Development of Pb-MnO$_2$ composite anodes for electrowinning application:

Electrochemical and corrosion evaluations

by

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Abstract

Electrowinning is the last step of the extraction of zinc in which aqueous zinc ions are electrodeposited to produce highly pure zinc metal. This process operates in highly acidic solutions and at high current densities. Conventional lead-based anodes used in the zinc electrowinning are associated with high corrosion rates and oxygen evolution overpotential in the electrowinning process. These result in some problems such as Pb contaminating the zinc cathode, shortened anode lifetime, and high energy consumption in the process.

Lead-based composite anodes have been introduced to address these issues by using electroactive oxide particles dispersed in the Pb anode. Manganese ions, which typically exist in the zinc electrowinning electrolyte, can influence the anode performance, depending on their concentration and the anode material. The main aim of this work was to develop a new composite anode using MnO₂ particles in a Pb matrix to improve the anode performance in the zinc electrowinning operating conditions in Mn-free and Mn-containing electrolytes.

A combination of electrochemical and analytical methods was used to understand the oxidation, electrocatalytic activity, and corrosion performance of the Pb-MnO₂ composite anodes compared to the conventional PbAg anode. Potentiometric titration was utilized to measure the oxidation rate of manganese ions. The anodic corrosion layers and the MnO₂ deposited layers were characterized by Scanning Electron Microscopy and X-Ray Diffraction. A new electrochemical method was also developed for an on-site investigation of the deposited MnO₂ layer on the anodes.

The Pb-MnO₂ composite anodes showed higher catalytic activity and better corrosion resistance than the PbAg anode under the zinc electrowinning operating conditions. The Pb-MnO₂ anode can decrease the energy consumption in the electrowinning process in the Mn-
free electrolyte by up to 5%. The composite particles were not effective in decreasing the anode potential in the Mn-containing electrolyte. The MnO$_2$ particles catalyzed Mn(III) disproportionation, contributing to the deposition of a uniform, adherent, and protective MnO$_2$ layer. Formation of this layer decreased the lead dissolution and manganese consumption rates. The Pb-MnO$_2$ composite anode can be put into service without any pre-treatment since it quickly develops a stable MnO$_2$ layer and generates very low MnO$_2$ mud.
Preface

All of the work presented henceforth was conducted in the Electrochemistry and Corrosion Laboratory of the Materials Engineering department at the University of British Columbia under the supervision of Professor Akram Alfantazi. This research work has been granted by NSERC, Hydro-Quebec, and Xstrata Zinc. The journal and conference papers listed below have been prepared from work presented in the dissertation. I am the primary author of all the published work in which Professor Akram Alfantazi helped me extensively with. Dr. Farzad Mohammadi contributing to the first paper.

Journal papers:


Conference presentations with proceeding


**Conference presentation:**

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<td>$E^\circ$ (V)</td>
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<tr>
<td>E (V)</td>
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<td>$V_\Omega$ (V)</td>
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<td>$\chi^2$</td>
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List of abbreviations

RLE           Roasting-Leaching-Electrowinning
HPAL          High-Pressure Acid Leaching
OER           Oxygen Evolution Reaction
ORR           Oxygen Reduction Reaction
EW            Electrowinning
DSA           Dimensionally-Stable Anode
SHE           Standard Hydrogen Electrode
Ag/AgCl       Silver/Silver Chloride Reference Electrode
OCP           Open Circuit Potential
PD            Potentiodynamic Polarization
PS            Potentiostatic Polarization
CV            Cyclic Voltammetry
GS            Galvanostatic Polarization
EIS           Electrochemical Impedance Spectroscopy
SEM           Scanning Electron Microscopy
FESEM         Field Emission Scanning Electron Microscopy
EDX           Energy Dispersive X-Ray Spectroscopy
XRD           X-Ray Diffraction
ICP           Inductively Coupled Plasma
AAS           Atomic Adsorption Spectroscopy
CPE           Constant Phase Elements
ppm           parts per million
ERC           Endpoint Recognition Criterion
RDS           Rate Determining Step
ECE           Electrochemical-Chemical-Electrochemical
EMD           Electrolytical Manganese Dioxide
ARB           Accumulative roll bonding
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Dedication

To my inspiring parents,
without whom none of my success would be possible.

To my dear and loving wife,
for her patience, support, and motivation.

To my beloved siblings,
who have given me dreams to look forward to.
Chapter 1

Introduction

Electrowinning is an important process in the extraction of metals such as nickel, copper, and zinc. Laterite and sulfide ores are the main source of nickel, which has a consumption rate in excess of 1,000,000 tons per year, and a significant proportion of this metal is produced through the electrowinning process. In the case of copper, electrowinning plants contribute to the production of approximately 20% of the world's product. According to the figures released by the London Metal Exchange (LME), approximately 7,000,000 tons of zinc is produced annually in the world by the electrowinning process [1-5].

Electrowinning is an electrolytic process in which metallic ions are electrodeposited from solutions on the cathode to produce high purity metals. Approximately 80% of the power requirement for a zinc refinery is consumed by the electrowinning process. Moreover, the quality of the final products is determined at this stage. In this process, metal reduction occurs on the cathode and the oxygen evolution reaction (OER) is the main anodic reaction [5, 6].

The electrical energy consumption during the electrowinning process depends on the current density that passes through the cell, which determines the production rate and the required potential difference between anode and cathode. At a constant applied current, the lower cell potential means the lower energy consumption for a given production rate. Therefore, minimizing the cell potential is essential in the electrowinning process [7, 8].
Although the equilibrium potential for the OER is 1.23V\textsubscript{SHE}, the reaction does not happen until a significant overpotential is applied [9, 10]. The oxygen evolution overpotential causes approximately 25\% of the electrowinning cell potential and the zinc electrowinning power consumption. The oxygen overpotential on the anode electrodes depends on the electrocatalytic properties of the anode materials [11]. Thus, the type of material used for the anode and its electrocatalytic properties determine the OER overpotential, cell potential and, consequently, the energy consumption during the electrowinning process.

The zinc electrowinning process is usually performed at high current densities (450-550 A/cm\textsuperscript{2}), which can result in a high anode potential and, consequently, the significant corrosion rate of the anodes. Although the price of a single commercial anode may seem insignificant, the overall cost of the corrosion of these anodes is considerably high. Therefore, stability of the anodes and their corrosion resistance in acidic solutions are also very important factors for the evaluation of the electrowinning anodes. These properties determine the service life of the anodes, potential of the cells during the process, and the purity of the metal deposited on the cathode [7, 8, 12].

Lead alloys are the most commonly used anodes in electrowinning processes due to the special properties of lead, such as its low solubility in the solutions containing sulfuric acid, relative low cost, low melting point, and the high conductivity in both metallic and the highest oxidized states (PbO\textsubscript{2}) [9, 13]. However, the OER overpotential on these anodes is high and their degradation resistance is relatively low [14].

Manganese ions usually exist in the zinc electrowinning electrolyte, which either originate from the ores or are added intentionally [15]. These ions are oxidized to form an MnO\textsubscript{2} oxide layer on the anode surface during the electrowinning process. This layer may improve the corrosion performance of the anodes and decrease lead contamination in the zinc
product [16, 17]. However, its protection performance strongly depends on the physical properties of the layer.

Lead-based composite anodes are a new type of the electrowinning anodes that have been developed in order to address the problems associated with the conventional lead-based anodes. The composite anodes are composed of the active metal oxide particles dispersed in the lead or lead-dioxide matrices. The presence of the active particles can facilitate the oxygen evolution reaction and decrease the anode potential. The concerns in application of a new composite anode are the efficiency of the composite particles on promoting the oxygen evolution reaction, their effects on the electrowinning process and the deposition of the anodic MnO₂ layer, and its durability and corrosion performance under the electrowinning operating conditions. Among all the options for the active composite particles, MnO₂ is one of the strongest candidates since it is catalytically active for OER and its dissolution does not negatively affect the zinc electrowinning process.

The following is a summary of the results on the electrochemical evaluation of the Pb-MnO₂ composite anodes in the zinc electrowinning operating conditions. This work hopes to contribute to the roles of the manganese dioxide composite phase in the composite anode to oxygen evolution depolarization, corrosion resistance of the anodes, and the electrodeposition of the MnO₂ protective layer on the anodes. It is believed that this project provides a baseline for electrochemical performances of the Pb-MnO₂ composite anodes in the zinc electrowinning operating condition in Mn-free and Mn-containing sulfuric acid solutions.
Chapter 2

Literature review

2.1 Introduction

Zinc has a wide range of applications in different industries, especially galvanized steel and brass productions. High global demand for zinc caused growth of its production from 5 to 13.5 million tons from 1970 to 2013 [18, 19]. Approximately 640 kilotons of zinc was produced in Canada in 2012, mostly through a hydrometallurgical process, which is nearly 5% of the global zinc production [19, 20]. Canada has some of the largest zinc processing complexes in the world, i.e. Trail (British Columbia), Valleyfield (Quebec), and Flin-Flon (Manitoba).

Sphalerite (ZnS) is the main and most frequent ore of zinc in the world and more than 90% of the zinc is mined from this source [21]. Traditionally, extraction of zinc from sphalerite is performed through the Roasting-Leaching-Electrowinning process [3, 22, 23]. Sphalerite ore is converted to zinc calcine (ZnO) after grinding and floatation steps. Then, zinc calcine is leached in different steps, which leads to the deliberation of zinc and other metallic impurities such as copper, nickel, and cobalt. Sphalerite can also be leached directly through the High-Pressure Acid Leaching process (HPAL) in autoclaves.
The resulted electrolyte after leaching contains a significant amount of the metallic ions that can cause problems in the zinc recovery stage. These ions will co-deposit with the cathodic zinc in the electrowinning process and contaminate the final product. Moreover, some of them, such as cobalt and copper, decrease the electrowinning current efficiency when co-deposited with zinc, as they can depolarize the hydrogen evolution reaction on the cathode [18]. Therefore, the leaching process is followed by the purification stage to remove the impurities that would interfere with the recovery process. In the last stage, the zinc is recovered by the reduction of zinc ions on the cathode. This process is called electrowinning (EW). The RLE and HPAL process stages are schematically shown in Figure 2-1.

Figure 2-1 Schematic of the RLE and HPAL processes of zinc extraction [18]
2.2 Zinc electrowinning process

Electrowinning is an electrolytic process that deposits high purity zinc metal on the cathode by applying external electrical energy. In the electrowinning process, zinc reduction, reaction (2-1), occurs on the cathode and water is decomposed at the anode surface to release oxygen, as shown in reaction (2-2) [5, 6]. The latter reaction is known as the oxygen evolution reaction (OER). Although these two reactions are the main redox reactions in the zinc electrowinning process, there are some other reactions happening on the surface of the electrodes. Proton reduction, also known as hydrogen evolution (reaction (2-3)), takes place at the cathode surface. This reaction is undesirable since it consumes electrons and reduces the zinc deposition current efficiency. In spite of the higher standard reduction potential of proton than zinc, the hydrogen evolution proceeds at significantly lower rates at the electrowinning operating conditions. This is the result of the high hydrogen evolution overpotential on the surface of zinc, which makes this reaction difficult to occur. Co-deposition of some other elements, such as cobalt and copper, which have low overpotential for the hydrogen evolution reaction, decreases the electrowinning current efficiency [18].

\[
\begin{align*}
Zn^{2+} + 2e^- & \rightarrow Zn & E^* = -0.76 \text{ V}_{\text{SHE}} \\
2H_2O & \rightarrow O_2 + 4H^+ + 4e^- & E^* = 1.23 \text{ V}_{\text{SHE}} \\
2H^+ & \rightarrow H_2 + 2e^- & E^* = 0.0 \text{ V}_{\text{SHE}}
\end{align*}
\]

Some of the impurities, such as manganese and chloride ions, react at the anode surface during the electrowinning process, which will be explained later. The zinc electrowinning process usually operates in highly acidic electrolytes and at high current densities. Typical electrowinning operating conditions are summarized in Table 2-1.
Table 2-1 Typical operating parameters of the zinc electrowinning process [18]

<table>
<thead>
<tr>
<th></th>
<th>Cathodes</th>
<th>Anodes</th>
<th>Current density (A/m²)</th>
<th>Current efficiency %</th>
<th>[H₂SO₄] (g/L)</th>
<th>[Mn²⁺] (g/L)</th>
<th>[Zn²⁺] (g/L)</th>
<th>[Cl⁻] (mg/L)</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum sheets</td>
<td>PbAg (0.5-.75 wt.% ) plates</td>
<td>Current efficiency %</td>
<td>88-93</td>
<td>165-180</td>
<td>1-6</td>
<td>50-65</td>
<td>0-250</td>
<td>37-40</td>
<td></td>
</tr>
</tbody>
</table>

The electrical energy consumption in the electrowinning process is approximately 80% of the power requirement for the entire zinc refinery process. The electrowinning process is operated under constant current density, therefore, the EW cell potential determines the energy consumption of this process. The cell potential ($\Delta V$) consists of several components:

$$\Delta V = \Delta E + \Delta \eta + \Delta V_\Omega + \Delta V_i$$  \hspace{1cm} (2-4)

where $\Delta E$ is the equilibrium potential of the overall cell reaction, $\Delta \eta$ is sum of the anodic ($\eta_a$) and the cathodic ($\eta_c$) overpotentials, $\Delta V_\Omega$ denotes the potential drop due to ionic resistance, electronic resistance of the connections and concentration polarization, and $\Delta V_i$ represents the stability of the anodes and shows the variation of the potential during service as a result of the anode degradation [7, 8]. Some of these components are shown in more detail in Figure 2-2. A decrease in each of the components results in lower cell potential and, consequently, better energy efficiency during electrowinning. The overpotential of the cathodic reactions is not considerable in the electrowinning process, however, decreasing the overpotential of the anodic reaction has been the subject of many studies.
2.3 Electrowinning anodes

The electrowinning process is usually carried out in the concentrated sulfuric acid solutions at a pH of 0 or lower and at high potentials. These conditions are very aggressive and corrosive, which limit the options for the electrowinning anode selection. Moreover, as previously mentioned, the anodes are preferred to have a high electrocatalytic activity for the OER in order to decrease the overpotential for this reaction, electrowinning cell potential, and the energy consumption [24-26]. In general, anode materials that are used in the zinc electrowinning should have the following special properties [27]:

- High electrical conductivity
- Good electrocatalytic capabilities (for OER)
- High mechanical strength to be resistant to bending and creep during long time service
- High corrosion resistance in the working conditions
Lead (Pb) is usually the preferred material for anode electrodes due to its special properties such as very low solubility in the solutions containing sulfuric acid, relatively low cost, low melting point, and high electrical conductivity of its highest oxidized states (PbO₂) [9, 13]. Since the surface oxide layer of an anode plays a determining role on its service lifetime and electrowinning efficiency, it is important to know the nature of this surface layer.

2.3.1 Electrochemical reactions and corrosion of lead

Figure 2-3 shows the Pourbaix diagram of lead in the presence of sulfate ions at 25°C [28]. As it shows, the composition of the corrosion product on the lead anode strongly depends on the applied potential. When the lead anode is anodically polarized in a sulfuric acid electrolyte, PbSO₄ forms initially. At the PbO₂ stability region, PbSO₄ is oxidized to PbO₂ and the oxygen evolution reaction can take place at potentials above the water stability line. Since the electrowinning electrolyte is highly acidic, the PbO₂ anodic layer is expected to be β-phase. However, Burbank [29] showed that the structure of the anodic layer formed on the lead anodes at each potential is not as simple as the one shown in the Pourbaix diagram of Figure 2-3. Burbank [29] developed two different Pourbaix diagrams for lead in sulfuric solutions, one for the oxide layer/electrolyte interface and one for the metal/oxide layer interface. The dependence of the corrosion product phases on the location in the layer and potential has been verified by the other researchers [30-32].

Figure 2-4 schematically shows the expected composition of the anodic surface layer on lead as a function of potential in an H₂SO₄ solution at 30°C [33]. Lead sulfate (PbSO₄) is the first layer that forms on the lead in sulfuric acid electrolytes. Formation of this layer prevents diffusion of SO₄²⁻ and Pb²⁺ ions, however, dissolved oxygen and hydrogen ions are
able to penetrate through the layer. As a consequence, some basic sulfates and oxides are formed in the layer including PbO.PbSO₄, 3PbO.PbSO₄, Pb(OH)₂, and PbO [32, 34].

As the potential increases, two modifications of PbO₂ can be formed. The orthorhombic, which is known as α-PbO₂, is the result of the oxidation of Pb, PbO, and basic sulfates in the basic and neutral environments. On the other hand, the oxidation of PbSO₄ leads to the formation of the tetragonal PbO₂, also known as β-PbO₂ [32, 35-38]. The latter transformation causes a decrease in the PbSO₄ layer thickness with potential [29]. Properties of the PbO₂ surface layer depend on the proportion of these two PbO₂ structures, which is a function of operating conditions such as the current density, electrolyte concentration, and alloying elements [10, 39, 40].

Figure 2-3 Pourbaix diagram of lead in sulfuric acid electrolyte
Formation of the PbO₂ phases on the anodic layer can slow further oxidation of lead as it is conductive, and let the OER occur on the anode surface [41]. Mohammadi et al. [12] concluded that only a small portion of the applied current in the EW process (0.05-0.1%) is consumed by the electrochemical oxidation of lead. Although corrosion is known as the destruction of materials by electrochemical reactions, an overestimation occurs if the anode’s service life is calculated based on this portion of the current density. Many studies measured several years for service life of these alloys [9, 12, 42, 43] while in practice, the anodes fail in a shorter period. Although the solubility of lead in sulfuric acid solutions is low and stable anodic layers form on the lead at the EW operating conditions, the degradation of lead is significant at these conditions, contributing to a short lifetime of this anode [14].

Figure 2-4 Schematic diagram of the composition of the corrosion film as a function of potential [33]
Corrosion of the EW anodes necessitates their frequent replacement, which imposes a heavy financial burden on zinc plants. Therefore, improvement of the corrosion performance of the lead-based anodes has been the subject of many research studies in the past years.

Furthermore, pure lead is not strong enough to resist against the creep or to guarantee a safe and long service life [27]. Elongation and deformation of the anode due to creep cause a generation of many cracks in the anodic oxide surface layer. As a consequence, a fresh lead surface is exposed to the electrolyte, contributing to further oxidation and rapid corrosion [13]. Alloying with other metals has been used to improve the properties of lead for a metal electrowinning anode application.

2.3.2 Lead-based alloys

Alloying with other elements has been used to improve both mechanical and electrochemical properties of lead for electrowinning anode applications. These alloying elements can be Ag, Sb, Sn, Ca, Co, Bi, As, Cd, Li, to mention a few [25, 27, 43-54]. Each of these alloying elements has special influences on the properties of the lead anode.

2.3.2.1 PbAg anodes

Among all of the alloying elements, silver has attracted significant attention. It has been widely accepted that the presence of Ag in the Pb anode as the main alloying element decreases the oxygen evolution reaction overpotential [25, 26, 44, 51, 55]. Figure 2-5 shows the oxygen evolution overpotential of the PbAg anodes containing different silver contents in the zinc electrowinning conditions. This figure confirms the positive effect of the silver alloying element on the oxygen evolution reaction [55, 56]. Pavlov and Rogachev [51] reported that the addition of 0.58% Ag to the Pb anode shifts its polarization curve by 30-
40mV in the negative direction. However, McGinnity and Nicol [57] showed that silver has poor electrocatalytic activity for the oxygen evolution reaction, which is believed to be due to either oxidation of the silver oxide to silver oxysulfate or the separation of Ag₂O₂ active sites by the formation of Ag₂SO₄ at the Ag/Ag₂O₂ interface.

Pavlov and Rogachev [51] attributed the positive role of silver alloying element on the catalytic activity of lead to its dissolution and the presence of silver ions in the vicinity of the anodes. However, it was reported that that silver ions at the layer/solution interface facilitate the adsorption of the electrolyte anions like SO₄²⁻ ions. The adsorbed ions can block the anode surface, contributing to the polarization of the OER [58, 59].

At the high potential of the electrowinning, Ag atoms are oxidized and penetrated through the anodic layer of the anode [58]. It is believed that silver can decrease the charge transfer resistance of the anodic layer by increasing the conductivity of the PbO layer at the layer/anode interface [60]. Furthermore, Ag ions change the density of the OER active sites on the anode surface. Pavlov and Monahov [61] proposed that oxygen evolves on the gel-zone in the anodic layer of the lead anodes. It was suggested that the silver alloying element increases the gel-zone in the anodic layer compared to the crystal zone [62].

In addition to the electrochemical performance, silver improves the mechanical properties of lead alloys since it may segregate in the grain boundaries and modifies the grain structure of lead [13, 63, 64]. As shown in Figure 2-6, the presence of silver in lead also results in higher corrosion-resistant anodes [45]. This can be due to either lower anodic potential [65] or the effects of silver on the structure of the alloy and the anodic layer [25, 51, 58, 66]. The densities of the PbSO₄ and PbO₂ anodic layers, as well as the α-PbO₂/β-PbO₂ ratio, are influenced by the silver content of the alloy [24, 51, 58]. PbAg alloys containing 0.5-1.0 wt.% silver are the most commonly used anodes in the electrowinning of zinc.
Figure 2-5 Overpotentials for OER on the PbAg anodes at 500 A/m$^2$ in acid electrolyte as a function of silver content [56]

Figure 2-6 Effect of silver content on the corrosion rate of PbAg alloys at 10000 A/m$^2$ [45]
2.3.2.2 \textit{PbSnCa anodes}

The PbSnCa alloy was introduced by Prengaman in the 1980s for the first time. Each of the used alloying elements has special effects on the properties of lead [24]. Calcium is used to improve the mechanical properties rather than corrosion performance [45]. It has been shown that the optimum calcium content of 0.07-0.09 wt.% results in the maximum yield strength of Pb-Ca alloy [63]. On the negative side, calcium weakens the corrosion resistance of the lead anodes [63, 67, 68]. The presence of calcium in the lead causes the precipitation of Pb$_3$Ca, which reduces the grain size and increases the intercrystalline area of the corrosion layer. Consequently, intergranular corrosion is promoted in the PbCa alloys [69, 70].

Addition of tin to the PbCa decreases the amount of the Pb$_3$Ca phase at the grain boundaries through the formation of the Sn$_3$Ca phase that is more stable. Therefore, tin reduces the intergranular corrosion in the PbCa anodes [46, 69]. Moreover, the presence of tin in the anodic layer causes higher conductivity of the layer and inhibits the anode passivation problem [69, 71-73]. The mechanical properties of lead alloys can also be improved by the tin alloying element. Since tin might be trapped in the large (Pb$_{1-x}$Sn$_x$)$_3$Ca precipitations in PbSnCa alloys, its effective amount depends on the amount of calcium in the lead alloy [72, 74]. PbCaSn alloys are the most popular lead-based anodes in the copper electrowinning process [24].
2.3.2.3 Alternative lead-based alloys

Industrial zinc electrowinning anodes commonly contain between 0.5 to 1.0wt% silver [25, 55]. The cost of alloying with silver is very considerable because of the high price of this metal and the significant amount required for the large number of anodes used in a typical electrowinning plant. As a consequence, many research studies have been performed in order to find an alternative for silver as well as to lower the content of this element in the zinc electrowinning anodes [44, 69, 75, 76].

Cobalt can be a suitable alternative for silver in lead anodes. The effects of cobalt as an alloying element and additive ions on performance of lead anodes have been the subjects of studies for many years [41, 77]. It has been widely accepted that the cobalt, either as the alloying element or as ions in the electrolyte, catalyzes the oxygen evolution reaction, reduces the lead anode potential, and improves the corrosion performance of lead [25, 26, 41, 77]. As shown in Figure 2-7, the effect of cobalt is more significant than silver in similar content [27].

![Graphs](image.png)

Figure 2-7 (a) Weight loss of PbCo and PbAg anodes as a function of the alloying elements content, (b) Anodic potential of PbCo and PbAg anodes as a function of the alloying elements content at 500 A/m² [27].
Although the suitable properties of PbCo alloys as the electrowinning anodes have been widely accepted, they could not find industrial applications because of the problem associated with alloy production. This problem is due to the very low solubility of cobalt in lead, which causes segregation of cobalt during the casting process and, consequently, non-uniform distribution of this element in the alloy [27, 41, 78]. Moreover, as mentioned earlier, cobalt ions can have harmful effects on the current efficiency of the zinc deposition, which limits the application of the PbCo alloys in the electrowinning of zinc [41].

Bismuth is another alloying element that can be used in lead-acid battery electrodes since its physical and chemical properties are close to those of lead. In addition, the separation of bismuth from lead is an irksome and costly process [52]. Byrnseva et al. [ref. 27 in [79]] investigated the PbBi anode containing a wide range of bismuth (0-40 wt.%). Although their results indicated that the corrosion attack increased with Bi content up to 3.6%, higher Bi content resulted in a more stable anode. Some other researches revealed that the presence of bismuth in the lead alloy resulted in lower corrosion resistance [9,80-83]. Lai et al. [84] investigated the influences of Bi on the performance of Pb-0.8Ag electrowinning anode and reported that a small addition of bismuth (<1.0wt.%) has a protective effect, while an increase in the corrosion rate was observed thereafter. On the other hand, it has been widely accepted that the oxygen evolution overpotential on PbBi alloys is lower than that on the Pb anode, an effect that is more considerable with higher Bi content [52, 85-91].

2.3.3 Dimensionally-stable anode

As mentioned before, oxygen evolution is the main anodic reaction in the electrowinning process and its overpotential determines the energy efficiency of the EW process. The dimensionally-stable anode (DSA) is one of the most important approaches in
lowering the OER overpotential and the EW energy consumption. DSA is a coated titanium substrate by the electrocatalyst metal oxides such as RuO$_2$ and IrO$_2$, which are usually prepared through thermal decomposition of suitable precursors $[7, 92]$. Electrocatalytic materials can decrease the OER overpotential either by decreasing the activation energy or changing the rate-controlling step of this reaction $[11]$. DSAs were developed in the 1960s for the chlorine and oxygen evolution reactions. The Sumitomo Metals and Mining Company used DSAs in commercial scale in 1975 for the electrowinning of nickel and cobalt from chloride solutions $[93]$. The DSAs provide lower OER overpotential and better corrosion resistance than the lead alloys. Figure 2-8 compares the corrosion rate of two DSAs with that of the PbSnCa anode in an electrolyte-containing sulfuric acid as a function of current density. It reveals that the corrosion rate of the PbSnCa anode is much higher than those of the DSAs and increases with the current density $[94]$. Improving the properties of these anodes has been the subject of many studies by changing the composition of the anodic layer and the substrate $[92, 93, 95-101]$. It has been shown that the electrocatalytic properties of the DSA is a function of RuO$_2$/IrO$_2$ ratio and improved by the addition of MnO$_2$ $[92,98]$. Smart anodes and green anodes for electrometallurgical industries have been developed based on the electrocatalytic properties of metals oxide $[102, 103]$.

Despite the desirable properties of the DSAs, problems such as the formation of a TiO$_x$ passive layer on the substrate and significant investment costs of these anodes have prevented widespread adoption of this technology $[14, 100, 101]$. Moreover, DSAs cannot function very well in Mn-containing electrolytes since the deposited MnO$_2$ layer covers the surface of the electroactive oxide layer and increases the anode potential.
2.3.4 Composite anodes

Composite anodes have been developed in order to combine the advantages of the commonly-used electrowinning anodes, i.e. lead-based alloys and DSAs. Composite anodes are composed of the active metal oxide particles dispersed in the lead or lead dioxide matrices. The electrocatalytic metal oxides can be selected among different categories of the metal oxides including [11]:

- **Rutile-type Oxides**: This group of oxides includes RuO$_2$, IrO$_2$, MnO$_2$, RhO$_2$, and PbO$_2$.

- **Spinel-type Oxides**: This type of oxide includes multiple substitutions of the transition metal cations and also two kinds of cation sites that are surrounded by oxygen anions. Co$_3$O$_4$, Co$_2$NiO$_4$ and Fe$_3$O$_4$ can be named as examples of this group.

- **Perovskite-type Oxides**: These oxides are ABO$_3$ oxides in which A is a large cation, such as La(III) or Sr(II), and B is a transition metal cation. La$_{0.7}$Pb$_{0.3}$MnO$_3$, La$_{0.2}$Sr$_{0.8}$Co$_{0.8}$Fe$_{0.2}$O$_3$ and La$_{0.9}$Sr$_{0.1}$CoO$_3$ are examples of these oxides [11].
The Sabatier principle of catalysis can be used to compare the catalytic properties of different oxides for the oxygen evolution reaction. According to this model, the best catalytic performance is observed when the reaction intermediate binding is neither too weak nor too strong [104]. If an oxide has a stable higher oxide state, the oxygen intermediates adsorb strongly on its surface and fail to dissociate, contributing to the surface blockage. On the other hand, if the interaction is weak, the intermediates fail to bond to the oxide surface and no reaction occurs. The volcano relation between the oxygen overpotential and the oxygen adsorption energy is shown in Figure 2-9 [105]. Note: the information presented in this might be associated with errors since the similarity of the real surface area of the oxide electrodes was not reported. According to this figure, PbO₂ is not highly active for the OER as its high enthalpy of transition to a higher oxidation state causes a weak M-O bond on its surface. The best catalysts among what are shown in Figure 2-9 should be around the top of the volcano curve. In general, the electroactive composite particles that are used in the zinc electrowinning anodes should have the following properties:

- Better electrocatalytic activity for the OER than PbO₂
- Stable in the electrowinning operating condition
- No negative effect on the electrowinning process, especially the current efficiency
- Economically attractive

RuO₂, IrO₂, and their combination with other oxides show excellent electrocatalytic properties for the OER. Musiani et al. [106] investigated the anodic performance of PbO₂-RuO₂ composite coatings. The influence of the RuO₂ composite particles on the OER overpotential on the PbO₂ coating is demonstrated in Figure 2-10.
Figure 2-9 Electrocatalytic activity for oxygen evolution at various oxides as a function of the enthalpy of the lower to higher oxide transition in an acidic solution [105].

Figure 2-10 Potentials of the PbO₂ and PbO₂-RuO₂ coated anodes in 0.5 M H₂SO₄ solution at different current densities [106].
It was also shown that higher content of RuO$_2$ leads to better electrocatalytic properties of the PbO$_2$-RuO$_2$ coating. Despite the desirable catalytic performance of these oxides (RuO$_2$ and IrO$_2$), using them is very costly [92, 93, 96, 106-110].

Spinel-type oxides, especially cobaltites (Co$_3$O$_4$ and NiCo$_2$O$_4$), show high electrocatalytic activity for the OER. Figure 2-11 reports the potential of the Pb-Co$_3$O$_4$ composite anode as a function of Co$_3$O$_4$ particles content at constant current density of 100 A/m$^2$ [111]. This figure shows that the potential of the Pb-Co$_3$O$_4$ anode decreases as the content of the composite particles increased, which is due to catalytic activity of the Co$_3$O$_4$ particles.

Although Co$_3$O$_4$-containing composite anodes can be used in the copper electrowinning, they are associated with a problem in the zinc electrowinning applications. According to the Pourbaix diagrams of cobalt and nickel (not presented here), their ionic states (M$^{2+}$) are stable under zinc electrowinning operating conditions. To illustrate, consider the dissolution rate of cobalt from a Pb-Co$_3$O$_4$ anode during anodic polarizations, which is shown in Figure 2-12. Dissolution of these ions and their co-deposition with the cathodic zinc can significantly drop the electrowinning current efficiency as they catalyze the hydrogen evolution reaction [11, 18, 112].

Manganese dioxide can be considered as a suitable candidate to be used as the composite particles in the lead-based composite anodes as it satisfies all the required criteria listed at the beginning of this section.
Figure 2-11 Potentials of the Pb–Co$_3$O$_4$ anodes as a function of Co$_3$O$_4$ content [111].

Figure 2-12 Dissolution of cobalt from Pb-Co$_3$O$_4$ anode during anodic polarization [41].
2.3.4.1 Pb-MnO₂ composite anodes

As suggested by Tseung and Jasem [114], in a good OER electrocatalyst, the redox potential of \( M^{n+/M^{(n+1)+}} \) reaction should be lower or similar to that of the \( H₂O/O₂ \) couple in the same media. The redox potential of Mn(III)/Mn(IV) in the acidic solution is 0.96-0.98 V\textsubscript{SHE} (for MnOOH/MnO₂ and Mn₂O₃/MnO₂), which is lower than that of the OER [115]. As Figure 2-9 shows, adsorption of oxygen atoms on MnO₂ is stronger than PbO₂ and its catalytic activity for the OER is higher [105, 116]. Therefore, MnO₂ can be considered as the active oxide for the OER. Catalytic activity of this Rutile-type oxide for OER in acidic and alkaline solutions has been previously reported [11, 117-120].

The Pourbaix diagram of manganese is shown in Figure 2-13. It shows that MnO₂ can be stable in a wide range of pH and at potentials more positive than OER equilibrium potentials. However, its oxidation to permanganate (MnO₄⁻) or its reduction to Mn(III) can take place at the electrowinning operating conditions. Moreover, the dissolution of MnO₂ particles does not disturb the deposition of the cathodic zinc. Besides, MnO₂ particles are economically more attractive than the other mentioned oxides (according to the analytical grade prices). During the electrowinning process in Mn-containing electrolytes, MnO₂ is produced either on the anodes or in the electrolyte. Depending on the impurities, these precipitated MnO₂ can be an available source of the MnO₂ composite particles.

Li et al. [110] and Lai et al. [121, 122] prepared the Pb-MnO₂ composite anode through co-deposition of MnO₂ particles into the Pb surface coating by the electrodeposition method. The potential of the anodes during the polarization reveals the positive effect of MnO₂ particles on the catalytic activity of the lead anode for the OER (Figure 2-14(a)). It was also reported that the composite-coated anode had better corrosion resistance than the lead anode in the zinc electrowinning application, as shown in Figure 2-14(b).
Figure 2-13 Pourbaix diagram of Mn-H$_2$O system

Figure 2-14 Potential (after 72 h) (a) and corrosion rate (after 33 h) (b) of Pb/Pb-MnO$_2$ anodes as a functions of MnO$_2$ content [110]
These results, however, indicate that the composite-coated anodes did not perform better than the PbAg anode. Schmachtel et al. [123] prepared the Pb/Pb-MnO$_2$ composite anodes containing different MnO$_2$ contents and using different structures of MnO$_2$. Their short-term results (6 hours) demonstrated that the MnO$_2$-containing composite anodes can have better catalytic activity for the OER than the PbAg anode.

It was reported that the service life of the composite coatings can be very limited. They may be corroded or detached from the surface of the substrate during service operation [106, 107, 124]. An alternative to this may be the use of bulk composite anodes, which contain the electrocatalytic phase dispersed in the body of the anode, not only on the surface. Therefore, the MnO$_2$-containing bulk composite electrode potentially can be used in the zinc and copper electrowinning process with better anodic performance than the conventional PbAg and PbSnCa anodes. Thus, an investigation of the electrochemical behavior and corrosion performance of Pb-MnO$_2$ bulk composite anodes with different contents of MnO$_2$ particles can be the subject of further studies. Furthermore, the composite particles might affect the performance of the anodes in the actual electrowinning electrolyte, which contains manganese and chloride ions.

### 2.4 Electrowinning electrolyte composition

#### 2.4.1 Chloride ions

Chloride usually exists in the zinc electrowinning electrolyte, coming from the ores or wash water. Many research studies have shown that the presence of chloride ions, regardless of their sources, increase the corrosion rate of lead anodes. However, this effect is a function of its concentration as well as the alloy composition. For instance, the corrosion rate of a pure lead anode sharply increases with the chlorine concentration while that of the PbAg anode
containing more than 0.5 wt.% silver is not very sensitive to chlorine concentration [27, 125, 126]. Mohammadi et al. [12] reported a positive effect of chloride at low concentrations on the corrosion of PbCa and PbAg by potentiodynamic polarization studies in the nickel electrowinning electrolyte. It is noteworthy to mention that the significant corrosion attack of the anode in the presence of chloride is observed well above the electrolyte level [126]. Consequently, the main issue associated with chloride in the electrowinning process is its oxidation on the anode surface through reaction (2-5), resulting in the evolution of chlorine gas and severe chemical attack.

\[
Cl_2 + 2e^- \leftrightarrow 2Cl^- \quad E^\circ = +1.161 \text{ V}_{Ag/AgCl} \quad (2-5)
\]

Corrosion attack is not the only problem associated with chloride in the electrowinning electrolyte. Dissolved chlorine gas that is formed through reaction (2-5) can be reduced on the surface of the cathode and consume a small portion of electrons, contributing to the lower current efficiency of the zinc electrodeposition [127].

### 2.4.2 Manganese ions

Manganese ions are usually encountered as an impurity in the zinc electrowinning electrolyte. Part of the manganese comes with the zinc ore. It might also be introduced to the electrolyte during the leaching process through the addition of manganese dioxide or potassium permanganate in order to oxidize iron impurities [15, 16].

Manganese ions are oxidized on the anodes during the electrowinning process, resulting in the formation of an MnO\(_2\) layer on the anode as well as MnO\(_2\) particles in the electrolyte, which are also known as cell mud [15]. The MnO\(_2\) layer deposited on the anode may improve the corrosion performance of the anode and decrease the lead contamination in
the zinc product [128]. Moreover, the evolution of chlorine as a hazardous and corrosive gas can be hindered in the presence of manganese [127]. Mraz et al. [129] reported that, at high potentials, the activation energy of the chlorine evolution on the MnO₂ surface is higher than on the PbO₂. Proposed scavenging reactions (2-6) and (2-7) also occur to limit dissolved chlorine in the Mn-containing electrolytes and reduce the chlorine release [127]. The presence of the Mn(II) ions in the electrolyte can also decrease the OER overpotential on the lead-based alloys [17, 45, 56, 59].

\[ 2\text{Mn}^{2+} + \text{Cl}_2 \rightarrow 2\text{Mn}^{3+} + 2\text{Cl}^- \]  \hspace{1cm} (2-6)

\[ \text{Mn}^{2+} + \text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+ + 2\text{Cl}^- \]  \hspace{1cm} (2-7)

The effects of the Mn(II) ions and its oxidation products are not always positive. High concentration of the manganese ions in the electrowinning electrolyte causes some problems in the electrowinning process such as drop-in current efficiency and increasing cell potential. Moreover, if the MnO₂ layer deposit on the anodes grows too thick, it causes electrical shorting between anode and cathode, resulting in a low quality zinc product and damage to the anode [15, 16, 130]. Optimum concentration of manganese ions in solution from the corrosion viewpoint is about 1-3g/L [15, 16, 131].

Depending on its concentration, the zinc electrowinning process might also be affected by the manganese and its oxidation products. For instance, the current efficiency of the zinc cathode production may decrease in the presence Mn(II) ions. Co-deposition of the MnO₂ particles with zinc on the cathode results in the formation of Zn/MnO₂ galvanic pairs. This can cause anodic dissolution of the deposited zinc and results in a lower current efficiency. Permanganate (MnO₄⁻) ions, as one of the manganese oxidation products, can also diffuse to the cathode surface, oxidize the cathodic product, and decrease the zinc deposition current.
efficiency [132, 133]. This was verified by Ivanov and Stefanov [16] through using separate electrode compartments with an exchange membrane that prevents the diffusion of anodic product to the cathodes.

The overall reaction for the electrodeposition of MnO₂ in Mn-containing electrolytes is given by reaction (2-8), which is proposed to occur in a sequence of steps.

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad E^\circ = 1.03 \text{ V}_{Ag/AgCl}$$ (2-8)

Many studies proposed the Electrochemical-Chemical-Electrochemical (ECE) mechanism for the MnO₂ electrodeposition. This mechanism, given by reactions (2-9)-(2-11), supports MnOOH as the main intermediate in the electrodeposition process [134-136].

$$Mn^{2+} \rightarrow Mn^{3+} + e^- \quad E^\circ = 1.31 \text{ V}_{Ag/AgCl}$$ (2-9)

$$Mn^{3+} + 2H_2O \rightarrow MnOOH + 3H^+$$ (2-10)

$$MnOOH \rightarrow MnO_2 + H^+ + e^- \quad E^\circ = 0.76 \text{ V}_{Ag/AgCl}$$ (2-11)

The other suggested mechanism for the MnO₂ electrodeposition is initiated by the formation of permanganate at high anodic potentials (reaction (2-12)). The chemical reaction of permanganate with Mn(II) results in Mn(III) ions, as shown in reaction (2-13). The disproportionation of Mn(III) ions can then yield an MnO₂ deposition, as shown in reaction (2-14) [127, 131, 137, 138]. Figure 2-15 proposed the scheme of this mechanism of the electrodeposition of an MnO₂ layer [127].

$$Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^- \quad E^\circ = 1.31V_{Ag/AgCl}$$ (2-12)

$$MnO_4^- + 4Mn^{2+} + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O$$ (2-13)

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+$$ (2-14)
Figure 2-15 Possible reaction scheme for the anodic oxidation of manganese ions and MnO₂ layer deposition.
The anodic electrodeposited layer is not the only form of MnO₂ that is generated at high anodic potentials. The MnO₂ particles that are suspended in the electrolyte and eventually settle as sludge on the bottom of the cell can originate during the electrowinning process. These particles might be the result of the detachment of the MnO₂ nucleated on the anode surface, especially when oxygen evolves from the surface. These nuclei can either remain in the electrolyte or relocate to provide suitable sites for further MnO₂ depositions [130, 139].

It can be stated that the rate of the cell mud formation depends on the properties of the deposited MnO₂ layer on the anode. Detachment of the MnO₂ layer as a source of the MnO₂ particles in the electrolyte is determined by the physical properties and mechanical stability of the layer [135]. Moreover, MnO₄⁻ formation also depends on the properties of the MnO₂ anodic layer. As McGinnity and Nicol reported, MnO₄⁻ is generated through the oxidation of Mn(II) on the lead dioxide surface when the MnO₂ layer on an anode breaks down [140].

It has been previously reported that the MnO₂ layer deposition and its properties depend on the chemical composition and pre-treatment of the lead-based anodes [135]. Therefore, the deposition of an MnO₂ layer on lead anodes might be affected by the composite particles on the composite anode surface. However, no comprehensive study on the electrodeposition of the MnO₂ layer on the composite anodes, especially Pb-MnO₂, has yet been performed.
Chapter 3

Objectives

Application of the conventional lead-based alloys as the electrowinning anodes is still associated with many problems such as high corrosion rates, shortened lifetime, and high energy consumption. Our literature review shows that these anodes can be replaced by new lead-based composite anodes as the presence of the electroactive composite particles can decrease the oxygen evolution overpotential and improve the electrowinning energy efficiency. High sensitivity of the zinc electrowinning process in the presence of impurities in the electrolyte limits the electroactive particle candidates for a zinc electrowinning composite anode. As was shown in the previous chapter, MnO$_2$ can be a suitable option for making new composite anodes for the zinc electrowinning application since the dissolution of MnO$_2$ does not negatively affect the zinc recovery process. To the best of our knowledge, only a few studies have been conducted on the fabrication and performance of the MnO$_2$-containing composite anodes, which focused on the Pb-MnO$_2$-coated anodes.

The broad scope of this work is to develop new bulk Pb-MnO$_2$ composite anodes for the zinc electrowinning and to investigate their performance to improve the energy efficiency of the electrowinning process and also extend the lifetime of the anodes. To accomplish this
objective, the roles of the MnO$_2$ composite particles on the oxidation of lead and the oxygen evolution mechanism on the lead anode must first be identified. Then, the performances of the composite anodes under the electrowinning operating conditions need to be studied. The zinc electrowinning electrolyte usually contains different concentrations of manganese ions. These ions can influence the performance of the anodes, depending on their concentrations, anode chemical composition, anodic potential, and properties of the MnO$_2$ deposited layer. Therefore, the electrochemical reactions on the composite anodes might be influenced by manganese ions, which should be acknowledged. Finally, an investigation of the electrochemical and corrosion performance of the Pb-MnO$_2$ composite anodes under electrowinning conditions in Mn-containing solutions is also required.

This research work involves various types of electrochemical experiments to investigate the electrocatalytic activity and anodic behavior, corrosion resistance, and corrosion layer properties of the Pb-MnO$_2$ anodes in Mn-free and Mn-containing sulfuric acid solution electrolytes. Some conventional lead-based electrowinning anodes are tested similarly as benchmarks for comparison. Therefore, the following steps need to be pursued to achieve the objective of this research study:

- To investigate the effects of the MnO$_2$ composite particles and their content on the electrochemical oxidation of the lead anode.
- To evaluate the oxygen evolution mechanism on the Pb-MnO$_2$ composite anodes and the effect of the MnO$_2$ particles content on the catalytic activity of the composite anodes.
- To study the anodic stability and corrosion performance of the composite anodes in the sulfuric acid electrolyte solution in comparison to the conventional electrowinning anodes.
• To study the effect of manganese ions on the anodic oxidation and the oxygen evolution rate on the Pb-MnO₂ composite anodes.

• To have a better understanding of the role of anode chemical composition on the properties of the electrodeposited MnO₂ layer.

• To investigate the role of the deposited MnO₂ anodic layer and its properties on the anodic performance and corrosion resistance of the composite anodes under the zinc electrowinning operating conditions in the presence of manganese ions in the sulfuric acid solution electrolytes.
Chapter 4

Experimental

The aim of this work is the electrochemical evaluation of the Pb-MnO$_2$ composite anodes in comparison to the conventional lead-based anodes in the zinc electrowinning operating conditions. In order to achieve this purpose, this work included comprehensive sets of experiments. Each set of experiments is carried out through a combination of electrochemical techniques. Characterization techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) were employed to study the features of the anodic layers of the polarized samples.

4.1 Anode materials

4.1.1 Lead-based alloys

Three industrially-supplied lead alloys of PbAg, PbSnCa, and PbCa were used in this work. The PbSnCa and PbCa anodes were examined in some of the electrochemical experiments. The PbAg anode was subjected to most of the electrochemical experiments and was used as a benchmark for comparison. Compositions of these alloys were determined using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique completed by Inspectorate IPL in Richmond, BC. Table 4-1 shows the chemical composition of these alloys.
Table 4-1 Chemical composition of the lead-based alloys used in this study

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sn wt.%</th>
<th>Ca wt.%</th>
<th>Ag wt.%</th>
<th>Mn ppm</th>
<th>Bi ppm</th>
<th>Al ppm</th>
<th>Fe ppm</th>
<th>Mg ppm</th>
<th>Cu ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbAg</td>
<td>0.003</td>
<td>&lt;0.01</td>
<td>0.746</td>
<td>&lt;5</td>
<td>33</td>
<td>&lt; 100</td>
<td>&lt; 100</td>
<td>&lt; 100</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>PbSnCa</td>
<td>1.3</td>
<td>0.11</td>
<td>&lt;10 ppm</td>
<td>≈40</td>
<td>&lt; 10</td>
<td>&lt; 100</td>
<td>&lt; 100</td>
<td>&lt; 100</td>
<td>&lt; 13</td>
</tr>
<tr>
<td>PbCa</td>
<td>&lt; 0.003</td>
<td>0.05</td>
<td>&lt;10 ppm</td>
<td>≈90</td>
<td>&lt; 10</td>
<td>&lt; 100</td>
<td>&lt; 100</td>
<td>&lt; 100</td>
<td>&lt; 15</td>
</tr>
</tbody>
</table>

4.1.2 Pb-MnO$_2$ composite anodes

Pb-MnO$_2$ composite anodes were fabricated through a single-action pressing of the Pb/MnO$_2$ powders mixture. This method has been used in some other studies to prepare different electrowinning anodes [141-146]. A positive effect of this fabrication technique on the corrosion resistance of the anodes was also reported compared to the cast alloys with similar composition [41]. A cold-pressing process takes place at the ambient temperature while hot press is performed at higher temperatures, which usually provides higher compactness. In the case of lead, however, room temperature-pressing can also be considered as hot compaction since lead has a very low melting point (327°C) [147]. So the sintering process after pressing does not seem very necessary.

Manganese dioxide particles with diameters less than 100μm (Baker & Adamson) were used to fabricate the composite anodes. The particle size distribution of the MnO$_2$ particles was analyzed by a particle size analyzer (Malvern Mastersizer 2000 Laser Diffraction Particle Size Analyzer). The results showed that 80% of the MnO$_2$ particles were smaller than 40 μm (P$_{80}$=40 μm). The XRD pattern of the MnO$_2$ particles is shown in Figure 4-1, indicating that the MnO$_2$ particles contained the Mn(III) oxide (MnOOH) and different phases of manganese dioxide. It should be noted that the catalytic activity of MnO$_2$ strongly depends on its phase structure. Therefore, the results of this study might be varied with a change in the type of
\textit{MnO}_2\textsubscript{2} composite particles. Lead powders were purchased from Sigma-Aldrich (>99\% pure) with diameters of less than 44\textmu m. Figure 4-2 presents the XRD pattern of the lead particles. Bulk and SEM images of the \textit{MnO}_2 and Pb powders are shown in Figure 4-3.

The \textit{MnO}_2 particles were dispersed by stirring magnetically in acetone for 2 hours followed by 10 minutes of ultrasonic dispersion. Different proportions of \textit{MnO}_2 and Pb powders were mixed before pressing the Pb-(0, 5, 10, 15, and 20) wt.\% \textit{MnO}_2 samples. Disk-shaped samples with a diameter of 16 mm was prepared through the single-action pressing of the powder mixture at 25 kg/mm\textsuperscript{2} load for 5 minutes in a stainless steel mold. The mentioned force is relevant to what was reported by Kiryakov and Dunaev [41]. The components of the stainless steel mold and cross section of a composite anode are shown in Figure 4-4. Figure 4-4(b) reveals uniform distribution of the \textit{MnO}_2 composite particles in the lead matrix. It was assumed that different phases of the \textit{MnO}_2 particles are uniformly distributed among the particles that were used to fabricate the composite samples.

4.2 Electrochemical measurements

Before each set of electrochemical experiments, the samples were ground using 320, 400, and 600-grit SiC papers. The specimens were rinsed in distilled water after each step. Depending on the type of experiment, an area of 1 or 2 cm\textsuperscript{2} of the disk-shaped samples was exposed to the electrolyte using either Teflon sealing rings or epoxy resin.

Electrochemical experiments were performed in the sulfuric acid electrolytes (\textit{H}_2\textit{SO}_4, ACS grade, Fisher Scientific) with a concentration of 180 g/L, which is relevant to the acid concentration of the zinc electrowinning electrolytes. The effects of manganese ions in the electrolyte were investigated with the addition of 0.5, 1.5, 3, and 6 g/L Mn(II) ions to the electrolyte.
Figure 4-1 XRD spectrum of the MnO₂ powders used to fabricate the composite anodes

Figure 4-2 XRD spectrum of the lead powders used to fabricate the composite anodes
Figure 4-3 Bulk and SEM images of the MnO$_2$ (a) and Pb powders (b)

Figure 4-4 Schematic of pressing mold components (a) and cross sectional SEM image of the as-pressed Pb-MnO$_2$ anode (b)
The Mn(II) ions were introduced into the electrolyte through the addition of MnSO$_4$.H$_2$O (ACS grade, Fisher Scientific). The electrochemical tests were performed in a water-jacketed glass container in a standard three-electrode cell. A silver/silver chloride electrode (Ag/AgCl, E=199 mV vs. SHE) and a graphite rod were used as the reference and counter electrodes, respectively. This cell will be connected to a Cole-Parmer heater and water circulating system to maintain the temperature of the electrolyte at 37±1°C. The electrolytes were slowly agitated during the electrochemical experiments using a 40 mm magnet bar at a stirring rate of 60 rpm. In this work, all the potentials are reported versus an Ag/AgCl reference electrode. A Gamry Reference 600 and a 1286 Solartron Schlumberger potentiostats were utilized to perform the electrochemical experiments. All the electrochemical experiments were repeated at least two times to ensure the obtained data are reproducible.

4.2.1 Cyclic voltammetry

Cyclic voltammetry is a useful technique in understanding the electrochemical reactions and activity of an electrode surface in certain environments. Cyclic voltammetry experiments were performed in two potential ranges of -1.0 – +2.1 and +0.4 – +2.0 V. The former potential range was conducted at a scan rate of 10 mV/s to study the general oxidation and reduction reactions of the anode surface. This technique was also employed to study the barrier properties of the anodic layer formed during the anodic polarizations. The narrower potential range was used to study the formation of different PbO$_2$ phases and conducted at different scan rates.
4.2.2 Potentiodynamic polarization

A potentiodynamic polarization experiment was performed to study the electrocatalytic properties of the anodes for oxygen evolution reaction (OER) as well as to determine the mechanism of this reaction on the anodes. This experiment was carried out on the fresh anodes at the potential range of $+1.5 - +1.95$ V at a scan rate of 0.5 mV/s.

4.2.3 Galvanostatic and potentiostatic polarization

The zinc electrowinning process usually operates at a constant current density of 500-550 A/m$^2$. In order to study the electrochemical performance of the anodes as well as the formation of the MnO$_2$ layer on the anodes, the galvanostatic experiments were carried out at a constant current density of 500 A/m$^2$. Potentiostatic polarization was also used to investigate the electrodeposition of the MnO$_2$ layer on the anodes at a constant potential and its effects on the oxidation of the anodes.

4.2.4 Linear sweep voltammetry

Linear sweep voltammetry (LSV), also called the cathodic potentiodynamic polarization, was carried out after potentiostatic polarizations of the samples in Mn-free and Mn-containing electrolytes. The potential was sweep at 5 mV/s. This technique was used to study the role of manganese concentration on the deposition of the MnO$_2$ layer on the anodes and their possible effects of the oxidation of the anode.

4.2.5 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was employed to investigate the properties of the anodic layers formed on the anodes at different anodic potentials in the
sulfuric acid electrolyte. It was also performed at a potential range of 1.7-1.9 V to observe the variation of the charge transfer resistance for the OER on the composite anode. The EIS measurements were performed in the frequency range of $10^4$-$10^1$ Hz with amplitude of 10 mV. The obtained impedance data was analyzed using Zsimwin software.

4.3 Analytical measurements

4.3.1 Inductively coupled plasma and atomic adsorption spectroscopy

Concentration of the dissolved lead during the anodic polarizations of the anodes, as an indication of the corrosion performance of the anodes, was measured by an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). A lead reference electrolyte with a concentration of 1000 ppm (Fisher Scientific) was used to prepare the standard solutions to calibrate the ICP equipment before analyzing the electrolyte samples.

Atomic adsorption spectroscopy (AAS) was used to measure the concentration of the manganese that remained in the Mn-containing electrolytes during the anodic polarization. The standard solutions with known Mn(II) concentrations were prepared using a manganese reference electrolyte with a concentration of 1000 ppm (Fisher Scientific). The AAS machine was calibrated using the standard solutions before measuring the Mn(II) concentration of the electrolyte samples. The ICP and AAS analyzes were repeated for several samples to ensure the obtained data is accurate and reproducible.

4.3.2 Titration

Electrolyte titration was used to measure the concentration of Mn(III) (manganic) and precipitated MnO$_2$ in the electrolyte during the polarization of the anodes in the Mn-containing electrolytes.
This analysis was carried out using two solutions in two steps:

First, the electrolyte samples reacted with ferrous ammonium sulfate (\((\text{NH}_4)_2(\text{SO}_4)_{2.6}\text{H}_2\text{O})\) in order to reduce Mn(III) ions and MnO\(_2\) by ferrous ions through reactions (4-1) and (4-2), respectively. The ferrous ammonium sulfate solution of 0.01 M was prepared by dissolving its powders (Fisher Scientific), which were left in an oven overnight, in the 0.2 M sulfuric acid.

Then, the leftover ferrous ions were back titrated by permanganate solution through reaction (4-3). The permanganate solution of 0.001 M was prepared by diluting the standard potassium permanganate solution (1N, Fisher Scientific). The concentration of Mn(III) ions and MnO\(_2\) precipitates were calculated from the amount of consumed ferrous ions to reduce Mn(III).

\[
\text{Mn}^{3+} + \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + \text{Fe}^{3+} \quad (4-1)
\]

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

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

The accuracy of the results was verified by potentiometric titrations that were performed using Metrohm 888 Titrando auto-titrant. Monitoring the potential of the solution during the addition of titrant is employed in this technique to detect the endpoint. Figure 4-5 shows an example of the electrolyte potential and ERC variations as a function of the titrant volume. The sharp increase in the electrolyte potential and the maximum value of the Endpoint Recognition Criterion (ERC) represents the end point of the titration (EP), which is shown by a vertical line. Titration of each sample was carried out three times to ensure the obtained data is accurate and reproducible.
4.4 Characterizations

4.4.1 Morphology and composition

The morphology of the anodic layers formed during the galvanostatic and potentiostatic experiments was studied using Field Emission Scanning Electron Microscopy (Sigma FESEM, Zeiss). The energy dispersive X-ray spectroscopy (EDX) coupled with the FESEM was used to analyze the composition of the anodic layers on the anodes.

4.4.2 Phase analysis

The phase structure of both the anodic surface layers on the polarized anodes and the deposited MnO₂ layers were analyzed by X-ray diffraction (MultiFlex XRD, Rigaku) using Cu-Kα radiation. To prevent the effects of substrates on diffraction patterns of the MnO₂ layers, the layers were detached from the anodes and put on a zero diffraction plate (SiO₂ single crystal, MTI Corporation) for XRD analysis. This analysis was carried out at 20 mA and 1°/minute, and 30 mA and 0.1°/minute for the anodes and MnO₂ layers, respectively.

![Figure 4-5](image.png)

Figure 4-5 Potentiometric determination of ferrous ions with permanganate (blue = titration curve, red = ERC)
Chapter 5

Physical features and electrochemical characterizations in the sulfuric acid electrolyte

5.1 Introduction

It is well known that the electrochemical responses of an electrode strongly depend on its surface characteristics. For instance, the surface roughness can affect the real surface area of the electrode and, consequently, the current response of the anode at an applied potential. The reaction of electrodes and their activity for other reactions like oxygen evolution depend on their surface area, surface defects, and morphology, which, in turn, are functions of the methods employed to prepare or pre-treat the electrodes. As mentioned in the experimental section, the single-action pressing of the powder mixture was used to fabricate the composite anodes. Therefore, preparation of the composite anodes by pressing of the powder mixture can cause different surface features of the anodes compared to the cast alloys, which will be studied in this chapter. This chapter also investigates and discusses the electrochemical oxidation of fresh composite anodes. Since the MnO₂ composite particles are used to enhance the oxygen evolution reaction, the performance of the composite anodes regarding this reaction will be investigated and discussed in this chapter.
5.2 Physical characterization of the composite anodes

Volume measurements of the pressed samples were carried out in water knowing that a submerged object displaces a volume of water equal to its volume. The bulk volume of each sample was calculated by measuring the weight of the displaced water and knowing the density of water. The porosity of each of the samples (Po) then was calculated as follows [75, 148]:

\[ Po = 1 - \frac{V_T}{V_b} \] (5-1)

where \( V_b \) and \( V_T \) are the bulk specific volume and true specific volume of the samples, respectively. \( V_b \) can be calculated as:

\[ V_b = m(x, \rho^{-1}_{MnO_2} + (1 - x), \rho^{-1}_{Pb}) \] (5-2)

where \( m \) is the mass of the sample, \( x \) is mass fraction of MnO\(_2\) in the samples, and \( \rho_{MnO_2} \) and \( \rho_{Pb} \) are the densities of Pb and MnO\(_2\), respectively.

Figure 5-1 shows the variation of the porosity of the Pb-MnO\(_2\) composite samples as a function of MnO\(_2\) content of the samples. It is apparent that the pressing of the Pb powders had a porosity of 3.5%. Increasing the MnO\(_2\) fraction in the initial powder mixture increased the porosity. This influence was more significant when the MnO\(_2\) content was higher than 10 wt.%. The compactness of a cold-pressed sample depends on the plastic deformation of the initial powders [148]. As MnO\(_2\) is a ceramic material, its malleability is much lower than that of lead, which is well known as a highly ductile metal [149]. Consequently, the addition of MnO\(_2\) particles decreased the plastic deformability of the mixed powder, contributing to further porosity and lower bulk density of the pressed samples. Distortion resistance of the composite anodes might be influenced by the internal porosities, which may result in warping during the electrowinning process [13, 150].
Figure 5-1 Porosity of the fabricated Pb-MnO$_2$ samples as a function of MnO$_2$ content

Surface morphology of the pressed samples are shown in Figure 5-2. These images revealed that the surfaces of the Pb-MnO$_2$ anodes contain some micro-cracks and pores that are imposed on the surface of the samples during the fabrication process. As seen in Figure 5-2, number and size of the cracks increased when the MnO$_2$ content increased in the anodes.

The presence of these defects might affect the electrochemical performances of the anodes. Despite the same geometry of the anodes, the real surface area of the composite anode is likely to be higher than that of the lead alloys due to the presence of the surface defects. In this study, the current density refers to the geometric current density that is measured based on the geometric dimensions of the samples rather than their actual surface area.
Figure 5-2 SEM surface morphology of the pressed samples: Pb (a), Pb-5MnO$_2$ (b), Pb-10MnO$_2$ (c), Pb-15MnO$_2$ (d), and Pb-20MnO$_2$ (e)
5.3 Electrochemical characterization in H$_2$SO$_4$ electrolyte

5.3.1 Cyclic voltammetry studies

Cyclic voltammetry was utilized to characterize the electrochemical behavior of the composite anodes in comparison with the PbSnCa and PbAg anodes. The cyclic voltammetry experiments were performed on the fresh samples at 10 mV/s. The potential was scanned from -1.0 V and reversed at 2.1 V.

Figure 5-3 and Figure 5-4 show the cyclic voltammograms of the PbAg, PbSnCa, and Pb-MnO$_2$ anodes obtained in sulfuric acid solution. In all of the cyclic voltammograms, one anodic peak and one anodic branch appeared during forward scanning, marked as A1 and A2. Peak A1 corresponds to the oxidation of metallic lead to lead sulfate (PbSO$_4$), reaction (5-3) [34]. At this potential, PbSO$_4$ is precipitated on the anode by either dissolution-precipitation or solid state mechanisms and caused the anodic current to increase. Beyond this potential, the electrode surface is passivated and the current decreased as the potential increased.

The current increase in the last stages of the forward scan (branch A2) is the consequence of both the formation of lead dioxide (PbO$_2$) through the oxidation of either lead (reaction (5-4)) or lead sulfate (reaction (5-5)) and the oxygen evolution reaction. As equation (5-4) shows, the formation of PbO$_2$ is possible at 0.467 V. However, PbO$_2$ is not stable at potentials lower than 1.22 V due to its tendency to react with H$_2$SO$_4$ at the oxide layer/electrolyte interface, and with lead in the lead/oxide layer interface to form PbO [6, 9, 30, 33, 39, 82, 117, 151].

\[
Pb + H_2SO_4 \leftrightarrow PbSO_4 + 2H^+ + 2e^- \quad E^\circ = -0.554 \text{ V}_\text{Ag/AgCl} \quad (5-3)
\]

\[
Pb + 2H_2O \leftrightarrow \alpha - PbO_2 + 4H^+ + 4e^- \quad E^\circ = 0.467 \text{ V}_\text{Ag/AgCl} \quad (5-4)
\]

\[
PbSO_4 + 2H_2O \leftrightarrow \beta - PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \quad E^\circ = 1.485 \text{ V}_\text{Ag/AgCl} \quad (5-5)
\]
Figure 5-3 Cyclic voltammograms of the PbAg, Pb-5MnO₂, and Pb-10MnO₂ samples in 180g/L H₂SO₄ solution at 37°C (initial potential: -1.0 V, reverse potential: 2.1 V, scan rate: 10 mV/s, fresh samples)

Figure 5-4 Cyclic voltammograms of the PbSnCa, Pb-15MnO₂, and Pb-20MnO₂ samples in 180g/L H₂SO₄ solution at 37°C (initial potential: -1.0 V, reverse potential: 2.1 V, scan rate: 10 mV/s, fresh samples)
In the backward scan, a cathodic peak and two anodic peaks were observed in the potential range of 1.2−1.5 V, which are marked as C1, B1, and B2, respectively. Cathodic peak C1 represents the reduction of PbO₂ to PbSO₄ through reaction (5-5). According to Sharpe [152], the small anodic peak that was observed just before the PbO₂ reduction peak was a result of the further generation of Pb²⁺ to form PbO and PbSO₄. Since molar volume of PbSO₄ (48 cm³/mol) is higher than that of PbO₂ (∼ 25 cm³/mol), conversion of PbO₂ to PbSO₄ (peak C1) causes cracks in the surface layer. Consequently, the metallic lead surface is partially exposed to the electrolyte after this reaction. Immediate oxidation of Pb at this potential range results in B1 and B2 anodic peaks [153, 154]. At the negative potentials, two cathodic peaks of C2 and C3 were observed in the backward potential scan, corresponding to the reduction of lead oxide and lead sulfate to lead, respectively [53, 155].

With regards to peak A1, as observed in Figure 5-3 and Figure 5-4, PbAg had the lowest peak current density compared to the other samples. The PbSnCa anode showed the second lowest current of peak A1. The magnitude of this peak depends on some other factors including history of the samples prior to the potential sweep and potential sweep parameters like the scan rate. Since all the anodes had been pre-treated in the same way prior to running the cyclic voltammetry experiments, the Pb oxidation peak in the cyclic voltammograms can be used to compare instant oxidation rates of the anodes [156,157]. The intensity of the Pb oxidation peak increased as the MnO₂ content of the composite anodes increased. This indicates that the amount of lead sulfate that was formed on the surface of the composite anodes increased with MnO₂ content [158]. The larger A1 peak in the cyclic voltammograms of the composite anode can be first attributed to the larger surface area of the composite anodes. The presence of micro cracks on the surface of the composite anodes increases the surface roughness and actual surface area of the anode.
Moreover, the presence of the MnO$_2$ particles in the composite samples might influence the oxidation rate of lead. The MnO$_2$ particles can accept electrons and accelerate the rate of electron consumption. According to the manganese Pourbaix diagram (Figure 2-13), MnO$_2$ is not stable at negative potentials. During the electrochemical experiment at negative potentials, Mn(IV) can be reduced to Mn(II) by accepting an electron. This electron exchange takes place in the solid phase without changing the positions of the ions [159]. Mn(IV) and Mn(III) can also be reduced to Mn(II) in the electrolyte. Thus, MnO$_2$ particles can provide new cathodic reactions that can cause an increase in the oxidation rate of lead. The similar effect of MnO$_2$ particles on the oxidation of lead was previously reported by Lai et al. [121]. Comparing branches A2 in the voltammograms reveals that catalytic activity of the anodes was affected by the MnO$_2$ particles. This effect will be further discussed in the following sections.

At a potential range higher than 1.65 V, the oxidation of lead to lead dioxide and the OER are the dominant reactions. The majority of the current density is due to the OER, while a small contribution is made by the PbO$_2$ formation [12]. The current densities of the samples were higher in the reverse scan compared to those of the forward scan. This difference can be attributed to the higher anode surface coverage with PbO$_2$ in the reverse scan. In the forward scan, the surface is covered mostly with PbO and PbSO$_4$, which are non-conductive phases, whereas in the reverse direction, the surface is more likely covered by the conductive PbO$_2$ phase facilitating the OER [137].

The voltammogram of the PbAg anode, unlike those of the others, did not show peak B1. This peak in the voltammograms of the composite anodes was larger than that of the PbSnCa anode. However, it did not change directly with the MnO$_2$ content of the composite anodes. The same trend was observed for peak C1.
Insets in Figure 5-3 and Figure 5-4 show enlarged curves in the potential range of 0.4-0.6 V. It is apparent that the graphs related to the composite anodes deviated from the horizontal axis (i=0) in this potential range and the deviation increased with the MnO₂ content of the samples. This can be attributed to the capacitance-like behavior of the MnO₂ present on the surface of the anode. Manganese dioxide serves as an active material to store charge via the insertion of protons from the aqueous electrolyte. This process goes along with the reduction of manganese sites in the MnO₂ oxide by the electrons coming from the external circuit. This electrochemical characteristic of MnO₂ is called pseudocapacitive behavior, which can be simplified in reaction (5-6). A large capacitance-like current was also reported for MnO₂ coatings in a sulfuric acid solution, which was prepared using the thermal decomposition method [115]. This property makes MnO₂ applicable in electrochemical energy storage systems, especially the electrochemical capacitor [160].

\[
Mn^{IV}O_2 + xe^- + xH^+ \leftrightarrow H_xMn^{III}_{1-x}Mn^{IV}_{1-x}O_2
\] (5-6)

### 5.3.2 Surface layer characterization

In this section, properties of the anodic layers of a Pb-MnO₂ composite sample at different anodic potentials were studied by the electrochemical impedance spectroscopy and XRD techniques. The composite anode containing 10 wt.% MnO₂ and the PbAg anode were subjected to study in this section.

#### 5.3.2.1 Open circuit system

The anodes were immersed in the sulfuric acid electrolyte for 2 hours. Variations of the open circuit potentials (OCP) of the Pb-MnO₂ and PbAg anodes in the naturally-aerated electrolyte are shown in Figure 5-5. The potential of the PbAg anode was stable at
approximately -0.48 V. The composite anode, however, became stable at a potential of +0.2 V. This difference can be explained by the mixed potential theory and considering different cathodic reactions during oxidation of lead on the samples.

According to the water stability lines in a Pourbaix diagram (Figure 2-3, for instance), the oxygen reduction reaction (ORR) and proton reduction reaction could be the cathodic reactions taking place on the PbAg anode at its OCP. Proton reduction reaction, however, is not thermodynamically possible at the OCP of the Pb-MnO₂ sample, as its potential is in the water stability region in the Pourbaix diagram of water. The ORR is thermodynamically favorable at this potential. Thus, the ORR can be considered as a cathodic reaction taking place on the composite anode when it is immersed in the electrolyte, especially because this reaction is catalyzed by the MnO₂ composite particles [161]. Moreover, according to the manganese Pourbaix diagram (Figure 2-13), the MnO₂ composite particles are not thermodynamically stable at potentials below 1.03 V. Therefore, the MnO₂ particles on the composite sample surface are susceptible to reduce when the sample is immersed in the sulfuric acid solution. This means that MnO₂ reduction can also occur on the surface of the composite sample at its OCP, which can be written as reaction (5-7).

\[ MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \]  \hspace{1cm} E°=1.03 \text{ V} \hspace{1cm} (5-7)

In order to find the main cathodic reactions taking place on the samples during their OCP measurements, the samples were immersed in a deaerated sulfuric acid solution and their OCPs were monitored. The electrolyte was deaerated by the continuous purging the pure N₂ gas. OCP variation of the samples in the deaerated solution is reported in Figure 5-6. As can be seen, the OCP of the PbAg did not change noticeably by deaerating the solution.
Figure 5-5 Variation of open circuit potential of the Pb-MnO₂ and PbAg anodes in the naturally-aerated sulfuric acid electrolyte at 37°C

Figure 5-6 Variation of open circuit potential of the Pb-MnO₂ and PbAg anodes in the deaerated sulfuric acid electrolyte at 37°C
This verifies that proton reduction is the main cathodic reaction on the PbAg sample. Very similar electrochemical behavior of lead alloys in the aerated and deaerated sulfuric acid solutions was also shown by Tunnicliffe et al. [6]. The OCP of the Pb-MnO₂ composite sample, on the other hand, changed when the electrolyte was deaerated. In the absence of oxygen, the OCP of this sample decreased to 0.08 V, which is still higher than that of the PbAg sample. This reveals that both of the proposed cathodic reactions, i.e. ORR and MnO₂ reduction, take place on the surface of the Pb-MnO₂ sample during its OCP monitoring in the naturally-aerated H₂SO₄ electrolyte.

Based on the different cathodic reactions on the samples, the observed difference in the OCP of the PbAg and Pb-MnO₂ samples (Figure 5-5) can be explained by the mixed potential theory. The polarization plot of a lead sample and the schematic of the Tafel lines of the cathodic reactions are shown in Figure 5-7. The OCP of the samples can be determined from the intersection of the cathodic and anodic polarization curves, in which the anodic and cathodic currents are the same. As schematically shown in Figure 5-7, the different cathodic reactions on the surface of the composite sample caused the OCP of the lead in the H₂SO₄ electrolyte to increase significantly.

The SEM morphology of the Pb-MnO₂ and PbAg anodes are shown in Figure 5-8. Formation of PbSO₄ crystals on the surface of both anodes can be observed. Generally, lead is dissolved at the lead/basic sulfate or lead/lead oxide interfaces. However, the layer is deposited at the basic sulfate/electrolyte interface. The lead ions diffuse and precipitate on to the lead sulfate crystals. Diffusion of the Pb²⁺ ions within the crystal boundary of PbSO₄ is easier than SO₄²⁻ ions due to their smaller sizes. Thus, PbSO₄ crystals grow out from the film/solution interface toward the bulk [162-165]. This phenomenon can be observed in the SEM morphology of the tilted PbAg anode (Figure 5-8(b)).
Figure 5-7 Pb polarization curve and schematic of the Tafel plots of the cathodic reactions occurring on the PbAg and Pb-MnO₂ anodes in the acid electrolyte.
Figure 5-8 Morphologies of the PbAg (a, b) and Pb-MnO$_2$ anodes (c, d) after 2 hours of monitoring the Open Circuit Potential in the sulfuric acid electrolyte
Figure 5-9 shows the XRD spectra of the Pb-MnO₂ and PbAg anodes after 2 hours of monitoring their open circuit potential in the sulfuric acid electrolyte. According to the XRD patterns, the corrosion layer on the composite anode was mainly composed of PbSO₄ and PbO. Therefore, the layer formed on this sample can be described as the Pb/PbO/PbSO₄ electrode system. On the other hand, no PbO diffraction peak was observed in the XRD pattern of the PbAg sample. This indicates that the layer formed on this anode was mostly the PbSO₄ phase.

Phase composition of the anodic layer on the lead anode in the sulfuric acid solutions depends on the anode potential [30, 32, 166]. According to studies by Pavlov et al. [30, 32, 35, 162], the anodic potential can be divided into three regions based on the composition of the anodic layer of the lead alloys in sulfuric acid solutions:

**A: Lead sulfate region**: potential range of -500 to +70 mV: interaction of lead surface with sulfuric acid solution at this potential range results in the formation of lead sulfate crystals on the lead surface [30]. Motion of SO₄²⁻ ions through this layer was hindered by the growth of PbSO₄ crystals, contributing to the formation of basic lead sulfate between the crystals. Therefore, this layer contains both PbSO₄ and basic lead sulfates (xPbO·PbSO₄) [32].

**B: Lead oxide region**: potentials between +70 to 1430 mV: the layer at this potential range contains tetragonal lead oxide (PbO) and PbSO₄ and minor amounts of basic lead sulfates.

**C: Lead dioxide region**: potentials more positive than 1430 mV: the anodic layer build on the anode at potentials higher than 1.43 V is mainly composed of the two polymorphs of PbO₂.

Note: the potential values reported in the above categorization are not exact values since the values reported in different references are not exactly the same.
Figure 5-9 XRD pattern of the Pb-MnO$_2$ (a) and PbAg (b) samples after 2 hours of monitoring the open circuit potential in the sulfuric acid solution
As the XRD results (Figure 5-9) reveal, the compositions of the anodic layers formed on the anodes are matched with the mentioned categorization. According to Figure 5-5, the OCP of the Pb-MnO$_2$ and PbAg samples were in the lead oxide and lead sulfate potential regions, respectively. Figure 5-10 schematically shows the structure of the anodic layer formed on the PbAg anode and the Pb-MnO$_2$ anode based on their OCP values and the XRD results [30].

![Figure 5-10](image.png)

Figure 5-10 Schematic model of the anodic layer on the lead anode in the lead sulfate (a) and lead monoxide potential regions (b) [30]
Figure 5-11 shows the Nyquist plots of the Pb-MnO₂ and PbAg anodes recorded after 2 hours of immersion in the sulfuric acid electrolyte. The composite anode exhibited a depressed capacitive semi-circle Nyquist plot. The PbAg anode showed a high frequency loop and a line at the low frequency region. The high frequency loop in the Nyquist plot of the PbAg anode is significantly smaller than that of the composite anode. The low frequencies impedance data in Figure 5-11 (b) could be the start of a second loop. However, this was considered as a Warburg diffusion line in literature [53, 88, 170]. The presence of this diffusion line shows that a diffusion process controls the growth of the PbSO₄ layer [167]. Growth of this layer makes it a perm-selective membrane, which hinders the diffusion of SO₄²⁻ ions (Figure 5-10(b)). According to the XRD results, the larger size of the semi-circle Nyquist plot of the composite anode and the absence of the low frequency diffusion line in this plot can be attributed to the formation of the PbO layer beneath the PbSO₄.

To analyze the EIS results, an equivalent circuit model should be developed from the physical grounds. In a simpler term, the proposed equivalent electrical circuit has to match the physical properties of the surface layer [171]. Thus, the elements of the equivalent circuit need to be in the same order as that of the anodic layers. Based on the above discussion and the scheme of the layers structure presented in Figure 5-10, the impedance results of the Pb-MnO₂ and PbAg anodes were modeled using the equivalent circuits shown in Figure 5-12 and Figure 5-13, respectively. These circuits have been previously used to model the EIS results of different lead-based alloys in different applications [167-170].
Figure 5-11 Experimental and simulated Nyquist plots of the Pb-MnO$_2$ (a) and PbAg (b) anodes obtained after 2 hours of immersion in the sulfuric acid electrolyte.
When capacitance C was used as an element in these circuits, the fitting results were not matched and showed larger departure. This deviation can be attributed to inhomogeneities of the anode surfaces, such as surface roughness, geometry-induced, non-uniform current, potential distributions, and porosity [171]. Therefore, the capacitance elements in the circuits were replaced by constant phase elements (CPE), whose impedance is

$$Z_{CPE} = (Q (j\omega)^n)^{-1}$$

where “Q”, “ω”, and “n” are the frequency-independent real constant, the angular frequency, and the CPE power, respectively. The value of “n” can vary from −1 to 1. For n = 0 and 1 and -1, CPE represents a resistance, a capacitance, and an adsorption, respectively.

In the proposed equivalent circuits, Rs is the electrolyte resistance. Two time constants correspond to the external (PbSO₄) and internal (oxide or basic sulfate) layers. Therefore, R1 represents the resistance of the PbSO₄ layer. R2 corresponds to the charge transfer resistance of the PbO layer in the circuit of Figure 5-12 and to that of the basic sulfate layer in the circuit of Figure 5-13. The R1 and R2 elements of the circuits were assigned to the mentioned layers based on their physical order in the anodic surface layer. The impedance results were modeled using the proposed equivalent circuits and the simulated Nyquist curves are shown in Figure 5-11. The simulated results show a good match with the experimental data. The value for chi squared was less than 10⁻³ in all cases, representing an acceptable fit between the simulated and experimental results.

The calculated value of the electrical circuit components for the Pb-MnO₂ and PbAg anodes are reported in Table 5-1. These results show larger values for the resistance of the layers on the composite anode. The R1 resistance values on both samples were lower than the R2 values. This can be due to the lower electrical resistance of PbSO₄ in comparison with PbO as well as the porous structure of the PbSO₄ layer [172].
Figure 5-12 Proposed equivalent circuit used to model the impedance data of the Pb-MnO₂ at open circuit potential

Figure 5-13 Proposed equivalent circuit used to model the impedance data of the PbAg at open circuit potential

Table 5-1 Impedance parameters obtained by fitting the experimental results for the Pb-MnO₂ and PbAg anodes after 2 hours at open circuit potential

<table>
<thead>
<tr>
<th>Material</th>
<th>Rs (Ω cm²)</th>
<th>Q₁ (Ω⁻¹ cm⁻² s⁻¹ x 10⁶)</th>
<th>n₁</th>
<th>R₁ (Ω cm²)</th>
<th>Q₂ (Ω⁻¹ cm⁻² s⁻¹ x 10⁶)</th>
<th>n₂</th>
<th>R₂ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-MnO₂</td>
<td>1.44</td>
<td>25.5</td>
<td>0.81</td>
<td>26.4</td>
<td>4.17</td>
<td>0.78</td>
<td>1340</td>
</tr>
<tr>
<td>PbAg *</td>
<td>1.41</td>
<td>33.7</td>
<td>0.93</td>
<td>0.428</td>
<td>3962</td>
<td>0.26</td>
<td>56.79</td>
</tr>
</tbody>
</table>

* W=0.27 (Ω⁻¹ cm⁻² s⁻¹)
5.3.2.2 Passive potential region

Impedance spectroscopy analysis was conducted on the Pb-MnO$_2$ anode at potentials of -100, 500, and 1300 mV. These potentials were chosen to study the corrosion properties of the anodic layer and its composition variation at the passive potential region. Prior to the each impedance measurement, the sample was immersed in the electrolyte for 1 hour at OCP and then polarized for 1 hour in the sulfuric acid electrolyte at the assigned potentials.

Note: the potentiostatic EIS measurements were conducted only on the Pb-MnO$_2$ anode.

The Nyquist plots of the composite anode sample at different potentials are shown in Figure 5-14. At each of these potentials, the composite anode showed a semi-circle Nyquist plot. The equivalent circuit shown in Figure 5-12 was used to model the results. The simulated Nyquist curves are also presented in Figure 5-14, which show a reasonable match with the experimental data ($\chi^2 < 4 \times 10^{-4}$). According to Figure 5-14, the size of the semi-circle Nyquist plot increased with potential. The calculated values of the elements of the equivalent circuit are shown in Table 5-2. The resistance of the corrosion layer (R1 and R2) increased with potential and showed the maximum values at 1.3 V. The effect of the applied potential on the resistance of the corrosion layers was more significant on R2, which is associated with the PbO layer. This verifies that the PbO formation is enhanced at higher potential within the investigated potential range.

The XRD pattern of the composite anode after polarization at 500 mV is shown in Figure 5-15. Comparing the PbO characteristic peaks in the patterns of Figure 5-9(a) and Figure 5-15 verifies growth of the PbO region of the anodic layer at more positive potentials.
Figure 5-14  Experimental and simulated Nyquist plots of the Pb-MnO\textsubscript{2} anode obtained after 1 hour polarization in sulfuric acid electrolyte at -0.1 (a), 0.5 (b), and 1.3 V (c)
Table 5-2 Impedance parameters obtained by fitting the experimental results for the Pb-MnO₂ anode at different potentials

<table>
<thead>
<tr>
<th>Potential</th>
<th>Rs ((\Omega \cdot \text{cm}^2))</th>
<th>Q1 ((\Omega^{-1} \cdot \text{cm}^2 \cdot \text{s}^{-n} \times 10^{-6}))</th>
<th>n1</th>
<th>R1 ((\Omega \cdot \text{cm}^2))</th>
<th>Q2 ((\Omega^{-1} \cdot \text{cm}^2 \cdot \text{s}^{-n} \times 10^{-6}))</th>
<th>n2</th>
<th>R2 ((\Omega \cdot \text{cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.1</td>
<td>1.33</td>
<td>29</td>
<td>0.85</td>
<td>15.1</td>
<td>7.2</td>
<td>0.91</td>
<td>1027</td>
</tr>
<tr>
<td>0.5</td>
<td>1.37</td>
<td>7.3</td>
<td>0.69</td>
<td>163</td>
<td>2.89</td>
<td>0.87</td>
<td>4729</td>
</tr>
<tr>
<td>1.3</td>
<td>1.28</td>
<td>3.05</td>
<td>0.825</td>
<td>412.4</td>
<td>1.61</td>
<td>0.692</td>
<td>11410</td>
</tr>
</tbody>
</table>

Figure 5-15 XRD pattern of the Pb-MnO₂ after polarization at 500 mV in the sulfuric acid solution
5.4 Electrochemical performance for the OER

The OER is the main anodic reaction during the electrowinning process. The oxygen evolution overall reaction was shown in equation (2-2). The catalytic performance of the composite anodes for oxygen evolution in comparison with those of the conventional anodes was studied using potentiodynamic polarization at the OER potential range.

Figure 5-16 shows the measured current density variations of the PbAg, Pb, and Pb-MnO$_2$ anodes as a function of the potential obtained during the potentiodynamic polarizations. During the potential sweep, the current density of the Pb anode showed a peak at around 1.68-1.7 V. This peak corresponds to the oxidation of lead sulfate to lead dioxide (reaction (5-5)) [173]. This peak also appeared in the voltammogram of the PbAg and Pb-5MnO$_2$ samples, however, further addition of MnO$_2$ to the electrode caused this peak to disappear.

As reported by Mohammadi et al. [12], the oxidation current of a lead alloy is very low compared to the OER current when it is polarized at the OER potential range. The portion of the anode oxidation current might be higher during the transient measurements such as the potentiodynamic sweeps. In this study, it was assumed that the contribution of the anode oxidation in the anodic currents during the potentiodynamic polarizations within OER potential range is negligible. In other words, the measured current during the potential sweep was assumed to be that of the OER. According to Figure 5-16, the PbAg anode showed a better catalytic activity for the OER than the Pb sample. The positive effect of the silver alloying element on OER overpotential was previously shown [55, 56].

Figure 5-16 also indicates that the presence of MnO$_2$ particles in the lead electrode shifted the potentiodynamic polarization curves to lower potentials, an effect that was enhanced by an increase in the MnO$_2$ fraction. This means that the overpotential for the oxygen evolution reaction decreased as the MnO$_2$ fraction of the composite anode increased.
At a given current density of 20 mA/cm², for instance, the OER overpotential on the surface of the Pb anode was 880 mV, while it was 760 and 670 mV on the surfaces of Pb-10MnO₂ and Pb-20MnO₂, respectively. Moreover, all the composite anodes showed lower oxygen evolution overpotential than the PbAg anode. This can be attributed to the higher electrocatalytic activity of MnO₂ for the oxygen evolution reaction compared to PbO₂ [129].

The observed effect of MnO₂ particles on the oxygen evolution performance of the anodes can be due to a change in the mechanism of this reaction or in its activation energy, which can be identified by the Tafel characteristics of the oxygen evolution reaction on the anodes.

Figure 5-17 compares the iR-corrected E-log (i) plots of the PbAg, PbSnCa, Pb, and Pb-MnO₂ anodes in the sulfuric acid electrolyte at 37°C. As can be seen, all the samples show two linear segments in the investigated potential range.

Figure 5-17 reveals that the PbSnCa and Pb samples behaved similarly in the linear regions. For these two samples, the slope of the E-log i linear region at lower potentials was 50-60 mV/decade and became approximately twice as much at the higher potential region. This change likely resulted from the different surface compositions and the reactions that happened at each region [116]. The first linear part can be attributed to the oxidation reaction of PbSO₄ to PbO₂ as well as the OER. The second linear region mostly represents the Tafel line for the OER on the samples, since the rate of the other reactions is negligible compared to that of the OER [12]. Similarly, the Tafel line of the PbAg and Pb-5MnO₂ samples showed a rapid variation at potential ranges of 1.80-1.85 and 1.75-1.80 V, respectively.

Upon further increase in the MnO₂ content of the anodes, a different behavior appeared in the potentiodynamic experiment. No initial linear part and sudden change in the plot slope was observed in the results of the Pb-MnO₂ samples containing 10 wt.% and more MnO₂.
Figure 5-16  Potentiodynamic polarization curves of the PbAg, Pb, and Pb-MnO\textsubscript{2} composite samples in 180 g/L H\textsubscript{2}SO\textsubscript{4} solution at 37°C

Figure 5-17  Tafel lines of the PbSnCa, Pb, and Pb–MnO\textsubscript{2} composite samples in 180 g/L H\textsubscript{2}SO\textsubscript{4} solution at 37°C.
The effect of MnO$_2$ particles on the rate-determining step of the oxygen evolution reaction can be identified through comparing the OER Tafel slope of the anodes. The slopes for each linear part are reported in Table 5-3. This table does not include the first linear region of the Pb, PbAg, PbSnCa, and the Pb-5MnO$_2$ samples since they are not representatives of only the OER and should not be considered as the Tafel line for this reaction. As previously mentioned, the oxidation rate of the anodes is assumed to be negligible compared to OER rate in the reported linear regions. The exchange current density for the OER on the anodes was calculated based on the linear relationship between $\eta_c$ (overpotential) and log($i$) in the polarization graph [174]. The OER exchange current densities are also presented in Table 5-3.

Table 5-3 Calculated Tafel slopes and exchange current density of the OER on the Pb, PbSnCa, PbAg, and Pb-MnO$_2$ composite samples

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Tafel slope (mV/dec)</th>
<th>Exchange current density (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low potentials</td>
<td>High potentials</td>
</tr>
<tr>
<td>PbSnCa &amp; Pb</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>PbAg</td>
<td>121.5</td>
<td>-</td>
</tr>
<tr>
<td>Pb-5MnO$_2$</td>
<td>122</td>
<td>-</td>
</tr>
<tr>
<td>Pb-10MnO$_2$</td>
<td>127</td>
<td>164</td>
</tr>
<tr>
<td>Pb-15MnO$_2$</td>
<td>122</td>
<td>205</td>
</tr>
<tr>
<td>Pb-20MnO$_2$</td>
<td>126</td>
<td>215</td>
</tr>
<tr>
<td>MnO$_2$*</td>
<td>110</td>
<td>-</td>
</tr>
</tbody>
</table>

* $\beta$-MnO$_2$ in 0.5 M H$_2$SO$_4$, 2 mm thick tablet-shaped sample [11]
Results shown in Table 5-3 reveal that the OER Tafel slope on the anodes did not noticeably change with the MnO₂ content of the anodes at low current densities. The Tafel slopes of all the samples at low current densities were in the range of 120-127 mV/decade. The difference in the Tafel slope of the Pb-MnO₂ samples may be due to either a change in the OER mechanism or different surface morphology [175].

The OER exchange current density of MnO₂ is also reported in Table 5-3 for comparison [11]. This value is lower than expected, especially when it is compared to that of the Pb-20MnO₂ sample. This can be attributed to its different structure than the MnO₂ particles used in this study and also different type of sample, which can affect the conductivity of the electrode.

The suggested mechanism for the oxygen evolution on the surface of metal oxides in acidic solutions is applicable to the surfaces of PbO₂ and MnO₂ [11, 176]. This mechanism involves electrochemical and chemical steps as shown in equations (5-8)-(5-10). S represents the active sites of the oxide surface for the oxygen evolution reaction.

\[
S + H₂O \rightarrow S - OH_{ads} + H^+ + e^- 
\]  
(5-8)

\[
S - OH_{ads} \rightarrow S - O_{ads} + H^+ + e^- 
\]  
(5-9a)

\[
S - OH_{ads} + S - OH_{ads} \rightarrow S - O_{ads} + S + H₂O 
\]  
(5-9b)

\[
S - O_{ads} + S - O_{ads} \rightarrow 2S + O₂ 
\]  
(5-10)

According to this mechanism, OER occurs through the formation of S-OHₐds and S-Oₐds intermediates. Two reactions have been proposed for the second stage. Steps (5-9a) and (5-9b) have been proposed in the “Electrochemical oxide path” and “Oxide path” mechanisms, respectively [176, 177]. As mentioned, the OER Tafel slope represents the rate-determining step (RDS) in the mechanism shown above [122, 178].
When the Tafel slope is equal or larger than 120 mV/decade, the first step of the oxygen evolution mechanism is the slowest step and formation of S-OH bond is the RDS. The Tafel is predicted to be 40 and 30 mV/decade when equations (5-9) and (5-10) are the RDS, respectively [179]. The small changes of the slopes at low potentials indicate that the rate-determining step was not altered by the addition of MnO$_2$ particles. These variations may simply be the result of the different surface morphologies of the anodes. According to references [122, 178], the Tafel slope of the Pb alloy and the composite anodes indicate that the formation of the S-OH$_{ads}$ intermediate, equation (5-8), is the RDS for the OER on the PbO$_2$ and MnO$_2$ surfaces.

The exchange current density for the OER on the surface of the PbSnCa and Pb anodes was approximately $7.4 \times 10^{-10}$ A/cm$^2$. The obtained Tafel slope (120 mV/decade) and the calculated OER exchange current density of these samples are in agreement with the data reported for the β-PbO$_2$ [11, 38, 180]. This suggests that β-PbO$_2$ sites are the favored regions on the lead anode surface for the OER.

As Table 2-1 shows, composite anodes have higher exchange current densities than the lead alloys. The exchange current density of the composite anode also increased with the MnO$_2$ content of the anodes. This can be attributed to the lower oxygen evolution overpotential on the MnO$_2$ surface than the PbO$_2$ surface, which is due to the difference in bond strength of oxygen atoms adsorbed on their surfaces [11, 105]. It has been shown that MnO$_2$ can be a nonstoichiometric oxide due to the presence of Mn(III) compounds in its structure, such as MnOOH [159, 181]. In fact, composition of the MnO$_2$ composite particles can be written as:

$$Mn(IV)_n Mn(III)_{1-n} O_m$$

(5-11)
An increase in the oxidation state of an oxide at the OER potential range is responsible for its catalytic activity for the OER [11, 117, 178]. The enthalpy of the transition of an oxide to a higher oxidation state determines the strength of M-O bond and, in turn, the catalytic activity for OER [105, 116]. The oxidation of metal cation (Mn(III)) expresses the initial stage of the OER on the surface of MnO$_2$ [115]. This process causes stronger adsorption of oxygen atoms on the MnO$_2$ surface compared to the PbO$_2$ surface, resulting in its higher catalytic activity for the OER. As proposed by Wei et al. [182], Mn(III) species are the intermediates for oxygen evolution reaction on the MnO$_2$ surface. Mn(III)-OH forms on the surface of MnO$_2$ and then oxidizes to Mn(III)-O by a proton transfer. Two adjacent Mn(III)-O species transform into two Mn(IV)=O, which couple to evolve O$_2$ gas. Based on this description, the proposed oxygen evolution mechanism on the MnO$_2$ surface can be schematically shown by Figure 5-18. The Mn(III) species can either exist on the MnO$_2$ or generate through the first step in Figure 5-18.

![Figure 5-18 Schematic of the oxygen evolution mechanism on the surface of MnO$_2$ based on the proposed mechanism by Wei et al. [182].](image-url)
According to the results, the OER activation energy decreased in the presence of the MnO₂ particles. Therefore, these particles are the main sites for the OER on the surface of the composite anodes.

As Figure 5-17 and Table 5-3 show, at very high current densities (log i>-1.2), the Tafel slope of Pb-10MnO₂, Pb-15MnO₂, and Pb-20MnO₂ samples increased to 160, 205, and 215 mV/decade, respectively. This can be attributed to the surface defects on the composite anode. Micro-pores on the surface of these samples might be blocked by the oxygen bubbles, contributing to the decrease in the mass transfer that can also affect the charge transfer. Therefore, the sample polarization and, consequently, their Tafel slope, was amplified [183, 184]. Variation of the active surface area with potential can be roughly examined by calculating the roughness factor (RF) using the EIS technique. The impedance spectroscopy analyzes were performed on the Pb-10MnO₂ anode at potentials of 1.7, 1.8, and 1.9 V.

Figure 5-19 shows the obtained Nyquist plots of this sample. As can be seen, these diagrams include a single loop. Other authors also reported single-loop Nyquist plots for the oxygen evolution on different Pb alloys [135, 155, 185] and Pb-based composite anodes [186]. This loop results from adsorption of the reaction intermediate.

The main reaction on the composite anode at the potential range of 1.7-1.9 V is the oxygen evolution. Thus, the impedance results obtained within this potential range could not be modeled using the equivalent circuits shown in Figure 5-12, which was used to model the anodes oxidation at its OCP. In order to simplify the reaction modeling to calculate the roughness factor, the equivalent circuit of Figure 5-20 was proposed to model the OER. This circuit has been used by other researchers to model oxygen evolution on the lead-based anodes [169, 185, 187, 188].
Figure 5-19 EIS Nyquist plots of the Pb-MnO₂ anode in the H₂SO₄ electrolyte at 1.7 (a), 1.8 (b), and 1.9 V (c) (T=37°C)
In this circuit, \( R_s \) corresponds to electrolyte resistance, CPE represents the constant phase element of the electrode/electrolyte interface, and \( R_{ct} \) is the charge transfer resistance of the electrochemical process. The simulated Nyquist curves are also shown in Figure 5-19.

Roughness factors (RF) were calculated from equation (5-12):

\[
RF = \frac{C_{dl}}{C^*}
\]  

(5-12)

where \( RF \) is the roughness factor, \( C_{dl} \) is the capacitance of the double layer and \( C^* \) is the reference value for the capacitance, which is proposed to be 20 \( \mu \)F.cm\(^{-2} \) for the smooth Hg electrode [185].

\( C_{dl} \) can also be calculated using equation (5-13), in which \( n \) represents the deviation of the double layer from the ideal capacitance.

\[
Q_{dl} = [C_{dl}] [ (R_s)^{-1} + (R_{ct})^{-1} ]^{1-n}
\]  

(5-13)

The calculated values of the roughness factor are plotted in Figure 5-21 as a function of anodic potential. As it shows, the RF values of the anode at 1.7 and 1.8 were very close, while it decreased when the potential increased to 1.9. This reveals that a fraction of the surface of the composite anode was blocked at high anodic potentials due to the oxygen bubbles shielding [189]. Therefore, electrochemical access of the electrolyte to these areas was limited at higher potentials, contributing to the lead surface area of the anode available for the OER.

As previously mentioned, this can be a reason for the observed two linear regions in the E-log (i) plots of the composite anodes. It should be noted that using the capacitance of smooth mercury as the reference can cause overestimation on the resulted roughness factor. Thus, the results presented in Figure 5-21 qualitatively compared the roughness factor of the composite anode at different potentials.
Figure 5-20 Electrical equivalent circuit used to simulate the impedance data

Figure 5-21 Calculated roughness factor of the Pb-10MnO₂ anode as a function of anodic potential
5.5 Summary

In this chapter, some physical features and electrochemical behaviors of the Pb-MnO₂ composite anodes containing different MnO₂ content in the H₂SO₄ electrolytes were studied in comparison with the PbAg and PbSnCa conventional anodes. Cyclic voltammetry analysis was utilized to characterize the oxidation of the anodes. The properties of the anodic layer formed on the composite anode at open circuit potential and at different anodic potentials were characterized using the electrochemical impedance spectroscopy technique. The catalytic activity of the anodes for the oxygen evolution reaction was characterized by the potentiodynamic polarization technique. The results presented in this chapter can be summarized as follows:

- The fabrication process can cause the formation of some surface defects on the anode surface, which increases with the MnO₂ content of the composite anode.
- The presence of MnO₂ can increase the instant oxidation rate of the anode.
- The corrosion layer formed on the composite anode at the open circuit potential showed higher charge transfer resistances than that formed on the PbAg anode. This was attributed to the oxidizing effect of the MnO₂ particles. Increasing the anodic potential caused the formation of thicker PbO/PbSO₄ anodic layer with higher charge transfer resistance.
- The addition of MnO₂ particles to the Pb anode catalyzed the OER and decreased the OER overpotential. This effect was more pronounced for a higher fraction of MnO₂ in the anode. The MnO₂ particles decreased the activation energy at the oxygen evolution reaction.
- In the case of the Pb-MnO$_2$ anodes with high MnO$_2$ content (>15wt.%), OER was slightly depolarized at high potentials. This behavior is believed to be due to the partial blockage of the anode surface and the electrode shielding by the oxygen bubbles.
Chapter 6

Anodic performance of the composite anodes in the sulfuric acid electrolyte

6.1 Introduction

The Pb-MnO$_2$ composite anodes have been developed in order to be used in the zinc electrowinning process. The zinc electrowinning process operates at very aggressive conditions, i.e. high acid concentration (160-180 g/L H$_2$SO$_4$) and a high current density of 500-550 A/m$^2$. Degradation and corrosion resistance of the anodes, as well as the stability of the anodic corrosion layer, are important factors of the anode selections for the zinc electrowinning process. Anode degradation can contribute to an increase in the anode potential as well as Pb contamination in the final zinc product. In this chapter, the anodic performance of the Pb-MnO$_2$ composite anodes under the electrowinning operating conditions in the sulfuric acid solution is investigated. Corrosion resistance of these anodes, as well as the quality of their surface layer formed during anodic polarization in the acidic solution, were studied and compared with those of the PbAg and PbSnCa anodes.
6.2 Galvanostatic study

Anodic performances of the anodes under the zinc electrowinning operating conditions were studied through galvanostatic polarization at a current density of 500 A/m². This current density is relevant to what is used in typical zinc electrowinning plants. The PbAg, PbSnCa, and Pb-MnO₂ samples were subjected to this experiment and their potentials were recorded during polarization. During the galvanostatic tests, the electrolyte was slowly stirred using a 40 mm magnet bar at 60 rpm. Potential variations of the PbAg, PbSnCa, and Pb-MnO₂ samples during the galvanostatic experiments are shown in Figure 6-1. The positive effect of the silver alloying element on the catalytic properties of lead can be observed by comparing the potentials of the PbAg and PbSnCa anodes. This difference was anticipated from the potentiodynamic results reported in section 5.4. The graphs presented in Figure 6-1 also revealed that the presence of the MnO₂ particles in the lead anode resulted in lower anodic potentials at the initial stages, an effect that was enhanced by increasing the MnO₂ fraction in the anodes. This means that the OER overpotential decreased when the MnO₂ content of the sample increased.

As shown in Figure 6-1, the potential of the samples did not change in a similar fashion during the experiments. Potentials of the PbAg and PbSnCa anodes, after a rapid decline, remained unchanged at 1.9 and 1.94 V until the experiment was finished, respectively. The initial potential drop can be attributed to the formation of PbO₂ on the surface, which causes higher surface area of the sample. As suggested by Ruetschi and Delahay [116], oxidation of Pb(II) products such as PbO and PbSO₄ to PbO₂ during the experiment also causes lower anodic potential, since the higher oxidation state of a metal usually shows lower OER overpotential.
As shown in Figure 6-1, the potential of the Pb-5MnO₂ and Pb-10MnO₂ anodes decreased continuously during the experiments. To illustrate, consider the potentials of the Pb-5MnO₂ and Pb-10MnO₂ samples, which were 1.90 and 1.84 V after one hour and reduced to 1.80 and 1.77 V after 72-hour polarization, respectively.

Further increase in the MnO₂ content of the anodes resulted in different anodic behaviors. As was expected, the Pb-20MnO₂ samples showed the lowest OER overpotential at
the initial stages of the galvanostatic experiments. However, according to Figure 6-1, failure occurred after a short period of the anodic polarization. This might be due to the high porosity of the sample (~15%) and a significant number of cracks on its surface. Different mechanical properties of MnO₂ and Pb can cause a weak mechanical bond between these particles [148]. This means that MnO₂ particles detachment is probable. As a result of the lower OER overpotential, the MnO₂ particles are the main sites for the OER to take place on the surface of the composite anodes [129]. However, since the MnO₂ particles have low electrical conductivity, the Pb matrix and PbO₂ surface layer carry most of the electrons through the Pb-MnO₂ composite anodes. The density of the OER, therefore, would be the maximum at the Pb/MnO₂ interface, as suggested by Schmachtel et al. [123]. Significant evolution of the oxygen bubbles from the Pb/MnO₂ boundaries could increase local pressure in these regions, contributing to microscale fracture of the anode and separation of the MnO₂ particles from the surface [94]. The SEM surface morphology of the a Pb-20MnO₂ samples after 24-hour polarization is presented in Figure 6-2, which shows the presence of a large crack as the main reason for the failure of this sample and the holes on the surface of the sample that might result from the MnO₂ particles detachment.

As shown in Figure 6-1, the composite sample containing 15 wt.% MnO₂ showed the anodic behavior between Pb-10MnO₂ and Pb-20MnO₂ in terms of oxygen overpotential and stability. The potential variation of this sample indicates that the Pb-15MnO₂ sample might also be subject to mechanical wear, MnO₂ detachment, and formation of micro cracks, however, they were not significant compared to those of the Pb-20MnO₂ anode.

The potentials of the composite anodes after 72-hour galvanostatic polarizations are compared with those of the PbAg and PbSnCa anode in Figure 6-3.
Figure 6-2 SEM morphology of the Pb-20MnO₂ anodes after 24-hour polarization in the in sulfuric acid solution at 500 A/m² and 37°C

Figure 6-3 potential of the PbSnCa, PbAg and Pb-MnO₂ anodes after 72-hour polarization at 50 A/m² and 37°C
The experimental conditions, including the acid concentration and the applied current density, are relevant to the zinc electrowinning process. Moreover, the PbAg alloy is the most commonly used anode in the zinc electrowinning process. Thus, according to Figure 6-3, using the composite anodes, cell potential can be lowered, contributing to better energy efficiency in the electrowinning process. As the galvanostatic results show, the composite anode containing less than 15 wt.% MnO$_2$ showed reasonable performance regarding the OER overpotential and the short-term stability among the investigated composite anodes.

It should be noted that most of the electrowinning electrolyte contain impurities that can affect the anodic performance of the anodes. Manganese is the one of the main impurities in the zinc electrowinning electrolyte that can change the anodic behavior of the anodes. Effects of the manganese ions in these regards will be discussed in the following chapters.

6.3 Corrosion performance during galvanostatic polarization

6.3.1 Degradation resistance

The corrosion layers on lead anodes are typically removed by immersing the samples in the stripping solutions containing NaOH, mannitol, or ammonium acetate. In this study, however, the samples were not subjected to the stripping process since dissolution of the MnO$_2$ particles of the composite samples in the stripping solution might negatively affect the accuracy of the weight loss results. Moreover, the amount of detached corrosion products is more significant than the amount of the corrosion products that remained on the surface of lead alloys. In other words, weight loss of lead anodes is mostly determined by the detachment of the corrosion product. Therefore, in this study, the anode degradation is defined as the weight loss of the anodes considering that the remaining corrosion product on the surface is part of the anodes.
After the GS polarization, the samples were rinsed in DI water and dried quickly using a wiper tissue and an air stream. The samples were weighed before and after the galvanostatic polarizations. Weighing of each sample was repeated several times to make sure no solution remained in the pores of the samples. The degradation rates of the samples are shown in Figure 6-4.

According to these results, the pure Pb sample showed the lowest degradation resistance followed by the PbCa anode. Addition of tin to the PbCa anode resulted in an anode with higher corrosion resistance. The degradation rate of the PbSnCa anode is approximately 40% lower than that of the PbCa anode. The positive effect of Sn on the corrosion resistance of lead anodes has been previously shown [69, 71, 73].

![Figure 6-4 Degradation rate of the anodes during anodic polarization at 500 A/m² and 37°C](image-url)
The presence of Ca in the lead alloy causes precipitation of Pb$_3$Ca, which reduces the grain size of the corrosion layer and promotes in the PbCa alloy [69, 70]. Tin prevents the intercrystalline corrosion of the surface layer as it decreases the Pb$_3$Ca precipitates through the formation of (Pb$_{1-x}$Sn$_x$)$_3$Ca, which is more corrosion resistant compared to Pb$_3$Ca [46, 69].

The PbAg anode showed the lowest degradation rate among the lead alloys. It has been reported that the presence of silver in the lead can cause the formation of a denser anodic layer on the surface which, in turn, decreases the degradation rate of the anodes [25].

The lower degradation rate of the Pb-MnO$_2$ composite anodes, except the Pb-20MnO$_2$, was anticipated since their potential, as the main driving force for the electrochemical reactions, was lower during the anodic polarization compared to the lead alloys. The measured degradation rates showed negative values for the composite samples. This indicates that, unlike the typical lead-based anodes, the weight of the Pb-MnO$_2$ anodes increased during the anodic polarization under the electrowinning conditions.

The negative weight loss of the electrowinning anodes was also reported by Rey et al. [190] for lead in the presence of cobalt ions at concentrations higher than 20 mg/L. The weight gain of the composite samples can be attributed to the corrosion products on the surface of the samples, which are mostly PbO$_2$ and PbSO$_4$. This may be the result of a very low detachment rate of the corrosion products from the surface, as will be discussed later.

Porosity of the anodes may affect the amount of the corrosion products and their adhesion to the surface of the samples. As shown in the last chapter, the porosity of the composite samples increased with their MnO$_2$ contents. Therefore, the surface area of the sample that was exposed to the solution and, hence, the corrosion product on their surface, increased when the MnO$_2$ content increased. Furthermore, disengagement of the corrosion products that formed in the microcracks and porosities of the surface seems less likely. As a
result, the integrity of the corrosion products was expected to be enhanced in the presence of the surface defects. The significant degradation rate of the Pb sample with approximately 3.5% porosity, however, reveals that there should be another reason for the observed degradation rates of the composite anodes, which would be related to the MnO$_2$ particles.

The presence of MnO$_2$ particles might affect the detachment rate of the corrosion products. As mentioned earlier, the MnO$_2$ particles are the preferred sites for the OER on the surface of the composite anodes. Therefore, contribution of the other parts of the surface in the OER, which were mostly covered by PbO$_2$, decreased as the MnO$_2$ content of the anode increased. Formation of oxygen bubbles can impose stress on the surface of the anodes and cause their surface layer to detach [106, 107, 124]. Hence, the destructive effect of the OER on the PbO$_2$ region of the surface may decrease when the MnO$_2$ content is increased, contributing to a lower degradation rate of the composite anodes.

6.3.2 Corrosion and dissolution resistance

Corrosion resistance of the anodes and, consequently, the concentration of dissolved lead can be a determining factor for the selection of anodes in the electrowinning industries. Purity of the final products depends on the amount of lead dissolved in the electrolyte [12, 75]. Concentration of the dissolved lead during the anodic polarization is another indicator to study the corrosion performance of lead-based anodes. Corrosion resistance of the composite anodes was examined and compared with those of the lead alloys through measuring the concentration of the dissolved lead in the electrolyte during the anodic polarization using Inductively Coupled Plasma (ICP). To do this, three samples were taken from each of the solutions at 24-hour intervals and up to $t = 72$ hours and filtered by a 0.4μm PTFE syringe filter. The measured concentrations of the dissolved lead in the electrolyte during anodic
polarizations are reported in Figure 6-5. All the data points shown in this figure represent the mean values of the results from three replicated experiments, while the error bars represent the variance of the results. In the case of the Pb and PbCa anodes, dark precipitations in the cells were observed during the polarization. These precipitations demonstrated that the electrolyte reached the Pb-saturated level within 72 hours when these anodes were polarized. These precipitations were not observed in the case of the other samples. The ICP results reveal lower corrosion rate of the PbAg than that of the PbSnCa anode, which was anticipated from the weight loss results. As can be seen in Figure 6-5, the presence of the MnO₂ particles in the composite anodes, even at low contents, significantly reduced the amount of the dissolved lead and increased the corrosion resistance of lead.

Figure 6-5  Concentration of lead in the electrolyte during anodic polarization at 500 A/m² and 37°C
It is noteworthy that the concentration of lead in the electrolyte decreased as the MnO$_2$ content of the anodes increased. However, the results of the Pb-10MnO$_2$ and Pb-15MnO$_2$ anodes were very close. As discussed in the previous section, the MnO$_2$ particles of the composite anodes caused these anodes to operate at lower potentials. This results in less driving force (overpotential) for the oxidation of the anode and dissolution of lead. Moreover, oxygen evolution reaction prefers to take place on the composite particles due to the lower activation energy for this reaction on MnO$_2$ in comparison to PbO$_2$ [129]. Consequently, a negative effect of oxygen evolution on the anode oxidation and detachment of the PbO$_2$ layer would be less significant on the composite anodes.

The results of the ICP analysis also demonstrated that the amount of dissolved manganese increased with the MnO$_2$ content of the composite anodes, whereas the concentrations were several times higher than the lead concentration. For instance, 24-hour anodic polarization of the composite samples containing 5, 10, and 15 wt.% MnO$_2$ resulted in a manganese concentration of 4.3, 5.7, and 6.3 mg/L in the electrolyte, respectively. As previously mentioned, manganese ions are usually present in or added to the zinc electrowinning electrolytes. Therefore, dissolution of the manganese in the electrolyte does not affect the zinc electrowinning process. However, small amounts of manganese in the electrolyte have been found to be detrimental as the products of Mn oxidation can result in degradation of organic extractants in the solvent extraction circuit. Therefore, the Pb-MnO$_2$ anodes cannot be used in the copper electrowinning process.

At high anodic potentials, both dissolution and deposition of MnO$_2$ are possible, which may affect the anodes surface characteristics. Although no evidence has been found by the morphological study of the polarized samples, the dissolved Mn(II) ions might be re-deposited as MnO$_2$ on the anode surface. If this happens, the precipitations of MnO$_2$ can cause a larger
surface area of the anode to be covered by the MnO₂ phase, contributing to more MnO₂ active sites for the OER and further OER depolarization. This might be considered as another reason for the continuous reduction of the potentials of the composite anodes containing 5 and 10 wt.% composite particles during the galvanostatic polarization (Figure 6-1). It should be noted that the re-deposited MnO₂ at very low Mn(II) concentrations cannot contribute to a continuous MnO₂ layer on the anode surface. As explained in the previous section, different potential variations of the Pb-15MnO₂ anode in the course of polarization could be attributed to possible detachment of the MnO₂ composite particles from the anode surface.

6.4 Anodic surface layers characterization

6.4.1 Morphological studies

Surface morphologies of the 72-hour polarized Pb alloys and Pb-MnO₂ anodes are presented in Figure 6-6. As it shows, the anodic layer formed on the lead alloys had coral-like morphologies. The morphologies of the anodic layers formed on the composite anodes were different. Figure 6-6(d) indicates that the surface layer formed on the Pb-5MnO₂ composite anode included grain structure. The presence of larger MnO₂ content in the anode led to the formation of a finer-grained anodic layer, as shown in Figure 6-6(e)-(f).

The anodic surface layer that formed on the composite anodes containing 10 and 15 wt% MnO₂ seemed more compact than those of the Pb, PbAg, and PbSnCa anodes. This could be a reason for the lower degradation and dissolution rates of the composite anodes compared to the lead alloys. A more compact and denser anodic layer can lower the diffusion of the corrosive species such as SO₄²⁻, HSO₄⁻, and atomic oxygen to the anode metallic surface, providing a higher level of protection for the anode.
Figure 6-6  Morphology of the anodic layer formed on the surface of the Pb (a), PbSnCa (b), PbAg (c), Pb-5MnO₂ (d), Pb-10MnO₂ (e), and Pb-15MnO₂ (f) anodes in 72-hour anodic polarization at 500A/m² and 37°C
6.4.2 Electrochemical studies

The surface layer that formed on the composite anodes had different morphologies, which can contribute to different barrier properties of these layers. In order to compare the barrier properties of the anodic layers, cyclic voltammetry experiments were performed on the PbAg, PbSnCa, Pb-10MnO$_2$, and Pb-15MnO$_2$ samples at three stages: at the beginning of the experiment, after 24-hour, and after 72-hour galvanostatic polarization at 500 A/m$^2$. The cyclic voltammetry experiments were performed right after the galvanostatic polarizations at 10 mV/s. The potential was scanned from -1.0 V and reversed at 2.1 V. Characteristic peaks in cyclic voltammograms are a suitable criterion to compare barrier properties of the anodic layers [191, 192]. Hereinafter in this chapter, the cyclic voltammograms obtained on the fresh anodes will be represented by CV0 and those obtained after the 24-hour and 72-hour polarizations will be represented by CV24 and CV72, respectively.

The CV0, CV24, and CV72 voltammograms of the PbSnCa and PbAg anodes are shown in Figure 6-7 and Figure 6-8, respectively. These voltammograms are characterized by some anodic and cathodic peaks, which were introduced in chapter 5. The reactions of the peaks are as follows:

Peak A1: oxidation of lead to lead sulfate, reaction (5-3),

Branch A2: oxygen evolution reaction (equation (2-2)) and the formation of lead dioxide through oxidation of lead (reaction (5-4)) or lead sulfate (reaction (5-5)),

Peak A3: oxidation of Pb to PbSO$_4$ and PbO, resulted from the cracks in the surface layer,

Peak C1: reduction of lead dioxide to lead sulfate; reaction (5-5),

Peak C2: reduction of lead oxide to lead,

Peak C3: reduction of lead sulfate to lead; reaction (5-3).
Figure 6-7  Cyclic voltammograms of the PbSnCa anode obtained before (CV0) and after 24-hour (CV24) and 72-hour anodic polarization (CV72) (initial potential: -1.0 V, reverse potential: 2.1 V, scan rate: 10 mV/s)

Figure 6-8 Cyclic voltammograms of the PbAg anode obtained before (CV0) and after 24-hour (CV24) and 72-hour anodic polarization (CV72) (initial potential: -1.0 V, reverse potential: 2.1 V, scan rate: 10 mV/s)
The CV24 graph of the PbSnCa anode showed the same number of peaks, however, their characteristics were different. In this graph, the intensity of peak A1 was significantly higher than that of the fresh sample. Branch A2 shifted to lower potentials after the 24-hour polarization, meaning depolarization of the OER. Peak A3 obtained after the 24-hour polarization was notably higher than that observed for the PbSnCa fresh surface. This may represent the weak barrier properties of the surface layer formed in the 24-hour polarization. The larger cathodic peaks that appeared in the reverse scan direction of the CV24 compared to the CV0 is due to the growth of the anodic layer during the polarization. The CV72 graph of the PbSnCa anode (Figure 6-7) was similar to the corresponding CV24 graph. These results indicate that the surface layers that were formed in the 24-hour and 72-hour polarizations had similar properties.

The voltammograms of the PbAg anode (Figure 6-8) changed similarly to those of the PbSnCa with the polarization time. All the oxidation and reduction peaks grew with polarization time. Peak A3 appeared in the voltammogram of the PbAg anode after the 24-hour polarization and its intensity slightly increased with longer polarization. Lower intensities of the A1 and A3 peaks in the voltammograms of the PbAg anode compared to those of the PbSnCa demonstrate that the layer formed on the PbAg anode is more protective than that on the PbSnCa. This is in agreement with the corrosion results.

Figure 6-9 depicts the CV0, CV24, and CV72 voltammograms of the Pb-10MnO2 anode. As shown, the effects of the 24-hour polarization on the cyclic voltammogram of the Pb-10MnO2 sample were similar to what was observed for the PbSnCa and PbAg samples; i.e. an increase in the intensity of the anodic and cathodic peaks and a shift in branch A2 to lower potentials. After prolonged polarization, however, the cyclic voltammogram showed different properties of the anodic layer. As can be seen in curve CV72 in Figure 6-9, peak A1, which
represents the oxidation of lead to lead sulfate, disappeared. This reveals that the anodic layer formed on the Pb-10MnO₂ sample after the 72-hour polarization was dense enough to prevent diffusion of the electrolyte through this layer and the oxidation of Pb to PbSO₄ [122].

Moreover, the absence of anodic peak A3 in the reverse scan direction of CV72 voltammogram verified high compactness and protection properties of this anodic layer. Since the MnO₂ particles are the preferred sites for the OER, the actual current density on the other parts of the Pb-MnO₂ anode surface would be lower than the lead alloys. Therefore, the anodic layer of the Pb-MnO₂ anode was formed at lower actual current density, contributing to a denser layer formed on the Pb-10MnO₂ that can provide higher protection for the anode [75].

If the CV72 graphs of the PbAg and PbSnCa anodes are compared with that of the Pb-10MnO₂ anode, it can be observed that the cathodic peaks were shifted negatively and were intensified significantly in the presence of MnO₂ particles. This demonstrates larger amounts of corrosion products remaining on the surface of the Pb-10MnO₂ anode during the polarization time. This also verifies the discussions on the weight loss results.

The cyclic voltammograms of the Pb-15MnO₂ sample before and after anodic polarizations are presented in Figure 6-10. The number of the characteristic peaks and their variations after the 24-hour polarization were similar to what were observed for the other samples. The prolonged anodic polarization (curve CV72) lowered peak A1 significantly and also caused peak A3 to disappear. These influences show higher compactness of the layer formed in the 72-hour polarization on the Pb-15MnO₂ sample compared to that formed in the 24-hour polarization and also compared to those of the PbSnCa and PbAg alloys. The presence of peak A1 in CV72 of this sample demonstrated lower protection of this layer compared to the anodic layer formed on the Pb-10MnO₂ at the same polarization time [122].
Figure 6-9  Cyclic voltammograms of the Pb-10MnO$_2$ anode obtained before (CV0) and after 24-hour (CV24) and 72-hour anodic polarization (CV72) (initial potential: -1.0 V, reverse potential: 2.1 V, scan rate: 10 mV/s)

Figure 6-10  Cyclic voltammograms of the Pb-15MnO$_2$ anode obtained before (CV0) and after 24-hour (CV24) and 72-hour anodic polarization (CV72) (initial potential: -1.0 V, reverse potential: 2.1 V, scan rate: 10 mV/s)
6.4.3 Structural studies

The X-ray diffraction spectra of the 72-hour polarized PbAg and Pb-10MnO₂ samples are shown in Figure 6-11. This figure also shows the XRD characteristic peaks of Pb, PbSO₄, and PbO₂. It should be noted that reduction of PbO₂ to PbO was possible while the samples were washed. However, this is not a major concern in this study since removing the samples were from the solution, their rinsing and drying were done quickly.

Figure 6-11  XRD pattern of the anodic layers formed on the surface of the PbAg and Pb-10MnO₂ anodes in 72-hour anodic polarization at 500 A/m² and 37°C
These spectra reveal that both of the anodic layers were mainly composed of α- and β-PbO₂ as well as PbSO₄. The presence of the Pb peak in the XRD spectra demonstrated that the anodic layers were relatively thin [121]. Lower Pb peak in the XRD pattern of the Pb-10MnO₂ may indicate that the anodic layer formed on this sample was either more compact or thicker than those of the PbAg anode, which is in line with the results of the cyclic voltammetry investigations. Other peaks of the XRD spectra demonstrate higher amounts of corrosion products in the anodic layer of the Pb-10MnO₂ sample, which was also shown in the last section and matched well with the weight loss results. Although the content of MnO₂ composite particles in the composite anode was significant, no significant MnO₂ diffraction peak was observed in the XRD spectrum of this sample. This could be attributed to the more amorphous nature of the MnO₂ particles that was shown in Figure 4-1.

6.5 Summary

In this chapter, the anodic performance of the Pb-MnO₂ composite anodes containing different MnO₂ content in the H₂SO₄ electrolytes under the electrowinning conditions was investigated and compared to those of the PbAg and PbSnCa conventional anodes. Morphology and barrier properties of the corrosion product layers on the anodes were studied. The experimental results presented in this chapter can be summarized as follows:

- The Pb-MnO₂ composite anodes, regardless of their MnO₂ content, had lower potentials than the PbAg and PbSnCa anodes under the zinc electrowinning operating conditions. Using the Pb–MnO₂ anode can decrease the energy consumption in the industrial electrowinning process by 5%. 

The electrocatalytic capacity of the composite anodes was enhanced when their MnO₂ content increased, however, the anode stability decreased the MnO₂ contents at higher than 15 wt%. The composite anode containing 20 wt.% MnO₂ failed during the galvanostatic polarization after a short period of time.

The Pb-MnO₂ composite anodes had better degradation resistance under the electrowinning conditions and showed a very low dissolved lead concentration compared to the PbAg and PbSnCa anodes.

The anodic layers formed on the composite anodes in 72-hour polarization were either more compact or thicker than that of the PbAg anode, contributing to higher levels of protection. Accordingly, the Pb-10MnO₂ anode showed the optimum behavior among the investigated composite anodes.
Chapter 7

Electrochemical behavior in Mn-containing H₂SO₄ solution electrolytes

7.1 Introduction

Manganese ions usually exist in the zinc electrowinning electrolyte coming from different sources, including the zinc ore, with the addition of manganese dioxide and potassium permanganate [15, 16]. Mn(II) ions are oxidized on the anodes during the electrowinning process, resulting in the formation of an MnO₂ layer on the anode as well as MnO₂ particles in the electrolyte [15]. It has been previously shown that the influences of manganese ions depend on the chemical composition and pre-treatment of the anode [135]. In this chapter, the electrochemical reactions of the composite anode and oxygen evolution reaction in the sulfuric acid solution containing different Mn(II) concentrations are studied. The roles of Mn(II) ions on the oxidation of the composite anodes are also discussed. Based on the results of the studies on the composite anodes that were presented in the last chapter (anode potential, corrosion resistance, and anodic layer properties), the composite anode containing 10 wt.% MnO₂ had been used in the next stages of this study. Thus, hereinafter, the Pb-MnO₂ composite anode in the thesis represents the Pb-10MnO₂ anode.
7.2 Cyclic voltammetry study

The cyclic voltammetry experiments were carried out on the Pb-MnO$_2$ and PbAg anodes at the potential range of 0.4-2.0 V in order to study the formation of $\alpha$-PbO$_2$ and $\beta$-PbO$_2$ and the influences of manganese in this regard. In this experiment, the potential was scanned from 0.4 V and reversed at 2.0 V at different scan rates while the electrolyte was agitated at 60 rpm using a 40 mm magnet bar. Prior to the cyclic voltammetry analysis, the samples were subjected to a 10-minute potentiostatic polarization at 0.4 V.

7.2.1 Cycling effects

Figure 7-1 compares the first and fifth cycles of the voltammograms of the Pb-MnO$_2$ and PbAg anodes obtained in Mn-containing electrolytes at a potential scan rate of 5mV/s.

As Figure 7-1 shows, no anodic peak appeared in the forward scan in the first cycles of the cyclic voltammograms of the anodes except the OER anodic branch. Some anodic peaks appeared in the voltammograms with the cycling, which are shown by arrows in Figure 7-1. These peaks correspond to the formation of different PbO$_2$ modifications. This observation reveals that oxidation of the Pb(II) compounds (PbSO$_4$, PbO, and $x$PbO.PbSO$_4$) to PbO$_2$ is depolarized by cycling and, therefore, by the residual PbO$_2$ that formed during the previous potential scan cycles, which was also suggested by Simon et al. [193].

In addition to the formation of PbO$_2$, oxidation of manganese ions on the PbAg electrode depends on the cycling. Based on the visual observations, no MnO$_4^-$ ions were produced on this anode during the forward scan of the first cycle. In the reverse scan at 10 mV/s, a significant amount of dark species was produced on the anode at a potential of 1.95 V and diffused into the electrolyte (Appendix A- Figure A-1(a)). This dark solution contains small solid particles, indicating the detachment of MnO$_2$ particles and MnO$_4^-$ formation. The
dark solution slowly disappeared as reacted with the solution. This shows that permanganate ions are not stable in the presence of Mn(II) ions, which was previously established [194, 195].

In the next cycles, the permanganate formation on the PbAg anode started in the forward scan and at lower potentials. These observations verified the catalytic and depolarization effect of PbO₂ on the manganese oxidation on lead anodes. This has been previously shown regarding MnO₂ formations [135]. It was also noticed that the amount of permanganate generated on the anode decreased with cycling (Appendix A, Figure A-1). This can be attributed to the blocking effect of the MnO₂ layer. The MnO₂ layer deposited on the anode during the previous cycles inhibits the formation of permanganate.

![Graph showing voltammograms of Pb-MnO₂ and PbAg](image)

Figure 7-1 First and fifth cycles of the voltammograms of the Pb-MnO₂ and PbAg obtained in an Mn-containing electrolyte (initial potential: 0.4 V, reverse potential: 2.0 V, scan rate: 5 mV/s, after 10-minute polarization at 0.4 V)
This effect of MnO₂ layers was also shown by Zhang and Park [194] through comparing the observations during the cyclic voltammetry of the PbO₂ and MnO₂-coated PbO₂ anodes in Mn-containing solutions. It should be noted that, regardless of the cycle number, the formation of permanganate was very low on the Pb-MnO₂ composite anode during the cyclic voltammetry experiments in the Mn-containing electrolytes. The quantitative study of the Mn(II) oxidation on the surface of the anodes will be presented and discussed in the following section.

7.2.2 Roles of Mn(II) concentration

In order to investigate the effect of Mn(II) on the oxidation of the anodes, the cyclic voltammetry experiments were performed on the anodes in the presence of Mn(II) ions at different concentrations. Based on the discussion in Figure 7-1, the fifth cycles of the voltammograms were used in this regard. Figure 7-2 and Figure 7-3 show the 5th cycle of the cyclic voltammograms of the Pb-MnO₂ and PbAg anodes in the H₂SO₄ electrolyte containing different Mn(II) concentrations, respectively. The observed difference between the voltammograms in Figure 7-2 and Figure 7-3 and those reported in Figure 5-3 and Figure 5-4 could be attributed to the difference in the employed scanned potential range as well as to the history of the anodes prior to running this experiment (pre-polarization step). Moreover, as mentioned previously, these figures present the fifth cycles of the voltammograms while the first cycles were reported in the cyclic voltammograms in section 5.3.1.

Regardless of the Mn(II) concentrations, two anodic peaks appeared in the forward scan of the voltammograms of the PbAg anode (Figure 7-3), marked as peaks I and II. As these peaks appeared in the absence of Mn(II) ions, none of these peaks could be attributed only to the Mn(II) oxidation, although this reaction could be possible at this potential range.
As previously mentioned, these anodic peaks correspond to the formation of two different structures of PbO\(_2\) on the anode surface. The first anodic peak represents the oxidation of lead oxide (PbO) and basic lead sulfates (\(x\)PbO.PbSO\(_4\)) to \(\alpha\)-PbO\(_2\) through reactions (7-1)-(7-3). The equilibrium potentials of these reactions were calculated assuming pH=0 and \(a_{SO4(2-)} = C_{SO4(2-)} = 1.83\)M.

\[
PbO + 2H_2O \rightarrow \alpha - PbO_2 + 2H^+ + 2e^- \quad E = 0.907 \ V_{Ag/AgCl} \quad (7-1)
\]

\[
PbO.PbSO_4 + 3H_2O \rightarrow 2PbO_2 + HSO_4^- + 6H^+ + 4e^- \quad E = 1.26 \ V_{Ag/AgCl} \quad (7-2)
\]

\[
3PbO.PbSO_4.H_2O + 4H_2O \rightarrow 4PbO_2 + HSO_4^- + 10H^+ + 8e^- \quad E = 1.13 \ V_{Ag/AgCl} \quad (7-3)
\]

The second anodic peak that appeared in the voltammograms of the PbAg anode (peak II) resulted from the formation of PbO\(_2\) through the oxidation of PbSO\(_4\), reaction (5-5). This reaction takes place at the anodic layer/electrolyte interface and results in the tetragonal structure of PbO\(_2\), known as \(\beta\)-PbO\(_2\). Unlike what was observed in the voltammograms of the PbAg anode, those of the Pb-MnO\(_2\) sample showed only one anodic peak in the forward scan, which likely corresponds to the formation of \(\alpha\)-PbO\(_2\) (peak I).

As a result of the presence of the MnO\(_2\) particles in the composite anode, the OER started at lower anodic potentials compared to the PbAg anode. Therefore, peak II could be hidden by the OER branch in the cyclic voltammograms of the composite anode (Figure 7-2).

A reduction peak appeared at the potential range of 1.2-1.5 in the backward scan of the voltammograms (peak III), which represents a reduction of PbO\(_2\) to PbSO\(_4\). It was shown that a small portion of PbO\(_2\) might not get reduced during this peak. However, the remained amount of unreduced PbO\(_2\) is negligible in comparison with amount of PbO\(_2\) that is reduced at this potential range (peak III) [193]. Thus, peak III and the associated charge could be used to compare the amount of PbO\(_2\) formed on the anodes during the forward scan direction.
Figure 7-2 The cyclic voltammograms of the Pb-MnO\(_2\) anodes in the sulfuric acid electrolyte containing different concentrations of manganese ions (initial potential: 0.4 V, reverse potential: 2.0 V, scan rate: 10 mV/s, 5\(^{th}\) cycle, after 10-minute polarization at 0.4 V)

Figure 7-3 The cyclic voltammograms of the PbAg anodes in the sulfuric acid electrolyte containing different concentrations of manganese ions (initial potential: 0.4 V, reverse potential: 2.0 V, scan rate: 10 mV/s, 5\(^{th}\) cycle, after 10-minute polarization at 0.4 V)
Figure 7-2 and Figure 7-3 reveal that the addition of Mn(II) ions to the electrolyte and an increase in its concentration led to a marked decrease in the current densities of peak \( r \) and peak \( III \). These variations demonstrate polarization of the PbO\(_2\) formation by Mn(II) ions. This can be attributed to the deposition of the MnO\(_2\) layer on the anodic surface during the cyclic voltammetry polarization. According to the model that was proposed by Pavlov \[196\], the flow of H\(^+\) and SO\(_4\)\(^{2-}\) ions is required between the reaction layer and the bulk of the electrolyte for the \( \alpha \)-PbO\(_2\) formation reaction to proceed. Diffusion of these ions can be slowed down by the MnO\(_2\) layer deposited on the anodes. Moreover, while at the potential range that transitions between Pb(II) and Pb(IV) is active, Mn(II) ions can be oxidized through getting electrons from the PbO\(_2\). Therefore, the Mn(II) ions in the vicinity of the anode can reduce PbO\(_2\) to Pb(II) compounds through reactions (7-4)-(7-6) \[135, 137\].

\[
2\text{Mn}^{2+} + \text{PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ \rightarrow 2\text{Mn}^{3+} + \text{PbSO}_4 + 2\text{H}_2\text{O} \quad (7-4)
\]

\[
4\text{Mn}^{2+} + 3\text{PbO}_2 + 4\text{H}^+ \rightarrow 4\text{Mn}^{3+} + \text{Pb}_3\text{O}_4 + 2\text{H}_2\text{O} \quad (7-5)
\]

\[
2\text{Mn}^{2+} + \text{PbO}_2 + \text{HSO}_4^- + \text{H}^+ \rightarrow 2\text{MnOH}^{2+} + \text{PbSO}_4 \quad (7-6)
\]

Despite the shown inhibiting role of Mn(II) on the PbO\(_2\) formation, current density of peak \( II \) in the voltammograms of the PbAg anode increased with Mn(II) concentrations (Figure 7-3). This variation does not indicate the increase in the PbO\(_2\) formation rate. The variation of peak \( II \) can be attributed to other reactions that are possible to occur at this potential range. These reactions can be either reactions of the manganese species or accelerated evolution of oxygen.

In the backward scan, two cathodic peaks were observed in the voltammograms of the Pb-MnO\(_2\) anodes at potentials below 1.2 V (Figure 7-2). The intensity of these two peaks increased with Mn(II) concentrations. These peaks represent a reduction of Mn-containing
species including MnO₂ and MnOOH. These peaks, however, were not observed in the cyclic voltammograms of the PbAg anode (Figure 7-3), regardless of the Mn(II) concentrations.

7.2.3 Effect of scan rate

Figure 7-4 and Figure 7-5, respectively, report the cyclic voltammograms of the Pb-MnO₂ and PbAg anodes obtained in the sulfuric acid electrolyte containing 3.0 g/L Mn(II) at the potential scan rates of 2, 5, 10, and 20 mV/s. As these figures show, variation of the sweep rates did not significantly change the shape of the cyclic voltammograms of the anodes. All the voltammograms in each of Figure 7-4 and Figure 7-5 show the same number of peaks, however, their intensities and position varied with scan rate.

According to Figure 7-4, potentials of anodic and cathodic peaks changed with the scan rate. When the potential scan rate increased, anodic peak I shifted to more positive potentials, while cathodic peak III shifted in the negative direction. The growing potential gap between these two peaks with scan rate suggests that the formation of PbO₂ is an irreversible reaction [157]. Similar effects of the scan rate on the potentials of anodic peaks I and II and anodic peak III can be observed in the voltammograms of the PbAg (Figure 7-5).

The increase in the scan rate led to an increase in the current density flowing along the entire potential range of the cyclic voltammograms including anodic and cathodic peaks. This is in agreement with the results of the cyclic voltammetry studies that were conducted on different lead-based alloys [153, 157, 197]. Although the peak current increased with the scan rate, the charge associated with each of the anodic and cathodic peaks decreased. This demonstrates that the lower amount of PbO₂ formed at higher scan rates, which might be explained by less time for the oxidation reactions to occur at the higher scan rates.
Figure 7-4 Cyclic voltammograms of the Pb-MnO$_2$ anode obtained in H$_2$SO$_4$+ 3.0 g/L Mn(II) electrolyte at different scan rates (initial potential: 0.4 V, reverse potential: 2.0 V, 5$^{th}$ cycle, after 10-minute polarization at 0.4 V)

Figure 7-5 Cyclic voltammograms of the PbAg anode obtained in H$_2$SO$_4$+ 3.0 g/L Mn(II) electrolyte at different scan rates (initial potential: 0.4 V, reverse potential: 2.0 V, 5$^{th}$ cycle, after 10-minute polarization at 0.4 V)
7.3 Oxygen evolution and Mn(II) oxidation

7.3.1 Potentiostatic polarization studies

Anodic potentiostatic polarizations were performed to study the effects of Mn(II) ions on the oxygen evolution reaction. The Pb-MnO₂ and PbAg anodes were polarized at a constant potentials in the sulfuric acid electrolytes containing different Mn(II) concentrations for a short period. Figure 7-6 compares the current density of the Pb-MnO₂ and PbAg anodes in the sulfuric acid electrolyte containing various Mn(II) concentrations at different potentials. The plotted current densities are the average of the last 2 minutes of the 10-minute potentiostatic polarizations at each potential. The OER is the dominant anodic reaction at the potential range of 1.7-1.9 V. However, as Tjandrawan and Nicol [198] reported, the oxidation rate of Mn(II) might be significant on lead anodes in Mn-containing electrolytes.

Figure 7-6 reveals that, regardless of the type of anode and the applied potential, the current density increased with the increase in Mn(II) concentration at each potential. Since manganese can be oxidized at this potential range, this variation could be the consequence of both OER depolarization and Mn(II) oxidation.

In order to distinguish between the rates of these two reactions, Mn(III) concentration in the electrolyte after 10-minute polarization was measured by the potentiometric titration. The Mn(III) concentrations in the electrolytes of 1.5 and 3 g/L Mn(II) were measured and used to calculate the average Mn(II) oxidation current densities. The average Mn(II) oxidation current density on the anodes are plotted in Figure 7-7. All the data points shown in this figure represent the mean values of the results obtained from the titration of five electrolyte samples, while the error bars represent the variance of the results.
Figure 7-6  Current densities of the fresh PbAg (a) and Pb-MnO$_2$ (b) anodes in the H$_2$SO$_4$ electrolyte with variable Mn(II) concentrations at 37°C.
Figure 7-7 indicates that the oxidation of Mn(II) on two anodes did not proceed at the same rates. The oxidation rate of Mn(II) on the Pb-MnO₂ anode was relatively slow and did not change notably with the applied potentials. Although the oxidation rate of Mn(II) on the PbAg anode at 1.7 V was close to that on the Pb-MnO₂ anode, it significantly increased as the polarization potential increased. According to these results, the variation of the current of the Pb-MnO₂ with Mn(II) concentration could mostly represent the depolarized oxygen evolution reaction as the Mn(II) oxidation rate on this anode was very low compared to the total current. On the other hand, a portion of the increase in the current of the PbAg anode with Mn(II) concentration can be attributed to the Mn(II) oxidation.

The average oxygen evolution current density on the PbAg anode at each potential was calculated using equation (7-7):

\[
i_{\text{OER}} = i_{\text{anodic}} - i_{\text{Mn}}
\]  

where \(i_{\text{OER}}\) was the oxygen evolution current density, \(i_{\text{anodic}}\) and \(i_{\text{Mn}}\) were the total anodic current density, and the measured Mn(II) oxidation current density, respectively. The oxygen evolution currents on the PbAg anode are plotted in Figure 7-8 in logarithmic scale versus the polarization potential. The data for the 0.5 g/L Mn(II) experiments are not shown.

As Figure 7-8 shows, Mn(II) ions can depolarize OER on the PbAg anode. However, this effect was not as significant as that on the composite anode. The slope of the Tafel line of this sample slightly increased with Mn(II) concentrations. It should be noted that the values reported in Figure 7-8 for the Tafel slopes are not reliable since the number of points used to measure these values was not enough.
Figure 7-7 Current density of Mn(II) oxidation on the Pb-MnO\textsubscript{2} and PbAg anodes as a function of potential at different Mn(II) concentrations during 10-minute polarization.

Figure 7-8 E-log(i\textsubscript{OER}) of the PbAg anode at different Mn(II) concentrations obtained from the potentiostatic results.
7.3.2 Electrochemical impedance spectroscopy

The Nyquist plots of the Pb-MnO$_2$ anode at different potentials and Mn(II) concentrations are shown in Figure 7-9. The plots were obtained after 10-minute potentiostatic polarizations at the assigned potentials.

Figure 7-9 demonstrates that an increase in Mn(II) concentration decreases the size of the semi-circle Nyquist plots of the composite anode in all the potentials. Moreover, the Nyquist plots became smaller with applied potential. The Mn(II) oxidation current was very low compared to the total anodic current at OER potential range on the composite anode. Therefore, the oxygen evolution was the main reaction occurring on this anode in Mn-containing electrolytes. Consequently, the change in the size of the Nyquist plots of the Pb-MnO$_2$ anodes with Mn(II) concentration and applied potential represents the depolarization of oxygen evolution reaction [17, 59, 132, 135].

The depolarizing effect of Mn(II) did not change proportionally with its concentration on the Pb-MnO$_2$ anode. According to Figure 7-9 (b) and (c), the increase in the Mn(II) concentration from 1.5 to 3 g/L had little effect on the charge transfer resistance of the OER at 1.8 and 1.9 V.

A similar behavior was observed in the registered current of the polarized Pb-MnO$_2$ anode, which is shown in Figure 7-6(b).
Figure 7-9  EIS Nyquist plots of the Pb-MnO$_2$ anode at different potentials and in the H$_2$SO$_4$ electrolyte with variable Mn(II) concentrations (T=37°C)
7.4 Summary

In this chapter, the electrochemical reactions of the anodes in the Mn-containing sulfuric acid electrolytes were investigated using cyclic voltammetry techniques. Potentiostatic polarization and EIS techniques were employed to study the effect of Mn(II) ions on the oxygen evolution rates. The short-term oxidation of Mn(II) was also examined at different potentials and Mn(II) concentrations. The summary of the reported results is as follows:

- The presence of manganese ions in the electrolyte caused less PbO₂ formation on both Pb-MnO₂ and PbAg anodes despite more PbSO₄ formation. The latter effect is believed to be due to the inhibiting role of the Mn(II) ions on the oxidation of PbSO₄ to PbO₂.
- The charge transferred in the α-PbO₂ and β-PbO₂ formation and reduction peaks in the cyclic voltammograms of the anodes decreased with the potential scan rate, indicating a smaller amount of PbO₂ formed at higher potential scan rates.
- Visual observation verified the catalytic properties of PbO₂ and the inhibiting role of MnO₂ on the oxidation of Mn(II) to MnO₄⁻ ions on the surface of the PbAg anodes. A slower rate of permanganate formation on the composite anode was also observed.
- The Mn(II) ions catalyzed the oxygen evolution reaction on both types of the fresh anodes. This effect was a function of Mn(II) concentration and the anode material.
- The Mn(II) oxidation on the surface of the fresh Pb-MnO₂ anode proceeded at a slower rate than on the fresh PbAg anode during the short time polarization (10 minutes). The Mn(II) oxidation rate on the composite anode did not noticeably change with the Mn(II) concentrations and the applied potential. However, the Mn(II) oxidation on the PbAg anode strongly depended on the Mn(II) concentrations and the anodic potentials.
Chapter 8

Initial deposition of the MnO$_2$ layer and its effects

8.1 Introduction

It has been previously reported that the MnO$_2$ layer deposition and its properties depend on the type of anode material and its chemical composition. Moreover, visual observation during the cyclic voltammetry experiments (reported in the previous chapter) showed that oxidation of manganese ions on the Pb-MnO$_2$ and PbAg anodes did not proceed at a similar rate. This can contribute to different nucleation and growth rates of the MnO$_2$ layer on these two anodes. In this chapter, the initial growth of the MnO$_2$ layer on the Pb-MnO$_2$ composite anode will be studied using electrochemical techniques. Furthermore, the effects of this layer on the oxidation rate of the Pb-MnO$_2$ and PbAg anodes will be examined.

Since electrochemical techniques will be utilized to study the deposition of MnO$_2$ on the lead-based anodes, electrochemical characteristics of the MnO$_2$ deposition and reduction were studied first. A platinum electrode was used to investigate the oxidation/reduction reactions of Mn(II) and MnO$_2$. Platinum was selected to characterize the MnO$_2$ electrochemical reactions since it is an inert electrode and is not very active for the oxygen
evolution reaction (OER). Thus, Mn(II) oxidation reactions would have very low interference with the oxygen evolution reaction.

8.2 MnO₂ deposition and reduction characterization

Cyclic voltammetry experiments were performed on the platinum electrode in the sulfuric acid solution containing various Mn(II) concentrations (0-6 g/L) in the potential range of 0.4 to 1.8 V. In this experiment, the potential was scanned from 0.4 V and reversed at 1.8 V at a scan rate of 10 mV/s. Figure 8-1 depicts the voltammograms of the platinum electrode in the H₂SO₄ solution containing different Mn(II) concentrations. The curve obtained in the absence of Mn(II) showed no anodic or cathodic peak except the anodic branch A₃, which represents the OER. However, the voltammograms obtained in the presence of Mn(II) ions show a number of oxidation and reduction peaks, which are attributed to the reactions of manganese species on the electrode surface.

As is apparent, in all the graphs obtained in the Mn-containing electrolytes, two anodic peaks appeared in the forward potential sweep in addition to the OER branch, marked as A₁ and A₂. It reveals that the oxidation of Mn(II) to MnO₂ includes two electrochemical steps. Peaks A₁ and A₂ correspond to the oxidation of Mn(II) to Mn(III) (reaction (8-1)) and MnOOH to MnO₂ (reaction (8-3)), respectively. Consequently, as previously suggested [136, 199], MnO₂ formed on the platinum electrode through the Electrochemical-Chemical-Electrochemical (ECE) mechanism shown in reactions (8-1) to (8-3).

\[ \text{Mn}^{2+} \rightarrow \text{Mn}^{3+} + e^- \quad (8-1) \]

\[ \text{Mn}^{3+} + 2H_2O \rightarrow \text{MnOOH} + 3H^+ \quad (8-2) \]

\[ \text{MnOOH} \rightarrow \text{MnO}_2 + H^+ + e^- \quad (8-3) \]
Cyclic voltammograms of platinum in an agitated sulfuric acid electrolyte containing different manganese concentrations at 5 mV/s (0Mn graph at 10 mV/s)

The intensity of peaks A1 and A2 increased with the Mn(II) concentration in the electrolyte, indicating larger rate constants of the reactions at higher Mn(II) concentrations [200]. This is due to the larger amount of Mn(II) ions available for A1 reactions at higher manganese concentrations, which results in a larger quantity of MnOOH on the anode surface. Peak A1 was sharper at the higher Mn(II) concentration. Formation of a larger amount of MnOOH intermediate product on the Pt surface at higher Mn(II) concentrations insulates the electrode surface and prevents further oxidation of Mn(II) to Mn(III).
Two broad cathodic peaks appeared in the reverse scan direction of the cyclic voltammograms shown in Figure 8-1, marked as C_1 and C_2. The presence of two reduction peaks in the voltammograms of the MnO_2 layer in acidic solutions was also observed in other studies [136, 201, 202]. Peaks C_1 and C_2 have been suggested to represent the reduction of MnO_2 to MnOOH (reaction (8-3)) and that of Mn(III) to Mn(II) (reaction (8-1)), respectively. However, variations of the peak potential of C_2 with pH led to proposed reactions (8-4)-(8-6) for the MnO_2 reduction sequences in acidic solutions [201].

\[
\begin{align*}
MnO_2 + 4H^+ + 2e^- &\rightarrow Mn^{2+} + 2H_2O \quad (8-4) \\
MnO_2 + Mn^{2+} + 2H_2O &\rightarrow 2MnOOH + 2H^+ \quad (8-5) \\
MnOOH + 3H^+ + e^- &\rightarrow Mn^{2+} + 2H_2O \quad (8-6)
\end{align*}
\]

As expected from the anodic peaks, intensity of the cathodic peaks increased with Mn(II) concentrations. However, the intensities of the cathodic peaks were less than those of the anodic ones. This might reveal that either not all the deposited MnO_2 was reduced during the reverse potential scan or a portion of MnO_2 was detached from the surface due to the evolution of oxygen from the electrode surface and solution turbulence [202]. Moreover, transportation of Mn(III) to the bulk of the electrolyte could result in this observation.

### 8.3 MnO_2 deposition on the lead-based anodes

To compare the deposition of the MnO_2 layer on the Pb-MnO_2 and PbAg anodes, they were polarized at the constant potential of 1.9 V in the Mn-containing sulfuric acid electrolytes for different periods of time. Then cathodic potential sweep measurements (cathodic potentiodynamic) were conducted immediately after the potentiostatic polarization. The details of this experiment are schematically shown in Figure 8-2. The electrolytes were
stirred slowly at 60 rpm using a 40 mm magnet bar during this experiment. Figure 8-3 shows the cathodic voltammograms obtained on the previously polarized anodes in the electrolyte containing 3 g/L Mn(II) for different periods of 2.5, 5, 15, 30, 60, and 120 minutes.

The first cathodic peak of the voltammograms appeared in the potential range of 1.3-1.45 V. This peak represents the reduction of PbO₂ to PbSO₄ through reaction (5-5). The voltammograms of the composite anode (Figure 8-3(a)) show a cathodic peak at a potential range of 1.0-1.2 V. According to the cyclic voltammograms of platinum, this peak represents the reduction of the MnO₂ layer that was deposited on the anode. The MnO₂ reduction peak was not observed in the voltammograms of the PbAg anode (Figure 8-3(b)). Although the absence of this peak can be inferred as the absence of the MnO₂ layer, it would be wrong to assume that no MnO₂ deposited on the PbAg anode during the anodic polarization in the presence of Mn(II) ions. Lack of a physical connection between the MnO₂ layer and the anode can be the reason for the absence of an MnO₂ reduction peak.

Figure 8-2 Schematic presentation of the potentiostatic polarization experiment for different periods (t=2.5, 5, 15, 30, 60, and 120 minutes) followed by a cathodic potentiodynamic
Figure 8-3  Cathodic sweep voltammograms of the Pb-MnO₂ (a) and PbAg(b) anodes in sulfuric acid containing 3 g/L Mn(II) after polarization at 1.9 V for different periods of time (initial potential: 1.9 V, scan rate: 5 mV/s)
To understand the reason for this difference in the voltammograms of the anodes, the layers deposited on the anodes were characterized by SEM. The morphologies of the layers deposited on the Pb-MnO$_2$ and PbAg anodes after 30-minute polarization at 1.9 V in the Mn-containing electrolytes are presented in Figure 8-4. As Figure 8-4(a) shows, the MnO$_2$ layer deposited on the PbAg anode was relatively porous and flaky. This layer had been detached from the substrate in many spots. On the other hand, the Pb-MnO$_2$ anode formed a dense and uniform layer that covered the anode surface entirely and it nicely adhered to the substrate (Figure 8-4(b)). Therefore, the detachment of the MnO$_2$ layer from the PbAg anode and a lack of physical contact between this layer and the substrate were the most likely reasons for the absence of the MnO$_2$ reduction peak in the voltammograms of Figure 8-3(a).

The electrical contact between a porous MnO$_2$ layer and the electrode might become weak at the initial stages of the MnO$_2$ reduction. As reported by Lee et al. [201], Maskell [203], and Newman and Tobias [204], MnO$_2$ reduction proceeds at the deposit/substrate interface when the MnO$_2$ layer is porous. Formation of MnOOH at the deposit/substrate interface can lead to a very high electrical resistance between the layer and the electrode. This process might also physically separate parts in no electrical contact, resulting in no further MnO$_2$ reduction to occur. Therefore, the absence of the MnO$_2$ reduction peak in the voltammograms of the PbAg anode (Figure 8-3(b)) could be attributed to either a detachment of the MnO$_2$ layer from the electrode or a deposition of a highly porous MnO$_2$ layer.

Electrodeposition of the MnO$_2$ layer and its properties depend on the applied potential and current densities. Properties of the MnO$_2$ layer deposited at different potentials would be helpful to have a better understanding of the influences of the potential and current densities on the properties of the MnO$_2$ layer and the reason for the observed difference in the voltammograms of Figure 8-3.
Figure 8-4  SEM micrograph of the surface of PbAg (a) and Pb-MnO$_2$ (b) after 30 minutes of polarization in the Mn-containing electrolyte
8.4 Role of potential/current density on the MnO₂ deposition on PbAg

To find the role of potential and current density on the MnO₂ deposition on lead anodes, the PbAg electrode was polarized at different potentials (1.6-1.9V) in the Mn-containing electrolytes followed by a cathodic potential sweep. The current variation of the PbAg anode and the obtained voltammograms of this sample are plotted in Figure 8-5. As can be seen in Figure 8-5(b), the MnO₂ reduction peaks (peaks at 1.0-1.2 V) appeared in the voltammograms of the samples polarized at 1.6 and 1.7 V. However, no MnO₂ reduction peak appeared after the polarizations at 1.8 and 1.9 V. Considering this difference, it can be stated that the MnO₂ layers deposited at 1.6 and 1.7 V are likely to be denser and in better contact with the substrate compared to those deposited at the higher potentials. This was verified by the SEM morphologies of the polarized PbAg samples at 1.7 and 1.9 V, which are presented in Figure 8-6. As Figure 8-6(a) shows, the MnO₂ layer deposited at 1.7 V was relatively dense and uniform and nicely adhered to the substrate. On the other hand, the layer deposited at 1.9 V was relatively porous and flaky. These results verified that the presence or absence of the MnO₂ reduction peak in a cathodic voltammogram of a polarized sample represents the physical properties of the deposited MnO₂ layer. They also demonstrated that the anodic potential and current density determine the properties of deposited MnO₂ layer.

As Figure 8-5(a) shows, the anodic current increases with the applied potential. This means a higher rate of oxygen evolution reaction at more positive potential. Evolution of oxygen bubbles prevents deposition of a uniform and mechanically-stable MnO₂ layer and make it porous. The higher efficiency of the MnO₂ deposition at a lower current density was also previously shown [205, 207]. Newnham [45] also observed that the ability of the MnO₂ anodic layer to protect the PbAg anode was lower at higher current densities.
Figure 8-5  Anodic current of the PbAg anode at different potentials (a) and the obtained voltammograms of this sample after 30-minute polarization at 1.6, 1.7, 1.8, and 1.9 V in the presence of 3 g/L Mn(II) (b)
In spite of the higher current density of the Pb-MnO₂ anode (Figure 7-6), it formed a denser and more uniform MnO₂ layer than the PbAg did (Figure 8-4). Although the cause for this observation was not established, possible scenarios can be suggested by considering the catalytic activity of the MnO₂ particles for OER and Mn(II) disproportionation reaction, which will be discussed in the next chapter.

8.5 Role of Mn(II) concentration on the primary anode oxidation

The potentiostatic/LSV experiments at different polarization times (Figure 8-2) were repeated on the Pb-MnO₂ and PbAg anodes in the electrolyte containing different Mn(II) concentrations. Figure 8-7 and Figure 8-8 report the cathodic voltammograms of the polarized Pb-MnO₂ and PbAg anodes, respectively. The results obtained after 2.5-, 15-, and 60-minute polarizations are not shown for the sake of clarity. However, the results will be discussed and compared.
Figure 8-7  Cathodic cyclic voltammograms of the Pb-MnO₂ anode after polarization at 1.9 V for 5 (a), 30 (b), and 120 minutes (c) (initial potential: 1.9 V, scan rate: 5 mV/s)
Figure 8-8 Cathodic cyclic voltammograms of the PbAg anode after polarization at 1.9 V for 5 (a), 30 (b), and 120 minutes (c) (initial potential: 1.9 V, scan rate: 5 mV/s)
Comparing the voltammograms of the anodes obtained in the Mn-free electrolyte (Figure 8-7 and Figure 8-8) demonstrates that PbO₂ reduction peaks of the Pb-MnO₂ anode were larger than those of the PbAg anode. This suggests that the oxidation of lead in the Pb-MnO₂ anode was slightly higher than that in the PbAg anode in the absence of Mn(II) ions.

The size of the PbO₂ reduction peak, regardless of the polarization time and the type of anode, became smaller when the Mn(II) ions were introduced into the electrolyte. This variation suggests that the addition of Mn(II) ions reduced the formation of lead dioxide on the surface of the anodes. The charge associated with the PbO₂ reduction peaks were used to estimate the amount of this corrosion product formed on each anode during the polarization.

Figure 8-9 shows the variation of the calculated amount of the reduced PbO₂ on the anodes at different polarization times as a function of Mn(II) concentration. This data confirms that formation of the MnO₂ layer on the anodes decreased the oxidation rate of the anodes; an effect that was more significant at higher Mn(II) concentrations.

The inhibiting role of the MnO₂ layer on PbO₂ formation can be studied by considering the proposed PbO₂ growth mechanisms. There are two proposed mechanisms for growth of PbO₂ on lead-based anodes.

According to many studies, the surface of the existed PbO₂ layer is the active site for the further oxidation of Pb(II) and the growth of the PbO₂ layer. The Pb(II) ions are transported to these reaction sites on which they get oxidized to PbO₂ through reaction (8-8) to grow the PbO₂ of the anodic layer [30, 32, 35, 37, 206].

\[
Pb^{2+} + 2H_2O \leftrightarrow PbO_2 + 4H^+ + 2e^- \quad (8-8)
\]
Figure 8-9 Variation of the calculated amount of the reduced PbO$_2$ on the Pb-MnO$_2$ (a) and PbAg (b) anodes at different polarization times as a function of Mn(II) concentration.
Growth of the PbO$_2$ layer through the mentioned mechanism might be influenced in the presence of Mn(II) ions. It has been reported that the MnO$_2$ layer is not deposited on the lead anodes unless a PbO$_2$ layer forms. In fact, PbO$_2$ regions are the proper reaction sites for the MnO$_2$ deposition [135]. Therefore, a significant portion of the PbO$_2$ region on the surface, which is the reaction site for further PbO$_2$ formation, is covered by the MnO$_2$ layer in the Mn(II)-containing electrolytes. Thus, the formation of the MnO$_2$ layer can inhibit growth of the PbO$_2$ layer by blocking the active sites for this reaction.

Lander [82] proposed another mechanism for the growth of the PbO$_2$ layer. According to this mechanism, the growth of a PbO$_2$ layer is the result of the PbO$_x$ layer (1.5<x<2) reacting with the oxygen species. These oxygen species can either be oxygen atoms (O) or oxygen ions (O$^-$ and O$_2^-$) that result from the oxygen evolution reaction. Among these species, the diffusion of atomic oxygen is more likely to occur due to its smaller radius in comparison with the other species [29, 35, 37]. In the Mn-free electrolyte, OER takes place on the PbO$_2$ region of the surface, leaving oxygen species on the surface. These species diffuse through the PbO$_2$ to react with either Pb(II) or PbO$_x$ to form further PbO$_2$. This process is controlled by the diffusion of oxygen species and lead ions through the anodic layer [29, 37]. Diffusion of the oxygen species can be changed in the presence of Mn(II) ions in the electrolyte.

When the surface of an anode is entirely covered by an MnO$_2$ layer, the OER takes place mostly on this layer. This reaction leaves the oxygen species on the MnO$_2$ layer. These species need to diffuse through the MnO$_2$ layer to react with the lead compounds. This suggests that the MnO$_2$ layer acts as an additional diffusion barrier that could slow the growth of the PbO$_2$ layer. It should be noted that the surface of the MnO$_2$ layer is not the main reaction site for OER when a portion of this layer flakes off. If this happens, the OER prefers
to proceed at the PbO$_2$ region of the anode surface because the electrical resistance of the MnO$_2$ layer was relatively high and electrons prefer to flow in the path of the least resistance.

The data presented in Figure 8-9 indicates that the inhibiting effect of MnO$_2$ on the PbO$_2$ formation was slightly more significant on the Pb-MnO$_2$ anode. For instance, when 6 g/L Mn(II) was added to the electrolyte, the amount of PbO$_2$ on the Pb-MnO$_2$ anodes after 120 minutes decreased by 81% while that of the PbAg anode reduced by 47%. This difference might be ascribed to the different properties of the MnO$_2$ layer on the anodes. Diffusivity of the solid layer depends on its physical properties. A thicker and denser MnO$_2$ layer has a lower diffusivity compared to a porous layer, contributing to a slower diffusion of oxygen species.

8.6 Summary

In this study, the anodic deposition of the MnO$_2$ layer on the Pb-MnO$_2$ composite anode and the PbAg alloy was investigated by electrochemical techniques. Scanning electron microscopy was employed to verify the results of the electrochemical experiments. The effects of the MnO$_2$ layer and its properties on the growth of PbO$_2$ on the surface of the anodes were also studied. The results of these studies can be summarized as follows:

- The MnO$_2$ layer deposition on the platinum electrode, which takes place by Electrochemical-Chemical-Electrochemical (ECE) mechanism, is a function of Mn(II) concentrations.
- The appearance or the absence of the MnO$_2$ reduction peak in the cathodic potential sweep following the anodic polarization can represent the properties of the deposited MnO$_2$ layer. The absence of this peak might be due to the deposition of a porous, spongy, and flaky
layer of MnO$_2$ on the anode. This technique can be used for in-situ evaluation of the deposited MnO$_2$ layers.

- Deposition of the MnO$_2$ layer on the lead-based anodes is influenced by the MnO$_2$ composite particles in the electrode. The Pb-MnO$_2$ composite anode formed a uniform and dense MnO$_2$ layer while the layer deposited on the smooth PbAg anode was flaky and porous.

- The oxidation of the anodes was inhibited when Mn(II) was introduced into the electrolyte. This effect directly increases with the concentration of the manganese ions in the electrolyte. The MnO$_2$ anodic layer acts as a diffusion barrier layer for the oxygen species and decreases the oxidation and corrosion rate of the lead anodes. The dense MnO$_2$ layer deposited on the Pb-MnO$_2$ composite anode can provide a stronger barrier against the diffusion of the oxygen species.
Chapter 9

Anodic performance in the Mn-containing sulfuric acid electrolytes

9.1 Introduction

The positive effect of Mn(II) on the oxygen evolution rate on the fresh Pb-MnO$_2$ and PbAg anodes was shown in chapter 7 by the results of the potentiostatic polarization experiments. This effect of the manganese is prone to change, depending on the properties of the electrodeposited MnO$_2$ layer. Deposition of the MnO$_2$ layer depends on many factors such as the anodic current, Mn(II) concentration, polarization time, and the anode material. Therefore, the properties of this layer and its effects on the anodic performance of the anodes can be different under the zinc operating conditions in the electrolyte containing different Mn(II) concentrations. In this chapter, properties of the MnO$_2$ layer formed on the Pb-MnO$_2$ anode during longer polarizations are investigated. Moreover, the effects of the MnO$_2$ layer on the anodic potentials, corrosion of the anodes, and cell mud formation rate are discussed based on the experimental results.
9.2 Morphological studies of the MnO₂ layers

The anodic performance of the Pb-MnO₂ composite anode in the Mn-containing electrolytes was examined using galvanostatic polarizations (GS) in different electrolytes. The PbAg and PbCa anodes were also examined for comparison. These experiments were performed at a constant current density of 500 A/m² in the 180 g/L H₂SO₄ solutions containing different Mn(II) concentrations. The Pb-MnO₂ and PbAg anodes were polarized in the presence of 0, 0.5, 1.5, and 3 g/L Mn(II). The PbCa anode was polarized in the absence and presence of Mn(II) ions (3 g/L) in the electrolyte. During the galvanostatic tests, the electrolytes were slowly stirred by a 40 mm magnet bar at 60 rpm.

Surface morphologies of the MnO₂ layers electrodeposited on the PbAg anodes after 72-hour galvanostatic polarization in the solutions of different Mn(II) concentrations are presented in Figure 9-1. Figure 9-2 shows the morphology of the MnO₂ layer formed on the Pb-MnO₂ composite anodes in different Mn(II) concentrations. The morphology of the PbCa anode after GS polarization in the Mn-containing electrolyte can be seen in Figure B-1 (Appendix B). These results reveal significant differences among the MnO₂ layers electrodeposited on different anodes.

According to Figure 9-1, in the presence of 0.5 g/L Mn, the MnO₂ layer rarely remained on the PbAg anode after rinsing and drying. In the solutions of higher Mn(II) concentrations, the electrodeposited MnO₂ was composed of two distinct layers, a relatively compact layer on the anode and a thick and porous layer on top of the first one. Formation of an MnO₂ double layer on lead anodes was also observed by Ipinza et al. [208, 209]. It was reported that the MnO₂ layer deposited on the lead anode in the copper electrowinning process composed of an internal thin and dense layer and an external thick and porous layer.
Figure 9-1 Morphology of the MnO₂ anodic layers formed on the surface of the PbAg anode in 72-hour anodic polarization at 500 A/m² in the solution of 0.5 g/L Mn (a), 1.5 g/L Mn (b) and 3 g/L Mn(c) and (d), MnO₂ porous layer on the PbAg anode (e)
The porous MnO$_2$ top layer loosely adhered to the surface and was easily removed by rinsing. This layer was spongy and very porous and its morphology was different in various regions, as shown on Figure 9-1(e). The adhesion of the internal MnO$_2$ layer to the anode was relatively strong, however, it also flaked off easily. Only a small portion of this layer remained on the PbAg anode after rinsing the sample. The MnO$_2$ layer deposited on the PbCa anode showed similar properties to that of the PbAg anode (Appendix B).

As shown in Figure 9-2, the features of the MnO$_2$ layer deposited on the Pb-MnO$_2$ composite anode were different from those of the PbAg alloy. Unlike what was reported for the PbAg anode, no porous layer was observed on the composite anode. The MnO$_2$ layer on the composite anode contained only one dense layer. According to Figure 9-2, these layers were relatively dense and uniform, regardless of the Mn(II) concentration. They also exhibited cracks on their smooth surfaces. The cracking is likely due to either high stress levels in the coating or the drying process, which are common once thick coatings are formed [210, 211]. These MnO$_2$ layers exhibited strong adhesion to the substrate and covered the entire surface of the composite anodes. Moreover, the thickness of this layer increased and its surface became smoother at higher Mn(II) concentrations.
Figure 9-2 Morphology of the MnO₂ anodic layers formed on the surface of the Pb-MnO₂ anode in 72-hour anodic polarization at 500 A/m² in the solution of 0.5 g/L Mn (a)-(b), 1.5 g/L Mn (c)-(d), and 3 g/L Mn(II) ions (e)-(f)
9.3 Anode potential during the galvanostatic polarization

The potential variations of the PbAg and PbCa anodes during the galvanostatic experiments in the Mn-containing electrolytes are shown in Figure 9-3 and Figure 9-4, respectively. Figure 9-5 reports the potential variation of the Pb-MnO$_2$ composite anode during the GS polarization in the electrolyte containing different Mn(II) concentrations. The better catalytic activity of the Pb-MnO$_2$ anode than the Pb alloys can be observed by comparing their potentials in the Mn-free electrolytes. However, the presence of manganese ions may cast doubt on this conclusion.

As Figure 9-3 shows, the potential of the PbAg anode decreased with an increase in the Mn(II) concentration during the initial 1-2 hours of the polarization. In the solutions of 0.5 and 1.5 g/L Mn(II), this effect remained unchanged during the 72-hour polarization. During this period, the potential of the PbAg anode polarized in the presence of Mn(II) ions at the mentioned concentrations was lower than its potential in the Mn-free electrolyte.

In the presence of 3 g/L Mn(II), however, the potential of the PbAg anode raised gradually after 2 hours. This behavior caused the PbAg potential in the presence of 3 g/L Mn(II) to be higher than its potential in the Mn-free electrolyte at polarization longer than 15 hours. A similar behavior was observed when the PbCa anode was polarized in the presence of Mn(II). The potential of the PbCa anode in the Mn-containing electrolyte gradually increased and caused the anode potential to be higher compared to that in the Mn-free electrolyte.

As Figure 9-5 shows, Mn(II) had positive effects on the potential of the Pb-MnO$_2$ anode at the initial stages of the polarization, i.e. lower anodic potential at higher Mn(II) concentrations. This effect is shown in the closer view of the potential-time of the Pb-MnO$_2$ (Figure 9-5(b)) and is in agreement with the potentiostatic results reported in chapter 7.
Figure 9-3  Potential variations of the PbAg anodes during anodic polarization in the H$_2$SO$_4$ electrolyte containing different Mn(II) concentrations at 500 A/m$^2$ and 37°C

Figure 9-4  Potential variations of the PbCa anodes during anodic polarization in the Mn-free and Mn-containing H$_2$SO$_4$ electrolytes at 500 A/m$^2$ and 37°C
According to Figure 9-5(a), the negative effect of the MnO$_2$ layer on the anodic potential was more significant for the composite anode compared to the lead alloys. Regardless of the Mn(II) concentrations, the potential of the composite anode in the Mn-containing electrolyte was higher than that in the Mn-free electrolyte. As explained, this behavior could have resulted from the low conductivity of the electrodeposited MnO$_2$ layer on the anode surface. Therefore, the MnO$_2$ composite particles are not very effective in decreasing the oxygen evolution overpotential in the presence of manganese ions in the electrolyte.

The final potential of the PbAg and Pb-MnO$_2$ after the 72-hour polarization in the presence of different Mn(II) concentrations are compared in Figure 9-6. These results clearly show the effect of the electrodeposited MnO$_2$ layers on the potential of these anodes. Although the MnO$_2$ layer deposited at 3 g/L Mn(II) caused a significant increase in the potential of the Pb-MnO$_2$ anode, the final potential of this samples is slightly lower than that of the PbAg. The similar features of the MnO$_2$ layers deposited on the PbCa and PbAg anodes in the presence of 3 g/L Mn(II) caused their similar potential variation during the GS polarizations. Unlike the PbO$_2$ anodic layer, the MnO$_2$ layer does not have good electrical conductivity [11, 117]. Therefore, the MnO$_2$ layer can decrease the conductivity of the anode surface as it covers the surface and causes the potential drop on the anode surface, resulting in the higher anodic potentials at a constant current density. Moreover, as mentioned, the MnO$_2$ layers on the Pb alloys were loosely adhered and might be partially detached from the anode surface. If this happens, the OER prefers to occur on the PbO$_2$ region of the surface. This results from the low conductivity of the MnO$_2$ layer.
Figure 9-5 Potential variations of the Pb-MnO₂ anodes during anodic polarization in the H₂SO₄ electrolyte containing different Mn(II) concentrations at 500 A/m² and 37°C
Since the MnO₂ layer covered part of the anode surface, the area of the exposed PbO₂ surface was smaller than the entire electrode surface area. Therefore, the current density in these areas is higher than the applied current density, which can cause a higher potential of the alloys in the Mn-containing electrolyte.

The dense and uniform MnO₂ layer deposited on the composite anode prevents the solution to be in contact with the anode surface. Therefore, the OER mostly occurs at the MnO₂ layer. The dense and thick MnO₂ layer could cause a significant decrease in the surface conductivity, contributing to the increase in the anodic potential [15, 16]. This effect was more significant when the thicker MnO₂ layer was deposited at higher Mn(II) concentrations.

The deposited MnO₂ layer on the composite anode might also influence the anode potential by changing the surface roughness of the anode. Figure 9-7 compares the surface morphology of the composite anode and that of the deposited MnO₂ layer. This figure reveals that the deposited MnO₂ layer was smoother than the anode surface. Therefore, despite the same geometry of the anodes, the real surface area of the composite anode decreased by deposition of the MnO₂ layer. It reveals that the deposition of the MnO₂ layer on the composite anodes contributed to a higher actual current density and, consequently, a higher anode potential. The effects of the MnO₂ layer on the real surface area and the charge transfer resistance cannot be distinguished [177].
Figure 9-6  Anodic potential of the PbAg and Pb-MnO$_2$ anodes after 72-hour polarization at 500 A/m$^2$ and 37°C in electrolytes containing different Mn(II) concentrations

Figure 9-7  Profile of the MnO$_2$ layer deposited on the composite anode
9.4 MnO$_2$ suspended particles in the solution

The formation rate of the MnO$_2$ suspended particles was visually different when the PbAg and Pb-MnO$_2$ anodes were examined. The electrolytes in the cells of the Pb-MnO$_2$ and PbAg anodes after 24-hour polarizations are compared in Appendix C. During the galvanostatic polarization of the PbAg anode, a significant amount of MnO$_2$ fine particles was generated in the electrolyte, turning the electrolyte color to black after several hours. The deposition of the MnO$_2$ layer on the inert surfaces, such as the PTFE sample holder and the glass cell walls, was also observed in this case. However, no significant amount of MnO$_2$ particles in the electrolyte or MnO$_2$ deposited on the inert surfaces was observed when the Pb-MnO$_2$ anode was polarized at the same conditions. In this case, the electrolyte turned pink after several hours, which is due to the formation of Mn(III) ions.

This difference could be attributed to the different rate of Mn(II) oxidation on the surface of the anodes. The properties of the MnO$_2$ layer play an important role in this regard. The MnO$_2$ particles in the electrolyte are believed to result from the reaction of permanganate with manganous ions, which is known as the Guyard reaction (reaction (9-1)) [212].

$$2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+ \quad (9-1)$$

Tompkins [213] suggested a skeleton for this reaction, which is shown in reactions (9-2)-(9-6). The Guyard reaction proceeds at a slow rate since steps 9-3 and 9-6 are slow [213, 214]. However, this reaction is catalyzed by the manganese dioxide previously formed in or added to the electrolyte [212, 213, 215]. According to Tompkins [213], the rate of MnO$_2$ formation in the electrolyte is proportional to the amount of manganese dioxide present in the electrolyte. Therefore, detachment of the MnO$_2$ particles from the deposited layer on the anode can catalyze the formation of MnO$_2$ particles in the electrolyte.
\[ \text{MnO}_4^- + \text{Mn}^{2+} + \text{H}_2\text{O} \rightarrow \text{Mn}^{3+} + \text{HMnO}_4^- + \text{OH}^- \] (9-2)

\[ \text{HMnO}_4^- + \text{Mn}^{2+} + \text{OH}^- \rightarrow 2\text{MnO}_2 + \text{H}_2\text{O} \] (9-3)

\[ 2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+} \] (9-4)

\[ \text{Mn}^{4+} + \text{OH}^- \rightarrow \text{Mn(OH)}^{3+} \] (9-5)

\[ \text{Mn(OH)}^{3+} + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 3\text{H}^+ \] (9-6)

As previously shown, the MnO\(_2\) layer deposited on the PbAg anode was porous and did not strongly adhere to the substrate. This layer might be partially detached during the polarization, providing catalytic sites for the MnO\(_2\) cell mud formation. On the other side, detachment of MnO\(_2\) from the surface of the composite anode is negligible since the MnO\(_2\) layer strongly adhered to the anode. Thus, the Guyard reaction is not catalyzed when the Pb-MnO\(_2\) anode was polarized, resulting in no visible MnO\(_2\) particles in the electrolyte.

The amount of sludge at the bottom of a cell is a function of the formation rate of MnO\(_2\) particles in the electrolyte. The precipitated sludge may lead to anode/cathode short circuits if it touches the electrodes. This contributes to the short-circuit-induced corrosion of anodes and high lead contamination of the zinc product. The MnO\(_2\) suspended particles can also have a negative influence on the morphology of the zinc deposit and current efficiency [130, 139]. None of these would be a concern when the Pb-MnO\(_2\) anode is used, as no MnO\(_2\) particle was created during the polarization of this anode, at least in a short period of time.

Many factors can be considered as causes for the different properties of the MnO\(_2\) layers and, consequently, formation of the MnO\(_2\) mud in the electrolyte. These factors can be the deposition mechanism of the MnO\(_2\) layers and their structure, working potentials of the anodes, their chemical composition, and surface roughness, which will be discussed in the following sections.
9.5 XRD studies and MnO$_2$ phases

X-ray diffraction was used to investigate and compare the structure of the deposited MnO$_2$ layers and generated particles in the electrolyte. The suspended particles were collected through the filtering of the Mn-containing electrolyte after 72-hour polarization of the PbAg anode. The X-ray diffraction pattern of the MnO$_2$ layers that formed on the PbAg and Pb-MnO$_2$ anodes as well as that of the MnO$_2$ particles are shown in Figure 9-8. Characteristic peaks of different MnO$_2$ phases are also presented in this figure. Many of these peaks overlap each other. Therefore, some of the observed peaks in the diffraction patterns may represent more than one phase.

In Figure 9-8(a), the MnO$_2$ suspended particles exhibit relatively sharp diffraction peaks, indicating a noticeable level of crystallinity in their structure. The diffraction patterns indicate the presence of a combination of orthorhombic (ramsdellite), tetragonal (pyrolusite, β-MnO$_2$ and cryptomelane, α-MnO$_2$), and hexagonal (Akhtenskite, ε-MnO$_2$) structures of MnO$_2$ [216, 217].

In comparison, the MnO$_2$ layers deposited on the anodes are characterized by lower and broader peaks. These features indicate that the MnO$_2$ layers have a more amorphous structure compared to the MnO$_2$ suspended particles [161]. Moreover, this difference can be attributed to the higher density of defects in the structure of the MnO$_2$ layer, which are known as microtwinning and De Wolff disorders [161, 216].

Similar to what was observed for the MnO$_2$ suspended particles, the MnO$_2$ layers are a combination of different phases. However, some differences can be observed.
Figure 9-8 XRD patterns of the MnO₂ suspended particles in the electrolyte (a) and the MnO₂ layers deposited on the Pb-MnO₂ (b) and PbAg (c) anodes in addition to characteristic peaks of different MnO₂ modifications.
First of all, the XRD pattern of the layer deposited on the Pb-MnO$_2$ anode shows some unexpected peaks. These peaks are related to Pb-containing phases. Since the MnO$_2$ layer deposited on the composite anode strongly adhered to the anode, it was removed mechanically. This process could detach some lead corrosion products mixed with the MnO$_2$ layer. Furthermore, $\alpha$-MnO$_2$ phase did not appear in the MnO$_2$ layers, indicated by the absence of its characteristic peaks at 2\(\theta\)=12.8, 18.06, and 49.85°. The diffraction peak at 2\(\theta\)=28.3 in this XRD pattern (shown by arrow in Figure 9-8(b)) might correspond to either PbSO$_4$ or Pyrolusite ($\beta$-MnO$_2$).

Presence of ramsdellite and pyrolusite phases in addition to the mentioned defects in the structure of MnO$_2$ layers are the typical responses for the $\gamma$-MnO$_2$ phase [161, 216]. $\gamma$-MnO$_2$, also known as Nsutite, has been depicted as an irregular intergrowth of pyrolusite in the ramsdellite structure. Poor quality of XRD pattern is believed to be a problem in structural studies of $\gamma$-MnO$_2$. The presence of microtwinning can shift the $\gamma$-MnO$_2$ diffraction peaks, depending on its percentage [216]. In a comparison of the peak (110) of $\gamma$-MnO$_2$ among the XRD patterns (Figure 9-8), it can be seen that this peak shifted to lower degrees in the patterns of the MnO$_2$ layers. This reveals a larger percentage of microtwinning in the MnO$_2$ layers than the MnO$_2$-suspended particles. This deviation was more pronounced in the pattern of the layer deposited on the PbAg, indicating more significant defects in this layer compared to the layer deposited on the composite anode.

A wide range of microtwinning percentages (6-100%) has been reported for electrochemically-deposited MnO$_2$, depending on the operating conditions [216, 218]. Based on the categorization of $\gamma$-MnO$_2$ that was proposed by Chabre and Pannetier [216], the electrodeposited MnO$_2$ layers in this study were “extremely twinned” $\gamma$-MnO$_2$. This was concluded from the presence of only two broad peaks in the range of 2\(\theta\)=54-71°, and also the
shift in peak (130) to larger diffraction angles. Formation of the $\varepsilon$-MnO$_2$ phase in the MnO$_2$ layers can also be attributed to a significant amount of microtwinning and De Wolff disorders. Very high percentages of the structural defects lead to a partial change of the MnO$_2$ structure from orthorhombic ($\gamma$-MnO$_2$) to hexagonal ($\varepsilon$-MnO$_2$) [216].

According to the XRD results, $\gamma$-MnO$_2$ and $\varepsilon$-MnO$_2$ are the dominant phases of the electrodeposited MnO$_2$ layers. The appearance of the deposited layers on the composite anode matched with that previously reported for $\gamma$-MnO$_2$ [219]. This layer was hard, bright, and grey-black in color. Structural features of the MnO$_2$ layers deposited on the Pb-MnO$_2$ and PbAg anodes were generally consistent with those reported for EMD (Electrolytical Manganese Dioxide) deposited at room temperature, which has been known to be either $\gamma$ structure or poorly crystallized in nature [219-221]. The MnO$_2$ suspended particles, however, were shown to consist of $\alpha$-MnO$_2$, $\beta$-MnO$_2$, and low-defect $\gamma$-MnO$_2$ phases.

Comparing these features, it might be concluded that the mechanism of MnO$_2$ deposition on the anodes is the same. However, it might be different from that of the formation of suspended MnO$_2$ particles. This reveals that the detachment of the MnO$_2$ layer is not the only source for the MnO$_2$-suspended particles. The XRD results also demonstrated that the observed different physical properties of the MnO$_2$ layers on the PbAg and Pb-MnO$_2$ anodes could not be attributed to the mechanism of the MnO$_2$ deposition and structure of the layers. Therefore, it is more likely that the working potential of the anodes and the anode properties caused these differences.
9.6 Role of the anode electrochemical and physical properties on the MnO$_2$ layer

9.6.1 Electrocatalytic activity

As an electrochemical reaction, MnO$_2$ electrodeposition is a function of the anode potential [135]. The galvanostatic results show that, in the solutions of the same Mn(II) concentration, the initial potential of the Pb-MnO$_2$ anode was lower than those of the PbAg anode. This difference might affect the MnO$_2$ electrodeposition and properties of this layer. The role of potential on the properties of the deposited MnO$_2$ layer on the PbAg anode was shown in section 8.4. The results of this study demonstrated that the MnO$_2$ layer deposited on the PbAg anode at lower potentials and current densities was denser and more uniform.

In order to examine whether the initial potential difference of the Pb-MnO$_2$ and PbAg anodes caused the different properties of the deposited MnO$_2$ layers, the anodes were subjected to potentiostatic polarization at 1.9 V in the Mn-containing electrolytes for 3 hours. The morphologies of the deposited MnO$_2$ layers during this experiment, which are presented in Figure 9-9, show the role of the potential. As seen in Figure 9-9(a), the MnO$_2$ layer of the PbAg anode was flaky and loosely adhered to the anode surface. On the other hand, the composite anode was entirely covered by a very uniform, thick, hard, and strongly adhered MnO$_2$ layer (Figure 9-9(b)). Since current density controls properties of the MnO$_2$ layer, variations of the anodic currents during the potentiostatic polarizations were recorded and are shown in Figure 9-9(c). These results demonstrate a higher current density of the composite anode in comparison with the PbAg anode at the same potential. The potentiostatic results, i.e. deposition of the dense MnO$_2$ layer on the composite anode despite its higher current density, reveal that none of the applied potential and current density is the dominant cause for the different properties of the MnO$_2$ layer formed on the anodes during the galvanostatic and potentiostatic polarizations.
Figure 9-9 Morphology of the MnO₂ layers deposited on the surface of the PbAg (a) and Pb-MnO₂ (b) anodes (after 3 hours) and variation of the current density of the anodes during potentiostatic polarization at 1.9V in the H₂SO₄ electrolyte containing 3 g/L Mn(II) at T=37°C
9.6.2 Fabrication process and surface defects

Surface defects that are present on the composite anode might influence the deposition of the MnO$_2$ layer on the anode surface and enhance its properties. Morphological studies of the Pb-MnO$_2$ anodes showed that the surface of this anode contains surface defects, including microcracks and pores. These irregularities might enable the MnO$_2$ layer to provide interfacial mixing with the anode surface, resulting in a strongly-adhered MnO$_2$ layer on the composite anode. Mechanical interlocking, also known as interfingering, has been shown as a mechanism of adhesion between electrodeposited coatings and substrates. According to this mechanism, the penetration of a coating into the pores, holes, and cracks of the substrate surface locks the coating layer mechanically to the substrate [222].

Figure 9-10 shows the cross section of the Pb-MnO$_2$ anode after the 72-hour galvanostatic polarization in the electrolyte containing 3 g/L Mn(II). Deposition of a uniform MnO$_2$ layer on the composite anode can be observed in this figure. It also reveals that the MnO$_2$ deposition was able to penetrate into the irregularities of the anode surface and provide anchors for the films, preventing film delamination [223]. This may verify the role mechanical interlocking in formation of a strongly-adhered MnO$_2$ layer on the composite anode. It should also be noted that the composite MnO$_2$ particles in the anode cannot be distinguished from the penetrated MnO$_2$ layer.

To investigate whether the surface defects resulted from the fabrication process are the main reasons for the observed properties of the MnO$_2$ layer on the composite anode or not, two different anodes were fabricated using the same process as was used to fabricate the Pb-MnO$_2$ composite anodes. These samples include a pure Pb without any composite particles and a composite anode containing magnetite particles (Pb-Fe$_3$O$_4$).
In the first step, the Pb-Fe₃O₄ composite was subjected to the potentiostatic-linear sweep voltammetry cycle in sulfuric acid solution containing 3 g/L Mn(II). The potentiostatic polarization was performed at a potential of 1.9 V for periods of 5, 15, 30, 60, and 120 minutes followed by the cathodic potentiodynamic polarization (Figure 8-2). The obtained voltammograms are shown in Figure 9-11. For comparison, the voltammograms of the PbAg and Pb-MnO₂ obtained after 120 minutes in the same solution are also presented in Figure 9-11.

The voltammograms of the Pb-Fe₃O₄ electrode are similar to that of the PbAg in terms of the number of cathodic peaks in the shown potential range. Therefore, unlike the Pb-MnO₂ anode, the Pb-Fe₃O₄ sample did not show any MnO₂ reduction peaks, although both of these samples were fabricated by the same process and contained the same surface defects. This reveals that the presence of the surface defects on the Pb-MnO₂ anode is not the main factor that caused different properties of the MnO₂ layer on this anode compared to the layers deposited on the lead alloys.

In the next step, the pressed Pb and Pb-Fe₃O₄ samples were polarized in the Mn-containing electrolyte at 500 A/m² for 72 hours. The MnO₂ layers deposited on these samples were characterized by the SEM. Figure 9-12 and Figure 9-13 show the morphologies of the MnO₂ layer deposited on the Pb and Pb-Fe₃O₄ samples during the 72-hour polarization in the presence of 3 g/L Mn(II), respectively.
Figure 9-10 Cross section of the Pb-MnO$_2$ anode after 72-hour galvanostatic polarization in H$_2$SO$_4$ electrolyte containing 3 g/L Mn(II)

Figure 9-11 Cathodic sweep voltammograms of the Pb-Fe$_3$O$_4$ sample in sulfuric acid containing 3 g/L Mn(II) after polarization at 1.9 V for different periods of time and those of the PbAg and Pb-MnO$_2$ samples obtained after 120 minutes polarization in the same conditions (initial potential: 1.9 V, scan rate: 5 mV/s)
Figure 9-12 Morphology of the MnO₂ anodic layer formed on the surface of the Pb sample in 72-hour anodic polarization in the presence of 3 g/L Mn(II) at 50 mA cm⁻². (a) and (b) internal MnO₂ layer; (c) porous outer layer.

Figure 9-13 Morphology of the MnO₂ anodic layers formed on the surface of the Pb-Fe₃O₄ sample in 72-hour anodic polarization in the solution of 3 g/L Mn(II) at 500 A/m². (a) internal layer, (b) porous outer layer.
Similar to what was observed on the PbAg and PbCa samples, the MnO$_2$ layer deposited on the Pb and Pb-Fe$_3$O$_4$ samples composed of a continuous and thin internal layer and a porous and thick external layer. Both of these layers were easily removed from the anode surface by rinsing the samples with water. These results demonstrate that the special properties of the MnO$_2$ layer deposited on the Pb-MnO$_2$ anode cannot be only due to the fabrication process and the resulting surface properties. Therefore, the other significant difference of the Pb-MnO$_2$ composite anode compared to the lead alloys should be studied, which is its chemical composition.

9.6.3 Chemical composition and the presence of MnO$_2$ composite particles

It has been shown by other authors that the deposition of an MnO$_2$ layer and its effects depend on the chemical composition of the lead-based anodes [135]. Whether the presence of MnO$_2$ particles in the composite anode could modify the MnO$_2$ deposition process is still unknown. However, the MnO$_2$ composite particles might affect the electrodeposition of this layer through affecting the current distribution and providing nucleation sites for this reaction.

In order to examine if the MnO$_2$ particles on the anode can affect the MnO$_2$ layer deposition, a lead sample was prepared with a thin surface layer containing MnO$_2$ particles (Pb/Pb-MnO$_2$). The same MnO$_2$ powder that was used to fabricate the Pb-MnO$_2$ composite anodes was also used to prepare the Pb/Pb-MnO$_2$ sample. The MnO$_2$ particles were dusted on the surface of the PbAg substrate and the anode material was rolled. This process causes the MnO$_2$ particles to embed in the lead substrate, as detailed in Figure 9-14. After the first rolling pass, excess MnO$_2$ which did not adhere to the anode, was brushed off and collected, whereupon the dusting and rolling sequence was repeated. This sequence was repeated to reduce the thickness of the substrate to 45% of its original thickness.
The new Pb/Pb-MnO₂ anode was subjected to the potentiostatic (1.9 V)-linear sweep voltammetry cycle in a sulfuric acid solution containing 3 g/L Mn(II). The potentiodynamic curves of this sample obtained after the polarization for different periods of time are shown in Figure 9-15. Similar to what was observed in the voltammograms of the composite anodes (Figure 8-3(a)), a cathodic peak was observed in the voltammograms of the Pb/Pb-MnO₂ in the potential range of 1.0-1.2 V in addition to the PbO₂ reduction peak. This peak corresponds to the reduction of MnO₂. Since this peak enlarged with prolonged polarization, it represents the reduction reaction of the MnO₂ deposited layer rather than the reduction of the MnO₂ particles that were embedded on the anode surface in the pre-treatment rolling process.

Comparing the voltammograms of the Pb/Pb-MnO₂ with those of the PbAg and Pb-MnO₂ anodes reported in Figure 8-3 demonstrates that the MnO₂ layer deposited on the Pb/Pb-MnO₂ sample is likely to be dense, uniform, and in good physical and mechanical contact with the sample surface.

The prepared Pb/Pb-MnO₂ sample was polarized at a constant current density of 500 A/m² in the sulfuric acid solution containing 3 g/L Mn(II) for 72 hours. The morphology and profile of the MnO₂ layer deposited on this sample are shown in Figure 9-16. As was observed on the Pb-MnO₂, the Pb/Pb-MnO₂ sample formed a single and dense layer of MnO₂ that uniformly covered the entire surface.

The results of the linear sweep voltammetry and galvanostatic studies on the Pb/Pb-MnO₂ samples indicate that the presence of the MnO₂ particle could be the reason for the deposition of the uniform MnO₂ layer on the Pb-MnO₂ anode. The MnO₂ particle might influence the deposition of the MnO₂ layer in different ways, which will be discussed in the following sections.
Figure 9-14  Schematic of MnO$_2$ particles being set into the lead anode with the use of a rolling mill and making the Pb/Pb-MnO$_2$ anode

Figure 9-15  Cathodic sweep voltammograms of the Pb/Pb-MnO$_2$ sample in sulfuric acid containing 3 g/L Mn(II) after polarization at 1.9 V for different periods of time (initial potential: 1.9 V, scan rate: 5 mV/s)
Figure 9-16 Morphology (a, b) and the profile (c) of the MnO$_2$ anodic layers formed on the surface of the Pb/Pb-MnO$_2$ sample in 72-hour anodic polarization in solution of 3 g/L Mn(II) at 500 A/m$^2$. 
9.6.3.1 Current distribution

As was shown in the previous chapter, the anodic current density has a determining effect on the properties of the deposited MnO₂ layer. It is well known that the deposition of the non-uniform MnO₂ coating is promoted at higher current densities [205, 207]. According to the results presented in section 8.4, polarization at a lower current density results in the deposition of a more uniform and denser deposited MnO₂ layer. Incorporation of oxygen bubbles at high current density inhibits homogenous deposition of MnO₂ layer [207]. Therefore, the MnO₂ layer can deposit uniformly when the current density is lower or the OER proceeds at a lower rate.

According to the galvanostatic polarization results, the MnO₂ layers on the Pb-MnO₂ and PbAg anodes were different even at the same current density. Moreover, in spite of the higher current density of the Pb-MnO₂ anode during the potentiostatic polarization, the MnO₂ layer deposited on this anode was denser and more uniform than the layer deposited on the PbAg (Figure 9-9). Although the cause for this observation was not established, a possible scenario can be suggested by considering the catalytic activity of the MnO₂ particles for OER [129].

The presence of the MnO₂ particles on the composite anode surface might affect the MnO₂ deposition by changing the current distribution. As a consequence of the better catalytic activity of MnO₂ than PbO₂ for the OER, oxygen prefers to evolve from the surface of the MnO₂ particles [129]. Therefore, the current density at other parts of the composite surface is lower than the recorded current density. The possible effects of the MnO₂ composite particles on the current distribution and oxygen evolution on the anode are schematically shown in Figure 9-17. According to this model, the current density and the OER rate would be lower on
the PbO$_2$ regions of the surface. This leads to the MnO$_2$ layer depositing uniformly on the PbO$_2$ regions of the anode, which covers most of the anode surface area.

Although this model can describe the formation of a uniform MnO$_2$ layer on the PbO$_2$ regions of the composite anode surface, it is unable to explain the formation of a uniform layer that covers the entire anode surface. According to this model, the deposition of a uniform MnO$_2$ layer on the MnO$_2$ particles of the composite anode is not very likely since the oxygen evolution rate is assumed to be higher on these sites compared to other regions of the anode surface. However, based on SEM observations, the MnO$_2$ layers covered the entire surface of the composite anodes, even the MnO$_2$ particles.

![Diagram](image)

**Figure 9-17** The schematic of the oxygen evolution and current distributions on a Pb alloy (left scheme) and the Pb-MnO$_2$ composite anode (right scheme)
9.6.3.2 Mn(III) generation and consumption rate

The MnO$_2$ composite particles might be influential on the deposition of the MnO$_2$ layer by affecting the disproportionation rate of the Mn(III) ions and providing the suitable sites for MnO$_2$ nucleation. Many studies proposed that the disproportionation of Mn(III) (reaction 2-4) causes the nucleation and formation of the MnO$_2$ layer on the lead-based anodes [123, 127, 131, 137, 138]. It was previously shown that MnO$_2$ particles have a catalytic effect on the disproportionation reaction of Mn(III) [135, 198, 226]. In addition, Fleischmann et al. [225] reported that the nucleation of the MnO$_2$ layer takes place at preferred sites. The MnO$_2$ particles on the composite anode might play the role of the preferred sites for this reaction, especially because they catalyze the disproportionation reaction of Mn(III) (reaction (2-14)) [135, 198, 226]. In other word, the MnO$_2$ particles can increase the heterogeneous nucleation of the MnO$_2$ layer on the anode surface.

Welsh [224] found that the properties of the deposited MnO$_2$ layer depend on the ratio of the Mn(III) generation rate to its consumption rate. As was reported, when this ratio is lower, a dense MnO$_2$ layer is more likely to deposit. Catalytic activity of the MnO$_2$ particles on the disproportionation reaction of Mn(III) can cause this reaction to proceed faster on the composite anode. This suggests that the consumption rate of the Mn(III) ions at the initial stages of the polarization on the surface of the composite anode is likely to be higher than that on the PbAg anode. Therefore, in the presence of the MnO$_2$ particles on the composite anode, the ratio of Mn(III) generation/Mn(III) consumption is expected to be lower, which contributes to the deposition of a uniform MnO$_2$ layer.

To compare the Mn(III) generation rate on the anodes, the Pb-MnO$_2$ and PbAg samples were polarized at 1.9 V$_{Ag/AgCl}$ in the electrolyte containing 3 g/L Mn(II) for 24 hours. During the polarization time, solution samples were taken and titrated to measure the concentration of
the Mn(III) in the electrolyte as well as the MnO₂ cell mud. The titration results were utilized to calculate the Mn(II) oxidation current, which is equal to that of the Mn(III) generation.

The concentration of the oxidized Mn(II) and the calculated Mn(II) oxidation current on the PbAg and Pb-MnO₂ anodes are shown in Figure 9-18. These results indicate that the manganese oxidation rate on the Pb-MnO₂ was significantly lower than that on the PbAg anode. This reveals that the Mn(III) generation rate on the Pb-MnO₂ anode was lower.

Considering the faster Mn(III) disproportionation and lower Mn(III) generation rate on the composite anode, the ratio of “Mn(III) generation rate/Mn(III) consumption rate” is smaller on the Pb-MnO₂ anode, which contributes to the deposition of a uniform and adherent MnO₂ layer.

Now, the question is “why was the oxidation of manganese on the composite anode slower than that on the PbAg anode?” To determine the reason of the slower Mn(III) generation on the composite anode, the sources of the Mn(III) ions are listed as follow:

- Direct oxidation of Mn(II) ions: manganic ions can be produced by the oxidation of Mn(II) on the anode surface through reaction (8-1).

- Decomposition of permanganate ions: permanganate ions are produced on the anode surface through the oxidation of Mn(II) at high anodic potentials. These ions, however, are not stable in the electrowinning electrolytes and react with Mn(II) ions to form Mn(III) ions through reaction (2-13) [127, 131, 137, 138].

- Oxidation of Mn(II) by PbO₂: as previously mentioned, Mn(II) can reduce PbO₂ on the anode surface through reactions (7-4) and (7-5), which result in Mn(III) ions generation. This mechanism is active only at the potential range in which transition between the Pb(IV) species (i.e. PbO₂) and Pb(II) species (e.g. PbSO₄) is thermodynamically favorable [135].
Figure 9-18  Concentration of the oxidized Mn(II) (a) and Mn(II) oxidation current density (b) on the anodes during the polarization at 1.9 V in the electrolytes containing 3 g/L Mn(II)
As reported by Zhang and Park [194], permanganate is the dominant oxidation product of the manganese oxidation at the potentials more positive than 1.7 V_{Ag/AgCl}. Based on this report, the second listed method can be considered as the main source of the Mn(III) generation in the electrolyte during the zinc electrowinning process and the performed experiments. Therefore, the lower rates of the Mn(III) generation on the Pb-MnO_2 anode can be attributed to the slower generation of permanganate on this anode. The different rate of the formation of permanganate ions roots in the different properties of the deposited MnO_2 layer on the PbAg and Pb-MnO_2 anodes. It is worth pointing out that oxidation of Mn(II) to permanganate is polarized by the MnO_2 surface, while it is catalyzed on the PbO_2 surface [140, 194].

As explained, the presence of the MnO_2 composite particles on the composite anode caused the deposition of the uniform MnO_2 layer at the initial stages of the polarization, which covered the PbO_2 oxide layer on the anode. The uniform and dense MnO_2 layer deposited on the composite anode avoids further oxidation of manganese on the PbO_2 surface and inhibits the permanganate formation. However, the MnO_2 layer on the PbAg anode was porous and flaky, which allowed the solution to react on the PbO_2 surface. Consequently, manganese can be oxidized catalytically on the PbO_2 surface, resulting in the significant formation of permanganate.

To verify the proposed model for the role of the MnO_2 composite particles on the MnO_2 layer development and the Mn(II) oxidation rate, the Pb-MnO_2 composite anode was subjected to a two-step polarization experiment. The first step was polarization at 1.9 V in the Mn-free electrolyte for 2 hours. This step was carried out in order to oxidize the anode surface, resulting in a PbO_2 layer. Then, at the second step, an Mn(II) concentrated solution was added to the electrolyte to adjust the Mn(II) concentration of the entire electrolyte at 3 g/L and the
polarization continued for 2 more hours. During the second polarization step, electrolyte samples were taken and the concentration of Mn(III) ions was measured by titration.

The Mn(III) concentration and Mn(II) oxidation current on the pre-polarized composite anode are presented in Figure 9-19. The results obtained in the cases of the Pb-MnO₂ and PbAg anodes without the pre-polarization step are also shown in this figure for comparison. According to these results, the oxidation rate of Mn(II) significantly increased by the pre-polarization of the anode. The Mn(II) oxidation current on the pre-polarized composite anode was even higher than that on the PbAg anode during the first 30 minutes of polarization. To illustrate, consider the Mn(III) generation current density on the pre-polarized composite anode after 10 minutes of polarization, which was approximately 16 and 1.4 times higher than those on the Pb-MnO₂ and PbAg anodes, respectively. The initial high Mn(II) oxidation rate on the pre-polarized anode can be attributed to the PbO₂ surface layer that was formed during the pre-polarization step and can catalyze the permanganate formation [140, 194].

Although the Mn(II) ions were initially oxidized relatively fast on the pre-polarized composite anode, its rate decreased slowly over the course of polarization. This caused the Mn(III) concentration to become less than that formed during the polarization of the PbAg anode. This behavior could be attributed to the formation of an MnO₂ layer on the anode surface. According to Figure 9-19, this layer covered the surface of the pre-polarized composite anode in the first 30 minutes of the second polarization step. This MnO₂ layer inhibited the Mn(II) oxidation reaction and formation of the permanganate and Mn(III) ions. These results verify the catalytic effect of PbO₂ on the Mn(II) oxidation and the role of the MnO₂ composite particles on the deposition of the uniform MnO₂ layer and, consequently, the Mn(II) oxidation rate.
Figure 9-19 Measured concentration of Mn(III) (a) and Mn(III) generation current density (b) on the anodes during polarization at 1.9 V in the electrolytes containing 3 g/L Mn(II)
9.7 Structure of the anode layers

The X-ray diffraction spectra of the 72-hour polarized PbAg and Pb-MnO\textsubscript{2} anodes in Mn-free and Mn-containing electrolytes are presented in Figure 9-20. This figure also shows the XRD characteristic peaks of Pb, PbSO\textsubscript{4}, and PbO\textsubscript{2} phases. The XRD spectra of the anodes reveal that all the anodic layers were mainly composed of PbSO\textsubscript{4} and PbO\textsubscript{2} phases.

Comparing the XRD diffraction patterns of Figure 9-20(a) and (b) reveals that Mn(II) modified the structure of the anodic layer of the PbAg anode. The intensity of the PbO\textsubscript{2} peaks decreased when Mn(II) was added. This shows that Mn(II) ions polarize PbO\textsubscript{2} formation, which was shown previously using the cyclic voltammetry and potentiostatic polarization studies. As previously mentioned, a portion of current is used to oxidize Mn(II) on the anodes’ surface in the presence of Mn(II) ions. Moreover, the deposited MnO\textsubscript{2} layer on the anode protects the anodes against further oxidation reactions by decreasing the diffusion rate of the oxygen species from the oxygen evolution sites to the lead oxide layer. Therefore, the oxidation rate of lead on the anodes’ surface is lower in the Mn-containing electrolyte.

A lower Pb peak in the XRD pattern of Figure 9-20(a) than that in Figure 9-20(b) may indicate that the anodic layer deposited in the presence of Mn(II) was either less compact or thinner.

Comparing the XRD patterns in Figure 9-20(c) and (d) reveals that the effects of Mn(II) on the phases of the corrosion product on the Pb-MnO\textsubscript{2} anode was more significant than those on the PbAg anode. These changes can be attributed to the even, dense, and nicely adhered MnO\textsubscript{2} layer deposited on the Pb-MnO\textsubscript{2} anode. This layer can separate the anodes’ surface from the electrolyte and prevent further oxidation of lead. This can also be observed through the comparison of Pb peaks in the spectra. The higher intensity of this peak in the XRD pattern of Figure 9-20(d) demonstrates lower thickness of the corrosion product layer formed in the presence of Mn(II).
Figure 9-20 XRD patterns of the anodes after 72-hour anodic polarization at 500 A/m² and 37°C in addition to characteristic peaks of Pb, PbSO₄, and PbO₂. (a) PbAg in 0 g/L Mn, (b) PbAg in 1.5 g/L Mn, (c) Pb-MnO₂ in 0 g/L Mn, and (d) Pb-MnO₂ in 1.5 g/L Mn.
9.8 Corrosion and lead dissolution rate

In the presence of the manganese ions in the electrolyte, weight loss measurement could not be used to compare the corrosion resistance of the anodes. The MnO$_2$ layer and its removal by either mechanical or chemical methods can cause error on the weight loss results. Therefore, the concentrations of the dissolved lead during the GS polarization were measured as an indicator of the corrosion resistance of the anodes. The Pb-MnO$_2$ and PbAg anodes were polarized at a constant current of 500 A/m$^2$ in the sulfuric acid electrolyte containing different Mn(II) concentrations. The electrolytes were slowly agitated during the polarization using a 40 mm magnet bar at 60 rpm. The solution samples were taken from each of the electrolytes at 24-hour intervals and up to 72 hours. Three samples of each solution were analyzed by Inductively Coupled Plasma (ICP) to measure the lead concentrations.

Variation of the concentrations of lead during the 72-hour polarization of the PbAg and Pb-MnO$_2$ anodes in different solutions are shown in Figure 9-21 and Figure 9-22, respectively. As these figures show, regardless of the type of anode, the rates of lead dissolution in the Mn-containing electrolytes were less than that in the Mn-free electrolyte. This observation demonstrates the protection property of the deposited MnO$_2$ layer. Moreover, the oxidation of manganese that takes place on the anodes in the presence of Mn(II) ions might decrease the contribution of lead in the anodic reactions.

The positive effect of the MnO$_2$ layer on the dissolution of the PbAg anode increased with Mn(II) concentration in the electrolyte (Figure 9-21). For instance, the concentration of lead after 48 hours polarization decreased by approximately 40 and 70% with the addition of 0.5 and 3 g/L Mn(II), respectively. According to the morphological study (Figure 9-1), the MnO$_2$ layer deposited on the PbAg anode at the higher Mn(II) concentrations was more stable, which can provide a higher level of protection.
Concentration of lead in the electrolyte during anodic polarization of the PbAg anode at 500 A/m² in the electrolyte containing different Mn(II) concentrations.

Concentration of lead in the electrolyte during anodic polarization of the Pb-MnO₂ anode at 500 A/m² in the electrolyte containing different Mn(II) concentrations.
The lower lead dissolution rate in the presence of manganese ions was also observed in the results of the polarized Pb-MnO₂ composite anode.

The SEM observations reveal that a thicker MnO₂ layer formed on the Pb-MnO₂ anode in the solutions of higher Mn(II) concentration. The thicker layer is expected to be more protective. However, the dissolution rate of lead from the Pb-MnO₂ composite anode did not decrease directly with the Mn(II) concentrations (Figure 9-22). This could be due to the higher operating potential of the anode in the presence of higher Mn(II) concentration (Figure 9-6). Comparing the results in Figure 9-21 and Figure 9-22, it can be seen that the Pb-MnO₂ had higher corrosion resistance than the PbAg anode in similar operating conditions.

9.9 Manganese consumption rate

The presence of manganese ions in the electrowinning electrolyte is uninvited when Dimensionally-Stable Anodes (DSA) are used since the deposited MnO₂ layer can block the electroactive oxide layer. However, they need to present at a minimum concentration in the zinc electrowinning electrolyte when the lead-based anodes are in service. The manganese ions are necessary to promote the formation of the MnO₂ protective layer on the anode surface and decrease the concentration of dissolved lead and, thus, the lead-contamination content in the final zinc product [16, 17]. Manganese ions can also hinder the evolution of chlorine gas, which is hazardous and corrosive [127].

The concentration of manganese in the zinc electrowinning electrolyte is usually monitored during the process to make sure the electrolyte contains the minimum level of manganese ions. When the Mn(II) concentration gets low, operators increase the Mn(II) concentration through the addition of manganese flakes or MnO₂ particles.
Formation of the MnO₂ anodic layer and precipitation of MnO₂ sludge in the electrolyte (cell mud) are the only sources of manganese consumption. Since the rate of MnO₂ sludge formation was shown to be different when different anodes (Pb-MnO₂ and PbAg) were examined, the consumption rate of manganese is anticipated to be dependent on the type of anode material. The electrolyte samples after 72-hour polarizations of the Pb-MnO₂ and PbAg anodes at 500 A/m² in the Mn-containing electrolytes were utilized to compare the manganese consumption during polarization of these two anodes. The electrolyte samples were filtered using 0.4μm PTFE syringe filter and their Mn(II) concentrations were measured by the Atomic Absorption Spectroscopy (AAS) technique.

Figure 9-23 reports the manganese consumption rate on the Pb-MnO₂ and PbAg in the electrolytes containing different Mn(II) concentrations. This indicates that the Mn(II) consumption rate was higher when the anodes were polarized in solution of higher Mn(II) concentrations. Regardless of the Mn(II) initial concentrations, the Mn(II) ions consumed at higher rates when the PbAg anode was polarized. For instance, in the solution of 3 g/L Mn(II), the Mn(II) consumption rate in the case of the polarized PbAg anode was 25 times higher than that in the solution of the composite anode.

The Mn(II) consumption rates on the PbAg anode were higher than those reported in literature [130, 134, 139, 205]. This difference is due to the different history of the investigated anodes. Other studies investigated the Mn(II) consumption on the aged PbAg anodes, which had been operated for a long time (≥1 year). Anodes newly introduced to service produce a large amount of MnO₂ cell mud before the stable anodic MnO₂ layer is established [130]. The developed MnO₂ layer on the aged anodes inhibits the Mn(II) consumption.
The slower Mn(II) consumption in the case of the Pb-MnO₂ anode can be attributed to the development of the stable MnO₂ layer. Although the surface of the composite anode was ground and freshly subjected to the polarization, the measured Mn(II) consumption rates (4-5 mg/cm².day) were less than those of the aged PbAg anodes reported by Rodrigues and Meyer [130], Rodrigues et al. [139], and Clarke et al. [134] (6.5-11.5 mg/cm².day). It should be noted that the Mn(II) consumption rate reported by Rodrigues and Meyer [130] was measured based on an overall manganese balance for the Zincor cell house in South Africa. This cell house operates at a higher current density (550 A/m² average) and higher manganese concentration (7–13 g/L) than those used in this study. The Mn(II) consumption rate on the Pb-MnO₂ was also significantly less that the value reported by Ault and Bratt (37.4 mg/cm².day) [205]. The Mn(II) consumption results demonstrate that Pb-MnO₂ anodes can newly introduce in the service without being concerned about the drop in the Mn(II) concentration.

Figure 9-23 The manganese consumption rate during 72-hour polarization at 500 A/m² in the electrolytes containing different Mn(II) concentrations
It is worth noting that the Mn(II) ions at high concentrations increase the electrical resistance of the electrolyte, which causes an increase in the electrowinning energy consumption [18]. Therefore, Mn(II) concentration needs to be adjusted to prevent it from both dramatically increasing and decreasing.

### 9.10 Potentiostatic studies

In order to study the effect of manganese ions on the oxidation of the Pb-MnO₂ composite anode at different potentials, this sample was subjected to polarization at the constant potentials of 1.8 and 1.9 V in two electrolytes of the sulfuric acid with and without Mn(II) ions. The electrolyte of 3 g/L Mn(II) was used to examine the oxidation of the anode in the presence of manganese. To keep the electrolyte composition uniform during the experiment, the electrolyte was stirred slowly at 60 rpm using a 40 mm magnet bar. The polarization proceeded for periods of 10, 20, 30, and 40 hours. The potentiostatic polarizations were followed by a cathodic LSV. The potential scan was carried out from the polarization potential in the negative direction at a scan rate of 5 mV/s.

The variation of the anodic current during the first 10 hours of the polarizations at different potentials and Mn(II) concentrations are shown in Figure 9-24. As expected, the anodic currents initially increased with the potentials and addition of manganese into the electrolyte. With prolonged polarization, however, the potential of the anode in the Mn-containing electrolyte decreased gradually. As explained in section 9.3, this variation in the anodic current could be attributed to the deposition of the uniform and dense MnO₂ layer on the composite anode.

Figure 9-25 and Figure 9-26 show the voltammograms of the Pb-MnO₂ anode after polarization at 1.8 and 1.9 V in the Mn-free electrolyte, respectively. Based on the Pourbaix
diagram of lead (Figure 2-3), PbO$_2$ is the stable phase of lead at potentials of 1.8 and 1.9 V. However, it would be wrong to assume that this is the only existent phase in the oxide layer that is formed at this potential range. In fact, the corrosion layers on these samples contain Pb(II)-compounds in addition to the PbO$_2$ phase. This could be verified by the XRD results reported in previous sections.

The anodic peak that appeared at 1.3-1.4 V represents the reduction of PbO$_2$ to PbSO$_4$. This peak was followed by a small anodic peak in the voltammograms obtained after the polarization at 1.8 V (Figure 9-25(a)). As previously mentioned, this peak resulted from the oxidation of Pb, which is exposed to the electrolyte as a result of the crack formations in the anodic layer [152]. The absence of this peak in the voltammograms of Figure 9-26(a) reveals a thicker oxide layer formed at higher potentials. This can also be observed by comparing the PbO$_2$ reduction peaks in the voltammograms of Figure 9-25 and Figure 9-26.

![Figure 9-24 Anodic current of the Pb-MnO$_2$ composite anode during polarizations at 1.8 and 1.9 V in Mn-free and Mn-containing electrolytes](image-url)
Figure 9-25  Cathodic potentiodynamic voltammograms of the Pb-MnO₂ anode after polarization at 1.8 V in the Mn-free electrolyte (initial potential: 1.8 V, scan rate: 5 mV/s)

Figure 9-26  Cathodic potentiodynamic voltammograms of the Pb-MnO₂ anode after polarization at 1.9 V in the Mn-free electrolyte (initial potential: 1.9 V, scan rate: 5 mV/s)
Comparing the PbO₂ reduction peaks reveals that the oxidation of the anode proceeded faster at the higher anodic potential. This can be attributed to the higher overpotential for this reaction and also the higher rate of oxygen evolution reaction.

The anodic peaks that appeared at the negative potentials of the voltammograms can be attributed to the reduction of Pb(II) compounds. The reduction reactions of PbO and basic sulfates are shown in reactions (9-7) to (9-9). The equilibrium potentials of these reactions were calculated assuming pH=0 in the acidic solution and \( a_{SO4^{2-}} = C_{SO4^{2-}} = 1.83 \text{M} \). The standard reduction potentials of PbO, basic sulfate (xPbO.PbSO₄), and PbSO₄ suggest that the reduction of PbO and basic sulfate is the first stage of the reduction followed by the reduction of PbSO₄ [196]. Therefore, the first small cathodic peak in Figure 9-25(a) represents the reduction of PbO and basic lead sulfate and the second peak corresponds to the reduction of PbSO₄.

\[
PbO + 2e^- + 2H^+ \rightarrow Pb + 2H_2O \quad E = 0.049 \text{ V}_{\text{Ag/AgCl}} \quad (9-7)
\]

\[
3PbO.PbSO_4.H_2O + 8e^- + 8H^+ \rightarrow 4Pb + 4H_2O + H_2SO_4 \quad E = -0.173 \text{ V}_{\text{Ag/AgCl}} \quad (9-8)
\]

\[
PbO.PbSO_4 + 4e^- + 4H^+ \rightarrow 2Pb + H_2O + H_2SO_4 \quad E = -0.321 \text{ V}_{\text{Ag/AgCl}} \quad (9-9)
\]

The Pb-MnO₂ was subjected to the same potentiostatic-LSV experiments in the solution containing 3 g/L Mn(II). The cathodic voltammograms of the Pb-MnO₂ anode obtained after polarization at 1.8 and 1.9 V in this solution are reported in Figure 9-27 and Figure 9-28, respectively. The effects of the polarization time and potential on the voltammograms of the Pb-MnO₂ sample in the Mn-containing electrolyte were similar to what was observed in the absence of manganese.
Figure 9-27 Cathodic potentiodynamic voltammograms of the Pb-MnO₂ anode after polarization at 1.8 V in the Mn-containing electrolyte (initial potential: 1.8 V, scan rate: 5 mV/s)

Figure 9-28 Cathodic potentiodynamic voltammograms of the Pb-MnO₂ anode after polarization at 1.9 V in the Mn-containing electrolyte (initial potential: 1.9 V, scan rate: 5 mV/s)
These observations include:

- Larger PbO₂ and Pb(II)-compound reduction peaks at higher anodic potential,
- Increase in the size of the Pb(II)-compounds and PbO₂ reduction peaks with polarization time,
- Presence of the lead oxidation anodic peak next to the PbO₂ reduction peak (E=1.4 V) in the voltammograms of the sample polarized at 1.8 V, which disappeared as the polarization potential increased.

The main difference between the voltammograms obtained in the Mn-containing electrolyte with those obtained in the Mn-free electrolyte was the presence of the MnO₂ reduction peak at a potential range of 0.9-1.2 V.

These results show that the PbO₂ reduction peaks that appeared in the Mn-containing electrolyte were smaller compared to those obtained in the absence of Mn(II) ions at the same polarization potential and time. This verifies that the amount of PbO₂ in the anodic layer decreased in the presence of Mn(II) ions in the electrolyte. This resulted from the protection property of the MnO₂ deposited layer.

The reduction peaks of PbO and PbSO₄ were changed in the presence of Mn(II) ions. The potential of these peaks in the Mn-free electrolyte did not noticeably change with the polarization time. However, as Figure 9-27(b) and Figure 9-28(b) show, the Pb(II)-compound reduction peak shifted to more negative potentials with the prolonged polarization.

According to reactions (9-7)-(9-9), protons need to diffuse from the electrolyte to react with the corrosion products. This diffusion can be slowed down by the MnO₂ layer deposited on the anode surface. This suggested that the reductions of the Pb(II)-compounds may proceed slower in the presence of the MnO₂ layer, contributing to wider reduction peaks at more negative potentials.
The charge associated with the reduction of PbO₂ was calculated from the integration of the area under its reduction peak at 1.3-1.4 V. Simon et al. [1975] showed that a small amount of PbO₂ is usually found within the lead sulfate after the discharge process. However, it can be assumed that this PbO₂ amount is negligible compared to the amount of PbO₂ reduced at this stage of potential scan. Furthermore, it was assumed that the reduction of the PbO₂ layer proceeds from the layer/solution interface and does not come to a stop by the reduction products. Therefore, the measured charge associated with the PbO₂ reduction peak can be a reasonable estimate of the amount of PbO₂ formed during the previous polarization to investigate the role of manganese in this regard.

Due to the presence of the large Pb oxidation peak next to the PbO₂ reduction peaks in Figure 9-27(a), the PbO₂ reduction charge of the sample polarized at 1.8 V cannot be calculated accurately. Therefore, the effect of Mn(II) ions on the anode oxidation at this potential may not be studied quantitatively.

The variations of the PbO₂ reduction charge of the sample polarized at 1.9 V with the polarization time in the absence and presence of manganese ions are presented in Figure 9-29. This figure reveals the growth of the PbO₂ layer on the composite sample in the course of the polarization and regarding effect of manganese ions. The PbO₂ reduction charge variation suggests that, regardless of the manganese concentration, the amount of PbO₂ on the anode surface increased linearly with polarization time in the investigated polarization period. The slopes of the PbO₂ reduction charge curves, however, were not similar. The amount of PbO₂ on the composite sample increases at a higher rate in the Mn-free electrolyte compared to that in the presence of manganese ions. This difference is due to the protective property and the MnO₂ layer deposited on the composite sample during the anodic polarization.
Figure 9.29  Variation of the charges associated with the PbO₂ reduction peak with the polarization time at 1.9 V in the Mn-free and Mn-containing electrolytes.
9.11 Long-term galvanostatic polarization

Cylindrical samples of the PbAg and Pb-MnO₂ anodes with a surface area of 2 cm² were prepared. These samples were connected to a plastic isolated copper wire and then cast in epoxy resin. The resistance between the copper wire head and the surface of the samples was measured by a low-resistance voltmeter to make sure the samples are electrically connected to the wires. The mounted samples were ground up to 600 SiC-sand papers. These samples were polarized at the same current density in the 180 g/L sulfuric acid electrolyte containing 3 g/L Mn(II) and 250 mg/L chloride. No control was applied to adjust on the Mn(II) concentration of the electrolyte at a constant level during the experiment. The temperature of the cells was maintained at 37°C through putting the cells in a water bath. No agitation was applied in the electrolyte during this experiment. Although the current was set to apply a constant current density of 500 A/m², the current density varied in the range of 500-540 A/m² during the polarization. The potential of the samples was measured every 2-3 days using an Ag/AgCl reference electrode. The current density applied to the anodes was measured and recorded at the same time. This experiment was performed for 33 days.

9.11.1 Anode potential

Variations of anode potential during polarization are presented in Figure 9-30. The recorded current densities were also shown in this figure. As can be seen, the potential of the anodes varied during the polarization. These variations are similar to that of the applied current density. Therefore, the fluctuation observed in the anode potential can be mainly due to variation of the applied current density.

After the first day of polarization, the potential of the PbAg anode was lower than that of the Pb-MnO₂, which was expected from the results of the 72-hour polarization. During the
rest of the polarization, however, the Pb-MnO₂ anode showed lower anodic potential than the PbAg anode did. Thus, the Pb-MnO₂ has better catalytic activity for oxygen evolution than the PbAg in the long-term polarization, even in the Mn-containing electrolyte. This behavior can be due to the porous MnO₂ layer deposited on the PbAg anode. This layer can trap the oxygen bubbles and block the anode surface, contributing to high anodic potential. Note: the difference between the results of Figure 9-30 and those that were presented in section 9.3 could be attributed to the different experimental conditions, including the sample size, solution volume, accuracy of the applied current, electrolyte agitation, and the potential measurement intervals.

Figure 9-30 Variations of the anode potentials and the applied current density during anodic polarization
9.11.2 Morphological study of the anode surface

After 33 days of polarization, the samples were taken out of the electrolytes, rinsed, and dried. During the washing of the sample, the entire porous MnO₂ layer on the PbAg anode was removed from the sample surface. Adhesion of the MnO₂ layer on the composite anode was relatively stronger and did not flake off the anode surface. The morphologies of the 33-day polarized Pb-MnO₂ and PbAg anodes are shown in Figure 9-31 at different magnifications.

The morphological study verifies that no MnO₂ layer remained on the PbAg anode surface after washing the anodes. The surface of this anode was also very rough. These results also demonstrate that one month is not long enough to develop an adherent layer of MnO₂ on the smooth PbAg anode. The surface of the Pb-MnO₂ anode, on the other hand, was covered by a uniform layer of MnO₂, like what was observed after the 72-hour polarization. The SEM picture of the tilted Pb-MnO₂ sample (Figure 9-31(e)) reaffirms that the MnO₂ layer deposited on the composite anode consists of one dense and uniform layer. The long-time polarization did not cause different properties of the MnO₂ layer on the composite anode, indicating the high stability of the MnO₂ layer on this anode.

The polarized samples were cast in another epoxy resin and cut to prepare the sample for cross section studies. The cross section of the samples were metallographically prepared and observed using the SEM. A semi-quantitative composition analysis of the anodic layers was also performed by EDX linear scan.
Figure 9.31 SEM morphologies of the PbAg (a-b) and Pb-MnO$_2$ anode (c-e) after 33-day polarization in the Mn-containing electrolyte at 500 A/m$^2$. 
Figure 9-32 presents the cross section of the Pb-MnO$_2$ and PbAg anodes after 33-day polarization. The corrosion layer formed on the PbAg anode was very porous and cannot provide the anode with a high level of protection. A small evidence of severe general corrosion attack was observed in the cross section of the composite anode. Figure 9-32(b) shows a dense and uniform layer of MnO$_2$ deposited on the surface of the composite anode.

Elemental composition profiles across the anodic layers of the 33-day polarized Pb-MnO$_2$ and PbAg anodes are shown in Figure 9-33. As evidenced by the EDX results, the outer layer on the composite anode mainly contains Mn and O. The Mn signals decreased gradually with distance from the surface after 15 μm, where the lead signal strengthened. After this point, the lead weight percentage was higher than that of manganese.

No Mn signal was detected in the linear EDX analysis of the cross section of the PbAg anode, Figure 9-33(b). The lead and oxygen signals respectively increased and decreased at the depth of 18μm from the anode surface. This point may determine the thickness of the corrosion layer on the PbAg anode. Due to the qualitative nature of the EDX results, the variation of the Pb-containing phases along the cross section of the corrosion layer could not be determined.

Although a significant general corrosion attack was not observed on the composite anode, some evidence of localized corrosion were found in the cross section of the composite anode. Figure 9-34 shows the formation of a crack on the anode surface that penetrated through the anode. This can represent the intergranular corrosion attack. The crack likely proceeded along the boundaries that were created during the anode fabrication process between the lead particles. Although the intergranular corrosion cracks can initiate at any particle/particle boundary on the anode surface, they mainly start where the MnO$_2$ layer cracked.
Figure 9-32 Cross section of the Pb-MnO₂ (a) and PbAg (b) anodes after 33-day polarization in the Mn-containing electrolyte at 500 A/m².
Figure 9-33  Element composition profiles (EDX linear scan) across the anodic layers on the 33-day polarized Pb-MnO$_2$ (a) and PbAg (b) anodes
Due to the low conductivity of the MnO₂ layer, oxygen evolution reaction prefers to proceed at the PbO₂ region of the anode surface if the MnO₂ layer cracks or flakes off the surface. The significant localized current density at this spot can promote the localized electrochemical corrosion attack.

Moreover, most of the corrosion products of lead occupy more volume than lead. For instance, oxidation of lead to PbO, PbSO₄, and PbO₂ caused volume expansions of approximately 28, 160, and 40% per mole of oxidized lead. Therefore, the oxidation of lead and formation of corrosion products in the cracks would contribute to substantial stress on the surrounding lead particles. The shrinkage that resulted from the oxidation of PbSO₄ to PbO₂
could cause penetration of the electrolyte in the crack, resulting in further oxidations taking place in the cracks.

Most of the oxidation reactions of lead compounds produce protons. Therefore, the local pH of the electrolyte in the cracks significantly decrease and provides a more aggressive environment in the cracks, contributing to a faster corrosion and cracks propagation. These observations demonstrate that the composite anode fabricated by the cold press technique is prone to failure in long-term polarizations.

9.11.3 Lead dissolution and manganese consumption

During the polarization, 25mL electrolyte samples were taken to measure the concentration of lead and manganese in the electrolyte. After taking the electrolyte samples, the same volume of fresh electrolyte was added to each cell to keep the electrolyte volume constant. The electrolytes of the cells were refreshed after the initial 3 days. Due to the high rate of MnO$_2$ sludge formation in the cell of the PbAg polarization, the electrolyte of this cell was replaced once more on 11$^{th}$ day of the experiment. The electrolyte samples were analyzed by the ICP and AAS techniques to measure the concentrations of lead and manganese ions in the electrolyte, respectively.

Figure 9-35 compares the concentration of lead in the electrolytes of the Pb-MnO$_2$ and PbAg polarization during the polarization. During the first 3 days of the polarization, the lead concentrations in both electrolytes were close. However, the significant difference in the lead concentrations began after 5 days and increased with prolonged polarization. These data reveal that the dissolution of lead from the PbAg was faster than from the Pb-MnO$_2$ anode, indicating better corrosion resistance of the latter one. The lower dissolution rate of lead in the case of the composite anode can be attributed to two separate reasons: first, the lower anodic potential
of the Pb-MnO₂ anode that caused less driving force for the oxidation of lead; second, the uniform and compact MnO₂ layer deposited on the composite anode. The difference between the results of Figure 9-35 and those presented in section 9.8 resulted from the difference in the conditions of the performed experiments such as the sample size, solution volume, accuracy of the applied current density, the solution composition, and the electrolyte agitation.

The measured concentrations of the manganese in the electrolyte during polarization are shown in Figure 9-36. As anticipated, the manganese concentration significantly dropped during the first days of the polarization of the PbAg anode. The appearance of the cells and samples after the 33-day polarization are presented in Appendix D, which shows a significant amount of MnO₂ in the electrolyte and on the inert surfaces, like the epoxy surrounding the sample in the cell of the PbAg polarization. The manganese consumption rate decreased slightly after the electrolyte was replaced. The MnO₂ layer that deposited on the anode could partially cover the anode surface and inhibit oxidation of the Mn(II) to permanganate and MnO₂. However, manganese concentration significantly dropped in the last week of polarization, which could result from the detachment of the MnO₂ layer at this stage.
Figure 9-35  Variations of dissolved lead concentrations in the electrolyte during anodic polarization

Figure 9-36  Variations of manganese concentrations in the electrolyte during the anodic polarization of the Pb-MnO$_2$ and PbAg anodes
According to Figure 9-36, the Mn(II) concentration in the electrolyte did not decrease significantly during the polarization of the composite anode. A very low rate of manganese consumption was expected from the results of the 72-hour polarization and the appearance of the electrolyte after the 33-day polarization (Appendix D). Surprisingly, the measured manganese concentration increased slightly with the concentrations higher than the initial Mn(II) concentration in the course of the polarization. This observation could be due to the slow evaporation of the electrolyte during polarization, which caused the concentration of species in the electrolyte to slightly increase.

Based on the AAS results and visual observations, the cleaning of the anodes and the cell, which is periodically performed in a zinc cell house, can be done either in a shorter period of time or with less frequency when the Pb-MnO₂ composite anodes are used.

9.12 Summary

In this chapter, the anodic performance of the Pb-MnO₂ composite anodes in the Mn-containing H₂SO₄ solution electrolytes under the electrowinning operating conditions were investigated and compared to those of the PbAg conventional anode. The properties of the deposited MnO₂ layers and corrosion product layers formed on the anodes were also studied. Moreover, the possible reasons for the different properties of the MnO₂ layers deposited on the anodes were examined. The potentiostatic studies were conducted in order to investigate the effect of potential and manganese on the oxidation of the composite anode. The summary of the results presented in this chapter is as follows:
- The Mn(II) ions catalyze the oxygen evolution reaction on both types of fresh anodes. Formation and growth of the MnO\textsubscript{2} anodic layer, depending on its properties, can reverse this effect and increase the anodic potential.

- The Pb-MnO\textsubscript{2} anode generates a very uniform, dense, and strongly-adherent anodic MnO\textsubscript{2} layer, which can cause higher charge transfer resistance and/or less surface area for the OER to occur. On the other hand, MnO\textsubscript{2} layers deposited on the smooth PbAg and PbCa anodes were flaky, porous, and loosely adherent.

- Polarization of the PbAg anode in the Mn-containing electrolytes caused the formation of a significant amount of MnO\textsubscript{2} precipitations in the electrolyte and on the inert surfaces. However, no MnO\textsubscript{2} precipitation other than on the anode surface was observed when the Pb-MnO\textsubscript{2} anodes were polarized.

- Formation of the uniform MnO\textsubscript{2} layers on the composite anode and no cell mud in the electrolyte were attributed to the presence of the MnO\textsubscript{2} composite particles embedded in the composite anode. These particles catalyze nucleation and the deposition of the uniform MnO\textsubscript{2} layer which, in turn, inhibits generation of permanganate and Mn(III) ions on the anode surface.

- Concentration of dissolved lead in the solution decreased in the presence of the Mn(II) ions due to the deposition of MnO\textsubscript{2} anodic layers. The uniform and dense MnO\textsubscript{2} layer on the Pb-MnO\textsubscript{2} composite anode significantly prevents the oxidation of lead and provides a high level of protection for the anode.

- The MnO\textsubscript{2} layer on the composite anode was stable during 33-day polarization and prevents extensive oxidation of the anode. This period was not enough for the PbAg anode to establish a stable MnO\textsubscript{2} layer. A high rate of MnO\textsubscript{2} mud formation caused drops in the
Mn(II) concentration in the electrolyte, necessitating the frequent adjusting of the Mn(II) ions in the electrolyte. Adjusting the Mn(II) to address its concentration drop would not be a serious concern when the Pb-MnO$_2$ composite anode is used. According to the MnO$_2$ mud formation rate, the cleaning of the anodes and the cell, which is periodically performed in zinc cell houses, can be done either in a shorter period of time or with less frequency when the Pb-MnO$_2$ composite anodes are used. This can lead to higher production efficiency of the electrowinning.
Chapter 10

Conclusions and recommendations

10.1 Conclusions

The chemical–electrochemical experiments and analysis presented in this dissertation resulted in the following conclusions:

- The oxidizing effect of the MnO$_2$ particles changes the composition and charge transfer resistance of the corrosion layer formed on the anode at open circuit potential. At OCP, the composite anode formed a PbO/PbSO$_4$ layer while the layer that formed on the PbAg anode composed of PbSO$_4$.

- The addition of MnO$_2$ particles to the Pb anode catalyzed the oxygen evolution reaction and decreased the OER overpotential. The Pb-MnO$_2$ composite anodes (regardless of their MnO$_2$ content) showed lower operating potential than the conventional PbAg and PbSnCa anodes under the zinc electrowinning operating conditions. The presence of MnO$_2$ composite particles can decrease the anode potential by 150 mV compared to the conventional EW anodes. Using the Pb–MnO$_2$ anode can decrease the energy consumption of the electrowinning process in the Mn-free electrolytes by up to 5%. The electrocatalytic capacity of the composite anode is enhanced with its MnO$_2$ content, however, the mechanical stability of the anodes fabricated by the cold-press technique decreases at high MnO$_2$ contents (higher than 15 wt.%).
The Pb-MnO$_2$ composite anodes had better corrosion resistance under the electrowinning conditions in the Mn-free sulfuric acid electrolyte in comparison with the conventional PbAg anodes. This behavior was attributed to the more compact anodic layers formed on the composite anodes, which provides higher levels of protection. The composite anode containing 10 wt.% MnO$_2$ showed the optimum corrosion performances among the investigated composite samples.

The manganese ions in the electrolyte catalyzed the oxygen evolution reaction on the fresh lead-based anodes. This effect was more significant on the fresh composite anode compared to the lead alloys. Development of the MnO$_2$ anodic layer, depending on its properties, can reverse this effect and increase the anodic potential. The charge transfer resistance and the density of active sites for oxygen evolution can respectively increase and decrease by the electrodeposition of the MnO$_2$ layer. This influence depends strongly on the properties of the MnO$_2$ layer which, in turn, are determined by the type of the anode materials and manganese concentration.

The deposition of the MnO$_2$ layer on the lead-based anodes was influenced by the MnO$_2$ composite particles in the electrode. The Pb-MnO$_2$ anode generated a very uniform, dense, and strongly-adherent anodic MnO$_2$ layer, while the layers deposited on the lead-based alloys are flaky, porous, and loosely adhered. The quickly-formed MnO$_2$ layer on the composite anode was stable during the 33-day polarization, however, this period is not enough for the PbAg anode to establish a stable MnO$_2$ layer.

Unlike the conventional lead alloys, the application of the Pb-MnO$_2$ composite anode prevents the formation of the cell mud and Mn(II) concentration drop in the electrolyte. The cleaning of the anodes and the cell can be done with less frequency when the Pb-
MnO\textsubscript{2} composite anodes are used, which can contribute to higher electrowinning production efficiency.

- The Mn(II) oxidation and formation of manganic and permanganate ions are inhibited on the Pb-MnO\textsubscript{2} composite anode. These reactions are independent of the Mn(II) concentrations and the anodic potential in the OER potential range on the composite anode. The Mn(II) oxidation on the PbAg anode is noticeably higher than that on the composite anode, which also increases with the Mn(II) concentration and the applied potentials. The difference in the performance of the composite anode in the Mn-containing electrolytes compared to the other anodes is attributed to the MnO\textsubscript{2} particles embedded in the composite anode. These particles catalyze nucleation and deposition of the MnO\textsubscript{2} layer through accelerating Mn(III) disproportionation, contributing to the deposition of a uniform MnO\textsubscript{2} layer which, in turn, blocks further Mn(II) oxidation, permanganate ions generation.

- Oxidation of the anodes is inhibited when Mn(II) is introduced into the electrolyte. The MnO\textsubscript{2} anodic layer acts as a diffusion barrier layer for oxygen species and decreases the oxidation and corrosion rate of the lead anode. The uniform and dense MnO\textsubscript{2} layer deposited on the Pb-MnO\textsubscript{2} composite anode significantly prevented the oxidation of lead and provided a high level of protection for the anode. Therefore, the composite anodes are anticipated to have a longer service lifetime than the conventional PbAg anode.

- Linear sweep voltammetry following the anodic polarizations can be employed to identify the properties of the MnO\textsubscript{2} deposited layer on the anodes. Appearance of the MnO\textsubscript{2} reduction peak in the cathodic voltammograms represents the deposition of the adherent MnO\textsubscript{2} layer, while porous and loosely-adhered layers do not show this peak.
10.2 Recommendations

This work formed a basis for the performance of the Pb-MnO₂ composite anodes in the zinc electrowinning application and its advantages and disadvantages in comparison with the conventional lead-based alloys. These anodes require further investigation and development to achieve successful industrial adoption. To this end, the following studies are recommended:

- Evolution of corrosive chlorine gas is inhibited by the addition of manganese ions and deposition of the MnO₂ layer. Since the properties that the MnO₂ layer deposited on the composite anode were shown to be different from those on the lead alloys, studying the chlorine evolution rate on the composite anode in the presence of chloride and manganese ions is recommended.

- The anodic performance of the Pb-MnO₂ composite anodes needs to be verified in long-term experiments under the electrowinning operating conditions in the actual electrowinning electrolyte. This is recommended to investigate the stability of the anode, the MnO₂ layer on the anodes, and the ability of the composite anode to build a similar layer when the MnO₂ layer flakes off.

- Higher anodic surface area is favourable for the oxygen evolution reaction during the electrowinning process. Thus, deposition of dense and rough surface on the anode is more beneficial than the smooth layer. Deposition of a rougher protective anodic layer can be the subject of further studies. Moreover, TEM study of the amount of microtwinning in the deposited MnO₂ layer is recommended to have a better understanding of the mechanism of the MnO₂ layer deposition.
• Powder metallurgy was utilized in this work to fabricate the composite anode. Although this technique can provide good mechanical properties for lead as a soft material, the creep resistance of these samples needs to be studied.

• Fabrication of the Pb-MnO$_2$ composite anodes by other production techniques is also recommended. The electrochemical and mechanical performances of the anodes depend on their phase and grain structure. Therefore, a different fabrication process of the composite anode can lead to its different electrochemical and mechanical properties. Due to a significant difference in density between lead and MnO$_2$, Pb-MnO$_2$ composite anodes cannot be fabricated by the traditional casting techniques. Thus, agitated continuous casting can be used to fabricate the composite anodes by the casting process. Powder rolling and powder extrusion are two techniques to fabricate solid anodes using the powder mixtures. Accumulative roll bonding (ARB) is also a new technique of fabricating composite materials. ARB is an intense plastic straining process introducing high strains in materials by rolling. The composite anode can also fabricated by applying the Pb-MnO$_2$ composite coating on different substrates using cold and thermal spray techniques.

• Using lead alloys such as PbAg and PbSnCa as a matrix for the MnO$_2$-based composite anode can provide better anodic performance and longer lifetime in the electrowinning application since these alloys have better corrosion resistance than pure lead. An investigation of these composite anodes and their anodic performance is also recommended.
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Appendices

Appendix A. Permanganate formation during cyclic voltammetry

Figure A-1 Appearances of the PbAg anode during the cyclic voltammetry polarization in the Mn-containing electrolyte, (a) first cycle at 1.9 V, backward scan, (b) fifth cycle at 2.0 V, forward scan
Appendix B. MnO$_2$ deposited layer on PbCa anode

Figure B-1 Morphology of the MnO$_2$ anodic layers formed on the surface of the PbCa anode in 72-hour anodic polarization in solution of 3 g/L Mn(II) at 500 A/m$^2$. (a) and (b) internal layer, and (C) MnO$_2$ porous layer
Appendix C. MnO$_2$ precipitations - Short-term polarizations

Figure C-1 Appearance of the Mn-containing electrolyte after 20-hour polarization of the Pb-MnO$_2$ (a) and PbAg (b) and the sample holder of the PbAg sample after 72-hour polarization (c)
Appendix D. MnO$_2$ precipitations - Long-term polarizations

Figure D-1 Appearance of cell and the sample holder after long-term polarization of the PbAg anode
Figure D-2 Appearance of cell and the sample holder after long-term polarization of the Pb-MnO₂ anode