CORROSION OF LEAD ANODES IN METALLIC ELECTROWINNING ENVIRONMENTS

by

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Abstract
The corrosion of anodes in electrowinning is costly because of their relatively short lifespan, material cost, and their impact on cathodic deposit quality. The objective of this thesis was to understand the corrosion behavior of Pb anodes in electrolyte simulating Zn and Ni electrowinning conditions. Pb-based alloys have been used because they are cheap, conductive and stable at high potential and low pH. Experiments in this thesis included open circuit potential (OCP), potentiodynamic, and potentiostatic polarizations. The parameters studied include; \( i_{\text{corr}}, E_{\text{corr}}, \) slope of the oxygen evolution region and \( O_2 \) potential.

For Zn electrowinning, variables changes included modifying \( \text{H}_2\text{SO}_4, \text{Mn}^{2+}, \text{Cl}^{-}, \text{Zn}^{2+} \) concentrations and increasing temperature. The best corrosion resistance in Zn electrowinning was achieved by increasing \( \text{H}_2\text{SO}_4 \) concentration, using 15 g/L \( \text{Mn}^{2+} \), 0 g/L \( \text{Cl}^{-} \), and increasing both \( \text{Zn}^{2+} \) temperature. Corrosion products were studied using SEM and EDX and the relationship between surface morphology of the working electrode and operating potential. Deaerating the cell reduced the dissolved oxygen in the cell and generally increased \( i_{\text{corr}}, \) oxygen evolution region slope and OER overpotential. For Ni electrowinning applications, three materials were used as cast PbAg, rolled PbAg, and as cast PbCaSn. The effects of \( \text{H}_2\text{SO}_4 \) and \( \text{Cl}^{-} \) on corrosion behavior were studied using both potentiodynamic and galvanostatic polarizations. Corrosion rates were determined by measuring the length of the discharge peak after 24 hours galvanostatic polarization and SEM and XRD were used to determine the surface morphology and phase composition of the anodes.
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<td>$b_a$</td>
<td>Anodic Tafel slope</td>
</tr>
<tr>
<td>$b_c$</td>
<td>Cathodic Tafel slope</td>
</tr>
<tr>
<td>$E_{corr}$</td>
<td>Corrosion potential</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EW</td>
<td>Electrowinning</td>
</tr>
<tr>
<td>Hg/HgSO$_4$</td>
<td>Mercurous sulfate reference electrode</td>
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<tr>
<td>$i_{corr}$</td>
<td>Corrosion current</td>
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<tr>
<td>LME</td>
<td>London Metal Exchange</td>
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<tr>
<td>OCP</td>
<td>Open circuit potential</td>
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<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
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<tr>
<td>SCE</td>
<td>Saturated calomel electrode (reference electrode)</td>
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<td>SHE</td>
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<td>XRD</td>
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1. Introduction

Electrowinning is a process through which metal ions are plated from solution onto a cathode using electrolytic principles. Electrowinning cell houses produce hundreds of thousands of tonnes of metal per year requiring a large number of cells and a large number of electrodes. A cell-house may contain hundreds of cells with up to 85 electrodes composed of 42 cathodes and 43 anodes.

The objective of electrowinning is to electroplate highly pure metals from a leach solution quickly and efficiently. Electrowinning cells are powered by a cell voltage of 3.2 to 3.7V to achieve reasonable kinetics. The large electricity requirement for electrowinning has inspired a large amount of research to focus on catalyzing the anodic and cathodic reactions using alloys and pretreatments.

For electrowinning to be thermodynamically feasible, a low pH is required to stabilize metallic ions in solution and a large voltage to reverse the thermodynamically favored reaction. Few materials exist that can be used in highly acidic electrolyte, the presence of Cl⁻, and high potentials used in electrowinning. Pb-based alloys have been used in Zn electrowinning since 1909 when it was first produced industrially (Newnham, 1991). These anodes are used because they are cheap, insoluble, conductive, electrocatalytic, and stable at high potentials (Ivanov et al. 2000A).

Pb passivates and inhibits the corrosion of the anode by acting as a physical barrier between the alloy and electrolyte. The presence of corrosion product layer on a Pb anode requires a large overpotential as the anode is fully passivated and limiting the OER from
occurring quickly. The presence of the Pb oxide layer increases the overvoltage, but the presence of alloying elements can catalyze the kinetics of OER (Newnham, 1992, Ivanov, et al.2000A, Rerolle, et al. 1996). For example, Ag passivates, increases the conductivity, and enhances the OER by increasing the number of sites for oxygen evolution. Due to the high cost of Ag, authors and industry have proposed alloying with multiple elements (such as Ca and Sn), and to physically or chemically treat anodes to enhance both mechanical and electrochemical properties.

Little research has been completed studying the effect of solution composition of leach solution on anode corrosion. Understanding each elements’ role on the corrosion resistance of a Pb anode will assist in optimizing physical or chemical pretreatments to both increase service life of Pb-based anodes and to decrease Pb contamination in the plated metal. The experiments in this thesis are based on a PbAg (as cast and rolled) and PbCaSn alloys in leach solutions based on Zn and Ni electrowinning environments.

The cost of anode corrosion in an electrowinning circuit is substantial. We assume that to produce 1 tonne of Zn will require 3200 kWh energy and the cost of electricity is $0.10/kWh, Moats, et al(2010). The electricity cost of a plant producing 300,000 tonnes of Zn a year is approximately 96 million dollars (or approximately $500,000,000 over 5 years). Such a plant contains 30,000 anodes which cost $300 each and over 5 years replacing all of the anodes would cost almost $9,000,000 (or ~2% of the total electricity cost of electrowinning). The cost of corrosion assumes that the processing plant uses a PbAg alloy and is capable of recovering the majority Pb and Ag making the anode cost approximately $300 each. Therefore, studying the corrosion behavior of the anodes is necessary and beneficial to industry.
i. Zn electrowinning

The London Metal Exchange (LME) reported that 12 million tonnes of metallic Zn was produced in 2007 and of that, 7 million tonnes are recovered through aqueous electrowinning, (Parada & Asselin, 2009). The largest producers were Australia, Canada, China, Peru, and the United States, (Zhang, 2010).

Zn exists in nature as sphalerite (ZnS) and the hydrometallurgical processing commonly includes roasting, atmospheric leaching, purification and electrowinning stages. Otherwise, the ore is leached at high temperature and pressure, purified and recovered using electrowinning (Habashi, 1997).

\[
\begin{align*}
\text{Zn}^{2+} + 2e^- &= \text{Zn} & \text{E}^* &= -1.00 \text{ V}_\text{SCE} \\
\text{H}_2\text{O} &= \text{O}_2 + 2\text{H}^+ + 2e^- & \text{E}^* &= 0.99 \text{ V}_\text{SCE}
\end{align*}
\]

Fundamentally, electrowinning is an electrolytic process composed of a metallic reduction at the cathode reaction (1-1) and oxygen evolution reaction (OER) (1-2) at the anode. The non-spontaneous cell voltage based on these oxidation and reduction reactions is -1.99 V. In order to produce metallic zinc, a higher potential must be applied to the cell. A cell house applies a voltage between 3.2 V and 3.7 V to achieve desired kinetics during electrowinning.

Zn electrowinning plants primarily use PbAg anodes because they have the best corrosion resistance and mechanical properties at high potentials. Ag content varies, but industrial anodes commonly use between 0.5 to 1wt%, (Newnham, 1992, Ivanov et al. 2000a,

Anodes are pretreated using physical treatments such as rolling, sandblasting or shot peening or chemical treating with leach solution to enhance the formation of stable oxide prior to being placed in service.

ii. Ni Electrowinning

1.5 million tonnes of Ni is produced annually (London metal exchange 2007) from laterite and sulfide ores. Laterite ores are recovered using aqueous electrowinning and sulfide deposits are readily processed using pyrometallurgical flow sheets, (Lanagan, 2002). The majority of Ni is refined from sulfide deposits despite, but because of, increased Ni demand, there has been more interest in processing Ni laterite ores, (Tzeferis, 1994).

The cell reactions in an electrowinning circuit consist of the reduction of Ni\(^{2+}\) (1-3) at the cathode and the evolution of oxygen at the anode (1-2). The standard reduction potential of Ni is \(-0.550 \text{ V}_{\text{SCE}}\) making the cell potential 1.480 \text{ V}_{\text{SCE}}.

\[ \text{Ni}^{2+} + 2e^- = \text{Ni} \quad \text{E}^\circ = -0.550 \text{ V}_{\text{SCE}} \]  

(1-3)

Ni electrowinning is highly dependent on the electrolyte composition represented by \(\text{H}_2\text{SO}_4\) concentration, temperature, current density, and presence of impurities. The hydrogen evolution reaction has potential that competes with the Ni plating reaction at the cathode. In order to maintain current efficiency, the \(\text{H}_2\text{SO}_4\) concentration is closely monitored. Additionally, the anodes are bagged to both contain both the anodic slime and
prevent generated H₂SO₄ (from reaction 1-2) from changing conditions that could promote hydrogen generation at the cathode. The presence of Cl⁻ is not clearly understood but clearly impacts both current efficiency and anode corrosion in Ni electrowinning, (Moskalyk & Alfantazi, 2002).
2. Objectives

Pb alloys have been used as anodes in electrowinning circuits because they are conductive, stable, and have satisfactory mechanical properties. Much research has been focused on minimizing energy consumption in electrowinning because of the costs associated with electricity and very little research has been completed establishing the corrosion behavior of Pb alloys in electrowinning cells.

This thesis will discuss the corrosion behavior of Pb anodes in electrolyte simulating both Zn and Ni electrowinning with changing electrolyte composition and anode material. The objectives of this thesis are primarily to:

- Study the effects of H$_2$SO$_4$, Mn$^{2+}$, Cl$^-$, Zn$^{2+}$ and temperature on the corrosion behavior of a PbAg alloys in Zn electrowinning. This knowledge will assist in optimizing anode service life and decrease the cost of maintaining and replacing PbAg alloys while in service.

- To study the corrosion behavior of three anode materials (as cast PbAg, rolled PbAg and as cast PbCaSn) in Ni electrowinning conditions to understand the effect of H$_2$SO$_4$, and Cl$^-$ concentration. This information can be used to optimize anode service lifespan and when choosing a suitable Pb-based alloy for Ni electrowinning.
3. Literature review

Pb based anodes are used in electrowinning because they are electrically conductive, electrocatalytic, and stable at high potential in concentrated H$_2$SO$_4$. The increased conductivity is required to optimize energy use, electrocatalytic to increase the product yield and to minimize corrosion and cathodic contamination, (Ivanov et al., 2000A).

Anodes in electrowinning are commonly Pb-based alloys containing Ag, Ca, and or Sn, to enhance mechanical properties and corrosion resistance. Anode materials are selected based on their corrosion resistance when placed in H$_2$SO$_4$ and their ability to remain stable in the presence of Cl$^-$. Anodes can be mechanically treated to improve the quality of microstructure and to enhance mechanical and electrochemical properties.

The development and destabilization behavior of Pb-based anodes has been investigated for their application to Pb-acid batteries. The composition of the oxide layer as a function of potential was first explored by Lander (1951), and Burbank (1959). The discharge behavior of a Pb oxide was initially studied by galvanostatic polarization for 24 hours and monitoring the potential when removing the applied current, (Rüetschi & Cahan, 1957, Rüetschi & Cahan, 1958).

In Zn electrowinning, the presence and characterization of the Mn oxide layer is important for maintaining pure leach solution and developing a better performing oxide layer to increase corrosion resistance, (Rodrigues et al. 1998, Yu & O’Keefe, 2002, Recéndiz et al.2009).
Publications in the last twenty years have developed methods to increase the quality of oxide layers using pretreatments. Some solutions for chemical pretreatments include fluoride, fluoride sulfate, sodium fluoride or potassium fluoride with H$_2$SO$_4$ solution, (Gonzalez, 2001, Ramachandran, et al. 1981, Ramachandran, et al. 1980). Mechanical pre-treatments can include sandblasting, shot-peening or rolling anodes to enhance the surface for optimal adhesion of the corrosion product, (Ramachandran & Balakrishnan, 1996), Jin, et al. 2003).

Publications outlining the impact of electrolyte constituents on oxide layer characterization and their effect on current efficiency have been completed, but few have focused on the corrosion resistance as a function of electrolyte composition. This review will discuss the current and established research on anodic corrosion and its effect on corrosion behavior of Pb-based anodes in Zn and Ni electrowinning.

3.1. **Lead (Pb)**

Pb oxidizes in atmospheric conditions and appears grey in color. Its valence includes both 2+ and 4+, and on the periodic table is located in the 14th group and its atomic number is 82. The melting and boiling point of Pb are 327.4°C and 1741°C respectively, and its density is reported as 11.34 g/cm$^3$. The metals crystal structure is face centered cubic with an atomic radius of 0.175 nm. Pb is soft and is cast and rolled easily, (Habashi, 1997). However, mechanically pure Pb is poor and it suffers from creep. Creep causes the anode to elongate under its own weight and if in an electrowinning environment, will cause cracking of the oxide layer that can cause spalling and increase
corrosion rates. To maximize mechanical properties, Pb has been alloyed with Ag, Sn, Ca, Ca and Sn for Zn electrowinning and Sb, Sn, and PbCaSn for Ni electrowinning.

In electrowinning, the reduction potential of Pb is between Zn$^{2+}$ and H$^+$ and will deposit onto the cathode and re-dissolve. This cycle of plating and dissolving will decrease the current efficiency, in addition to decreasing cathodic yield and quality.

3.2. Pb oxide layer

Zn electrowinning takes place at a pH of 0 or lower while Ni electrowinning requires a pH around between 1 and 3.5, (Newnham, 1992, Ji, 1994). Ni electrowinning requires a higher pH in order to avoid hydrogen evolution, but a low enough that Ni$^{2+}$ is stable over higher Ni oxides. Understanding the oxide layer formation and transformation is important because when an anode is placed into a sulfate based electrolyte at high potentials, PbSO$_4$ is the first oxide to form despite being thermodynamically unstable. This was shown by Pavlov & Lordanov, (1970) who used potentiostatic experiments with different current passed and used XRD to determine the quantity of oxide at high potentials, Figure 3.4.

The conditions of electrowinning (pH less than 0 for Zn and between 1 and 3.5 for Ni electrowinning) and at potentials above 1.8V$_{SCE}$, PbO$_2$ is clearly stable. These points are found on the Pb-H$_2$O Pourbaix diagram, Figure 3.1. The presence of a pH gradient within the oxide complicates the oxide by establishing sub-layers, (Laitinen, 1990). This section outlines the development of an oxide layer initially from OCP to high potentials used in electrowinning.
Figure 3.1 Pb-H$_2$O Pourbaix diagram, (Pourbaix 1974)

At OCP at a pH less than 0 in sulfate based electrolytes; Pb (3-1) and hydrogen (3-2) are stable phases.

\[
Pb^{2+} + 2e^- = Pb \quad E^* = -0.368 \text{ V}_{\text{SCE}} \quad (3-1)
\]

\[
2H^+ + 2e^- = H_2 \quad E^* = -0.242 \text{ V}_{\text{SCE}} \quad (3-2)
\]

\[
Pb(OH)_2 + 2H^+ + 2e^- = Pb + H_2O \quad E^* = 0.000 \text{ V}_{\text{SCE}} \quad (3-3)
\]

\[
PbO + 2H^+ + 2e^- = Pb + H_2O \quad E^* = 0.160 \text{ V}_{\text{SCE}} \quad (3-4)
\]

Increasing the potential between the Pb/Pb$^{2+}$ (line ‘16’ on Figure 3.1) and the hydrogen oxidation line (line ‘a’ on Figure 3.1), Pb oxides become thermodynamically stable in
reactions 3-3 and 3-4. In the region of Pb$^{2+}$, PbSO$_4$ is the stable phase and because of insolubility in solution, it tends to precipitate on top of the Pb oxides already formed on the anode by a solution-precipitation mechanism, (Archdale & Harrison, 1972). After the surface has been covered by PbSO$_4$, basic oxides will form at the Pb/oxide interface because of a pH gradient within the oxide layer. The gradient exists because of the alkalization of the Pb/oxide interface. After the PbSO$_4$ has covered the anode surface and its density is increased, it prevents the diffusion of Pb$^{2+}$ away from the anode to the electrolyte and SO$_4^{2-}$ from the bulk electrolyte to the corrosion product. In order to maintain electroneutrality, dissolved oxygen and hydroxide ions diffuse through the oxide and react with corrosion products. These ions and corrosion products form basic oxides including PbO-PbSO$_4$, 3PbO·PbSO$_4$·H$_2$O and 5PbO$_2$·H$_2$O, Pb(OH)$_2$ (3-3) and PbO (3-4), (Zhang, 2010). The change in oxide layer composition as a function of potential and is sketched in Figure 3.5 which represents the oxide development with increasing potential. The presence of these compounds was established using potentiodynamic experiments, Figure 3.3. Presence of sub-layer oxide in Figure 3.3 is established by the cathodic scans. Although only PbSO$_4$ is observed during the anodic scan, the presence of peaks during the cathodic scan suggests the presence of these oxides, (Rehim, et al. 1984).
Figure 3.2 The changing composition of the Pb oxide layer with increasing potential, (Valeriote & Gallop, 1977)

Figure 3.3 Potentiodynamic curve of pure Pb, 30% H₂SO₄, (Ljomah, 1987)
Figure 3.4 Intensity of diffraction lines when potentiostatically polarizing Pb anode as a function of amount of electricity passed in 1 M H₂SO₄ at 1.8Vₜₜ, reproduced from Pavlov & Lordanov (1970).

At potentials above the PbO₂ and PbSO₄ equilibrium (line ‘21’ on Figure 3.1), PbO, basic oxides and PbSO₄ are consumed by two forms of PbO₂, α and β, Figure 3.4, (Burbank 1959). The α-PbO₂ forms in basic and neutral environments by consuming the PbO and basic oxides. In the acidic environment at the oxide electrolyte interface, the PbSO₄ is consumed by the transformation to β-PbO₂, poorly bonded needle like crystals. The transformation of the oxide layer with increasing potential is presented in Figure 3.2 and Figure 3.5 and previously established by Burbank (1959), Lander (1951), Lander (1956), Pavlov & Popova (1970), Pavlov & Dinev (1980), Recéndiz et al. (2009), Garche (1990), Valeriote & Gallop (1977).

The volume change associated with transforming PbSO₄ (48 cm³/mol) to PbO₂ (25 cm³/mol) in reaction 3-5 is significant and often leads to the exposure of anode material
and increasing corrosion rates. During the oxidation and destabilization of PbSO$_4$ (reaction 3-5), decrease in volume exposes Pb alloy to corrosive conditions requiring further passivation. During a cathodic scan after of a potentiodynamic experiment or removing the current after a galvanostatic polarization, the transformation of PbO$_2$ to PbSO$_4$ causes cracking and destabilizing the oxide layer, (Czerwiński, et al. 2000).

$$\text{PbSO}_4 + 2\text{H}_2\text{O} = \text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \quad E^* = 1.43 \text{ V}_{\text{SCE}}$$ (3-5)

![Figure 3.5 Schematic of oxide layer formed on a Pb anode in H$_2$SO$_4$, (Ruetschi & Angstadt 1964)](image)

### 3.3. Manganese oxide layer development

PbO$_2$ and MnO$_2$ form a coliform structure that performs best with respect to minimizing corrosion and maximizing current efficiency when an optimal concentration of Mn$^{2+}$ and thickness of MnO$_2$ is obtained, (Chen & Dutrizac, 2009).
MnSO$_4$ is added to the leach solution in Zn electrowinning to precipitate Fe and other more electropositive metals from solution and assist in purifying the leach solution. Additional benefits by MnSO$_4$ are the formation of an oxide to inhibit the corrosion reaction of the Pb-based anode, (Recéndiz, 2009, Fukushima, 1960). The Mn oxide layer minimizes the effect of Cl$^-$ reaching the anode that would evolve Cl$_2$ that would decrease the current efficiency of electrowinning. Mn is avoided in Ni electrowinning because the cathodic deposit shows poor morphology and decreased current efficiency.

**Figure 3.6 Mn-H$_2$O Pourbaix diagram, (Pourbaix 1974)**

The development of the oxide layer is complex, and the stability of Mn at low pH and high potential is observed in the Mn-H$_2$O Pourbaix diagram, Figure 3.6. In electrowinning, Mn is stable as MnO$_2$ but the mechanism of formation is complicated. MnO$_2$ does not form immediately on a Pb-based anode until a Pb-based oxide layer has
already formed, (Yu & O'Keefe, 2002). The mechanism of MnO$_2$ formation was outlined by Rodrigues, et al. (1998) using cyclic voltammetry of a Pt electrode between 0.6 and 1.6V$_{SHE}$. The mechanism of MnO$_2$ formation are outlined in reactions 3-6 to 3-11.

\[
\text{Mn}^{2+}_{\text{bulk}} \rightarrow \text{Mn}^{2+}_{\text{surface}} \tag{3-6}
\]

\[
\text{Mn}^{2+}_{\text{surface}} \rightarrow \text{Mn}^{3+}_{\text{ads}} + e^- \tag{3-7}
\]

\[
\text{H}_2\text{O} \rightarrow \text{OH}_{\text{ads}} + \text{H}^+ + e^- \tag{3-8}
\]

\[
2\text{Mn}^{3+}_{\text{ads}} \rightarrow \text{Mn}^{2+}_{\text{ads}} + \text{Mn}^{4+}_{\text{ads}} \tag{3-9}
\]

\[
\text{Mn}^{2+}_{\text{ads}} + 2\text{OH}_{\text{ads}} \rightarrow \text{MnO}_2 + 2\text{H}^+ \tag{3-10}
\]

\[
\text{Mn}^{4+}_{\text{ads}} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+ \tag{3-11}
\]

The growth of the Mn oxide layer is dependent on the establishing MnO$_2$ which then reacts with Mn$^{3+}$ to form MnOOH. This oxide then reacts with hydrogen again forming MnO$_2$. This reaction is in solid state and requires excessive Mn$^{2+}$ in solution, (Kao & Weibel, 1992, Paliphot, et al.2006).

The presence of Mn$^{2+}$ in electrolyte changes the oxide layer in 4 time periods during galvanostatic experiments. Initially (0 to 5 min), the oxide layer is composed of Pb$_3$O$_4$ on the anode. When time equals 5 minutes, the Pb oxide is covered with conductive $\alpha$-MnO$_2$. The third stage (5 to 60 minutes) of oxide is composed of non-conducting MnO$_4^-$ and $\delta$-MnO$_2$, (also detected by Lee (1977)), and the fourth stage (60 minutes or more) is
fully δ-MnO₂. When the crystalline layer is transformed into an amorphous one, the oxide fractures exposed Pb to solution forming PbO₂, (Recéndiz, et al. 2009).

3.4. Pb base alloys

Although Pb is conductive and stable, it suffers from creep when loaded under its own weight. The addition of alloys and plastic treatment are required to engineer the microstructure to optimize electrochemical and physical properties. The three alloys used in this thesis were as cast and rolled PbAg and PbCaSn.

3.4.1. PbAg alloy

Both Pb and Ag have FCC structure and the difference in crystal size is approximately 17% resulting in limited solid solubility, (Heidenreich, 1955). Ag precipitates and tends to form in clusters and is not homogenously dispersed in the as cast structure.

The maximum solubility of Ag in Pb is 0.1wt%Ag, the eutectic temperature is 304°C and eutectic composition of 2.5wt%, (Petrova et al., 1996, Karakaya & Thompson 1987), Figure 3.7.
Ag particles are found within interdendritic regions and grain boundaries in an as cast alloy making it difficult for the oxide layer to adhere to, (Jin, et al. 2000).

PbAg alloys have proven to have the best mechanical properties and highest corrosion resistance required for electrowinning. Increasing the Ag content improves the alloys hardness and creep resistance. Electrochemically, there is a decrease in the OER overpotential, which decreases energy required to evolve O$_2$, and increases the number of sites for OER to take place, Figure 3.8, (Zhang, 2010, Monahov et al.,2000, Yu & O’Keefe, 1999).
The presence of Ag at the grain boundaries and interdendritic regions enhances mechanical properties of Pb via solid solution hardening and also improves the quality of PbO₂ layer. PbO₂ becomes thin and dense after a sufficient amount of time and progressively stabilizes, (Prengaman & Siegmund, 2000). During galvanostatic polarization, the PbAg alloy is covered with stable PbO₂ and the presence of AgSO₄₄ad, AgMnO₄₄ad and AgMnO₄₄ad has been reported, (Rerolle & Wiart, 1996). The presence of Ag oxide stabilizes the PbO₂ layer, decreases $E_{\text{corr}}$ and $i_{\text{corr}}$, decreases potential during galvanostatic experiments (Figure 3.8), and increases the conductivity and the number of sites for O₂ evolution, (Monahov, et al 2000, Zhang, et al., 2009, Taguchi 1996, Umetsu et al., 1985).

Hine et al.(1986) performed galvanostatic experiments at high current density to determine the effect of Ag content on corrosion rate, Figure 3.9. Results were duplicated by Newnham (1992) and both authors reported benefits are most significant between 0.7% and 1%.
Figure 3.8 Decreasing potential with increasing Ag content during galvanostatic experiments, 50mA/cm$^2$, (Zhang, 2010)

Figure 3.9 Effect of Ag content on corrosion rate, 1 M $\text{H}_2\text{SO}_4$, 10000 A/m$^2$ and 55°C, (Hine, 1988)
3.4.2. Rolled PbAg alloy

Rolled anodes have been used in electrowinning applications because they show higher corrosion resistance and reduced anodic polarization behavior. Rolling an anode develops a microstructure composed of fine elongated grains, removes casting defects and produces a homogenous microstructure, (Petrova, et al. 1996, St. Rashkov, et al. 1996).

3.4.3. PbCaSn alloy

Historically, Ni electrowinning used Pb-Sb anodes, but because these alloy are unstable and corrode at high potential, they have been replaced by PbCaSn, (Rogechev, 1988, Prengaman, 2001, Prengaman, 2000, Felder & Prengaman, 2006). Binary PbCa anodes suffer from alloy segregation but the addition of Sn improves alloy dispersion and improves both mechanical and electrochemical properties. PbCaSn anodes have been used in electrowinning operations because they form a hard and well adhered oxide layer, catalyze the OER and substantially more corrosion resistant, (Felder & Prengaman, 2006, Yu & O’Keefe, 1999, Čekerevac, et al 2010).

The PbCaSn alloy is characterized by much larger ‘puzzle’ shaped grains and large precipitates, (Boirden, et al.1991). With large grains, the PbCaSn alloy has a lower number of grain boundaries compared to the as cast and rolled PbAg alloys. The presence of large precipitates and low grain boundary density improved corrosion resistance, (Giess, 1995). The primary grains would be composed of Pb and the grain
boundaries have been reported to be composed of \((\text{Pb}_{1-x}\text{Sn}_x)_{3}\text{Ca}\) precipitates, \((\text{Rocca, et al. 2006, Boirden, et al. 1991})\)

PbCaSn alloys were tested using weight loss methods in addition to observations using SEM. Performance of the alloy is based on the Sn/Ca ratio, \((\text{Boirden, et al. 1991})\). Too much Sn and the oxide layer spalls easily and too little causes the oxide layer to be ineffective. \(\text{Rocca et al.}(2006)\) showed that increasing Sn decreased corrosion and increased the OER overpotential. Using a Sn/Ca ratio of 2.5 is optimal for good corrosion resistance and maintaining a low OER overpotential. For Pb-acid batteries, a Sn/Ca of 10 is desired because OER is detrimental to overcharging batteries.

Generally, increasing Sn content and decreasing Ca improved corrosion resistance, Table 3.1.

**Table 3.1 Effects of Ca and Sn on corrosion rate, \((\text{Prengaman, 1999})\)**

<table>
<thead>
<tr>
<th>Sn Content (wt%)</th>
<th>0.6</th>
<th>1.2</th>
<th>1.5</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 Ca</td>
<td>126</td>
<td>80</td>
<td>76</td>
<td>54</td>
</tr>
<tr>
<td>0.08 Ca</td>
<td>75</td>
<td>37</td>
<td>33</td>
<td>32</td>
</tr>
</tbody>
</table>

The lack of cohesion observed with high Sn is displayed in Figure 3.10, Figure 3.11, Figure 3.12, and Figure 3.13 by a decrease in the PbO layer destabilizing the oxide during cyclic experiments.
Figure 3.10 Cross section of PbCaSn after cycling testing test, 0 wt% Sn. (Rocca, et al. 2006)

Figure 3.11 Cross section of PbCaSn after cycling testing test, 0.6 wt% Sn. (Rocca, et al. 2006)
Figure 3.12 Cross section of PbCaSn after cycling testing test, 1.2 wt% Sn. Rocca et al. (2006)

Figure 3.13 Cross section of PbCaSn after cycling testing test, 2 wt% Sn. Rocca et al. (2006)
3.5.  Corrosion mechanism

The corrosion of Pb anodes in electrowinning has been discussed by Kabanov et al. (1964) to be a result of dissolved oxygen ability to travel through the PbO₂ and reach the Pb anode. This study established that the O²⁻ diffuses through the PbO₂ oxide layer but the mechanical effect of O₂ evolution at the anode causing the oxide to spall, Rocca et al. (2006). The oxide layer is continuously cycling through growth, breaking, peeling and growth and consuming the Pb alloy.

3.6.  Chemical and other physical pretreatments of Pb anodes

It is common for the PbO₂ layer to spall from the anode and fall to the bottom of the cell during conditioning. It can take as long as 30 to 60 days to establish a stable layer in highly concentrated H₂SO₄ used in Zn electrowinning. During that time, the Pb corrodes and Pb can be deposited within the metallic deposit at the cathode decreasing its quality, (Moskalyk, et al (1999, Ramachandran & Balakrishnan, 1996, Ramachandran, et al. 1980, Prengaman & Siegmund, 2000).

Sandblasting and shot peening anodes have been reported to increase the corrosion resistance of anodes. The shot peened anode showed the lowest corrosion rate compared to sandblasted and as cast anode, (Jin, et al. 2003).

Conditioning Pb based anodes in KF-H₂SO₄ bath, oxidizing in KMnO₄-H₂SO₄ or sandblasting to determine the improvement of PbO₂ oxide development and adhesion to prevent excessive corrosion. Sandblasting the anode was easy to develop a good surface
for oxides to adhere to and mud grew in a uniform manner. Chemical conditioning of anodes was difficult to produce anodic oxides consistently.

3.7. Effects of changing electrolyte composition

3.7.1. H$_2$SO$_4$ concentration

Decreasing H$_2$SO$_4$ concentration causes more PbO to form on the anode. Using linear sweep voltammetry and potential steps has determined that the lower H$_2$SO$_4$ concentration and the higher mass transfer of H$^+$ and SO$_4^{2-}$ increases the presence of basic oxides and PbSO$_4$. The increase is associated with the presence of larger crystal sizes of increasing porosity, (Guo, 1996).

When cycling Pb anodes, the composition and thickness of the oxide layer was determined in different concentrations of H$_2$SO$_4$. The oxidation rate of PbSO$_4$ to PbO$_2$ (reaction 3-5) is dependent on PbSO$_4$ solubility in H$_2$SO$_4$ which is a function of pH. At high pH, the solubility of PbSO$_4$ is high compared to low pH solutions, Figure 3.14. The thickness of the oxide layer is also a function of solubility and the thickness is largest between 0.5 and 2 M H$_2$SO$_4$, Figure 3.15, (Monahov, et al. 2000, Pavlov & Pashakova, 1987). The solubility falls off with increasing concentration and increases again when the electrolyte contains 70% H$_2$SO$_4$, (Crockford & Brawley, 1934).
Figure 3.14 Solubility of PbSO$_4$ as a function of H$_2$SO$_4$ concentration, (Danel & Plichon, 1982)

Figure 3.15 Anode layer thickness as a function of H$_2$SO$_4$ concentration, reproduced from Monahov et al. (2002)
Newnham (1992) and Hine (1988) showed increasing corrosion rates with increasing H$_2$SO$_4$ concentration. Newnham (1992) tested both pure Pb and PbAg anodes in the presence and absence of 10 g/L Mn$^{2+}$ to determine a general increase in corrosion rates (Figure 3.16). Both authors used a high current density (10,000A/m$^2$) for the purpose of accelerating experiments.

![Figure 3.16 Corrosion rate as a function of H$_2$SO$_4$ concentration, 10000A/m$^2$, created from (Newnham, 1992)](image)

Potentiodynamic polarizations showed the presence of PbSO$_4$, and PbO$_2$ during the anodic scan and PbO-PbSO$_4$, during the reduction, Figure 3.3. The stability of oxides in anodic layer as a function of potential is presented in Figure 3.5. Increasing H$_2$SO$_4$ concentration decreased $E_{corr}$ and the Pb dissolution was controlled by the HSO$_4^-$ ions and H$^+$ diffusion in the electrolyte, (Rehim, 1984, Ljomah, 1987, Yamamoto, et al.1991).
3.7.2. Mn$^{2+}$ concentration

Mn$^{2+}$ concentration in Zn electrowinning and its effect on current efficiency has been studied since the 1960’s by Fleischman et al, (1962), and Fukushima (1960). These authors determined Electrowinning is sensitive to impurities and Mn$^{2+}$ is added and regulated to precipitate Fe from the leach solution and to minimize anode corrosion. Mn$^{3+}$ is deposited onto the anode as MnO$_2$ and acts as a physical barrier to anode corrosion and minimizing Pb slime formation, (Fukushima, 1960, Chen & Dutrizac, 2009, Zhang & Cheng, 2007).

In small concentrations, Mn can minimize the corrosion of Pb based anodes by depositing anodic scale and minimizes the formation of anodic slime. However, too much scale tends to cause spalling and Pb can contaminate the cathodic deposit. Other ways to improve the quality of the anodic layer is to reduce the temperature and current density during galvanostatic experiments. Decreasing the temperature increased the quality of the oxide layer and minimized the current density which avoids excessive OER that displaces the oxide layer, (Fukushima, 1960, Zhang & Cheng, 2007).

A decrease in current efficiency is not observed until 10 g/L of what is added in 60 g/L Zn$^{2+}$, 150 g/L H$_2$SO$_4$ at 40°C using a Pb0.2%Ag anode and an aluminum cathode. Increasing Mn$^{3+}$ concentration unexpectedly catalyzed the OER during cyclic voltammetry, (Zhang & Hua, 2009).

Nijjer (2000) used cyclic voltammetry to determine the effect of H2SO4 and temperature on the presence of Mn$^{2+}$ in solution. It was observed that decreasing H$_2$SO$_4$ concentration and temperature increased the volume of MnO$_2$ present in the oxide layer.
Nijjer (2000) established that increasing temperature and decreasing H₂SO₄ concentration increased the oxidation rate of Mn²⁺ to MnO₂.

Mn oxide scales exist in a coliform structure (Figure 3.17) on the surface of and PbO₂ that can also contain AgCl in industrial Zn electrowinning plants. It is common for Ag to corrode and become entrapped in the Mn oxide layer as an Ag oxide, (Chen & Dutrizac, 2009).

Zn Electrowinning takes place at a pH of zero or slightly below and at a high potential where MnO₂ is stable and near the stability region of MnO₄⁻. The presence of MnO₄⁻ has been detected, but studies have shown that it will react with Mn²⁺ to form Mn³⁺ and hydrate and precipitate MnO₂. The increased thickness of the oxide decreasing activity and additional reactions are what decreases the current efficiency when too much Mn²⁺ present, (Zhang, 2009).

In higher concentrations of Mn²⁺, Ecorr increases with increasing concentration up to 5 or 10 g/L due to the depolarization when Mn oxide forms on the anode, (Ivanov, et al. 2000B). This concentration represents when MnO₂ occupies all of the sites available for O₂ evolution. It is likely for this reason that there is an increase in the oxygen evolution region slope, O₂ potential and decreased current efficiency above 5 or 10 g/L. The presence of an Ag oxide catalyzes OER, but too much Mn²⁺ can eliminate this behavior, (Ivanov. et al. 2000B, Yu & O’Keefe, 2002, Cachet, et al. 1999).

Characterization has been established by Recéndiz, et al. (2009) using x-ray diffraction after certain time intervals and the MnO₂ oxide layer forms on top of the PbO₂ as presented by Yu & O’Keefe (2002) in Figure 3.17. The oxide layer is dynamic and it can
take as long as 30 to 60 days before it stabilizes, (Prengaman & Siegmund, 2000). During the stabilization time, the oxide layer will crack and expose the metal anode liberating Pb ions.

There are no publications discussing the effect of Mn$^{2+}$ on anode corrosion in Ni electrowinning. However, Gogio & Das (1988) performed a study on the effects of Mn$^{2+}$ on current efficiency and determined that the current efficiency decreased the quality of the deposit diminished.

![Figure 3.17 Cross section of PbO2 and MnO2 oxide layer developed in 180 g/L H2SO4 and 0.2 g/L Mn2+, (Yu & O'Keefe, 2002)](image)

3.7.3. Cl$^-$ concentration

In electrowinning, Cl$^-$ ions are present in low concentration and appear due to their presence in wash water and in ore. In Zn electrowinning concentration is <500 mg/L and up to 1000 mg/L in Ni electrowinning.
Newnham (1992) added Cl\(^-\) as HCl in the presence and absence of Mn\(^{2+}\) and determined that when no Mn\(^{2+}\) was present, Cl\(^-\) had little effect on corrosion rates. In the presence of Mn\(^{2+}\), the corrosion increased and the system became more complex because of the presence of Cl compounds. In low concentration (~100 mg/L), AgCl\(_2\) formed on the surface of the anode which inhibited Pb\(^{2+}\) from dissolving into solution, (Kiryakov & Stender, 1951). Ivanov, et al. (2000) considered that in the presence of Cl\(^-\), Cl oxides would form, sealing the layer.

Ivanov, et al.(2000b) reported that Cl\(^-\) discharged onto the Pb anode potentially forming compounds that could protect the anode. Hampson (1981) suggested that Cl\(^-\) could destabilize SO\(_4^{2-}\) and inhibit the repassivation of the anode and could play a roll in decreasing the oxygen evolution region slope and OER potential.

Cl\(_2\) evolution (3-6) has a standard reduction potential of 1.16\(V_{SCE}\). Since the Cl\(_2\) reduction over potential is less then OER, it is more likely OER takes place, (Littauer & Shreir, 1967). With Cl\(^-\) in such low concentration in both forms of electrowinning, the Cl\(_2\) evolution is not likely to occur or decrease current efficiency substantially, (Alfantazi & Shakshouki, 2002).

At potentials between 1.7\(V_{SCE}\) and 2.0\(V_{SCE}\), Cl\(^-\) can be transformed to hypochlorite (ClO\(^-\)), chlorate (ClO\(_3^-\)) and or perchlorate (ClO\(_4^-\)). ClO\(_4^-\) has been proven to corrode Pb in H\(_2\)SO\(_4\) by decomposing the oxide layer, but optimal concentration of perchlorate can be beneficial, (Hampson & Lazarides, 1981).

\[
Cl_2 + 2e^- = 2Cl^- \quad E^\circ = +1.16V_{SCE}
\]  
\[\text{(3-12)}\]
Newnham, *et al.* (1995) found little agreement with the amount of Cl\(^-\) that can be tolerated in a Pb-acid battery during cyclic voltammetry. Results by Kiryakov & Stender (1951) over long-term immersion experiments (167 hours) showed that Cl\(^-\) has a large impact on pure Pb, but a small amount of Cl\(^-\) can increase corrosion resistance when using PbAg anodes, Figure 3.18.

The role of Cl\(^-\) in Ni electrowinning has been discussed by Alfantazi & Shakshouki (2002) between 0 and 1000 mg/L with respect to current efficiency, power consumption, and surface morphology of the Ni deposit. Improvements with the increasing Cl\(^-\) included decreasing power consumption, improved the current efficiency, and flat and ductile Ni deposits more fine morphology.

![Figure 3.18 Impact of Cl\(^-\) on the corrosion of Pb anodes, 167h, 400 A/m\(^2\), 1M H\(_2\)SO\(_4\) reproduced from Kiryakov & Stender (1951) via Ivanov (2000).](image)
3.7.4. Metal ion concentration

Both Zn and Ni electrowinning cell houses have the metal ions of interest between 0.5 and 1M, (Newnham 1992). Newnham (1992) varied the Zn concentration from 0 to 150 g/L with constant sulfate concentration composed of Zn$^{2+}$, H$_2$SO$_4$, and Mn$^{2+}$ to observe the impact on corrosion rate. There is no change in corrosion rate until concentration is increased to 100 g/L Zn$^{2+}$ where a distinct increase in corrosion rate in the presence and absence of Mn$^{2+}$ (Figure 3.19). The author maintained constant sulfate concentration because it had been reported to decrease corrosion by limiting the diffusion of SO$_4^{2-}$. It was thought that increasing H$_2$SO$_4$ without maintaining constant SO$_4^{2-}$, there would be an increase in corrosion rates with higher metal ion concentration above 60 g/L.

No studies exist on the corrosion of Pb anode in Ni electrowinning with changing Ni$^{2+}$ concentration, but a report by Holm & O’Keefe (2000) concluded that increasing Ni concentration improved the shape and coherency of the Ni deposit.
3.7.5. Temperature

Increasing temperature increases the kinetics of corrosion (Figure 3.20), Newnham (1992). Hine (1988) suggested that corrosion rates of pure Pb were independent of temperature when the electrolyte contained 1M H$_2$SO$_4$ when Mn was not present. Monahov & Pavlov (1998) showed that increasing temperature above 40°C, increased the thickness of the oxide layer and increased the amount of β-PbO$_2$. This author also presented evidence of increasing potential and activation energy until a critical value is reached.

Low temperatures in Ni electrowinning produced deposits that were brittle and had poor morphology. At 60°C, a ductile and smooth deposit was formed, (Holm & O’Keefe, 2000).

Figure 3.19 The effect of Zn$^{2+}$ on corrosion rate, 50°C, 10 000A/m$^2$ and constant sulfate(2.8M). Newnham (1992).
Figure 3.20 Corrosion rate as a function of increasing temperature, Pb-0.78%Ag, 1.5M H₂SO₄, (Newnham, 1992)
4. Experimental

To understand the corrosion behavior of different alloys in Zn and Ni electrolyte, in this thesis metallographic analysis was used to characterize the materials, electrochemical polarizations to observe corrosion parameters and energy dispersive x-ray spectroscopy and x-ray diffraction to understand the composition of oxides.

The Pb-based alloys were observed using a Hitachi S-2300 scanning electron microscope (SEM) to analyze the surface morphology of oxide layer at different potentiostatic and galvanostatic conditions. Chemical composition, microstructure, and oxide morphology of the alloy and oxide layer accomplished using energy dispersive X-ray spectroscopy attached to the SEM to observe microstructure and oxide layer morphology.

Electrochemical polarizations were used to determine the effect of changing electrolyte composition and anode material on corrosion parameters. The methods used in this experiment include OCP to ensure stability prior to potentiodynamic, potentiostatic, and galvanostatic polarizations.

4.1. Materials

Although the Zn component of this thesis used a PbAg alloy, the Ni component used an as cast PbAg, rolled PbAg and PbCaSn. The PbAg alloy was received from Xstrata Zinc and the PbCaSn alloy was received from Cominco Engineering Services Ltd.

Prior to observing the alloys microstructure, the samples were sequentially wet ground using SiC paper using #320, #600, #800, and #1200 grit followed by polishing with 6 and
1 micron diamond suspension. It was common for Si to be embedded into the sample surface requiring ultrasonic cleaning between each step of grinding and polishing. For metallographic observation, the samples were etched using 3 parts acetic acid to 1 part hydrogen peroxide to reveal grain boundaries.

4.1.1. PbAg alloy

Table 4.1 shows the composition of the PbAg obtained by fire assay and inductively coupled plasma (ICP) techniques completed by Inspectorate IPL in Richmond, BC. The primary grains contain 0.7% Ag and 99.3% Pb and the eutectic region is composed of 4.5% Ag, the microstructure is shown in Figure 4.1. The values corresponding to primary and eutectic regions of the microstructure were determined by applying the Lever Rule to that PbAg phase diagram presented in Figure 3.7. According to the Pb-Ag equilibrium phase diagram, the microstructure contains 22% eutectic phase. The ASTM macro grain size number for this alloy was calculated to be between 8 and 8.5 (ASTM E112) and the grains are orientated randomly in the as cast form. The lighter region represents the primary Pb grain and the dark represents the eutectic.

The second material tested was a PbAg alloy that was rolled at UBC using a rolling mill to reduce its thickness by 70%. The alloy was heat treated to relieve residual stresses and to slightly increase the grain size for 48 hours in an aerated furnace at 200°C. The grains of the rolled alloy (Figure 4.2) are elongated, aligned, and show a more uniform distribution of grain and grain boundaries compared to Figure 4.1.

Table 4.1 Composition of PbAg alloy, IPL

<table>
<thead>
<tr>
<th></th>
<th>Pb (wt%)</th>
<th>Ag (wt%)</th>
<th>As (ppm)</th>
<th>Bi (ppm)</th>
<th>Cu (ppm)</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbAg</td>
<td>99.22</td>
<td>0.78</td>
<td>5</td>
<td>40</td>
<td>15</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 4.1 Microstructure of as cast Pb-0.78% Ag, 50x magnifications

Figure 4.2 Microstructure of rolled Pb-0.78% Ag, 70% reduction and 48 hour heat treatment at 200°C, 50x magnification
4.1.2. PbCaSn alloy

The composition and microstructure of the PbCaSn alloy are displayed in Table 4.2 and Figure 4.3 respectively. The ICP by IPL Inspectorate determine the composition of the alloy, but the Sn content was too high to determine a specific value. The grain sizes of the PbCaSn were larger then the PbAg alloys used in this thesis and more irregularly shaped.

Table 4.2 Composition of the PbCaSn alloy, IPL

<table>
<thead>
<tr>
<th></th>
<th>Pb (wt%)</th>
<th>Sn (ppm)</th>
<th>Ca (wt%)</th>
<th>Ag (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCaSn</td>
<td>99.22</td>
<td>&gt;1000</td>
<td>0.09</td>
<td>9.18</td>
</tr>
</tbody>
</table>
4.2. Standard electrowinning electrolytes

4.2.1. Zinc

The standard electrolyte and variations in electrolyte for Zn electrolyte are outlined in Table 4.3. The standard electrolyte was composed of 180 g/L \( \text{H}_2\text{SO}_4 \), 60 g/L \( \text{Zn}^{2+} \), 2.5 g/L \( \text{Mn}^{2+} \), 0 g/L \( \text{Cl}^- \) and held at 37°C.

**Table 4.3 Zinc electrowinning test conditions, standard conditions are marked in italic**

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{SO}_4 )</td>
<td>0, 50, 100, 150, <strong>180</strong>, 200, 250</td>
<td>g/L</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} )</td>
<td>0, 30, <strong>60</strong>, 90, 120</td>
<td>g/L</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} )</td>
<td>0, 2.5, 5, 8, 15</td>
<td>g/L</td>
</tr>
<tr>
<td>( \text{Cl}^- )</td>
<td>0, 100, 200, 300, 500</td>
<td>mg/L</td>
</tr>
<tr>
<td>Temperature</td>
<td>20, <strong>37</strong>, 50, 65</td>
<td>°C</td>
</tr>
</tbody>
</table>

4.2.2. Nickel

Electrowinning cells operate at 3.6 V\text{SHE} to 3.9 V\text{SHE} in cells maintained at 60°C. The leach solution flowing into the electrowinning cells consist of 30 g/L \( \text{H}_2\text{SO}_4 \), 60 g/L \( \text{Ni}^{2+} \), and 400 mg/L \( \text{Cl}^- \). These concentrations were developed from industry and Alfantazi & Shakshouki (2002), Mohanty, *et al.* (2009).

**Table 4.4 Nickel electrowinning test conditions**

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{SO}_4 )</td>
<td>20, <strong>30</strong>, 40</td>
<td>g/L</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} )</td>
<td><strong>60</strong></td>
<td>g/L</td>
</tr>
<tr>
<td>( \text{Cl}^- )</td>
<td>0, <strong>400</strong>, 600, 800</td>
<td>mg/L</td>
</tr>
<tr>
<td>Temperature</td>
<td><strong>60</strong></td>
<td>°C</td>
</tr>
</tbody>
</table>
4.3. Experiments

Anode material received from Xstrata (PbAg) and Cominco Engineering Services Limited (PbCaSn) were cut into manageable disc shape coupons that would fit into a Tefzel® Dupont fluorocarbon electrode holder that would limit anode exposure to electrolyte to 1 cm$^2$. The disc shape coupons had a diameter of 16 mm and a varying thickness between 3 and 5 mm. All electrochemical experiments were repeated to ensure reproducibility of results were confirmed.

A 1L, 3 port water-jacketed glass cell was connected to a Cole-Parmer heater to maintain constant temperature while performing polarization. The temperature was set 2 degrees above the target temperature in order to obtain the desired temperature in the cell. A graphite rod was used as a counter electrode (CE) and all potentials were determined using a saturated calomel reference electrode (0.242V vs SHE) via a Luggin capillary filled with the same cell solution and a salt bridge. A Princeton Applied Research (PAR) Versastat 4 potentiostat was used for all electrochemical measurements.

Disk shaped samples with the diameter of 15 mm were cut from the original alloy sheets and the surface was ground smooth using SiC. No other treatment was completed on the alloy surface. Using a Teflon sealing ring, an area of 1 cm$^2$ of the sample surface was exposed to the solution.

All solutions in this thesis were prepared using analytical grade reagents manufactured by either Fisher or Alfa Aesar; Fisher chemicals included 98% ACS grade H$_2$SO$_4$ (H$_2$SO$_4$), Sodium chloride (NaCl), ACS grade Zinc sulfate hexahydrate (ZnSO$_4$ 6H$_2$O), and Manganese monohydroxide (MnSO$_4$ H$_2$O). Alfa Aesar Chemicals were limited to nickel
sulfate hexahydrate (NiSO₄·6H₂O) due to availability. Compositions for nickel and zinc electrowinning were based on industry concentrations and relevant literature.

Each experiment used a fresh batch of 750mL of electrolyte and was exposed to testing conditions (temperature and atmosphere) for 30 minutes to stabilize in aerated or deaerated conditions prior to running a polarization.

4.3.1. OCP

Electrochemical tests are highly dependent on surface preparation and the materials ability to form an oxide layer, (Jiménez, et al. 2009). Pb alloys were wet ground on silicon carbide paper to a 600 grit finish prior to degreasing in an ultrasonic bath before being placed in the corrosion cell. The Pb alloy, counter electrode, and reference electrode are connected to a potentiostat when no current is applied to the working electrode. The potential was then monitored for 3600 seconds for the electrode and oxide potential to stabilize. This allowed for a consistent surface layer prior to electrochemical experiments.

4.3.2. Potentiodynamic polarization

All of the potentiodynamic polarization experiments were conducted consistently with the procedures outlined in ASTM G5. In the Zn electrowinning component of this thesis, potentiodynamic polarizations were compared in both an atmospheric and a deaerated environment. Although electrowinning cell houses are exposed to aerated conditions and evolve oxygen, it was of interest to observe the impact of dissolved oxygen in the cells.
In Zn electrowinning, all experiments were run with a PbAg anode and in aerated and deaerated cells.

Potentiodynamic polarizations were used to determine corrosion parameters; $E_{\text{corr}}$, $i_{\text{corr}}$, oxygen evolution region slope and OER overpotential with respect to dissolved oxygen, and changing electrolyte and anode material. The potentiodynamic polarizations were completed after 30 minutes for the electrolyte to stabilize at temperature and 1 hour OCP. The scan started at -0.250 V$_{\text{OCP}}$ and was completed when 1.650 V$_{\text{SCE}}$ was reached using a scan rate of 0.166 mV/s.

Corrosion current, corrosion potential, and Tafel constants have historically been determined using Tafel extrapolation. Due to the importance and consistency required when determining corrosion parameters, Lorenz & Mansfeld (1981), fitting a modified Butler-Volmer equation (equation 4-1) to data points 25 mV above and below $E_{\text{corr}}$ was used. This method is accepted in literature and has been established to be in good agreement with both experimental and calculated curves (Figure 4.4).

\[
i = i_{\text{corr}} \left[ \exp \left( \frac{\eta}{b_a} \right) - \exp \left( \frac{\eta}{b_c} \right) \right]
\]

- $\eta$, is the overpotential
- $b_a$, is the anodic Tafel slope
- $b_c$, is the cathodic Tafel slope
- $i_{\text{corr}}$, corrosion current
Figure 4.4 Fitting equation 4-1 to the experimental data plus and minus 25mV to determine the corrosion current density

4.3.3. Oxygen evolution region slope and oxygen evolution potential

The oxygen evolution reaction (reaction 1-2) is intrinsically slow and limited by a large activation energy, limited number of sites that can be blocked by adsorbed OH\(^-\). It takes a large overpotential to displace the adsorbed oxides on active sites before \(O_2\) is evolved, Pavlov & Monahov (1996). The evolution of \(O_2\) disturbs the solution close to the anode and mass transfer limitations are not expected to have a large impact. To determine the oxygen evolution potential from a potentiodynamic polarization, a tangent line to both the passive and oxygen evolution regions were drawn (Figure 4.5). The slope of the OE region represented the rate of reaction as a function of potential, and the intersection between the two regions was taken to be the OER overpotential (Pajunen et al. 2003).

Maja, et al. (1985) showed that, at high potentials where both OER and PbO\(_2\) formation are possible, the rate of the former is much greater than the rate of the latter. Accordingly,
in this study it is assumed that the high potential portion of the curve in Figure 4.5 primarily represents the OER. Considering this assumption, complete results for oxygen evolution overpotential are reported and were used to compare the OER rates for different electrode materials/ solutions. Low oxygen evolution overpotential and smaller slopes are favorable for the electrowinning industry. A smaller slope represents the evolution of more oxygen at a lower potential and indirectly decreasing the electricity required to plate metal at the cathode.

4.3.4. Potentiostatic polarizations

Potentiostatic experiments were completed at three different potentials; -0.3, 0.9, and 1.3V_{SCE} (Figure 4.5). These potentials were chosen to study the oxide composition and morphology at the beginning, in the middle and close to the end of passive potential region on the potentiodynamic polarization curve of the Pb-Ag alloy. The chemical composition of each corrosion product formed at the three potentials was qualitatively measured using EDX.

Figure 4.5 determining the onset of oxygen evolution region behavior by drawing tangent lines and regions of potentiostatic
4.3.5. Galvanostatic polarization in nickel electrowinning

Typically, a current density of 200 A/m$^2$ is used in nickel electrowinning plants. By application of this current, the anode is pushed to the potential region where PbO$_2$ is a stable phase. Under these conditions, the surface of the anode is oxidized while oxygen evolves simultaneously. The oxide layer thickens with time until some parts begin to spall. This process reduces the anodes service life on one hand, and contaminates the solution and thus the final product on the other. Therefore, measuring the corrosion rate (rate of oxide formation) is important. In order to determine the corrosion rates and study the behavior of anode materials under different working conditions, it is necessary to distinguish between the current consumed for oxide formation and the current consumed by other anodic reactions. The following approach was chosen to measure the corrosion rate:

Polished samples were galvanostatically polarized for 24 hours at 20 mA/cm$^2$ (typical of nickel electrowinning plants). After the 24 hour period, the current was shut off and the PbO$_2$ was allowed to transform (be reduced) to PbSO$_4$, a process during which a plateau was observed on the potential-time curve (self discharge). Discharge current and plateau length together define the amount of PbO$_2$ that is transformed. However, conventional measurement methods were inconclusive for discharge current measurement mainly due to continuous conversion of the surface along the plateau. This inefficiency was observed experimentally by performing experiments similar to that shown in Figure 4.6.
Potentiodynamic scans were performed 20 mV above and below the OCP at different time intervals along the self discharge plateau. Experiments yielded variable discharge currents at different intervals. In order to overcome this difficulty, variable discharge currents were applied and the plateau lengths were measured.
Figure 4.7 Total charge as a function of discharge time for Pb-alloys in 400 mg/L Cl⁻ and 30 g/L H₂SO₄ at 60°C

Figure 4.7 shows the total charge (plateau length X applied discharge current) plotted as a function of discharge time for different discharge currents. An extrapolation to zero discharge time on Figure 4.7 gives the total charge consumed during the plateau since the self discharge effect is virtually eliminated. However, not all of the PbO₂ transforms to PbSO₄ along the plateau. Rüetschi and Cahan (1957) used microtitration and determined the remaining PbO₂ on the surface. They found that the amount of PbO₂ remaining on the surface after the plateau is independent of the discharge rate, (Rüetschi & Cahan, 1957).

In this thesis, immediately after the discharge plateau, samples were drawn out of the solution and were examined using XRD so the remaining PbO₂. By measuring the area under the PbO₂ and PbSO₄ peaks after discharge, a qualitative estimation of surface composition was determined. This was used to roughly calculate the remaining PbO₂ on
the surface relative to PbSO₄ content after discharge. It is noteworthy that according to previous studies, the remaining PbO₂ on the anode is at most 15% of total PbO₂, Rüetschi and Cahan (1957).

Anode materials were polished sequentially at 320, 400 and 600 grit SiC and then degreased ultrasonically before being galvanostatically polarized for 24 hours at 20 mA/cm². After 24 hours, the current was removed and a discharge current was applied (1, 10, or 20 mA/cm²) while the potential was observed. The potential would initially drop to a potential corresponding to the PbO₂/PbSO₄ equilibrium potential until all PbO₂ had transformed to PbSO₄ when it would further drop to OCP. Total charge can represent the total volume of oxide and when the length of the discharge plateau was multiplied by the discharge current, a discharge rate is determined. The discharge rate would be graphed using the three different discharge currents and three different anode materials. Fitting a line of best fit between multiple discharge rates and extrapolating to zero would represent the total charge required to form the oxide layer over 24 hours. The better performing anode material with respect to galvanostatic polarization would have a short discharge plateau because a smaller volume of corrosion product would be present.
Figure 4.8 Example of discharging alloys galvanostatically at 10 mA/cm$^2$ in 30 g/L H$_2$SO$_4$, 400 mg/L Cl$^-$, 60 g/L Ni$^{2+}$ at 60$^\circ$C

Using OCP, potentiostatic, potentiodynamic, and galvanostatic experiments will develop a strong understanding of Pb-based alloy corrosion in environments relative to electrowinning. The OCP will determine the corrosion tendency, the potentiodynamic will show the changing composition as a function of potential, and the galvanostatic will simulate actual electrowinning conditions.
5. Results and discussion; Zinc electrowinning

The effects of H$_2$SO$_4$, Mn$^{2+}$, Zn$^{2+}$, Cl$^-$ and temperature were studied using a large number of potentiodynamic experiments. The results can be used to study the corrosion behavior of anode material at a wide range of potentials, kinetics of oxygen evolution, and oxide layer development.

The corrosion product layer is complicated due to the number of possible reactions and products. The electrowinning process is carried out in concentrated H$_2$SO$_4$ solution (pH<0). The stable oxides of Pb at different potentials are presented in the Pb-S-H$_2$O
Pourbaix diagram that was constructed for this study (Figure 5.1). The sulfur content of the diagram is based on the addition of 1.8 M H$_2$SO$_4$, and 1 M Zn$^{2+}$ as ZnSO$_4$ (2.8 M of sulfate). The Pb concentration in Figure 5.1 is based on the 0.07 ppm from ICP analysis on spent industrial electrolyte. Some of the reactions that are likely to take place at the anode during potentiodynamic polarizations are:

\[
\begin{align*}
\text{Pb} + \text{SO}_4^{2-} &= \text{PbSO}_4 + 2e^- & E^* &= -0.601 \text{V}_{\text{SCE}} \\
2\text{H}^+ + 2e^- &= \text{H} & E^* &= -0.242 \text{V}_{\text{SCE}} \\
\text{Cl}_2 + 2e^- &= 2\text{Cl}^- & E^* &= 1.116 \text{V}_{\text{SCE}} \\
\text{Mn}^{2+}_{\text{surface}} &\rightarrow \text{Mn}^{3+}_{\text{ads}} &\rightarrow \text{Mn}^{4+} \rightarrow \text{MnO}_2 & 1.238 \text{V}_{\text{SHE}} < E^* < 1.288 \text{V}_{\text{SCE}} \\
\text{PbSO}_4 + 2\text{H}_2\text{O} &= \text{PbO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2e^- & E^* &= 1.308 \text{V}_{\text{SCE}}
\end{align*}
\]

According to Figure 5.1, no Pb oxides are stable and, therefore, not expected to be present on the surface. Increasing potential above $E_{\text{corr}}$, PbSO$_4$ and lower oxides of Pb (PbO) begin to form on the anode surface, Lander(1956). The PbSO$_4$ was observed at the oxide/electrolyte interface and the PbO was found at the alloy/oxide layer interface, Pavlov, et al.(2004). Both PbO and PbSO$_4$ are non-conductive and with increasing potential, the PbO and PbSO$_4$ oxides will protect the Pb-Ag alloy from corrosion and decrease the current density. Potentiodynamic experiments are relevant to simulating electrowinning conditions because PbO and PbSO$_4$ form prior to a transformation to PbO$_2$ even at high potentials.

The OER rate and overpotential is dependent on the stability of PbO$_2$ in reaction 5-5. At high potentials, the surface is covered with PbO$_2$ while the OER takes place. Maja et al.(1985) reported that both reactions 1-2 and 5-5 take place at high potentials, but the
OER occurs more extensively than the formation of PbO₂, (Maja, 1985). Therefore, within the oxygen evolution region, the current density primarily represents the rate of OER instead of the current consumed by the development of PbO₂. It is more favorable to have low oxygen evolution region slope and OER overpotential because they reflect an increase in Zn production using a lower current density.

5.1. Changes in electrolyte composition

5.1.1. Effect of H₂SO₄ concentration on corrosion behavior

H₂SO₄ is added upstream in the processing of Zn concentrates. Acid is generated during electrowinning from the OER reaction (1-2) where H₂SO₄ concentration is commonly between 150 and 200 g/L⁵,₁⁵. The acid concentrations in potentiodynamic experiments in this study ranged from 0 g/L up to 250 g/L in both aerated and deaerated cells. The purpose was to determine changes in E_corr, i_corr, oxygen evolution region slope, and OER overpotential (Table 5.1).

Table 5.1 Effect of H₂SO₄ concentration on potentiodynamic behavior of PbAg alloys in aerated and deaerated (*) cells.

<table>
<thead>
<tr>
<th>H₂SO₄ (g/L)</th>
<th>E_corr (V_SCE)</th>
<th>i_corr (A/cm²)</th>
<th>Slope of oxygen evolution region (V/dec)</th>
<th>OER Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.57</td>
<td>8.63E-06</td>
<td>0.071</td>
<td>1.30</td>
</tr>
<tr>
<td>50</td>
<td>-0.62</td>
<td>1.81E-05</td>
<td>0.053</td>
<td>1.45</td>
</tr>
<tr>
<td>100</td>
<td>-0.64</td>
<td>1.21E-05</td>
<td>0.076</td>
<td>1.43</td>
</tr>
<tr>
<td>150</td>
<td>-0.70</td>
<td>1.20E-05</td>
<td>0.063</td>
<td>1.47</td>
</tr>
<tr>
<td>180</td>
<td>-0.68</td>
<td>9.67E-06</td>
<td>0.073</td>
<td>1.48</td>
</tr>
<tr>
<td>200</td>
<td>-0.70</td>
<td>1.06E-05</td>
<td>0.071</td>
<td>1.47</td>
</tr>
<tr>
<td>250</td>
<td>-0.71</td>
<td>9.46E-06</td>
<td>0.048</td>
<td>1.43</td>
</tr>
<tr>
<td>*50</td>
<td>-0.55</td>
<td>1.74E-05</td>
<td>0.079</td>
<td>1.53</td>
</tr>
<tr>
<td>*100</td>
<td>-0.55</td>
<td>6.81E-05</td>
<td>0.091</td>
<td>1.55</td>
</tr>
<tr>
<td>*150</td>
<td>-0.55</td>
<td>1.79E-05</td>
<td>0.092</td>
<td>1.61</td>
</tr>
<tr>
<td>*180</td>
<td>-0.55</td>
<td>1.52E-05</td>
<td>0.157</td>
<td>1.62</td>
</tr>
<tr>
<td>*200</td>
<td>-0.56</td>
<td>3.11E-05</td>
<td>0.088</td>
<td>1.59</td>
</tr>
</tbody>
</table>
The potentiodynamic polarizations in both the aerated and deaerated cells have the same general behavior and are displayed in Figure 5.2. The aerated polarization curve shows more electrochemical noise than the deaerated cell likely due to the increase in dissolved oxygen. The presence of dissolved oxygen likely increases the presence and stability of PbO and PbSO₄. The increased oxygen facilitates the formation of PbO at the anode/corrosion product interface and thus reduces the formation of the PbSO₄ layer, hence the fluctuations when increasing potential between the primary passive potential (E_pp) and +0.25 V_SCE. Lander(1956). At high potentials, the anodic polarization curve shifts to the left with increasing H₂SO₄ concentration improving corrosion resistance. At all acid concentrations in a deaerated cell, a local increase in current density at ~1.0 V_SCE is observed. It is possible that this change in polarization behavior is caused by Mn²⁺ since the effect is more noticeable with increasing Mn²⁺ concentration (Figure 5.3).

With increasing acid concentration, a decrease in E_corr was observed in both aerated and deaerated cells. This was likely due to decrease in PbSO₄ solubility with increasing concentration and the presence of a thinner oxide layer, Guo(1997), Fontana & Greene(1978).

When oxygen was removed from the cell, the polarization curve shifted to the right as a result of a thinner PbO layer. Deaerating the cell shifts the polarization curve to the right while in the aerated cell shifted the curve to the left, decreasing corrosion rates. The lack of oxygen in the deaerated cell creates conditions for a poorly established oxide layer, Kim et al.(1985). Increasing dissolved oxygen and labile oxygen on the anode increased the oxide layer bond strength and decreased the OER overpotential, Danilov et al.(1994) and Rüetschi & Delahay(1955).
Figure 5.2 Effect of $\text{H}_2\text{SO}_4$ concentration on potentiodynamic behavior of PbAg alloys in aerated (top) and deaerated (bottom) figure.
The curve shift with increasing H\textsubscript{2}SO\textsubscript{4} has been reported to be as a result of the change in PbSO\textsubscript{4} solubility. It has previously been establish that maximum solubility of PbSO\textsubscript{4} is between 100 and 200 g/L H\textsubscript{2}SO\textsubscript{4} (6.5 mg/L) and the thickest layer was measured between 50 and 250 g/L H\textsubscript{2}SO\textsubscript{4} (5 microns thick after 16 hours of polarization), Monahov \textit{et al},(2000), Vinal & Craig(1939) and Danel & Plichon(1982). The deaerated cell shows a local minimum in $i_{corr}$ between 100 and 200 g/L H\textsubscript{2}SO\textsubscript{4} which is in agreement with previous authors, Guo \textit{et al}.(1996) and Yu & O’Keefe(2002). It is unclear what caused the decrease in corrosion resistance: Guo reported that increasing H\textsubscript{2}SO\textsubscript{4} concentration increased the density of the oxide layer and decreased the presence of pores in the oxide Guo \textit{et al}.(1996), and Yu & O’Keefe reported the presence of Pb oxides modifying the corrosion rate.

The oxygen evolution region slope is highest at 100 g/L H\textsubscript{2}SO\textsubscript{4} and 180 g/L for aerated and deaerated cells, respectively. The OER potential is highest in 180 g/L H\textsubscript{2}SO\textsubscript{4} in both aerated and deaerated cells. The lowest rates are observed at concentrations below 100 g/L and above 200 g/L. The role that PbSO\textsubscript{4} solubility plays is greater at high potentials because of the development of thicker oxide layer with increased stability of PbSO\textsubscript{4}. The increased thickness of the corrosion product at H\textsubscript{2}SO\textsubscript{4} concentrations with high solubility likely contribute to increasing oxygen evolution region slopes and OER potentials, (Newnham, 1992).

\textbf{5.1.2. Effect of Mn\textsuperscript{2+} on general corrosion behavior}

In Zn electrowinning, Mn\textsuperscript{2+} is added and regulated to precipitate Fe from the leach solution and to minimize anode corrosion. Mn\textsuperscript{2+} is deposited onto the anode as MnO\textsubscript{2}
and acts as a physical barrier to anodic corrosion during electrowinning, (Fukushima, 1960), (Habashi, 1997). At high potentials, Mn$^{2+}$ is oxidized in a series of reactions to form stable MnO$_2$, whose role is to inhibit the corrosion of Pb alloys. MnO$_2$ oxide only adheres to the established PbO$_2$ oxide layer forming a coliform structured composite oxide (Yu & O’Keefe, 2002).

The potentiodynamic experiments were completed in aerated and deaerated cells with Mn$^{2+}$ concentrations between 0 and 15 g/L. The OCP decreased with increasing Mn$^{2+}$ concentration in the aerated and deaerated cells. This is in agreement with Ivanov, et al. who reported that initially $E_{corr}$ decreased because of depolarization but increased with increasing concentration from the formation of a protective oxide layer (Ivanov et al. 2000b).

Potentiodynamic polarization curves are displayed in Figure 5.3 for both the aerated and deaerated cells. In the aerated cell, at potentials above $E_{pp}$ and up to +0.25 V$_{SCE}$ the presence of unstable oxides and the development of the oxide sub-layer can be observed. This behavior was not observed in the deaerated cell. With increasing Mn$^{2+}$ concentration, the reactions happening at potentials slightly above 1 V$_{SCE}$ in both the aerated and deaerated cells were more pronounced than in the aerated cell. This may suggest that they were a result of a Mn$^{2+}$ oxidation or adsorption. Both environments showed the lowest $i_{corr}$ when 2.5 g/L Mn$^{2+}$ was present in solution. These experiments showed that increasing the Mn$^{2+}$ concentration at high potential shifted the upper region of the polarization curve in an aerated cell up to 10 g/L Mn$^{2+}$, while a deaerated cell consistently shifted the polarization downwards in agreement with Cachet et al.(1999). Cachet et al.(1999) attributed this behavior to stimulating the OER reaction with
increased presence of Mn$^{2+}$ in an aerated cell up to 5 and 10 g/L when the electrolyte becomes saturated with Mn$^{2+}$ and the MnO$_2$ covers sites for oxygen evolution, Rerolle & Wiart(1996)
Figure 5.3 Effect of Mn$^{2+}$ concentration on potentiodynamic behavior of PbAg alloys in aerated (top) and deaerated (bottom) figure.
Potentiodynamic polarization curves are displayed in Figure 5.3 for both the aerated and deaerated cells. In the aerated cell, at potentials above \( E_{pp} \) and up to +0.25 V\textsubscript{SCE}, the presence of unstable oxides and the development of the oxide sub-layer can be observed. This behavior was not observed in the deaerated cell. With increasing Mn\(^{2+}\) concentration, the reactions at potentials slightly above 1 V\textsubscript{SCE} were more pronounced in both the aerated and deaerated cells. This may suggest that they were a result of a Mn\(^{2+}\) oxidation or adsorption. Both environments showed the lowest \( i_{corr} \) when 2.5 g/L Mn\(^{2+}\) was present in solution. These experiments showed that increasing the Mn\(^{2+}\) concentration shifted the upper region of the polarization curve in a negative direction in an aerated cell up to 10 g/L Mn\(^{2+}\). In a deaerated cell, the polarization curve shifted in a negative direction in agreement with Cachet, et al. (1999). This affect was considered to be a result of Mn\(^{2+}\) being saturated in the electrolyte and being adsorbed onto the PbAg anode as silver-salt with manganese.

The corrosion parameters (\( E_{corr} \), \( i_{corr} \), oxygen evolution region slope, and OER potential) are presented in Table 5.2. In an aerated cell, \( E_{corr} \) increased with increasing Mn\(^{2+}\) concentrations up to 10 g/L and \( i_{corr} \) increased up to 5 g/L. The deaerated cell showed a limited increase in \( E_{corr} \) up to 15 g/L and a fluctuation with \( i_{corr} \) with increasing concentration. Zhang & Hua (2009) observed a similar critical concentration when studying current efficiency. Although not directly related to this study, current efficiency was not affected until Mn\(^{2+}\) concentration was increased above 10 g/L. The cause of the current efficiency change was determined to be a result of MnO\(_4^-\) generation. This same reaction could potentially cause destabilization of the oxide layer and catalyze the OER.
Table 5.2 Effect of Mn$^{2+}$ concentration on potentiodynamic behavior of PbAg alloys in aerated and deaerated (*) cells.

<table>
<thead>
<tr>
<th>Mn$^{2+}$ (g/L)</th>
<th>E$<em>{corr}$ (V$</em>{SCE}$)</th>
<th>i$_{corr}$ (A/cm$^2$)</th>
<th>Slope of oxygen evolution region (V/dec)</th>
<th>OER Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.71</td>
<td>1.13E-05</td>
<td>0.068</td>
<td>1.52</td>
</tr>
<tr>
<td>2.5</td>
<td>-0.68</td>
<td>9.67E-06</td>
<td>0.073</td>
<td>1.48</td>
</tr>
<tr>
<td>5</td>
<td>-0.67</td>
<td>1.77E-05</td>
<td>0.062</td>
<td>1.42</td>
</tr>
<tr>
<td>10</td>
<td>-0.56</td>
<td>1.64E-05</td>
<td>0.067</td>
<td>1.62</td>
</tr>
<tr>
<td>15</td>
<td>-0.66</td>
<td>1.42E-05</td>
<td>0.051</td>
<td>1.44</td>
</tr>
<tr>
<td>*0</td>
<td>-0.56</td>
<td>2.69E-05</td>
<td>0.091</td>
<td>1.63</td>
</tr>
<tr>
<td>*2.5</td>
<td>-0.55</td>
<td>1.52E-05</td>
<td>0.157</td>
<td>1.63</td>
</tr>
<tr>
<td>*5</td>
<td>-0.56</td>
<td>2.59E-05</td>
<td>0.052</td>
<td>1.58</td>
</tr>
<tr>
<td>*10</td>
<td>-0.56</td>
<td>1.84E-05</td>
<td>0.672</td>
<td>1.62</td>
</tr>
<tr>
<td>*15</td>
<td>-0.56</td>
<td>6.64E-05</td>
<td>0.711</td>
<td>1.60</td>
</tr>
</tbody>
</table>

At high potentials, no clear relationship was observed between changing concentration and the oxygen evolution region slope. The OER potential showed a minimum at 5 g/L Mn$^{2+}$. The presence of Mn$^{2+}$ catalyzes the OER reaction when in optimal concentration, but it was reported to also impede it at high concentrations (Cachet et al. 1999). High concentrations increased the thickness of the oxide and also decreased the number of active sites for OER (Zhang & Hua, 2009).

In the deaerated experiments, the lack of dissolved oxygen is shown to decrease the stability of the oxide layer (Kim et al. 1997). OER potential was higher in deaerated experiments consistent with Danilov et al (1994) who observed a decrease in OER overpotential with increasing dissolved oxygen. This was ascribed to increased adsorbed OH$^-$.  

5.1.3. Effect of Cl$^-$ on general corrosion behavior

In Zn electrowinning, Cl$^-$ concentrations are commonly less than 500 mg/L. The effect of Cl$^-$ compounds on the anodic layer and their benefits to minimizing corrosion of anodes
has been discussed by multiple authors: Newnham (1992), Ivanov, et al. (2000), and Littauer & Shreir (1967).

It is unclear whether the effect of Cl\(^-\) on the anode is positive or negative. It has been reported that Cl\(^-\) forms a compound (AgCl\(_2\)) sealing the oxide layer, enhancing corrosion resistance, and depolarizing galvanostatic experiments (Ivanov et al. 2000b). However, Hampson (1981) reported that Cl\(^-\) destabilizes the SO\(_4^{2-}\) in the oxide layer, decreasing the quality of the oxide layer and inhibiting the passivation process, decreasing both the oxygen evolution region slope and OER potential. Cl\(^-\) has a very high reduction potential and destabilizes elements in the oxide and displaces them from the anode.

Cl\(^-\) concentrations were varied between 0 and 500 mg/L in potentiodynamic polarization experiments and are displayed in Figure 5.4. At low potentials and in the aerated cell, the largest variation in current density was likely due to the stabilization of oxides compared to the deaerated cell. In the passive region, the presence of Cl\(^-\) shifted the polarization curve to the left, showing lowest current densities when 500 mg/L Cl\(^-\) in the aerated cell and 100 mg/L in a deaerated cell. The highest current densities in the passive region corresponded to 300 mg/L Cl\(^-\) in the aerated cell and 0 g/L Cl\(^-\) in the deaerated cell. At high potentials, the polarization curve was shifted to more negative values when Cl\(^-\) concentration was increased to 200 mg/L in both the aerated and deaerated cell. The corrosion parameters (E\(_{corr}\), i\(_{corr}\), oxygen evolution region slope, and OER potential) are presented in Table 5.3.
In aerated cells, both $E_{\text{corr}}$ and $i_{\text{corr}}$ increased with increasing Cl$^-$ concentration. In both aerated and deaerated cells, $i_{\text{corr}}$ increased. However, $E_{\text{corr}}$ increased in the presence of oxygen and decreased in the absence of oxygen.

At high potentials in an aerated cell, the slope of the oxygen evolution region increased and the OER potential showed a minimum of 100 g/L Cl$^-$ concentration. In the deaerated cell, the slope was at a minimum between 100 and 300 mg/L of Cl$^-$ and the OER potential generally decreased with increasing concentration. In both environments, a low concentration of Cl$^-$ catalyzed the OER; the aerated cell was most affected in 100 mg/L Cl$^-$, and the deaerated cell was most affected by 200 mg/L Cl$^-$.

In the deaerated experiments, the lack of dissolved oxygen is shown to decrease the stability of the oxide layer (Kim et al. 1997). OER potential was higher in deaerated experiments consistent with Danilov et a(1994) who observed a decrease in OER overpotential with increasing dissolved oxygen. This was ascribed to increased adsorbed OH$^-$. 
Figure 5.4 Effect of Cl$^-$ concentration on potentiodynamic behavior of PbAg alloys in aerated (top) and deaerated (bottom) figure.
Table 5.3 Effect of Cl- concentration on potentiodynamic behavior of PbAg alloys in aerated and deaerated (*) cells.

<table>
<thead>
<tr>
<th>Cl (mg/L)</th>
<th>E$<em>{corr}$ (V$</em>{SCE}$)</th>
<th>i$_{corr}$ (A/cm$^2$)</th>
<th>Slope of oxygen evolution region (V/dec)</th>
<th>OER Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.68</td>
<td>9.67E-06</td>
<td>0.073</td>
<td>1.48</td>
</tr>
<tr>
<td>100</td>
<td>-0.65</td>
<td>1.46E-05</td>
<td>0.119</td>
<td>1.44</td>
</tr>
<tr>
<td>200</td>
<td>-0.68</td>
<td>1.53E-05</td>
<td>0.120</td>
<td>1.39</td>
</tr>
<tr>
<td>300</td>
<td>-0.66</td>
<td>1.62E-05</td>
<td>0.112</td>
<td>1.47</td>
</tr>
<tr>
<td>500</td>
<td>-0.61</td>
<td>1.87E-05</td>
<td>0.196</td>
<td>1.49</td>
</tr>
<tr>
<td>*0</td>
<td>-0.55</td>
<td>1.52E-05</td>
<td>0.144</td>
<td>1.62</td>
</tr>
<tr>
<td>*100</td>
<td>-0.57</td>
<td>6.44E-05</td>
<td>0.103</td>
<td>1.57</td>
</tr>
<tr>
<td>*200</td>
<td>-0.59</td>
<td>1.30E-05</td>
<td>0.104</td>
<td>1.54</td>
</tr>
<tr>
<td>*300</td>
<td>-0.59</td>
<td>1.73E-05</td>
<td>0.106</td>
<td>1.57</td>
</tr>
<tr>
<td>*500</td>
<td>-0.60</td>
<td>2.36E-05</td>
<td>0.153</td>
<td>1.50</td>
</tr>
</tbody>
</table>

5.1.4. Effect of Zn$^{2+}$ concentration on general corrosion behavior

Zn$^{2+}$ is plated onto the cathode and is not expected to play a large role in the anodic corrosion rate, but it may affect E$_{corr}$ and OER kinetics. Zn$^{2+}$ was added as ZnSO$_4$·7H$_2$O that also increased the SO$_4^{2-}$ concentration in electrolyte. Newnham$^4$ observed that increasing Zn$^{2+}$ concentration above 60 g/L increased the anodic corrosion, but maintained a constant SO$_4^{2-}$ by decreasing H$_2$SO$_4$ concentrations. Additional experiments in the presence and absence of Zn$^{2+}$ showed that the corrosion rate was more dependent on the concentration of SO$_4^{2-}$ in solution rather than Zn$^{2+}$(Ivanov et al.2000a).

OCP experiments were run in deaerated cells to observe the effect of Zn$^{2+}$ concentration. These experiments showed that the concentration of Zn$^{2+}$ had limited impact on the OCP at 6 different concentrations.

The potentiodynamic experiments with changing Zn$^{2+}$ concentration were completed using Pb-Ag anodes in both aerated and deaerated cells. Zn$^{2+}$ concentrations were varied.

66
between 0 and 130 g/L. The potentiodynamic polarization curves for both the aerated and deaerated cells are presented in Figure 5.5. For both cells, the polarization diagrams showed consistent behavior. Increasing Zn$^{2+}$ concentration generally shifted the curve to the left in an aerated cell, while the deaerated cell showed only a small shift to the left. In the deaerated cell at low potentials, the highest concentrations had the lowest current density and, at high potentials, the lowest Zn$^{2+}$ concentration had the lowest current density. At high potentials, the curve is generally shifted to a more negative value in an aerated cell and more positive in deaerated cell. The corrosion parameters ($E_{\text{corr}}$, $i_{\text{corr}}$, oxygen evolution region slope, and OER) are presented in Table 5.4.

In the aerated cell, both $E_{\text{corr}}$ and $i_{\text{corr}}$ decreased with increasing Zn$^{2+}$ concentrations in contrast with the results by Newnham(1992). Newnham used galvanostatic experiments with a constant sulfate concentration over long periods of time. The deaerated cell showed $E_{\text{corr}}$ independent of Zn$^{2+}$ concentration and $i_{\text{corr}}$ increased with increasing Zn$^{2+}$ concentration above 30 g/L. The increase in $i_{\text{corr}}$ was likely due to the increased SO$_4^{2-}$ instead of Zn$^{2+}$ concentration as concluded by Newnham(1992).
Figure 5.5 Effect of Zn\textsuperscript{2+} concentration on potentiodynamic behavior of PbAg alloys in aerated (top) and deaerated (bottom) figure.
At high potentials in the aerated cell, the oxygen evolution region slope was stable up to 100 g/L Zn^{2+} and the OER potential decreased with increasing concentration. The deaerated cell showed an increase in oxygen evolution region slope up to 60 g/L Zn^{2+} and similar behavior with the OER potential.

Table 5.4 Effect of Zn^{2+} concentration on potentiodynamic behavior of PbAg alloys in aerated and deaerated (*)& cells.

<table>
<thead>
<tr>
<th>Zn^{2+} (g/L)</th>
<th>E_{corr} (V_{SCE})</th>
<th>i_{corr} (A/cm^2)</th>
<th>Slope of oxygen evolution region (V/dec)</th>
<th>OER Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.71</td>
<td>1.46E-05</td>
<td>0.076</td>
<td>1.86</td>
</tr>
<tr>
<td>30</td>
<td>-0.67</td>
<td>1.85E-05</td>
<td>0.076</td>
<td>1.38</td>
</tr>
<tr>
<td>60</td>
<td>-0.68</td>
<td>9.67E-06</td>
<td>0.073</td>
<td>1.48</td>
</tr>
<tr>
<td>100</td>
<td>-0.67</td>
<td>7.03E-06</td>
<td>0.057</td>
<td>1.44</td>
</tr>
<tr>
<td>*0</td>
<td>-0.56</td>
<td>4.16E-05</td>
<td>0.055</td>
<td>1.55</td>
</tr>
<tr>
<td>*30</td>
<td>-0.56</td>
<td>5.24E-05</td>
<td>0.066</td>
<td>1.60</td>
</tr>
<tr>
<td>*60</td>
<td>-0.55</td>
<td>1.52E-05</td>
<td>0.144</td>
<td>1.62</td>
</tr>
<tr>
<td>*100</td>
<td>-0.56</td>
<td>2.94E-05</td>
<td>0.129</td>
<td>1.51</td>
</tr>
<tr>
<td>*130</td>
<td>-0.56</td>
<td>2.22E-05</td>
<td>0.061</td>
<td>1.61</td>
</tr>
</tbody>
</table>

In the deaerated experiments, the lack of dissolved oxygen is shown to decrease the stability of the oxide layer (Kim et al. 1997). OER potential was higher in deaerated experiments consistent with Danilov et al(1994) who observed a decrease in OER overpotential with increasing dissolved oxygen. This was ascribed to increased adsorbed OH^-.
5.1.5. Effect of temperature on general corrosion behavior

The temperatures were varied between 25°C and 85°C to determine corrosion parameters that are presented in Table 5.5. Increasing temperature is suspected to increase the kinetics of reactions in an electrowinning cell. Newnham(1992) showed that the corrosion rates of Pb-Ag anodes increased with increasing temperature. The author claimed that increasing the temperature of the cell has been reported to increase the hardness and stability of the oxide layer increasing corrosion resistance.

The potentiodynamic polarizations for the aerated and deaerated cell are presented in Figure 5.6. With the exception of the experiment in 37°C in an aerated cell, increasing temperature generally increased the current density at given potentials. At high potentials, the polarization curve was generally shifted to the more positive direction that would result in requiring a higher potential to plate metal.

Table 5.5 Effect of temperature on potentiodynamic behavior of PbAg alloys in aerated and deaerated (*) cells.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(E_{corr}) (V SCE)</th>
<th>(i_{corr}) (A/cm²)</th>
<th>Slope of oxygen evolution region (V/dec)</th>
<th>OER Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-0.67</td>
<td>7.58E-06</td>
<td>0.068</td>
<td>1.38</td>
</tr>
<tr>
<td>37</td>
<td>-0.68</td>
<td>9.67E-06</td>
<td>0.073</td>
<td>1.48</td>
</tr>
<tr>
<td>55</td>
<td>-0.72</td>
<td>1.44E-05</td>
<td>0.134</td>
<td>1.46</td>
</tr>
<tr>
<td>70</td>
<td>-0.69</td>
<td>1.56E-05</td>
<td>0.071</td>
<td>1.48</td>
</tr>
<tr>
<td>85</td>
<td>-0.71</td>
<td>3.16E-06</td>
<td>0.089</td>
<td>1.45</td>
</tr>
<tr>
<td>*25</td>
<td>-0.55</td>
<td>1.98E-05</td>
<td>0.075</td>
<td>1.57</td>
</tr>
<tr>
<td>*37</td>
<td>-0.55</td>
<td>1.52E-05</td>
<td>0.157</td>
<td>1.62</td>
</tr>
<tr>
<td>*55</td>
<td>-0.55</td>
<td>3.67E-05</td>
<td>0.144</td>
<td>1.62</td>
</tr>
<tr>
<td>*70</td>
<td>-0.55</td>
<td>3.56E-05</td>
<td>0.218</td>
<td>1.62</td>
</tr>
<tr>
<td>*85</td>
<td>-0.55</td>
<td>7.50E-05</td>
<td>0.155</td>
<td>1.60</td>
</tr>
</tbody>
</table>
Figure 5.6 outlines the corrosion parameters from the potentiodynamic experiments. In the aerated cell, $E_{\text{corr}}$ remained stable and $i_{\text{corr}}$ increased up to 70°C. At high potentials, the oxygen evolution region slope had maximum value at 55°C and the OER potential decreased with increasing temperature. The deaerated cell maintained a nearly constant $E_{\text{corr}}$ and $i_{\text{corr}}$ that both increased with increasing temperature. At high potentials, the oxygen evolution region slope was increased and the OER potential was stabilized from 37°C to 70°C.

In the deaerated experiments, the lack of dissolved oxygen is shown to decrease the stability of the oxide layer (Kim et al. 1997). OER potential was higher in deaerated experiments consistent with Danilov et al. (1994) who observed a decrease in OER overpotential with increasing dissolved oxygen. This was ascribed to increased adsorbed OH⁻.
Figure 5.6 Effect of temperature on potentiodynamic behavior of PbAg alloys in aerated (top) and deaerated (bottom) figure.
5.2. Potentiostatic polarization

The composition of the oxide layer was qualitatively analyzed using EDX. Samples were potentiostatically polarized for three hours to develop an oxide layer. These potentials included: -0.30 V\textsubscript{SCE}, 0.90 V\textsubscript{SCE}, 1.30 V\textsubscript{SCE}. These points were chosen to represent early stages of passivation, the passive region, and a potential just below the OER. These potentials are shown in Figure 4.5. Immediately after potentiostatic polarization, the samples were dried in air, observed under the SEM, and analyzed using EDX. The oxide morphologies are displayed in Figure 5.7 and the compositions are reported in Table 5.6.

<table>
<thead>
<tr>
<th>Element</th>
<th>Potential /Potential</th>
<th>-0.30 V\textsubscript{SCE} (%)</th>
<th>0.90 V\textsubscript{SCE} (%)</th>
<th>1.30 V\textsubscript{SCE} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td></td>
<td>17</td>
<td>63</td>
<td>13</td>
</tr>
<tr>
<td>Sulfur</td>
<td></td>
<td>6</td>
<td>17</td>
<td>3</td>
</tr>
<tr>
<td>Manganese</td>
<td></td>
<td>0</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>Lead</td>
<td></td>
<td>77</td>
<td>19</td>
<td>70</td>
</tr>
</tbody>
</table>
Figure 5.7 SEM images of potentiostatically polarized PbAg sample a) -0.3 V<sub>SCE</sub> b) 0.9 V<sub>SCE</sub> c) 1.3 V<sub>SCE</sub>.

At -0.3 V<sub>SCE</sub>, Pb is present primarily as pure Pb, but small amounts of PbSO<sub>4</sub> and PbO are likely to form and cover a small fraction of the surface (Rehim et al. 1984), (Burbank, 1956). Increasing the potential above -0.3 V<sub>SCE</sub> increased the surface coverage with a non-conductive oxide (PbSO<sub>4</sub>) that decreased the current density until conductive PbO<sub>2</sub> became stable at higher potentials. As apparent in Figure 5.7a, the crystals only cover a fraction of the alloy and the surface is only partially passivated. Thermodynamically, it’s possible that some PbSO<sub>4</sub> be present on the oxide, but the EDX only detected small amounts of oxygen and sulfur (Table 5.6).
The high values of sulfur and oxygen at 0.9\text{V}_{\text{SCE}} are representative of the sulfate stability region and the increasing Mn is in agreement with the formation of Mn oxide. As observed in Figure 5.7b, when the potential is increased to 0.9\text{V}_{\text{SCE}}, the anode is covered with small PbSO$_4$ particles and likely contains basic oxides below the sulfate layer. The decrease in Pb is likely a result of sulfate build up at the electrode electrolyte interface. Figure 5.7b also shows a larger fraction of the surface covered by coarse crystals when the potential is increased.

At 1.3\text{V}_{\text{SCE}}, the oxide layer has fully engulfed the anode surface and crystals began to coarsen. With further increase in potential above 1.3 \text{V}_{\text{SCE}}, the oxidation of Mn$^{2+}$ and OER will take place. Figure 5.7b shows a decrease in sulfur and an increase in manganese and Pb suggesting the destabilization of PbSO$_4$. Figure 5.7c shows that the alloy was completely covered by crystals and EDX has detected lower amounts of sulfur and higher amounts of manganese.

5.3. Summary

Potentiostatic experiments showed the presence and development of an oxide layer during potentiodynamic experiments. It is clear that the PbSO$_4$ forms at low potentials and with increasing potential, passivates the anode decreasing the current passing through it. Increasing the potential further, the oxide becomes composed of Pb, Mn and oxygen.

OCP and potentiodynamic experiments have been used to observe the changes in $E_{\text{corr}}$, $i_{\text{corr}}$, oxygen evolution region slope, and $O_2$ potential with changing $H_2SO_4$, Mn$^{2+}$, Cl$^-$, Zn$^{2+}$ and temperature.
Increasing H$_2$SO$_4$ concentration decreased E$_{cor}$ increasing the tendency for corrosion and i$_{corr}$ increased. With increasing concentration, the slope of the oxygen evolution region generally decreased and OER overpotential increased. When exposed to deaerated cells, E$_{corr}$ decreased slightly and i$_{corr}$, oxygen evolution region slope, and OER overpotential increased. The deaerated cell showed higher i$_{corr}$ and OER potential. The best concentration of H$_2$SO$_4$ to maintain a low oxygen evolution region slope and OER would be 250 g/L in the aerated cell.

Increasing concentration of Mn$^{2+}$ increased E$_{corr}$ and generally decreased i$_{corr}$ with increasing concentration. The oxygen evolution region slope and OER overpotential generally decreased with increasing concentration because of a catalytic effect. In a deaerated cell, i$_{corr}$ fluctuated and there was little impact on the OER overpotential. Using an aerated cell, the lowest oxygen evolution region slope and OER was observed using 15 g/L Mn$^{2+}$.

Increasing Cl$^-$ concentration increased E$_{corr}$ to a more positive value in aerated conditions and decreased it in deaerated cells. The i$_{corr}$ generally increased with increasing concentration despite a local minimum using a deaerated cell with 200 mg/L. The oxygen evolution region slope increased in the aerated cell and was stable when deaerated. The OER overpotential decreased with increasing Cl$^-$ in both environments. It is possible for a low concentration of Cl$^-$ to enhance corrosion resistance by minimizing i$_{corr}$ and catalyzing the OER. Using 0 mg/L, Cl$^-$ shows the best combination of oxygen evolution region slope and OER overpotential in an aerated cell, but a concentration between 100 and 400 in a
deaerated cell shows a significant decrease in oxygen evolution region slope and a decrease in OER.

- It is unclear the impact of Zn$^{2+}$ because of the presence of additional SO$_4^{2-}$. If we assume the corrosion behavior is due to Zn$^{2+}$ alone, $E_{\text{corr}}$ increases, $i_{\text{corr}}$ decreases, and oxygen evolution and OER are independent of concentration in an aerated cell. When deaerated, $E_{\text{corr}}$ is independent, $i_{\text{corr}}$ generally decreases, and maximum oxygen evolution region slope and OER overpotential are at 60 g/L. The best corrosion resistance is attained when using 100 g/L Zn$^{2+}$ with respect to both oxygen evolution slope and OER overpotential.

- Increasing temperature showed a slight decrease in $E_{\text{corr}}$, and at 55°C and 70°C the highest $i_{\text{corr}}$ values were observed. At high potentials, the OER overpotential decreased and oxygen evolution slope increased in an aerated cell. When deaerated, the oxygen evolution slope increased while OER overpotential decreased. With respect to minimizing both oxygen evolution region slope and OER overpotential in an aerated cell, electrowinning at 37°C shows the best corrosion resistance and lowest OER overpotential.

To maximize life span of anodes and decrease power consumption, a decrease in both the oxygen evolution region slope and OER overpotential is required. In Zn electrowinning, this would be optimized using an electrolyte composition composed of 250 g/L H$_2$SO$_4$, 15 g/L Mn$^{2+}$, 0 mg/L Cl$^-$, 100 g/L Zn$^{2+}$ in a cell at 37°C in atmospheric conditions.
6. Results and discussion; nickel electrowinning

Ni electrowinning is conducted at a higher pH and temperature compared to Zn electrowinning. The higher pH is required to minimize hydrogen evolution, but needs to be low enough to avoid the plating of Ni oxides. The thermodynamics of Ni electrowinning make anode corrosion less severe as compared to Zn electrowinning. This chapter not only discusses the effects electrolyte constituents but also the impact of changing anodic materials.

Although a large number of polarizations were completed discussing the effects of H₂SO₄, Mn²⁺, Cl⁻, Zn²⁺, and temperature with respect to Zn electrowinning. Although it was feasible to draw conclusions, to develop better conclusions an increased amount of time in electrolyte would be required to develop a stable oxide prior to experiments is required. This chapter uses additional galvanostatic experiments to assist developing stronger conclusions regarding electrolyte composition and anode material.

The composition of Ni leach solution is composed of H₂SO₄, Ni²⁺ and Cl⁻. The standard electrolyte used in this chapter are outlined in Table 4.4. The H₂SO₄ concentration is substantially lower then Zn electrowinning and the Cl⁻ concentration is much higher. In industry, electrowinning cells are exposed to 200 A/m² and maintained at a potential of ~1.8 V_{SCE}.

6.1. The effect of H₂SO₄ and Cl⁻ concentration

In order to study the overall corrosion performance of the samples, extensive potentiodynamic polarization experiments were carried out. The potentiodynamic
polarization experiments were also used to study the overpotential and kinetics of the OER for different anode material/solution combinations. Effects of H$_2$SO$_4$ and Cl$^-$ concentrations were investigated. Reactions 6-1, 6-2 and 6-3 are likely playing a role at OCP:

\[
\begin{align*}
\text{Ni}^{2+} + 2e^- &= \text{Ni} & E^* &= -0.250 \text{ V}_{\text{SHE}} \\
2H^+ + 2e^- &= H_2 & E^* &= 0.000 \text{ V}_{\text{SHE}} \\
Pb + H_2SO_4 &= PbSO_4 + 2H^+ + 2e^- & E^* &= -0.355 \text{ V}_{\text{SHE}}
\end{align*}
\]

where reactions 6-1 and 6-2 are possible cathodic reactions and reaction 6-3 is the anodic reaction. Looking at Figure 6.2 and Figure 6.1, one can observe a general behavior for all the anode materials/solutions combinations. As the potential is increased in the anodic region, the first reaction to happen is the formation of the PbSO$_4$ phase on the surface where the corresponding OCP is approximately -0.540 V$_{\text{SCE}}$. PbSO$_4$ is protective in nature and therefore a reduction in the current density was expected and observed. When the potential is further increased, $\alpha$- and $\beta$-PbO$_2$ phases may be present either individually or together with other phases depending on the applied conditions. At potentials higher than 1.684 V$_{\text{SHE}}$, PbO$_2$ is the only stable phase and it may exist in either of the $\alpha$ or $\beta$ forms, again, depending on the applied conditions, (Lander 1956).

Figure 6.2 shows the effect of H$_2$SO$_4$ concentration on potentiodynamic polarization curves of the PbCaSn samples. As apparent from Figure 6.2, the H$_2$SO$_4$ concentration does not have a significant effect on the curves of the PbCaSn samples, however, a small shift to the right is observed in the curves of the PbCaSn samples representing a small increase in the corrosion rate of the samples.
Figure 6.2 Effect of H$_2$SO$_4$ concentration on corrosion behavior of PbCaSn samples at 0 g/L Cl$^-$ concentration and 60°C.

Figure 6.3 Effect of Cl$^-$ concentration on corrosion behavior of PbCaSn samples at 30 g/L H$_2$SO$_4$ and 60°C.
Due to their similarity to the curves shown in Figure 6.2, the potentiodynamic polarization curves for the PbAg rolled and cast samples will not be presented here; however, their behavior as a function of H_2SO_4 and Cl^- concentrations will be described. Effect of solution acidity on the electrochemical behavior of PbAg as cast samples in the absence of Cl^- was studied and it was found that increasing the H_2SO_4 content of the solution from 20 g/L to 30 g/L shifts the curves to the right and increases the current density. This increase in the current may be attributed to the amount of PbSO_4 formed on the surface and its solubility in the solution. PbSO_4 forms on the surface through reaction 6-3. Vinal et al. (1939) reported that the solubility of PbSO_4 in solutions containing H_2SO_4 reached a maximum when the H_2SO_4 concentration was between 50 and 200 g/L. However, any further decrease or increase in the H_2SO_4 concentration decreased the solubility of PbSO_4. 20, 30 and 40 g/L H_2SO_4 concentrations used in this study correspond to 0.2, 0.3 and 0.4 M H_2SO_4 solutions. Therefore, according to Vinal et al. (1939), an increase in the amount of H_2SO_4 from 20 to 40 g/L increased the solubility of PbSO_4. Increased solubility of PbSO_4 resulted in the formation of thinner layers of PbSO_4, which may be less protective.

The effect of H_2SO_4 concentration on corrosion behavior of the PbAg rolled electrodes was also studied and a general behavior similar to that of cast PbAg samples was observed. Increasing the H_2SO_4 concentration from 20 g/L to 40 g/L caused a shift to the right in the polarization curve. However, rolled PbAg samples had an overall increase in current density compared to the cast PbAg samples. This might be due to relatively non-uniform grain structure of the rolled samples, which increases the chance of inter-granular corrosion.
In order to investigate the effect of Cl\textsuperscript{−} on the overall corrosion behavior of the samples, Cl\textsuperscript{−} was added to the solutions at concentrations of 0.4 g/L, 0.6 g/L and 0.8 g/L. Figure 6.3 shows the effect of Cl\textsuperscript{−} concentration on general corrosion behavior of the PbCaSn samples. It was found that an addition of 0.4 g/L Cl\textsuperscript{−} to the solution decreased the corrosion current density; however, further increase in the Cl\textsuperscript{−} concentration reversed this effect and the current density was shifted back to its value for the condition with no added Cl\textsuperscript{−} ions. This effect was also observed for the PbAg rolled and cast samples; however, the change in current density by addition of Cl\textsuperscript{−} was more evident in these cases. Cifuentes et al. (2005) suggested that the effect of Cl\textsuperscript{−} might be due to its high oxidizing power, which results in greater stability of the sulfate and oxide layers formed on the surface.

6.2. OER rate and overpotential

Formation of PbO\textsubscript{2} is probable at potentials lower than 1.684 V\textsubscript{SHE}; however, this phase is not stable and transforms to other lead compounds which cover the surface along with PbSO\textsubscript{4}. At higher potentials, PbSO\textsubscript{4} transforms to PbO\textsubscript{2} according to reaction 3-5 (charging reaction on positive plates of lead-acid batteries):

Therefore, at potentials higher than 1.43 V\textsubscript{SCE}, the surface is mostly covered by PbO\textsubscript{2}. When the potential is high enough, OER takes place on the surface according to reaction 1-2.
Table 6.1 Oxygen evolution overpotential and Tafel slopes for different anode material/solution combinations.

<table>
<thead>
<tr>
<th>Pb-Ag cast</th>
<th>H₂SO₄ (g/L)</th>
<th>Cl (g/L)</th>
<th>0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Overpotential (V)</td>
<td>0.448</td>
<td>0.488</td>
<td>0.458</td>
<td>0.438</td>
<td>0.478</td>
<td>0.538</td>
<td>0.528</td>
<td>0.498</td>
<td>0.550</td>
<td>0.450</td>
<td>0.440</td>
<td>0.410</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Slope (V/dec)</td>
<td>0.149</td>
<td>0.098</td>
<td>0.095</td>
<td>0.093</td>
<td>0.086</td>
<td>0.143</td>
<td>0.166</td>
<td>0.117</td>
<td>0.103</td>
<td>0.116</td>
<td>0.097</td>
<td>0.080</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pb-Ag rolled</th>
<th>H₂SO₄ (g/L)</th>
<th>Cl (g/L)</th>
<th>0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Overpotential (V)</td>
<td>0.368</td>
<td>0.408</td>
<td>0.388</td>
<td>0.398</td>
<td>0.458</td>
<td>0.428</td>
<td>0.468</td>
<td>0.518</td>
<td>0.570</td>
<td>0.410</td>
<td>0.430</td>
<td>0.420</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Slope (mV/dec)</td>
<td>0.111</td>
<td>0.118</td>
<td>0.076</td>
<td>0.086</td>
<td>0.095</td>
<td>0.115</td>
<td>0.093</td>
<td>0.143</td>
<td>0.146</td>
<td>0.094</td>
<td>0.114</td>
<td>0.113</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pb-Ca</th>
<th>H₂SO₄ (g/L)</th>
<th>Cl (g/L)</th>
<th>0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>0</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Overpotential (V)</td>
<td>0.448</td>
<td>0.268</td>
<td>0.308</td>
<td>0.308</td>
<td>0.448</td>
<td>0.448</td>
<td>0.518</td>
<td>0.498</td>
<td>0.510</td>
<td>0.250</td>
<td>0.280</td>
<td>0.350</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Slope (mV/dec)</td>
<td>0.135</td>
<td>0.330</td>
<td>0.123</td>
<td>0.124</td>
<td>0.061</td>
<td>0.079</td>
<td>0.060</td>
<td>0.081</td>
<td>0.213</td>
<td>0.186</td>
<td>0.187</td>
<td>0.077</td>
<td></td>
</tr>
</tbody>
</table>
It can be concluded from Table 6.1 that increasing the \(H_2SO_4\) content from 20 g/L to 40 g/L in the absence of \(Cl^-\) increases the oxygen evolution overpotential for all three anode materials, which is more pronounced in the case of PbCaSn anodes. This behavior may be rationalized through OER where increasing the concentration of hydrogen ions shifts the reaction to the left, hence the higher overpotential.

Further increase in the solution acidity from 30 g/L to 40 g/L in the absence of \(Cl^-\) also increases the oxygen evolution overpotential; however, when 0.4 g/L \(Cl^-\) is added to the solution, increasing the \(H_2SO_4\) content from 30 g/L to 40 g/L has very little effect on the oxygen evolution overpotential. This may be a result of \(Cl_2\) evolution (reaction 5-3) being added to the group of anodic reactions (OER and oxide formation), which, in part, reduces the share of OER in the overall anodic current.

At 0.6 g/L and 0.8 g/L \(Cl^-\) concentrations increasing the \(H_2SO_4\) content from 30 g/L to 40 g/L reduces the oxygen evolution overpotential significantly.

In general, the minimum oxygen evolution overpotential is observed on PbCaSn samples at both low and high \(H_2SO_4\) concentrations and 0.4 g/L \(Cl^-\) concentration. On the other hand, these conditions do not represent the smallest slopes on the curves. Table 6.2 shows that PbCaSn samples have generally larger slopes at both low and high \(H_2SO_4\) concentrations, especially in the absence of \(Cl^-\) ions. At medium \(H_2SO_4\) concentration, both in the presence and absence of \(Cl^-\) ions, the smallest slopes belong to the PbCaSn anodes. The question of what part of this current is consumed by OER and chlorine evolution or how much of this current is the corrosion contribution needs further experimental observations, which will be addressed later in the discussion.
6.3. **Determining corrosion current during electrowinning**

In the determination of the corrosion current during electrowinning, Figure 6.4, Figure 6.5, and Figure 6.6 show the XRD patterns along with SEM images for the discharged samples both in the presence and absence of Cl⁻. PbO₂ peaks are marked with stars whereas the remaining peaks belong to PbSO₄ and Pb. In general, it is apparent from the XRD patterns that the addition of Cl⁻ to the solution reduced the height of the peaks for PbAg samples indicating smaller amounts of both PbSO₄ and PbO₂ were present on the surface after discharge. Furthermore, sulfate or oxide phases of other alloying elements cannot be defined in the XRD patterns.

As apparent from Figure 6.4, porous layers exist on the surface of PbCaSn samples both in the presence and absence of Cl⁻. However, in the presence of Cl⁻, deposits have a cubic shape and have larger sizes compared to those formed in the absence of Cl⁻. Moreover, in Cl⁻ containing solutions the surface layer is smoother compared to those of Cl⁻ free solutions. Depicted in Figure 6.5 is the surface morphology of PbAg cast samples. It is apparent that the layer formed on the surface is more porous when Cl⁻ is present. Introducing Cl⁻ to the solution changes the shape of the deposits from a cubic shape to an elongated pin shape which are also more coarse. On the other hand, the surface morphologies of the rolled samples do not change significantly upon addition of Cl⁻ to the solution. A porous layer with pin shaped deposits was observed on the surface of rolled PbAg samples (Figure 6.5).

The area under each peak in Figure 6.4, Figure 6.5, and Figure 6.6 was measured and used to relatively quantify the remaining PbO₂ and the PbSO₄ present on the surface after discharge. Table 6.2 presents the total charge measured from the plateau and the ratio of
the remaining \( \text{PbO}_2 \) to \( \text{PbSO}_4 \). Using the sum of these two values, the total mass of \( \text{PbO}_2 \) formed was calculated 24 hours after the experiment, which is also presented in Table 6.2. The data of Table 6.2 was used to calculate the corrosion current density and corrosion rate, which are shown in Figure 6.7. As apparent from Figure 6.7, the corrosion current density for all anodes was between 10 and 20 \( \mu \text{A/cm}^2 \). These values indicate that the assumption made in section 4.3.3 for studying OER rate and overpotential were valid (corrosion current very small compared to OER current).
Figure 6.4 SEM and XRD patterns of PbCaSn samples discharged after being galvanostatically polarized for 24 hrs at 20 mA/cm² and 30 g/L H₂SO₄ concentration and 60°C.
Figure 6.5 SEM and XRD patterns of cast Pb-Ag samples discharged after being galvanostatically polarized for 24 hrs at 20 mA/cm² and 30 g/L H₂SO₄ concentration and 60°C.
Figure 6.6 SEM and XRD patterns of rolled Pb-Ag samples discharged after being galvanostatically polarized for 24 hrs at 20 mA/cm² and 30 g/L H₂SO₄ concentration and 60°C.
Figure 6.17 Corrosion current density of samples obtained from electrochemical measurements under typical nickel electrowinning conditions.

Figure 6.7 also shows the corrosion rate of all anodes. As apparent, PbCaSn samples have the highest corrosion rate among all samples, both in the presence and absence of Cl⁻. Therefore, PbCaSn samples are not recommended for use in nickel electrowinning conditions. The corrosion rates of PbAg rolled and cast samples do not vary greatly, however, the cast samples are slightly more corrosion resistant, both in the presence and absence of Cl⁻. This may be attributed to the more uniform grain structure of the PbAg cast samples. It can be summarized from Figure 6.7 that the corrosion rate of all the samples are lower in the presence of Cl⁻ while cast PbAg samples have the lowest corrosion rate. This behavior is in agreement with what was observed in Figure 6.4, Figure 6.5, and Figure 6.6 where the addition of Cl⁻ to the solution reduced the overall
height of the peaks in the XRD patterns of PbAg samples. However, an attempt to correlate the surface morphology of the samples after discharge (Figure 6.4, Figure 6.5 and Figure 6.6) with their corrosion behavior was inconclusive. Accordingly, in order to observe the surface morphology of the samples in early stages of the process, XRD and SEM experiments were performed after 2 hours of polarization at operating potential just before the discharge (Figure 6.8 and 12).
Figure 6.8 XRD patterns of samples after being galvanostatically polarized for 2 hrs at 20 mA/cm² at 30 g/L sulfuric acid concentration and 60°C.

Figure 6.8 shows the XRD patterns for all samples both in the presence and absence of Cl⁻. The peaks that are not marked in Figure 6.8 represent Pb and its oxides. It is apparent that addition of Cl⁻ to the solution increased the intensity of the Pb peaks for the PbCaSn samples. This indicated that the surface was covered with a thinner layer so the Pb underneath had larger peaks. Formation of a thinner oxide layer corresponds to a
lower corrosion rate. Interestingly, it was found that, despite the expectations, some PbSO₄ was formed on the surface of all samples at the operating potential. No phases other than Pb, its oxides, and its sulfate were present on the surface under all conditions tested (before or after the discharge, in the presence and absence of Cl⁻). Littauer, et al. (1967) reported that only at Cl⁻ concentrations higher than 1.3 M, chloro-complexes form and deposit on the surface of lead anodes.
Figure 6.9 Surface morphology of samples after being galvanostatically polarized for 2 hrs at 20 mA/cm² at 30 g/L sulfuric acid concentration and 60°C.

Depicted in Figure 6.9 are surface morphologies of samples before discharge. It was found that the surface of cast PbAg samples were covered with a relatively smooth
deposit layer, both in the presence and absence of Cl\textsuperscript{−}. On the other hand, rolled PbAg samples are covered with layers of higher porosity. Addition of Cl\textsuperscript{−} increased both the number and size of pores and introduced a large number of cracks to the surface layer. According to Figure 6.8, with the addition of Cl\textsuperscript{−} to the solution, the height of the peaks for PbSO\textsubscript{4} slightly increased for both rolled and cast PbAg samples. PbSO\textsubscript{4} has a considerably lower density compared to PbO\textsubscript{2}. This difference in the densities causes mechanical stresses in the corrosion layer. Likely due to higher residual stresses present in the rolled samples than in the cast samples, more cracks and crevices form in the structure of the layers formed on them. It is apparent that in the absence of Cl\textsuperscript{−} a relatively smooth layer with small holes and randomly shaped deposits is present on the surface of PbCaSn samples; however, in the presence of Cl\textsuperscript{−} a highly porous and distorted layer can be observed.

Pavlov, et al. (1969) and Pavlov & Lordonov (1967) reported that, regardless of the potential applied to lead electrodes in the potential region where PbO\textsubscript{2} is stable, PbSO\textsubscript{4} is always present in the layers. They showed that, in the mentioned potential region, PbO\textsubscript{2} can form either directly from lead or by transformation of PbSO\textsubscript{4}. Based on the results presented in Figure 6.8 and Figure 6.9, in addition to the findings of Pavlov et al. (1969), it may be concluded that by adding Cl\textsuperscript{−} to the solution, reaction 6 is added to the group of anodic reactions. Since a constant current is applied to the system during the electrowinning process, the rate with which PbO\textsubscript{2} forms through reaction 5-5 is reduced. Presence of PbSO\textsubscript{4} may have two effects on the corrosion of lead anodes. First, once formed on the surface, PbSO\textsubscript{4} provides protection, as observed in low potential regions in Figure 6.2 and Figure 6.3. Secondly, its density is different from PbO\textsubscript{2}, which causes
mechanical stresses in the oxide layer, resulting in poor protection. Based on this, these factors should be considered in the effect of Cl\(^-\) on corrosion behavior of lead anodes. It may be concluded that under the electrowinning conditions used in this study, the surface oxide layers contain large number of cracks and crevices (micro and macro) so that with the addition of Cl\(^-\) to the solution, the second effect of PbSO\(_4\) is not significant compared to the first one. Therefore, adding Cl\(^-\) slightly improves the corrosion resistance of the alloys through PbSO\(_4\) present in the surface layer. It has been observed that addition of silver to lead results in the formation of more continuous layers of PbO\(_2\) on the surface, (Littauer & Shreir, 1967). Therefore, better corrosion properties of PbAg alloys can be considered the result of more continuous layers compared to PbCaSn samples (Figure 6.9).

The results in Figure 6.7 confirm that the thickness of a typical 6-8 mm thick lead calcium anode reduces to half in 4-5 years of operation in nickel electrowinning conditions at a rate of approximately 27 mpy.
### Table 6.2 Calculation of the total mass of oxidized Pb from the plateau length and XRD patterns after 24 hours of galvanostatic polarization at 20 mA/cm^2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PbCaSn</th>
<th>PbCaSn</th>
<th>Cast PbAg</th>
<th>Cast PbAg</th>
<th>Rolled PbAg</th>
<th>Rolled PbAg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 (g/L) Acid</td>
<td>0 mg/L Cl^-</td>
<td>400 mg/L Cl^-</td>
<td>0 mg/L Cl^-</td>
<td>400 mg/L Cl^-</td>
<td>0 mg/L Cl^-</td>
<td>400 mg/L Cl^-</td>
</tr>
<tr>
<td>Charge Extrapolation (C)</td>
<td>1.30</td>
<td>1.25</td>
<td>1.05</td>
<td>0.87</td>
<td>1.07</td>
<td>0.87</td>
</tr>
<tr>
<td>PbO_2/PbSO_4</td>
<td>0.11</td>
<td>0.08</td>
<td>0.11</td>
<td>0.07</td>
<td>0.15</td>
<td>0.19</td>
</tr>
<tr>
<td>Total mass of PbO_2 (g)</td>
<td>1.79 E-3</td>
<td>1.68 E-3</td>
<td>1.45 E-3</td>
<td>1.16 E-3</td>
<td>1.53 E-3</td>
<td>1.28 E-3</td>
</tr>
</tbody>
</table>

### 6.4. Summary

This chapter outlined the behavior of different anode materials in electrolyte with changing H_2SO_4 and Cl^- concentration. In summary:

- Increasing H_2SO_4 did not have as great an impact as it did in Zn electrowinning because of the different anode material. For OCP, the PbCaSn potential decreased above 30 g/L, the as cast anode potential increased with increasing concentration and the rolled anode increased from 20 to 30 g/L.
  - The lowest and most stable OCP was observed using the PbCaSn
- Increasing H_2SO_4 concentration on potentiodynamic experiments, the primary variables to minimize corrosion and power consumption at high potentials was both the oxygen evolution region slope and OER. By increasing H_2SO_4 concentration, the oxygen evolution region slope and OER overpotential decreased using a PbCaSn alloy, the as Cast PbAg showed an increase in oxygen
evolution region slope and decrease in OER overpotential and the rolled PbAg alloy increased both the oxygen evolution region slope and OER overpotential.

- With increasing Cl\(^-\) concentration on potentiodynamic experiments, minimizing the oxygen evolution region slope and OER overpotential is required. All three alloys showed increasing oxygen evolution region slope and OER overpotential with increasing Cl\(^-\) concentration.

- The PbCaSn has the lowest OER overpotential (1.21 V\(_{SCE}\)) while the rolled anode has a lower oxygen evolution region slope (0.089 V/dec) in standard electrolyte. Being able to evolve oxygen at a lower potential decreases energy consumption making PbCaSn superior at lower currents.

- Galvanostatic experiments showed the largest volume of corrosion product on the PbCaSn and the least on the as cast PbAg alloy. Galvanostatic experiments are based on an established oxide and able to determine both the mass of the corrosion product and the corrosion rate. Both the as cast and rolled PbAg showed the best corrosion rates in standard Ni electrolyte.

After numerous OCP, potentiodynamic, and galvanostatic experiments, the best corrosion resistance is observed using as cast and rolled PbAg. Although OCP and potentiodynamic experiments are convenient, they do not best represent the conditions observed in electrowinning. Galvanostatic experiments better represent the conditions Pb-based anodes experience in industry and therefore conclusions will be based more on these experimental results.
7. Conclusion

The objective of this thesis was to understand the corrosion behavior of Pb-based anodes as a function of electrolyte composition and anode material. Electrolyte was varied in both Zn and Ni leach solutions based on industrial compositions using OCP, potentiostatic, potentiodynamic, and galvanostatic experiments.

For Zn Electrowinning the following conclusions can be drawn;

- Increasing $\text{H}_2\text{SO}_4$ concentration from 0 g/L to 250 g/L generally minimized $i_{\text{corr}}$ and OER potential while $E_{\text{corr}}$ and oxygen evolution region potential were decreased.
- In general, addition of Mn$^{2+}$ decreased $i_{\text{corr}}$ and OER potential. Optimum values of $i_{\text{corr}}$ and OER potential were found when a Mn$^{2+}$ concentration was 2.5 g/L.
- Small amounts of Cl$^{-}$ seem to be beneficial in decreasing the cost of Zn production in terms of optimizing the OER potential (100 mg/L).
- Increasing the Zn$^{2+}$ concentration from 0 g/L to 100 g/L decreased the $i_{\text{corr}}$ and catalyzed the OER.
- Increasing temperature did not affect $E_{\text{corr}}$, but slightly increased $i_{\text{corr}}$.
- Higher $i_{\text{corr}}$ and OER potentials were consistently observed in the deaerated cell compared to the aerated conditions.
- SEM images revealed that, as the potential was increased, the deposited crystals on the surface became coarser and had higher Mn content.
For Ni electrowinning:

- Increasing the H\textsubscript{2}SO\textsubscript{4} content of the solutions shifted the potentiodynamic polarization curves to the right, indicating higher corrosion currents at the passive potential region.

- Adding up to 0.4 g/L Cl\textsuperscript{-} to the solutions reduced the corrosion current in the passive potential region, however, a further increase in the Cl\textsuperscript{-} content of the solution shifted the potentiodynamic polarization curves back to the values obtained in the absence of Cl\textsuperscript{-}.

- The corrosion current density is negligible compared to that of the OER at the nickel electrowinning operating potential.
8. Future work

Although potentiodynamic experiments offered valuable data on the $E_{\text{corr}}$, $i_{\text{corr}}$, OER overpotential, and oxygen evolution region slope, it represented the corrosion properties of a fresh anode placed into service. The objective of this thesis is to understand the corrosion behavior of Pb-based anodes and to increase the service life in electrowinning conditions. The accelerated tests did not achieve this result since the oxide layer can take as long as 60 days to stabilize before optimal corrosion characteristics are achieved.

For this subject to move forward and further the knowledge of anode corrosion in metallic electrowinning, subjects of research should include:

- Completing experiments similar to those in Chapter 6 with application to anode corrosion in Zn electrowinning.
- Exploring other alloying systems and alloys such as the Mn-Co system, PbAgCa alloys or alloying with bismuth. This could remove or reduce the amount of Ag currently used in anodes in both Ni and Zn electrowinning.
- Treating anodes during solidification to understand the impact of crystalline structure and to observe the effect of grain boundaries using a PbAg alloy to stabilize.
References


formation of lead sulphate and the phase change to lead dioxide. Transactions of the Faraday Society 51:71-95.


Gogia, S.K., Das, S.C (1988). The effects of Mg\(^2+\), Mn\(^2+\), Zn\(^2+\), and Al\(^3+\) on the nickel deposit during electrowinning from sulfate bath. Metallurgical Transactions B 19B:823-30.


