charge Fraction for O₂ Evolution, $Q_{O2}/Q_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidation at 1.8 V</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1.083</td>
<td>0.911</td>
<td>0.089</td>
</tr>
<tr>
<td>100</td>
<td>0.598</td>
<td>0.905</td>
<td>0.095</td>
</tr>
<tr>
<td>150</td>
<td>0.303</td>
<td>0.858</td>
<td>0.142</td>
</tr>
<tr>
<td>200</td>
<td>0.464</td>
<td>0.791</td>
<td>0.209</td>
</tr>
<tr>
<td><strong>Oxidation at 1.9 V</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.738</td>
<td>0.147</td>
<td>0.853</td>
</tr>
<tr>
<td>100</td>
<td>2.096</td>
<td>0.206</td>
<td>0.794</td>
</tr>
<tr>
<td>150</td>
<td>1.859</td>
<td>0.145</td>
<td>0.855</td>
</tr>
<tr>
<td>200</td>
<td>1.577</td>
<td>0.199</td>
<td>0.801</td>
</tr>
<tr>
<td><strong>Oxidation at 2.0 V</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>94.800</td>
<td>0.006</td>
<td>0.994</td>
</tr>
<tr>
<td>100</td>
<td>66.698</td>
<td>0.007</td>
<td>0.993</td>
</tr>
<tr>
<td>150</td>
<td>62.479</td>
<td>0.007</td>
<td>0.994</td>
</tr>
<tr>
<td>200</td>
<td>48.277</td>
<td>0.010</td>
<td>0.990</td>
</tr>
</tbody>
</table>
Figure 4.2 Reduction sweep after oxidation of Pb-0.42%Ag anodes at various sulphuric acid concentrations
Figure 4.2 shows the cathodic sweeps at 1 mV s\(^{-1}\) after each of the oxidation periods with the inset showing the voltammograms between 1.4 and 1.7 V. As the potential was swept in a negative direction, two cathodic peaks are observed which are due to the reduction of PbO\(_2\) to PbSO\(_4\) at 1.6 to 1.5 V followed by that of PbO and PbSO\(_4\) to Pb at -0.2 to -0.6 V with a passive region between 1.4 to -0.2 V. The charges associated with the oxidation of lead (\(Q_{\text{Pb}}\)) were obtained from the integration of the area under each of these peaks and the results are also shown in Table 4.1. The appearance of anodic current peaks during the reduction of PbO\(_2\) to PbSO\(_4\) (1.5 to 1.6 V) has been attributed to the oxidation of lead exposed in the process of reduction of PbO\(_2\) to PbSO\(_4\). The magnitude of these peaks can be correlated to the small cathodic peak appearing at -0.25 to -0.35 V which has previously been assigned to the reduction of PbO (Sharpe 1975).

It has been suggested by Sharpe (1975) that PbSO\(_4\) formed on the surface of the discharging PbO\(_2\) might possess perm-selectivity, so that OH\(^-\) ions become localized in the interior of the corrosion film and are responsible for the reaction.

\[
Pb + 2OH^- = PbO + H_2O + 2e^- \tag{4.1}
\]

The charge for oxygen evolution (\(Q_{O_2}\)) during oxidation was calculated from the difference between the total charge (\(Q_T\)) and the charge for the oxidation of lead (\(Q_{\text{Pb}}\)). As can be seen from Table 4.1, after 2 hours at 1.8 V, about 90 % of the total charge is utilised for oxidation of lead. The experiment at 1.8 V was repeated with 100 g L\(^{-1}\) H\(_2\)SO\(_4\) for 300 and 1650 seconds until the current reached the first and the second maxima respectively and then the potential was swept cathodically as shown in Figure 4.3. At this potential, decreasing acid concentration resulted in an increase of the extent of PbSO\(_4\) formation and slower kinetics of the oxidation of PbSO\(_4\) to PbO\(_2\). However,
at higher potentials, where oxygen evolution is the main reaction, increasing acid concentration does not affect the fraction of the charge involved in the oxidation of lead. Another notable feature is that the cathodic peaks for the reduction of PbO₂ to PbSO₄ shift to a more positive potential with increasing acidity (Figure 4.2). Also the cathodic peak for reduction of PbO to Pb only appears at the higher acidities of 150 and 200 g L⁻¹ sulphuric acid. This is contrary to what could be expected on the basis of the reverse of reaction (4.1). An alternative explanation is that PbSO₄ formed by the oxidation of exposed lead at 1.5 V is more readily reduced to metal. Thus, direct oxidation may occur at 1.5 V to form an amorphous PbSO₄ phase as opposed to the accepted dissolution-precipitation model for PbSO₄ formation at lower potentials.
Figure 4.3 Current-time transients during oxidation of Pb-0.42%Ag anodes at 1.8 V in 100 g L$^{-1}$ H$_2$SO$_4$ for 300 and 1650 seconds and the subsequent potential sweep in a negative direction
4.1.2 Effect of Varying Oxidation Time

In a series of tests, the anodic behaviour of a Pb-0.42%Ag anode in acid solution was studied by varying the oxidation time from 15 minutes up to 48 hours at a constant potential of 1.8 V (Figure 4.4) or 2.0 V (Figure 4.5), followed by negative potential sweeps as described above. The acid concentration in the 100 mL solution was 150g L$^{-1}$ H$_2$SO$_4$ which is typical of that used in plant zinc electrolytes. The measurements were performed at a rotation speed of 500 rpm at 40°C.

![Figure 4.4 Current-time transients during oxidation of Pb-0.42%Ag anodes at 1.8 V in 150 g L$^{-1}$ H$_2$SO$_4$ for various times](image)

Figure 4.4 Current-time transients during oxidation of Pb-0.42%Ag anodes at 1.8 V in 150 g L$^{-1}$ H$_2$SO$_4$ for various times
Figures 4.6 and 4.7 show the reduction scans of the anode surfaces after oxidation at 1.8 and 2.0 V respectively. Only the relevant sections of the potential region have been shown. The charges involved in the oxidation of lead and oxygen evolution are summarized in Table 4.2. The charges associated with the formation of PbO\textsubscript{2} were obtained from the integration of the area under the reduction peaks of PbO\textsubscript{2} to PbSO\textsubscript{4} at 1.6 to 1.5 V. The charges associated with the formation of PbSO\textsubscript{4} were calculated from the difference between the total charge for the reduction peaks of PbSO\textsubscript{4} to Pb at -0.2 to -1.0 V and the charges for formation of PbSO\textsubscript{4} from PbO\textsubscript{2} reduction. It is apparent that there was a significant amount of lead sulphate on the anodized surface after long times compared to short times. The rate of oxidation of lead decreases with time at both potentials and the rate is almost an order of magnitude greater at 2.0 V than 1.8 V. The rate of oxidation of lead decreases as the thickness of the oxide layer increases. On the other hand, the rate of oxygen evolution increases with time at both potentials.
confirming that PbO$_2$ is a superior electrocatalyst for O$_2$ evolution than a PbSO$_4$ covered lead surface (Pourbaix 1974). Table 4.3 shows that there is a good correlation between the magnitude of the anodic peaks (shown by arrows in Figure 4.6) that appear either before or after the reduction of PbO$_2$ to PbSO$_4$ and the peak attributed to the reduction of basic lead oxide to metallic lead at -0.25 to -0.35 V.

Table 4.2 Effect of time on the charge fractions during oxidation of a Pb-0.42%Ag anode in 150 g L$^{-1}$ H$_2$SO$_4$ at 1.8 V and 2.0 V

<table>
<thead>
<tr>
<th>Time / hours</th>
<th>Charge Fraction at 1.8 V</th>
<th>Charge Fraction at 2.0 V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{\text{PbSO}_4}$ / Coulomb</td>
<td>$Q_{\text{PbO}_2}$ / Coulomb</td>
</tr>
<tr>
<td>0.25</td>
<td>0.137</td>
<td>0.015</td>
</tr>
<tr>
<td>0.5</td>
<td>0.212</td>
<td>0.012</td>
</tr>
<tr>
<td>1</td>
<td>0.190</td>
<td>0.013</td>
</tr>
<tr>
<td>2</td>
<td>0.214</td>
<td>0.023</td>
</tr>
<tr>
<td>5</td>
<td>0.309</td>
<td>0.023</td>
</tr>
<tr>
<td>24</td>
<td>0.797</td>
<td>0.030</td>
</tr>
<tr>
<td>48</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.3 Correlation of the ‘anodic current peaks’ to the reduction of ‘PbO’

<table>
<thead>
<tr>
<th>Time / hours</th>
<th>Charges for the anodic current peaks at 1.7 to 1.4 V / Coulomb</th>
<th>Charges for the cathodic peak at -0.25 to -0.35 V / Coulomb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.036</td>
<td>0.029</td>
</tr>
<tr>
<td>0.5</td>
<td>0.058</td>
<td>0.084</td>
</tr>
<tr>
<td>1</td>
<td>0.041</td>
<td>0.036</td>
</tr>
<tr>
<td>2</td>
<td>0.033</td>
<td>0.035</td>
</tr>
<tr>
<td>5</td>
<td>0.038</td>
<td>0.040</td>
</tr>
<tr>
<td>24</td>
<td>0.025</td>
<td>0.030</td>
</tr>
</tbody>
</table>
Figure 4.6 Reduction sweep after oxidation of Pb-0.42%Ag anodes at 1.80 V in 150 g L\(^{-1}\) H\(_2\)SO\(_4\) for various times

\[
PbSO_4 \rightarrow Pb
\]

Figure 4.7 Reduction sweep after oxidation of Pb-0.42%Ag anodes at 2.00 V in 150 g L\(^{-1}\) H\(_2\)SO\(_4\) for various times

\[
PbO, PbSO_4 \rightarrow Pb
\]

\[
PbO_2 \rightarrow PbSO_4
\]
When the electrode was oxidised at 2.0 V for over 24 hours (Figure 4.7), there are additional broad reduction peaks at potentials below -0.4 V following the reduction peak of lead sulphate to metallic lead. Although the source of these peaks is not known, it is interesting to note that they only appear after extended times at potentials above ~2.0 V at which potentials O₂ evolution visibly occurred at a significantly increased rate.

4.2 Potentiostatic Oxidation of Lead-Silver Anodes in Sulphuric Acid Solutions Containing Manganese

4.2.1 Effect of Manganese at Various Potentials

Purified industrial zinc sulphate electrolytes often contain 1-10 g L⁻¹ Mn(II) that is oxidised at oxygen-evolving Pb/PbO₂ anodes. One of the objectives of this study is to investigate the fundamental electrochemistry of the oxidation of manganese on Pb-Ag anodes and the oxidation of these lead alloy anodes in the presence of manganese. The tests were conducted potentiostatically at 1.5, 1.6, 1.7, 1.8, 1.85, 1.9, 1.95 and 2.0 V for 2 hours at 40°C in 100 mL solutions containing either 150 g L⁻¹ H₂SO₄ or 150 g L⁻¹ H₂SO₄ and 5 g L⁻¹ Mn(II). After 2 hours, the electrode was subjected to a negative potential sweep. The rotating disc electrode made of Pb-0.42%Ag was used as the working electrode with a rotation speed of 500 rpm.

The oxidation of Mn²⁺ to Mn³⁺ and Mn²⁺ to MnO₄⁻ both have similar standard potentials of about 1.51 V.

\[
\begin{align*}
\text{Mn}^{2+} &= \text{Mn}^{3+} + e^- & \text{E}^0 &= 1.509 \text{ V} \quad (4.2) \\
\text{Mn}^{2+} + 4\text{H}_2\text{O} &= \text{MnO}_4^- + 8\text{H}^+ + 5e^- & \text{E}^0 &= 1.512 \text{ V} \quad (4.3)
\end{align*}
\]
However, the very low current densities observed in an acidic manganese solution (Figure 4.9) at potentials of 1.7 V and below suggest that there is little oxidation of manganese ions at these potentials. The current densities at 1.5 and 1.6 V are similar to those observed in the absence of manganese ions as shown in Figure 4.8. During oxidation at 1.7 V in both solutions, there is an indication that lead (and/or manganese ions) is undergoing a degree of oxidation in that the current tended to increase after longer times. At 1.8 V and above, the current in the presence of manganese ions is noticeably greater which suggests either that such potentials are required for the oxidation of manganese ions or that oxidation proceeds more readily on a PbO₂ surface.

The current density increased substantially at higher potentials and the steady state current densities during oxidation at 2.0 V were ~550 A m⁻² and ~900 A m⁻² in the absence and presence of 5 g L⁻¹ Mn(II) respectively.

Figure 4.8 Current-time transient during oxidation of Pb-0.42%Ag anodes at various potentials in a solution containing 150 g L⁻¹ H₂SO₄
The maximum increase in current density as a result of the oxidation of manganese ions is that for mass transport of manganese ions to the surface of the disk. This can be calculated from the Levich equation

\[ i_L = 41.8 \, n \, C \, D^{2/3} \, \omega^{1/2} \]

in which, \( i_L \) is the limiting current density in A cm\(^{-2} \), \( n \) the number of electrons involved, \( C \) the concentration in mol L\(^{-1} \), \( D \) the diffusion coefficient in cm\(^2\) s\(^{-1} \) and \( \omega \) the rotation speed in rev min\(^{-1} \).

Thus, for \( n=1 \) (i.e. Mn(III) as the product of oxidation), \( C = 5/55 \) mol L\(^{-1} \), assumed \( D = 5 \times 10^{-6} \) cm\(^2\) s\(^{-1} \) and \( \omega = 500 \) rev min\(^{-1} \),

\[ i_L = 247 \, A \, m^{-2} \]
which is similar to the increase in current density observed at 2.0 V on addition of 5 g L⁻¹ manganese ions. If permanganate were the product of oxidation this calculated maximum increase would be n=5 times greater.

Figure 4.10 shows the reduction sweeps after 2 hours potentiostatic oxidation in acid solution at 1.5 to 2.0 V and an enlarged view of the voltammograms between 1.4 and 1.7 V is presented in the inset. The cathodic peak at 1.55 V is due to the reduction of PbO₂ to PbSO₄ and only appeared after 2 hours oxidation at potentials of 1.7 V and above. Thus, as indicated above, oxidation of PbSO₄ to PbO₂ only occurs at potential of 1.7 V and above. The slow increase in current at 1.7 V after about 5000 seconds in Figures 4.8 and 4.9 is therefore probably due to the onset of formation of PbO₂. Oxidation of manganese ions appears to be dependent on the formation of PbO₂ in that the current density after 7000 seconds at 1.7 V is noticeably greater in the presence of manganese ions. The charge associated with the reduction of PbO₂ to PbSO₄ increases with increasing potential, while the charge associated with the reduction of PbSO₄ to Pb at around -0.375 V is greater and does not appear to vary consistently with increasing holding potential. The higher charge associated with the peaks in the lower potential region suggests that the layer produced by anodic oxidation consists of both PbSO₄ and PbO₂.
Figure 4.10 Reduction sweep after 2 hours oxidation of Pb-0.42%Ag anodes at 1.5-2.0 V in 150 g L$^{-1}$ H$_2$SO$_4$

Figure 4.11 shows the reduction sweeps after 2 hours oxidation in solutions with added manganese ions at 1.5 to 2.0 V with the inset showing the voltammograms between 1.2 and 1.7 V. It is interesting to note that there is no obvious peak for the reduction of PbO$_2$ after oxidation at all potentials. This suggests that the formation of PbO$_2$ is in some way inhibited in the presence of manganese ions and/or manganese ions are oxidized by PbO$_2$. Instead, a broad anodic peak appears in the region of 1.4 to 1.6 V which is most probably due to the oxidation of manganese ions. When the electrode was oxidised at 1.8 V and 1.85 V, there is also an additional reduction peak at ~1.275 V following the manganese oxidation peak. The magnitude of this reduction peak is lower after oxidation at 1.85 V. This peak probably corresponds to the reduction of MnO$_2$ to Mn(II) ($E^0$ for MnO$_2$/Mn$^{2+}$ is 1.223 V and for MnO$_2$/Mn$^{3+}$ is 0.98V).
Figure 4.11 Reduction sweep after 2 hours oxidation of Pb-0.42%Ag anodes at 1.5-2.0 V in 150 g L\(^{-1}\) H\(_2\)SO\(_4\) and 5 g L\(^{-1}\) Mn(II)

The oxidation of manganese ions during the potential sweeps in the region 1.6 to 1.4 V suggests that these reactions are more rapid on a lead alloy surface than on a PbO\(_2\) surface which is reduced to PbSO\(_4\) partially exposing the alloy in this potential region. Comparison of the peak areas for the reduction of PbSO\(_4\) shows that the amount of PbSO\(_4\) formed increases in the presence of manganese ions as shown in Table 4.4. This observation could possibly be explained by reduction of PbO\(_2\) by Mn(II) in the electrolyte according to reaction (4.4).

\[
2\text{Mn}^{2+} + \text{PbO}_2 + \text{HSO}_4^{-} + 3\text{H}^+ \rightarrow 2\text{Mn}^{3+} + \text{PbSO}_4 + 2\text{H}_2\text{O} \quad (4.4)
\]
Table 4.4 Effect of manganese on the charge involved in the oxidation of lead during oxidation of a Pb-0.42%Ag anode at various potentials

<table>
<thead>
<tr>
<th>Potential / V</th>
<th>150 g L⁻¹ H₂SO₄</th>
<th>150 g L⁻¹ H₂SO₄ + 5 g L⁻¹ Mn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>QₚbSO₄ / Coulomb</td>
<td>QₚbO₂ / Coulomb</td>
</tr>
<tr>
<td>1.5</td>
<td>0.301</td>
<td>0.000</td>
</tr>
<tr>
<td>1.6</td>
<td>0.232</td>
<td>0.000</td>
</tr>
<tr>
<td>1.7</td>
<td>0.263</td>
<td>0.001</td>
</tr>
<tr>
<td>1.8</td>
<td>0.237</td>
<td>0.023</td>
</tr>
<tr>
<td>1.85</td>
<td>0.236</td>
<td>0.014</td>
</tr>
<tr>
<td>1.9</td>
<td>0.258</td>
<td>0.012</td>
</tr>
<tr>
<td>1.95</td>
<td>0.288</td>
<td>0.028</td>
</tr>
<tr>
<td>2.0</td>
<td>0.335</td>
<td>0.073</td>
</tr>
</tbody>
</table>

4.2.1.1 Observations of the Oxidation of Manganese

At the start of potentiostatic oxidation at potentials of 1.8 V and higher, traces of purple MnO₄⁻ ion were observed streaming from the rotating anode. The permanganate ions were rapidly reduced by Mn(II) ions to precipitate MnO₂ (or MnOOH) on the surface of the lead anode and on the surrounding epoxy shroud of the rotating disc electrode. The colour of the electrolyte also became noticeably more red/pink due to the gradual formation of Mn(III) ions as is commonly found in the spent electrolyte in zinc electrowinning plants. The visible production of permanganate appeared to decrease with time of oxidation until no permanganate was observed at long times.

After the oxidation period, the electrolyte was analysed for manganese species by UV Visible Spectroscopy. The visible spectra which showed only a broad absorbance band around 485 nm, suggested that the electrolyte only contained manganic and not
permanganate ions. The manganic ion concentration was determined by first reacting the solution with excess ferrous ammonium sulphate and back titrating the excess ferrous ions with potassium dichromate. The manganese present as MnO₂ was also determined by reaction with excess ferrous ammonium sulphate and back titration with potassium dichromate. The charges equivalent to the oxidation of manganese ions to Mn³⁺ and MnO₂ measured after potentiostatic oxidation at 1.5 to 2.0 V and subsequent reductive sweeps are tabulated in Table 4.5.

Table 4.5 Charge associated with manganese oxidation at different potentials

<table>
<thead>
<tr>
<th>Potential of Oxidation</th>
<th>Q(Mn³⁺)/Coulomb</th>
<th>Q(MnO₂)/Coulomb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 V</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1.6 V</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1.7 V</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1.8 V</td>
<td>0.464</td>
<td>0.058</td>
</tr>
<tr>
<td>1.85 V</td>
<td>0.926</td>
<td>0.058</td>
</tr>
<tr>
<td>1.9 V</td>
<td>1.389</td>
<td>0.174</td>
</tr>
<tr>
<td>1.95 V</td>
<td>1.853</td>
<td>0.058</td>
</tr>
<tr>
<td>2.0 V</td>
<td>18.284</td>
<td>0.405</td>
</tr>
</tbody>
</table>

As can be seen from Table 4.5, the amount of manganese oxidised increases with increasing potential. This result is consistent with the results shown in Figure 4.9 in which the current density increased at the higher potentials during oxidation in the solution containing manganese ions. Manganese dioxide is probably formed by disproportionation of Mn³⁺ as suggested by Yu and O’Keefe (2002) and Kelsall et al. (2000). The Mn³⁺ ions are formed through reaction between Mn²⁺ and MnO₄⁻ and also possibly by direct anodic oxidation of Mn²⁺ or by oxidation of Mn²⁺ by PbO₂ (reaction 4.4).
4.2.2 Effect of Varying Concentration of Manganese(II) Ions

A series of experiments were carried out in 100 mL solutions of 150 g L\(^{-1}\) H\(_2\)SO\(_4\) containing 0.1, 1, 5 or 10 g L\(^{-1}\) Mn(II) at 40ºC. In each case, potentiostatic oxidation was carried out at 1.8, 1.85, 1.9, 1.95 and 2.0 V for 2 hours followed by a reduction sweep as before. The tests were performed using the Pb-0.42%Ag alloy at a rotation speed of 500 rpm.

At 1.8 V (Figure 4.12), the cumulative charge passed during potentiostatic oxidation increased with increasing manganese ion concentration and the current time transients exhibit a broad maximum indicating that continuous oxidation occurs at higher manganese concentrations. At this potential the rate of oxidation of manganese ions is not mass transport controlled as the increase in current density in the presence of manganese ions is considerably less than that estimated above for the limiting current density at all concentrations. During the reduction sweep, the peak for reduction of PbO\(_2\) is only observed at the lowest manganese concentration. At higher concentrations, a broad anodic plateau is observed at potentials above about 1.4 V with a slight peak at about 1.5 V. The anodic currents increase with increasing concentration of manganese ions in this potential region and it is possible that the peak at 1.5 V is due to enhanced oxidation of manganese ions on the surface after reduction of PbO\(_2\). The charge associated with the reduction of “MnO\(_2\)” is only a small fraction of the anodic charge due to oxidation of manganese ions which confirms that soluble manganese ions (Mn\(^{3+}\) and/or MnO\(_4^{-}\)) are the main products of oxidation at these potentials. The cathodic peak at 1.2 to 1.3 V due to reduction of MnO\(_2\) is observed for all manganese concentrations except the lowest. The charge associated with reduction of PbSO\(_4\) also increases with increasing manganese ion concentration.
Figure 4.12 Effect of manganese concentration on potentiostatic oxidation of Pb-0.42%Ag anodes at 1.8 V and the subsequent potential sweep in a negative direction.
At 1.85 V (Figure 4.13), the current-time transient exhibited a different shape in that, at longer times, the current decayed to roughly the same pseudo-steady-state values observed at 1.8 V. Although the peak currents increased with increasing manganese ion concentration, the current at longer times did not appear to be related to the concentration. Again, during the reduction sweep, the peak for reduction of PbO$_2$ is only observed at the lowest manganese ion concentration. At higher concentrations, a more prominent anodic peak due to oxidation of manganese ions is again observed in the region of 1.4 to 1.6 V. The cathodic peak at 1.2 to 1.3 V due to reduction of MnO$_2$ is again observed for all manganese concentrations except for the lowest but these peaks are significantly smaller than those observed after oxidation at 1.8 V. The charge associated with reduction of PbSO$_4$ also increases with increasing manganese ion concentration but is lower than observed after oxidation at 1.8 V. This could be expected in that oxidation of PbSO$_4$ is likely to be more rapid at the higher holding potential.

Similar trends were observed after oxidation at 1.9 V (Figure 4.14). However, the cathodic peak at 1.25 V was no longer present and this was also apparent in all subsequent experiments at higher potentials. The reason for this is not clear at this stage but could be due to the formation of a different manganese oxide at lower potentials which is more easily reduced.
Figure 4.13 Effect of manganese concentration on potentiostatic oxidation of Pb-0.42%Ag anodes at 1.85 V and the subsequent potential sweep in a negative direction
Figure 4.14 Effect of manganese concentration on potentiostatic oxidation of Pb-0.42%Ag anodes at 1.9 V and the subsequent potential sweep in a negative direction
After oxidation at 1.95 and 2.0 V (Figures 4.15 and 4.16 respectively) at which potentials O₂ evolution visibly occurred at a significantly increased rate, the magnitude of the anodic peak due to manganese oxidation and that of the reduction of PbSO₄ to Pb were not appreciably affected by the increase in the manganese concentration from 1 to 10 g L⁻¹. The considerable noise in the current during oxidation at these potentials in the presence of high concentrations of manganese suggests that the oxidation of manganese ions was occurring close to the mass transport controlled rate which is perturbed by the evolution of oxygen bubbles. Use of the Levich equation (Sec 4.2.1) for calculation of mass transport to a rotating disk electrode resulted in a limiting current density of about 250 A m⁻² for oxidation of manganese by a 1-electron process at a concentration of 5 g L⁻¹. This is consistent with the difference in final current densities observed at 1.95 V and at 2.0 V in the presence and absence of manganese ions.
Figure 4.15 Effect of manganese concentration on potentiostatic oxidation of Pb-0.42%Ag anodes at 1.95 V and the subsequent potential sweep in a negative direction
Figure 4.16 Effect of manganese concentration on potentiostatic oxidation of Pb-0.42%Ag anodes at 2.0 V and the subsequent potential sweep in a negative direction
In the presence of manganese, the total charge ($Q_T$) passed will be equal to the sum of 
the charge for the oxidation of lead ($Q_{\text{Pb}}$), the oxidation of manganese ($Q_{\text{Mn}}$) and that 
for the evolution of oxygen ($Q_{\text{O}_2}$). Figures 4.17 to 4.19 show the effect of varying 
manganese ion concentration on the fractions of the total charge attributable to these 
processes during oxidation at each potential. It can be seen that below 1.9 V the 
presence of manganese greatly suppresses the oxidation of lead and most of the charge 
is utilised for oxidation of manganese. The data for 0.1 g L$^{-1}$ manganese is probably not 
reliable given the very small amounts of oxidised manganese products at this potential. 
At potentials above 1.9 V where oxygen evolution occurs more readily, the effect of 
manganese on the extent of oxidation of lead is minimal. However, the rate of oxygen 
evolution is suppressed in the presence of manganese ions although the effect does not 
appear to be directly proportional to the manganese concentration.

Figure 4.17 Effect of manganese concentration on the charge fraction for lead oxidation 
at different potentials
Figure 4.18 Effect of manganese concentration on the charge fraction for manganese oxidation at different potentials

Figure 4.19 Effect of manganese concentration on the charge fraction for oxygen evolution at different potentials
It is apparent that these results are only indicative of the early stages of oxidation of the alloys and do not reflect the steady-state behavior in the various solutions. The results in the following section at longer times are a more realistic indication of the longer term behavior.

4.2.3 Effect of Time of Oxidation

In a series of tests in 200 mL of 150 g L\(^{-1}\) H\(_2\)SO\(_4\) with various Mn(II) ion concentrations (0.1, 1, 5 and 10 g L\(^{-1}\)), the oxidation time was varied from 15 minutes up to 48 hours at a constant potential of 2.0 V which most closely approximates the operating potential of an anode in practice. Each test was followed by a negative-going potential sweep and analyses of the solids and solutions for the oxidised forms of manganese. The temperature was held constant at 40°C and the Pb-0.42%Ag alloy electrode was rotated at 500 rpm. Figure 4.20 shows the current-time transient during oxidation of the lead anode at 2.0 V for 24 hours in each solution.

The linear sweep voltammograms obtained for the various manganese concentrations are shown in Figures 4.21 to 4.24 after various oxidation periods at 2.0 V. It can be seen that the peak for the reduction of PbO\(_2\) to PbSO\(_4\) at ~1.55 V was absent for periods up to 5 hours but reappeared after 24 and 48 hours in a solution of 5 and 10 g L\(^{-1}\) Mn(II) (Figures 4.23 and 4.24). At lower concentrations (0.1 and 1 g L\(^{-1}\)) of manganese ions, this peak was present after 5 hours oxidation (Figures 4.21 and 4.22). The charge associated with this peak was also reduced with increasing manganese ion concentration.
It was also noticed that after oxidation for 24 hours in 1 g L\(^{-1}\) Mn(II) and 48 hours in 5 g L\(^{-1}\) Mn(II), a black powder (presumably a form of MnO\(_2\)) also formed in the bulk electrolyte and on the walls of the cell as a result of a chemical precipitation reaction (Ipinza et al. 2003).

Figure 4.20 Current-time transient during oxidation of Pb-0.42%Ag anodes at 2.0 V for 24 hours in a solution containing various manganese concentrations
Figure 4.21 Voltammograms in 150 g L$^{-1}$ H$_2$SO$_4$ and 0.1 g L$^{-1}$ Mn after oxidation of Pb-0.42%Ag anodes at 2.0 V for various times

Figure 4.22 Voltammograms in 150 g L$^{-1}$ H$_2$SO$_4$ and 1 g L$^{-1}$ Mn after oxidation of Pb-0.42%Ag anodes at 2.0 V for various times
Figure 4.23 Voltammograms in 150 g L\(^{-1}\) H\(_2\)SO\(_4\) and 5 g L\(^{-1}\) Mn after oxidation of Pb-0.42\%Ag anodes at 2.0 V for various times

Figure 4.24 Voltammograms in 150 g L\(^{-1}\) H\(_2\)SO\(_4\) and 10 g L\(^{-1}\) Mn after oxidation of Pb-0.42\%Ag anodes at 2.0 V for various times
Figure 4.25 summarizes the relevant fractions of charge involved in the main reactions after various times of oxidation in the presence of increasing concentrations of manganese ions. It is apparent that the rate of oxidation (as reflected in the charge fraction) of lead is initially high but that it decreases significantly with increasing time of oxidation. This is consistent with previous studies of the corrosion of lead alloy anodes under similar conditions. Concentrations of manganese above 0.1 g L\(^{-1}\) appear to reduce the fraction of charge associated with the oxidation of lead. The oxidation of manganese is also initially greater and the fraction generally increases with increasing concentration of manganese except that shown for 1 g L\(^{-1}\) manganese which was also observed in other experiments (Figure 4.18). The reason for this apparently consistent but unusual trend is not known at this stage but may be associated with the relative rates of mass transport of Mn(III) or Mn(VII) ions from the surface of the electrode and disproportionation to MnO\(_2\) on the surface of the electrode. Thus, at high (>1 g L\(^{-1}\)) concentrations of manganese ions, the rate of the reaction (4.5) would proceed rapidly on the surface of the anode and the disproportionation reaction (4.6) would result in precipitation of MnO\(_2\) on the surface which may inhibit further oxidation. Additional experiments at varying electrode rotation speed could assist in the interpretation of this unusual observation.

\[
\begin{align*}
\text{MnO}_4^- + 4\text{Mn}^{2+} + 8\text{H}^+ &= 5\text{Mn}^{3+} + 4\text{H}_2\text{O} \quad \text{(4.5)} \\
2\text{Mn}^{3+} + 2\text{H}_2\text{O} &= \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+ \quad \text{(4.6)}
\end{align*}
\]

As could be expected at this potential, oxygen evolution is the main reaction and it becomes more dominant as the oxidation period increases. High concentrations of manganese ions do reduce the fraction of the charge associated with oxygen evolution even after long periods of oxidation.
Figure 4.25 Effect of manganese concentration on the charge fractions for (A) oxidation of lead, (B) oxidation of manganese and (C) evolution of oxygen at 2.0 V for Pb-0.42%Ag anode
Two sets of experiments were also performed at potentials of 1.95 and 2.05 V, at which potentials the main reaction is, as expected, oxygen evolution. The results show similar trends as those above in terms of the effects of increasing Mn(II) concentrations (Figures 4.27 and 4.28). The steady state current densities after 48 hours polarisation in 5 g L\(^{-1}\) Mn(II) were 250, 450 and 1100 A m\(^{-2}\) at 1.95, 2.0 and 2.05 V respectively (Figure 4.26). At the industrial operating current density of about 500 A m\(^{-2}\), the partial current density for the oxidation of manganese is about 25 A m\(^{-2}\) in a solution containing 5 g L\(^{-1}\) manganese. This would obviously account for the significant rate of production of manganese oxide scale and sludge in operating cells. Increasing the potential from 1.95 to 2.05 V increased the rate of oxygen evolution but also increased the amount of PbO\(_2\), and MnO\(_2\) formed as shown in Table 4.6.

Table 4.6 Effect of potential of oxidation on the charges during oxidation in a solution containing 150 g L\(^{-1}\) H\(_2\)SO\(_4\) and 5 g L\(^{-1}\) Mn(II) for 48 hours

<table>
<thead>
<tr>
<th>Potential of Oxidation / V</th>
<th>Q(Pb) / Coulomb</th>
<th>Q(Mn(^{3+})) / Coulomb</th>
<th>Q(MnO(_2)) / Coulomb</th>
<th>Q(O(_2)) / Coulomb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.95</td>
<td>1.481</td>
<td>40.292</td>
<td>2.721</td>
<td>900.5</td>
</tr>
<tr>
<td>2.0</td>
<td>1.620</td>
<td>25.287</td>
<td>67.211</td>
<td>1896.4</td>
</tr>
<tr>
<td>2.05</td>
<td>2.138</td>
<td>22.507</td>
<td>141.602</td>
<td>3486.0</td>
</tr>
</tbody>
</table>
Figure 4.26 Current-time transients during oxidation of Pb-0.42%Ag anodes at various potentials for 48 hours in a solution containing 150 g L$^{-1}$ H$_2$SO$_4$ and 5 g L$^{-1}$ Mn(II) and the subsequent potential sweep in a negative direction.
Figure 4.27 Effect of manganese concentration on the charge fractions for (A) oxidation of lead, (B) oxidation of manganese and (C) evolution of oxygen at 1.95 V for Pb-0.42%Ag anode
Figure 4.28 Effect of manganese concentration on the charge fractions for (A) oxidation of lead, (B) oxidation of manganese and (C) evolution of oxygen at 2.05 V for Pb-0.42%Ag anode
4.2.4 Effect of Varying Silver Content in the Alloy

Lead-silver anodes with a silver content ranging from about 0.5 to 1% are used in the zinc electrowinning process. It has been previously pointed out that silver has a significant effect in reducing the corrosion rate of the lead anode and in lowering the overpotential for oxygen evolution reaction. The superior performance of the lead-silver anode over pure lead anode is believed to be due to the presence of silver oxide, most probably Ag$_2$O$_2$, in the PbO$_2$ layer of the metal substrate (McGinnity 2008). Oxygen evolution occurs preferentially at lower overpotentials on this silver oxide surface. It was considered useful to assess the effect of varying the silver content of the anodes on the rates of oxidation of both lead and manganese as well as oxygen evolution. Samples of commercial materials with silver contents of 0.25, 0.42, 0.75, 1 and 2% were provided by RSR Technologies. The experiments were performed in 200 mL solution containing either 150 g L$^{-1}$ H$_2$SO$_4$ or 150 g L$^{-1}$ H$_2$SO$_4$ and 5 g L$^{-1}$ Mn(II) at 40°C with an electrode rotation speed of 500 rpm.

Cyclic voltammograms of the pure lead anode and the five different lead-silver alloys were obtained to identify the reactions occurring on the surface of the electrode in the absence and presence of 5 g L$^{-1}$ Mn(II) at 1 mV s$^{-1}$ scan rate. In all cases the scan was started from the open circuit potential at about -0.35 V to positive potentials, and reversed when the current density reached ~500 A m$^{-2}$. The scan was finished at -0.8 V at which potential the evolution of hydrogen commenced. This potential range was selected to cover all reactions of interest in the electrochemistry of lead.

Figure 4.29 summarizes the voltammetric scans of the anode surfaces in the absence of manganese. As the potential was swept in a positive direction, the first anodic peak is due to the oxidation of Pb to PbSO$_4$ at about -0.31 V. The anodic peak for the
formation of PbO\(_2\) which was coincided with the simultaneous evolution of oxygen gas occurs at potentials above 1.8 V. On the reverse scan, three cathodic peaks are observed which are due to the reduction of PbO\(_2\) to PbSO\(_4\) at about 1.56 V followed by that of (PbO.PbSO\(_4\)) to Pb, and PbSO\(_4\) to Pb at about -0.28 and -0.36 V respectively. It appears that increasing the silver content of the anodes resulted in a decrease of the anode overpotential for the oxygen evolution reaction. The extents of oxidation of lead on the lead-silver anodes were also lower compared to pure lead as shown by the smaller anodic peak at -0.31 V and the smaller cathodic peak at -0.2 to -0.7 V.

![Voltammetric scans of freshly polished lead-silver anodes with various silver content in 150 g L\(^{-1}\) H\(_2\)SO\(_4\) solution](image)

In the presence of 5 g L\(^{-1}\) manganese (Figure 4.30), again the anodic peak for the formation of PbSO\(_4\) at about -0.31 V and that for the formation of PbO\(_2\) and the simultaneous evolution of oxygen gas at potential above 1.8 V were observed. On the
reverse scan, an anodic peak is observed in the region of 1.55 to 1.8 V due to the “reactivation” of manganese ion oxidation which is associated with the reduction of PbO₂ (reaction 4.4) and followed by cathodic peaks for the reduction of (PbO.PbSO₄) to Pb, and PbSO₄ to Pb at -0.2 to -0.7 V. The addition of 0.25% Ag on the alloys revealed similar voltammetric scans to those of pure lead. When the silver content is above 0.25%, the magnitude of these peaks is higher confirming that silver has an electrocatalytic effect on the oxidation of manganese (Yu & O’Keefe 2002; Cachet, Rerolle & Wiart 1999).

![Voltammetric scans of freshly polished lead-silver anodes with various silver contents in 150 g L⁻¹ H₂SO₄ and 5 g L⁻¹ Mn(II) solution](image)

Potentiostatic oxidation tests at 2.0 V were carried out with each anode for 24 hours followed by a potential sweep in the negative direction (Figure 4.31). The measurements were performed at 40°C with a rotation speed of the rotating disc electrode of 500 rpm in 200 mL of solution containing 150 g L⁻¹ H₂SO₄ and 5 g L⁻¹ Mn(II). It is apparent that the rate of oxidation initially increased with increasing silver
content in the alloy. However, at longer times the current decayed to roughly the same pseudo-steady-state values of about 500 A m⁻². Increasing the silver content of the anodes also led to a decrease of the amount of lead oxidized.

Figure 4.31 Effect of silver content of the Pb-Ag anode on potentiostatic oxidation at 2.0 V and the subsequent potential sweep in a negative direction in 150 g L⁻¹ H₂SO₄ and 5 g L⁻¹ Mn(II) solution
Table 4.7 and Figure 4.32 summarize the relevant fractions of charge involved in the main reactions after 24 hours oxidation of the various alloys. It is noticeable that increasing the silver alloy concentrations increased the cumulative charge passed (increased current density at the same potential) and also increased the extent of oxidation of manganese and the formation of MnO$_2$ both on the anode and in the electrolyte. The rate of oxygen evolution was also reduced with increasing silver content. The behavior appears to be similar for silver contents of about 0.75% and greater.

Table 4.7 Effect of silver alloy content on the charge fraction for oxidation of Pb and Mn and evolution of O$_2$

<table>
<thead>
<tr>
<th>Ag %</th>
<th>Charge Fraction for Pb Oxidation, $Q_{\text{Pb}}/Q_T$</th>
<th>Charge Fraction for Mn Oxidation, $Q_{\text{Mn}}/Q_T$</th>
<th>Charge Fraction for O$<em>2$ Evolution, $Q</em>{\text{O}_2}/Q_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.005</td>
<td>0.039</td>
<td>0.956</td>
</tr>
<tr>
<td>0.25</td>
<td>0.001</td>
<td>0.013</td>
<td>0.986</td>
</tr>
<tr>
<td>0.42</td>
<td>0.001</td>
<td>0.026</td>
<td>0.973</td>
</tr>
<tr>
<td>0.75</td>
<td>0.001</td>
<td>0.106</td>
<td>0.893</td>
</tr>
<tr>
<td>1.00</td>
<td>0.001</td>
<td>0.076</td>
<td>0.923</td>
</tr>
<tr>
<td>2.00</td>
<td>0.001</td>
<td>0.092</td>
<td>0.908</td>
</tr>
</tbody>
</table>
Figure 4.32 Effect of silver content of the Pb-Ag anode on the charge fractions for oxidation of both lead and manganese and evolution of oxygen at 2.0 V

4.3 Potentiostatic Oxidation of Lead-Calcium-Tin Anodes in Sulphuric Acid

Alloys containing lead, calcium and tin are used extensively in the electrowinning of copper and low concentrations of manganese in the electrolyte are suspected as being responsible for greater contamination of the cathodes by lead. It was therefore considered relevant to investigate the behaviour of these anodes in the presence of manganese ions. In a series of tests, the anodic behaviour of a Pb-Ca-Sn anode in acid solution was studied by varying the oxidation time from 30 minutes up to 24 hours at a constant potential of 1.8, 1.9 or 2.0 V, followed by a potential sweep in the negative direction. The acid concentration in the solution was fixed at 150 g L\(^{-1}\) H\(_2\)SO\(_4\) at 40°C. The total volume of the solution was 200 mL. The working electrode was the rotating
disc electrode made from a commercial Pb-0.08%Ca-1.3%Sn-0.01%Al anode rotated at 500 rpm.

The cumulative charge ($Q_T$) passed during oxidation for 24 hours at each potential was obtained from the current-time curves shown in Figure 4.33. It is apparent from the current densities measured and the total charge passed that the rate of oxidation increases substantially with potential and time. Oxygen evolution was readily observed at 2.0 V. The steady state current density during potentiostatic oxidation of the Pb-Ca-Sn anode at 2.0 V in sulphuric acid electrolyte was ~80 A m$^{-2}$, which is about six times lower than that of a Pb-Ag anode under the same conditions.

![Figure 4.33](image)

Figure 4.33 Current-time transients during oxidation of Pb-Ca-Sn anodes at various potentials in a solution containing 150 g L$^{-1}$ H$_2$SO$_4$

Figure 4.34 shows the reduction scans of the Pb-Ca-Sn anode surfaces after oxidation at each potential for 24 hours. As the potential was swept in a negative direction, three cathodic peaks are observed which are due to the reduction of PbO$_2$ to PbSO$_4$ at ~1.55
V followed by that of (PbO.PbSO₄) to Pb, and PbSO₄ to Pb at -0.3 and -0.4 V respectively. The appearance of anodic current peaks during or after the peaks for the reduction of PbO₂ to PbSO₄ at about 1.55 V are due to oxidation of lead exposed in the process of reduction of PbO₂ to PbSO₄. The charge associated with these peaks can be correlated with that for the cathodic peak appearing at about -0.3 V which has previously been assigned to the reduction of “PbO” (Sharpe 1975). It can be seen that increasing the oxidation potential results in an increase in the extent of formation of PbO₂ and PbO. The oxidation of Pb-Ca-Sn anodes results in a greater amount of “PbO” than observed with Pb-Ag anodes. The broad reduction peak at potentials below -0.4 V which has been observed when using a Pb-Ag anode (Figure 4.7) also appears with the Pb-Ca-Sn anode when oxidized at 2.0 V for 24 hours. A comparison of the charges associated with oxidation of lead (Qₚb) and oxygen evolution (Qₒ₂) between the two different anodes are summarised in Table 4.8.

Figure 4.34 Reduction sweeps after oxidation of Pb-Ca-Sn anodes at each potential in 150 g L⁻¹ H₂SO₄ for 24 hours
Table 4.8 Charge fractions during oxidation of the Pb-0.75%Ag and Pb-Ca-Sn anodes in 150 g L\(^{-1}\) H\(_2\)SO\(_4\) for 24 hours at different potentials

<table>
<thead>
<tr>
<th>Potential / V</th>
<th>Total Charge, (Q_T) / Coulomb</th>
<th>Charge Fraction for Pb Oxidation, (Q_{Pb}/Q_T)</th>
<th>Charge Fraction for O(<em>2) Evolution, (Q</em>{O2}/Q_T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-Ag</td>
<td>Pb-Ca-Sn</td>
<td>Pb-Ag</td>
<td>Pb-Ca-Sn</td>
</tr>
<tr>
<td>1.8</td>
<td>2.611</td>
<td>0.250</td>
<td>0.275</td>
</tr>
<tr>
<td>1.9</td>
<td>65.869</td>
<td>0.012</td>
<td>0.087</td>
</tr>
<tr>
<td>2.0</td>
<td>867.129</td>
<td>0.002</td>
<td>0.011</td>
</tr>
</tbody>
</table>

As can be seen from Table 4.8, the charges attributable to the evolution of oxygen during oxidation of Pb-Ca-Sn anodes at all potentials for 24 hours were slightly lower than those of Pb-Ag anodes and this coupled with the considerably higher current densities observed on the Pb-Ag anodes confirms that silver exhibits a catalytic effect on the oxygen evolution reaction (Cachet, Rerolle & Wiart 1996; Ivanov et al. 2000).

### 4.4 Potentiostatic Oxidation of Lead-Calcium-Tin Anodes in Sulphuric Acid Solutions Containing Manganese

These tests were conducted potentiostatically at 1.7, 1.8, 1.9 and 2.0 V for 30 minutes up to 24 hours at 40°C in 200 mL of a solution containing 150 g L\(^{-1}\) H\(_2\)SO\(_4\) with either 0.1 or 1.0 g L\(^{-1}\) Mn(II). Each test was followed by a negative-going potential sweep and analyses of the oxidised forms of manganese present as solids or in solution after the cathodic sweep.
Figures 4.35 and 4.36 show the current-time transients during 24 hours oxidation of the Pb-Ca-Sn anodes at various potentials in 0.1 and 1.0 g L\(^{-1}\) acidic manganese solutions respectively. During oxidation at 1.7 V, there is little oxidation of lead and/or manganese ions in both solutions. However, at potentials of 1.8 V and above, it is noticeable that the current in the presence of manganese ions is greater and increases with increasing manganese ion concentration. After a certain period, there was a significant decrease in the current which suggests that the rate of oxidation of manganese is lower on an oxidised lead surface or a surface coated with manganese oxides. The current achieves a steady state value of \(~120\ A\ m^{-2}\) during potentiostatic oxidation at 2.0 V for 24 hours in both acidic manganese solutions compared to about 80 A m\(^{-2}\) in the absence of manganese.

![Figure 4.35 Current-time transients during oxidation of Pb-Ca-Sn anodes for 24 hours at various potentials in a solution containing 150 g L\(^{-1}\) H\(_2\)SO\(_4\) and 0.1 g L\(^{-1}\) Mn(II)](image-url)
Figure 4.36 Current-time transients during oxidation of Pb-Ca-Sn anodes for 24 hours at various potentials in a solution containing 150 g L\(^{-1}\) H\(_2\)SO\(_4\) and 1.0 g L\(^{-1}\) Mn(II).

Figure 4.37 shows the reduction sweeps after oxidation in 0.1g L\(^{-1}\) acidic manganese solution at 1.7-2.0 V for 2 hours. As expected there is no obvious peak for reduction of PbO\(_2\) after oxidation at all potentials. Instead, an anodic peak appears in the region of 1.4 to 1.6 V which is most probably due to oxidation of manganese ions. This suggests that the formation of PbO\(_2\) is in some way inhibited in the presence of manganese ions or that any PbO\(_2\) formed is reduced by oxidation of Mn(II) ions (reaction 4.4). The fact that an anodic peak appears during a cathodic sweep suggests that there is a thin PbO\(_2\) layer on the surface of the oxidized anode which inhibits oxidation of manganese ions. Removal of this layer at potentials in the region of 1.5 to 1.6 V where PbO\(_2\) is known to be reduced then allows for the oxidation of manganese ions. When the electrode was oxidised at 1.7 V for 2 hours, there is also an additional reduction peak at ~1.4 V.
following the manganese oxidation peak. This cathodic peak also appears when the electrode was oxidised at 1.7, 1.8 and 1.9 V for 24 hours (Figure 4.38), but these peaks shift to a lower potential of ~1.275 V. These peaks are probably due to the reduction of MnO$_2$ to Mn(III) and/or Mn(II) ($E^0$ for MnO$_2$/Mn$^{2+}$ is 1.223 V). It can also be seen from Figure 4.38 that the peak for the reduction of PbO$_2$ to PbSO$_4$ at ~1.55 V reappeared after 24 hours oxidation at 2.0 V.

Figure 4.37 Reduction sweeps after oxidation of Pb-Ca-Sn anodes at each potentials in 150 g L$^{-1}$ H$_2$SO$_4$ and 0.1 g L$^{-1}$ Mn(II) for 2 hours
Another notable feature on the linear sweep voltammograms of the PbCaSn anodes in the presence of manganese ions is that there is an additional broad cathodic peak in the region of -0.15 to 0.5 V during potentiostatic oxidation at 1.8 V and below (Figures 4.37 and 4.38). When compared with the cyclic voltammograms of a gold electrode in 0.5 M H₂SO₄ with various concentrations of manganese ions (Rogulski et al. 2003), this peak has been correlated to the reduction of MnOOH (reaction 4.9) formed by hydrolysis of Mn(III) ions in reaction (4.7) or reduction of MnO₂ as in reaction (4.8).

\[
\begin{align*}
\text{Mn}^{3+} + 2\text{H}_2\text{O} & \rightarrow \text{MnOOH} + 3 \text{H}^+ \quad (4.7) \\
\text{MnO}_2 + \text{H}^+ + \text{e}^- & = \text{MnOOH} \quad (4.8) \\
\text{MnOOH} + 3 \text{H}^+ + \text{e}^- & \rightarrow \text{Mn}^{2+} + 2 \text{H}_2\text{O} \quad (4.9)
\end{align*}
\]
Ipinza et al. (2007) suggested that amorphous MnOOH is formed in the oxide layer on a PbCaSn anode as the intermediate species in the oxidation to ε-MnO₂. However, further surface analyses are required to confirm the formation of MnOOH on a PbCaSn anode.

Figure 4.39 shows the reduction sweeps after oxidation in 1.0 g L⁻¹ acidic manganese solution at 1.7-2.0 V for 24 hours. Both of the reduction peaks of MnO₂ to Mn²⁺/MnOOH at ~1.2 V and MnOOH to Mn²⁺ ions at the region of 0 V increased with increasing manganese ion concentration and decreasing oxidation potential. There does not appear to be a correlation between the charges associated with the peaks at the 1.2 V and 0 V with that for the former being higher than that for the latter. This suggests that reduction to both soluble Mn²⁺ ions and insoluble MnOOH occurs at 1.2 V. In any event, the oxidation of Mn²⁺ ions during the cathodic sweep is a very small fraction of the oxidation products formed during anodization for 24 hours. Reduction of these oxidation products does not occur during the cathodic sweep. Increasing the concentration of manganese ions also resulted in a decrease of the extent of PbO₂ and PbSO₄ formation.
In the presence of manganese, the total charge ($Q_T$) passed will be equal to the sum of the charge for the oxidation of lead ($Q_{Pb}$), the oxidation of manganese ($Q_{Mn}$) and that for the evolution of oxygen ($Q_{O2}$). Figure 4.40 shows the effect of manganese on the fraction of the total charge attributable to these processes during oxidation at 2.0 V where $O_2$ evolution occurs more readily. It can be seen that the presence of manganese ions suppresses both the oxidation of lead and the evolution of oxygen, while most of the charge is utilised for oxidation of manganese ions. The rate of oxygen evolution is reduced by about 70 % after 24 hours oxidation of the PbCaSn anode at 2.0 V in the presence of 1.0 g L$^{-1}$ manganese. The data for 0.1 g L$^{-1}$ manganese is probably not reliable given the very small amounts of oxidised manganese products formed at this potential. These observations are very different to those made with Pb-Ag anodes and partially explain why the oxidation of manganese ions is a problem in the electrowinning of copper but not in the electrowinning of zinc.
Figure 4.40 Effect of manganese on the charge fractions for (A) oxidation of lead, (B) oxidation of manganese and (C) evolution of oxygen at 2.0 V for Pb-Ca-Sn anode
4.5 Galvanostatic Oxidation of Pure Lead and Lead Alloy Anodes in Acidic Manganese Solutions

In this section, the results of experiments will be presented in which the electrochemical behaviour of pure lead, lead-silver and lead-calcium-tin anodes with respect to the oxygen evolution reaction was studied by applying a constant current to the electrodes in the presence of manganese ions. This was followed by a voltammetric scan in a negative direction at a rate of 1 mV s$^{-1}$. The standard parameters for the galvanostatic oxidation tests were as follows: 200 mL solution containing 150 g L$^{-1}$ H$_2$SO$_4$ with various concentrations of manganese ions (0.1, 1 and 5 g L$^{-1}$), 24 hours oxidation time at 40°C, rotation speed of 500 rpm and current density of either 300 or 500 A m$^{-2}$.

4.5.1 Galvanostatic Oxidation of Pure Lead Anode

The pure lead anode was oxidized at 500 A m$^{-2}$ for 24 hours in electrolytes consisting of 0, 1 or 5 g L$^{-1}$ Mn(II) and 150 g L$^{-1}$ H$_2$SO$_4$. The potential-time curves during anodization are presented in Figure 4.41. In the absence of manganese, the steady state potential after 24 hours galvanostatic oxidation was 2.06 V. The addition of 1 g L$^{-1}$ manganese reduced the overpotential for oxygen evolution by about 30 mV. When the manganese concentration was increased to 5 g L$^{-1}$, the potential also decreased in the first 8 hours by about 40 mV and then started to increase as the thickness of the manganese dioxide layer on the surface of the anode increased, reaching a steady potential of 2.11 V after 24 hours. The considerable noise in the transient in this case is probably associated with the formation and cracking or spalling of this layer.
4.5.2 Galvanostatic Oxidation of Lead-Silver Anode

The Pb-0.75%Ag anode was anodized at 500 A m\(^{-2}\) for 24 hours with various manganese concentrations of 0.1, 1 and 5 g L\(^{-1}\) (Figure 4.42). The overpotential of the Pb-Ag anode was lower by about 60 mV compared to pure lead. The addition of 0.1 and 1 g L\(^{-1}\) manganese ions further decreased the potential by about 10 and 20 mV respectively. At the highest manganese concentration (5 g L\(^{-1}\)), the potential also decreased initially and then increased steadily as the MnO\(_2\) layer built up on the surface of the anode. The considerable oscillation in the potential during oxidation at this high concentration of manganese confirms the physical instability of the MnO\(_2\) layer.
Figure 4.42 Effect of manganese ions on the potential for oxygen evolution on a lead-silver anode at 500 A m$^{-2}$.

Figure 4.43 shows the cathodic sweeps after the galvanostatic oxidation periods of the pure lead and Pb-0.75%Ag anodes at various concentrations of manganese. A decrease in the extent of formation of PbO$_2$ can be seen both when lead-silver alloy was used and manganese ions were present in the electrolyte. Adding more manganese to the electrolyte further decreased the extent of formation of PbO$_2$. During the cathodic sweeps of both anodes in the solutions containing 1 g L$^{-1}$ manganese, an additional anodic plateau appeared in the region between 2.0 to 1.6 V which could be due to the formation of MnO$_2$ on the surface of the anode. However, the deposited MnO$_2$ was not found to be reduced in the cathodic sweep and some black MnO$_2$ was visibly present on the anode surface after the scan. Some MnO$_2$ particles were also observed suspended in the electrolyte.
It is apparent that for both anodes, low concentrations of manganese decreased the overpotential for the oxygen evolution. However, there is evidence for a steady increase in the anode potential with time, which is probably related to the formation of the MnO$_2$ layer on the surface of the anode. More MnO$_2$ was deposited on the anode surface as the manganese concentration in the electrolyte increased.

The following experiments were conducted to confirm this phenomenon. Various concentrations of phosphoric acid (1.78, 17.83 and 35.66 g L$^{-1}$) were added to a solution of 150 g L$^{-1}$ H$_2$SO$_4$ and 1 g L$^{-1}$ Mn(II) in order to complex the manganic ion and hence reduce its disproportionation to MnO$_2$. The Pb-0.75%Ag anode was oxidized at 500 A m$^{-2}$ for 24 hours in these solutions.
Figure 4.44 Effect of the addition of phosphoric acid on the potential for oxygen evolution on a lead-silver anode at 500 A m\(^{-2}\).

As shown in Figure 4.44, the anode potentials were lower when phosphoric acid was added to the electrolyte and the lower potential can be maintained for longer periods when there is sufficient phosphoric acid to complex the manganic ion. It is also apparent that the amounts of PbO\(_2\) and PbSO\(_4\) formed were higher in the presence of phosphoric acid confirming reduced formation of MnO\(_2\) on the anode as shown in Figure 4.45.
Figure 4.45 Voltammetric scan after 24 hours of oxidation of a lead-silver anodes at 500 A m⁻² in the presence of manganese ions and phosphoric acid.

4.5.3 Galvanostatic Oxidation of Lead-Calcium-Tin Anode

The current density applied in the experiments with a Pb-Ca-Sn anode was 300 A m⁻², which is typical of that used in the electrowinning of copper. Experiments at 500 A m⁻² were also included to compare the potentials with those of pure lead and lead-silver anodes. Each current density was kept constant for 24 hours. The variation of the anode potential with time for the various current densities and manganese concentrations is presented in Figures 4.46 and 4.47. It is apparent that the anode potentials were higher when operated at a higher current density with a steady state potential of 2.08 V after oxidation for 24 hours in sulphuric acid solution (Figure 4.46). The addition of 1 g L⁻¹ Mn(II) reduced the anode potential by about 20 mV.
Figure 4.46 Effect of manganese ions on the potential for oxygen evolution on a Pb-Ca-Sn anode at 500 A m$^{-2}$

Figure 4.47 Effect of manganese ions on the potential for oxygen evolution on a Pb-Ca-Sn anode at 300 A m$^{-2}$
At a current density of 300 A m\(^{-2}\) the anode potential reached a steady state value of 2.04 V after 24 hours of oxidation in 150 g L\(^{-1}\) H\(_2\)SO\(_4\) (Figure 4.47). This was about 20 mV lower compared to that of pure lead when oxidised at 500 A m\(^{-2}\) under similar conditions. The addition of 0.1 g L\(^{-1}\) manganese resulted in a similar potential-time transient on a Pb-Ca-Sn anode with no manganese. In the solution containing 1 g L\(^{-1}\) manganese, there was an initial drop of the potential during the first hour, which could be due to the concurrent oxidation of manganese ions. After 24 hours the anode potential increased slowly and reached a steady potential similar to that without manganese. As could be expected, increasing the concentration of manganese to 5 g L\(^{-1}\) resulted in an increase of the rate of deposition of manganese dioxide on the anode surface and hence the potential increased with time due to an increase in the ohmic resistance through the MnO\(_2\) layer.

Figure 4.48 summarises the effect of manganese ions when cobalt was present in the electrolyte. Experiments were conducted using a Pb-Ca-Sn anode oxidised at 300 A m\(^{-2}\) for 24 hours. The presence of 0.15 g L\(^{-1}\) Co\(^{2+}\) ions can be seen to lower the anode potential by about 120 mV. The steep decrease in the anode potential after 1 hour of oxidation occurred because of the increase in the rotation speed of the working electrode from 500 to 900 rpm. This was done to remove a large oxygen bubble that formed on the surface of the anode. The overpotential with both cobalt and manganese in the electrolyte was still well below that of the PbCaSn anode oxidised in acid solution only. However, when compared with that in cobalt alone, the potentials were about 6 and 15 mV higher with the addition of 0.1 and 1 g L\(^{-1}\) manganese respectively.
Figure 4.48 Effect of manganese on the potential for oxygen evolution on a Pb-Ca-Sn anode at 300 A m\(^{-2}\) in the presence of 0.15 g L\(^{-1}\) cobalt ions

The reduction sweeps after 24 hours galvanostatic oxidation of the Pb-Ca-Sn anode at 300 A m\(^{-2}\) in various manganese and cobalt concentrations are summarized in Figure 4.49 and enlarged views of the voltammograms from 1.3 to 1.7 V and -0.8 to -0.2 V are presented in Figure 4.50. It was observed that the amount of PbO\(_2\) and PbSO\(_4\) formed decreased with increasing manganese concentrations and this was more pronounced in the presence of both manganese and cobalt ions. When cobalt ion was present, less MnO\(_2\) formed on the surface of the anode and the pink manganic colour of the solution was less intense. As previously reported in the literature, cobalt ions reduce the rate of oxidation of manganese ions. It was also noticed that there was some evidence of the reduction of MnOOH (reaction 4.9) in the region of -0.15 to 0.5 V at the highest manganese concentration.
Figure 4.49 Reduction sweep after 24 hours oxidation of Pb-Ca-Sn anode at 300 A m\(^{-2}\) in 150 g L\(^{-1}\) H\(_2\)SO\(_4\) with various manganese and cobalt concentrations.

Figure 4.50 Enlarged views of the voltammograms in Figure 4.49 from 1.3 to 1.7 V and -0.8 to -0.2 V.
4.6 Effect of Manganese Ions on the Corrosion Rate of Lead-Silver and Lead-Calcium-Tin Anodes

In this section, the experimental results of corrosion tests carried out over three months as part of the AMIRA Project P705A at Murdoch University (McGinnity 2007) were included as part of this thesis to provide more representative long-term corrosion rates of both Pb-Ag and Pb-Ca-Sn anodes in the absence and presence of manganese ions. The various combinations of alloy composition, electrolyte composition and current density are detailed in Table 4.9. The corrosion rates of the anodes were determined from anode weight loss measurements after operation for 86 days as shown in Table 4.10.

Table 4.9 Experimental conditions the long term corrosion tests

<table>
<thead>
<tr>
<th>Anodes</th>
<th>Surface Pretreatment</th>
<th>Electrolyte</th>
<th>Current Density / A m⁻²</th>
<th>Temp / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rolled Pb-0.5%Ag-0.0023%C</td>
<td>Sand blasted</td>
<td>170 g L⁻¹ H₂SO₄</td>
<td>500</td>
<td>40</td>
</tr>
<tr>
<td>Rolled Pb-0.5%Ag-0.0023%C</td>
<td>Sand blasted</td>
<td>170 g L⁻¹ H₂SO₄ + 5 g L⁻¹ Mn</td>
<td>500</td>
<td>40</td>
</tr>
<tr>
<td>Rolled Pb-0.08%C-1.3%Sn-0.01%Al</td>
<td>600 SiC grit polished</td>
<td>170 g L⁻¹ H₂SO₄ + 50 mg L⁻¹ Co</td>
<td>300</td>
<td>40</td>
</tr>
<tr>
<td>Rolled Pb-0.08%C-1.3%Sn-0.01%Al</td>
<td>600 SiC grit polished</td>
<td>170 g L⁻¹ H₂SO₄ + 50 mg L⁻¹ Co + 50 mg L⁻¹ Mn</td>
<td>300</td>
<td>40</td>
</tr>
</tbody>
</table>
Table 4.10 Anode corrosion rates after 86 days operation

<table>
<thead>
<tr>
<th>Anodes</th>
<th>[Mn] /g L⁻¹</th>
<th>[Co] /g L⁻¹</th>
<th>Potential /V vs SHE</th>
<th>Corrosion rate / g kA⁻¹ h⁻¹</th>
<th>Mud generation rate / g kA⁻¹ h⁻¹</th>
<th>Mass of Pb formed on cathodes / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-Ag</td>
<td>0</td>
<td>0</td>
<td>2.002</td>
<td>4.25</td>
<td>1.8</td>
<td>19</td>
</tr>
<tr>
<td>Pb-Ag</td>
<td>5</td>
<td>0</td>
<td>1.989</td>
<td>1.13</td>
<td>14.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Pb-Ca-Sn</td>
<td>0</td>
<td>0.05</td>
<td>1.882</td>
<td>1.19</td>
<td>0.48</td>
<td>0.1</td>
</tr>
<tr>
<td>Pb-Ca-Sn</td>
<td>0.05</td>
<td>0.05</td>
<td>1.880</td>
<td>1.01</td>
<td>3.6</td>
<td>0.18</td>
</tr>
</tbody>
</table>

From the data it is evident that the anode potential for the Pb-Ag anode is lower by about 13 mV in the presence of 5 g L⁻¹ manganese ions over three months operation. For the Pb-Ca-Sn anode with the addition of cobalt ions, the potentials are as expected lower than that of the Pb-Ag anode by about 120 mV and are not affected by the addition of 0.05 g L⁻¹ manganese ions. The average corrosion rates for both types of anodes over 86 days operation were lower in the presence of manganese ions i.e. from 4.25 to 1.13 g kA⁻¹ h⁻¹ for the Pb-Ag anode and from 1.19 to 1.01 g kA⁻¹ h⁻¹ for the Pb-Ca-Sn anode. The rates of mud generation in the presence of manganese increased by up to a factor of 7.9 and 7.5 for Pb-Ag and Pb-Ca-Sn anodes respectively, with much larger amounts of anode mud and cell mud produced with a Pb-Ag anode in 170 g L⁻¹ H₂SO₄ containing 5 g L⁻¹ Mn. In contrast, the mass of lead product deposited upon the cathodes (made of lead) decreased from 19 g to 0.5 g in the presence of 5 g L⁻¹ Mn for the Pb-Ag anode and even lower to 0.18 g in the presence of 0.05 g L⁻¹ Co and 0.05 g L⁻¹ Mn for the Pb-Ca-Sn anode. These results illustrate the effect that both manganese and cobalt ions have on reducing the corrosion of the anodes and thereby the incorporation of lead on the cathodes.
These observations indicate that, consistent with the results shown in this study, the presence of manganese in the electrolyte decreases the rate of oxidation of lead and thereby the average corrosion rates of both Pb-Ag and Pb-Ca-Sn anodes. Increasing the concentrations of manganese decreases the extent of oxidation of lead as shown in Section 4.5.2 and 4.5.3 but also increases the amount of manganese oxidized (shown in Figures 4.25 and 4.40). The much larger amounts of mud produced with the higher manganese concentrations are primarily due to the spalling of the anode scale (predominantly manganese oxides) and the formation of fine MnO₂ precipitates in the electrolyte.

The formation of MnO₂ layer on the surface of the Pb-Ag anode seems to originate from the oxidation of Mn(II) to MnO₄⁻ ions (reaction 4.3), followed by the reduction of permanganate ions by Mn(II) ions to form intermediate Mn(III) species (reaction 4.5), which subsequently disproportionate to MnO₂ by reaction 4.6. High concentrations of manganese ions favor reactions 4.5 and 4.6, thus gradually increasing the concentrations of manganic ion in the electrolyte and the amount of MnO₂ precipitated both on the anode surface and in the electrolyte.

For the Pb-Ca-Sn anodes which have lower oxygen overpotentials, it is possible that a change in reaction mechanism of Mn³⁺ generation via a permanganate intermediate to direct Mn³⁺ formation on the anode has occurred, which can form a MnOOH intermediate layer (reaction 4.7) as shown in Section 4.4. The presence of cobalt ions in the electrolyte leads to a lower potential which results in decreased precipitation of MnO₂ both on the anode surface and in the electrolyte.
4.7 Electrochemical Oxidation of Iron(II) Ions on Lead Alloy Anodes

A preliminary study was made of the characteristics of the anodic oxidation of iron(II) ions on both Pb-Ag and Pb-Ca-Sn anodes for several reasons. Firstly, it was considered useful to study the electrochemical oxidation of iron(II) ions in comparison with that of manganese(II) ions and secondly, iron is always present in the electrolyte during the electrowinning of copper and iron(II) is oxidized at the anodes. Finally, it is of interest to establish the extent to which anodic reactions are possible on these anode materials in the potential region between formation of lead sulfate and its oxidation to lead dioxide.

Cyclic voltammograms of the Pb-0.42%Ag and Pb-Ca-Sn anodes at 1 mV s\(^{-1}\) scan rate in a solution containing 150 g L\(^{-1}\) H\(_2\)SO\(_4\) and 10 g L\(^{-1}\) Fe(II) were obtained. The measurements were performed at 40°C with a rotation speed of the disc electrodes of 500 rpm. The scan was started from the open circuit potential at about -0.35 V to positive potentials of about 2.1 V, and reversed. The scan was stopped at -0.8 V for the Pb-Ca-Sn anode and at 0.58 V for the Pb-Ag anode. The voltammograms are shown in Figure 4.51.

As the potential was swept in a positive direction, the oxidation of Pb to PbSO\(_4\) occurs at about -0.31 V and the surface of the lead anodes is coated with a passive lead sulphate layer. Oxidation of iron(II) could be expected at potentials above about 0.8 V given that the standard reduction potential for the reaction

\[
\text{Fe}^{2+} = \text{Fe}^{3+} + e^-
\]  \hspace{1cm} (4.10)

is 0.77 V. However, no significant anodic currents are obtained until the potential increases to about 1.5 V in the case of the Pb-Ca-Sn anode due to the formation of both \(\alpha\)- and \(\beta\)-PbO\(_2\) followed by the simultaneous evolution of oxygen gas at potentials
above about 2.0 V. In the case of the Pb-Ag anode, oxidation to PbO₂ coincided with the simultaneous evolution of oxygen gas at potentials above 2.0 V. The apparent current plateau observed in the potential region from 2.0 V to 2.1 V for both alloys is an experimental artifact associated with the current limitations of the potentiostat.

![Voltammetric scans of freshly polished lead-silver and lead-calcium-tin anodes in solution containing 150 g L⁻¹ H₂SO₄ and 10 g L⁻¹ iron(II)](image)

On the reverse scan, the current decreases rapidly to a steady limiting value of about 620 A m⁻² on both alloy electrodes at potentials between 1.5 and 2.0 V. The limiting current density for the oxidation of iron(II) under these conditions can be estimated from the Levich equation to be 621 A m⁻² for a diffusion coefficient of iron(II) of 7.1 x 10⁻⁶ cm² s⁻¹ (Lukomskij & Gamburg 2008). These observations suggest that oxidation of iron(II) only occurs on the surface of β-PbO₂ which is formed at higher potentials than α-PbO₂. The steep decrease of the current from the plateau at about 1.5 V
coincides with the potential at which PbO\textsubscript{2} is reduced to PbSO\textsubscript{4}. The absence of a cathodic peak could be due to the reduction of PbO\textsubscript{2} by iron(II) by a reaction such as
\[
PbO_2 + 2Fe^{2+} + HSO_4^- + 3H^+ = PbSO_4 + 2Fe^{3+} + 2H_2O \quad (4.11)
\]
the rate of which must be mass transport controlled on both anodes. This explains why there are no observed peaks for the reduction of PbO\textsubscript{2} but only the cathodic peaks for the reduction of (PbO.PbSO\textsubscript{4}) to Pb, and PbSO\textsubscript{4} to Pb at about -0.28 and -0.39 V respectively.

These results suggest that a more detailed study of reactions such as these allow one to probe the nature of the sulfate/oxide layer on the alloy surfaces. There are some interesting similarities with respect to the results obtained in solutions containing manganese ions (Sections 4.2.1 and 4.4). The oxidation of manganese(II) ions on the Pb-Ag and Pb-Ca-Sn anodes also appears to depend on the formation of PbO\textsubscript{2} at potentials of above 1.7 V. The favourable influence of manganese ions on reducing the rate of formation of lead dioxide might be as well explained by reaction 4.4 in which the lead dioxide formed may be reduced to lead sulphate by oxidation of Mn\textsuperscript{2+} ions to Mn\textsuperscript{3+} ions, which disproportionate to MnO\textsubscript{2}.
Chapter 5

CONCLUSIONS

The role of manganese ions in the corrosion and electrocatalytic behaviour for the oxygen evolution reaction of commercial Pb-Ag and Pb-Ca-Sn anodes under conditions typical of the electrowinning of zinc and copper has been studied using rotating disc electrodes involving potentiostatic and galvanostatic oxidation followed by negative potential sweeps and chemical analyses of the oxidized manganese species formed during the oxidation process.

Potentiostatic oxidation experiments in the range of 1.5 to 2.0 V followed by negative potential sweeps of surfaces of the Pb-Ag and Pb-Ca-Sn anodes in acidic manganese solution have revealed that the oxidation of manganese proceeds after the formation of PbO₂ at potentials above about 1.7 V and is also accompanied by evolution of oxygen at potentials above about 2.0 V. The amount of manganese oxidized increases with increasing potential, manganese ion concentration and time.

At 1.8 V, the rate of oxidation of manganese ions is not mass transport controlled. The main products of oxidation at this potential are soluble manganese ions (Mn³⁺ and/or MnO₄⁻). At 1.95 and 2.0 V, at which potentials O₂ evolution visibly occurred at a significantly increased rate, the oxidation of manganese ions was occurring close to the mass transport controlled rate. The presence of manganese in the electrolyte decreased the rate of formation of lead dioxide and also reduced the charge fraction for oxygen evolution. The high current densities observed during oxidation in the presence of
manganese might account for the significant rate of production of manganese oxide scale and sludge in operating cells, particularly during the electrowinning of zinc.

Increased silver content of the Pb-Ag alloys resulted in a decrease of the anode overpotential for the oxygen evolution reaction and a decrease in the extent of oxidation of lead. An increase in the silver concentration in the alloy, up to a saturation limit of about 0.75%, also increased the extent of the oxidation of manganese and the formation of MnO₂ both on the anode and in the electrolyte and reduced the rate of oxygen evolution.

The charge attributable to the evolution of oxygen during oxidation of Pb-Ca-Sn anodes at all potentials for 24 hours was slightly lower than those of Pb-Ag anodes and this coupled with the considerably higher current densities observed on the Pb-Ag anodes confirms that silver exhibits a catalytic effect on the oxygen evolution reaction. When Pb-Ca-Sn anodes were oxidized at 2.0 V for 24 hours in the presence of 1 g L⁻¹ manganese ions, 70% of the charge is utilized for oxidation of manganese ions. This value was reduced to about 10% when the Pb-Ag anodes were oxidized under the same conditions. In the presence of cobalt ions, the rate of oxidation of manganese ions decreased. Both cobalt and manganese have an effect on reducing the corrosion of the anodes and thereby the incorporation of lead on the cathodes.

The results observed in this study show that initial permanganate formation occurred with both Pb-Ag and Pb-Ca-Sn anodes but permanganate ions are not stable in the bulk electrolyte. Permanganate decomposition can result in the formation of either MnO₂ or Mn³⁺ ions depending on the concentration of manganese(II) ion, the oxidation potential and hydrodynamic conditions at the anode surface. The kinetics of the reduction of permanganate by manganese(II) ions is second-order with respect to manganese(II) and
therefore is a very sensitive function of the manganese(II) ion concentration. Thus, one will only observe permanganate in the electrolyte at low concentrations of manganese ions under which conditions it is metastable.

For the Pb-Ca-Sn anodes which have lower overpotentials for oxygen evolution, it is possible that a change in reaction mechanism occurs from manganese(III) formation via a permanganate intermediate to direct oxidation of manganese(II) ions on the anode. Subsequent slower precipitation of MnOOH and/or MnO₂ by disproportionation results in the formation of solids in the bulk electrolyte and on the walls of the cell. It is also possible that oxidation of manganese ions by anodically produced PbO₂ also occurs but confirmation will require additional experiments.

Preliminary results of the oxidation of iron(II) on the lead alloy anodes has shown some promising results as a probe of the nature of the sulfate/oxide layer on the surface of the alloys and further work should be conducted along these lines.
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