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# Effect of MnO<sub>4</sub><sup>-</sup> and silver content on electrochemical behaviour of Pb-Ag alloy anodes during potential decay periods

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**Abstract:** The effect of  $MnO_4^-$  and silver content on electrochemical behaviour of five commercial Pb–Ag alloy anodes was studied in acid zinc sulphate electrolyte with and without  $MnO_4^-$  ions at 38 °C during potential decay periods. When the anodes were immersed into acid zinc sulphate electrolyte without  $MnO_4^-$  ions, the Pb–0.72%Ag anode entered complete passivation state in the shortest time among the five anodes, followed by anodes Pb–0.67%Ag, Pb–0.60%Ag, Pb–0.58%Ag and Pb–0.29%Ag– 0.1%Ca by measurement of open circuit potential. During immersion of the anodes,  $MnO_4^-$  ions accelerated the passivation and increased the corrosion current density of the anodes. After immersion in zinc electrolyte with  $MnO_4^-$ , the anode Pb–0.72%Ag had the best corrosion resistance, followed by anodes Pb–0.67%Ag, Pb–0.60%Ag, then the close anodes Pb–0.58%Ag and Pb–0.29%Ag– 0.1%Ca by the electrochemical impedance spectroscopy (EIS) analysis.

Key words: electrochemical behaviour; Pb-Ag anode; permanganate ion; potential decay periods; zinc sulphate electrolyte

### **1** Introduction

In zinc electrowinning, the anode materials are lead alloys. However, pure lead has high overpotential and corrosion rate in the sulphuric acidic solution [1,2]. Small amount of Ag (0.7%-1.0%) alloyed with lead decreases the oxygen overvoltage, and increases the corrosion resistance of material. A well established custom in all electrolytic zinc plants is to use Pb-Ag alloys containing 0.7%-1.0% Ag as the anode material. The resulting benefits are a longer anode life and a lower Pb content in the cathodic zinc [3]. Also, Ag changes the structure of PbO [4] and increases the ratio of  $\alpha/\beta$ -PbO<sub>2</sub> in the corrosion layer for Pb-Ag alloy [5]. In addition, the introduction of silver in the alloy accelerates the oxygen evolution and the enhancement is proportional to the Ag content [6]. However, Pb-Ag has some shortages of higher overpotential of oxygen evolution and worse conductivity. Al/Pb-PANI-WC composite inert anode prepared by double pulse electrodeposition of WC and polyanilline particles with  $Pb^{2+}$  from an original plating bath, may be a suitable anode material in place of Pb–Ag alloy in zinc electrowinning [7–9].

During the polarization, the effects of Mn<sup>2+</sup> on the corrosion rate of lead alloy have been studied by many people.  $Mn^{2+}$  ions in the electrolyte could be oxidized to MnO<sub>4</sub><sup>-</sup> [10]. NEWHAM [11] established that the corrosion rate of Pb-Ag anodes in 1.8 mol/L H<sub>2</sub>SO<sub>4</sub> solution decreases in the presence of Mn<sup>2+</sup>. It was found that the presence of  $\mathrm{Mn}^{2\scriptscriptstyle +}$  in the electrolyte caused the formation of a thin layer of MnO<sub>2</sub> on the anode. IVANOV and STEFANOV [12] found that the addition of 1.5-3 g/L to the zinc electrolyte can minimize the corrosion of lead anodes and reduce the contamination of cathodic zinc with lead [12,13]. ZHANG and HOULACHI [14] found that the addition of Mn<sup>2+</sup> from 4 to 8 g/L to the zinc electrolyte gave almost the same overpotentials and then the overpotentials increased at concentration of  $Mn^{2+}$  of 10 and 12 g/L for Pb-Ag anode. Also, the corrosion rate of Pb-Ag alloy anode decreased with the MnSO<sub>4</sub> addition.

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In addition, adding  $MnSO_4$  to the zinc electrolyte could improve the structure of zinc deposit at low concentrations but decrease the current efficiency by few percent at concentration above 10 g/L [15,16]. However, higher concentration of manganese in the electrowinning can cause a significant decrease in current efficiency [14]. Also, with a longer operation time, the formation of  $MnO_2$  may increase the corrosion of lead anode [17,18].

Most electrolytes in zinc electrowinning contain  $Mn^{2+}$  ranging from 2 to 15 g/L. When manganese ions are oxidized at the anode,  $MnO_2$  and  $MnO_4^-$  are formed. Generally, industrial zinc electrolyte contains 100 mg/L  $MnO_4^-$  [1]. It is necessary to study the anodic corrosion behavior in zinc electrolyte containing manganese ion  $(Mn^{2+})$ . In this work, 8 g/L  $Mn^{2+}$  in the form of  $MnSO_4 \cdot H_2O$  was added to the supporting electrolyte. After 5 h of electrolysis at 60 mA/cm<sup>2</sup> using a Pb-Ag anode, the solution became violet red because of the formation of permanganate ions.

In some Zn plants, there are significant periods (potential decay period) of time when the current is off, 2 h once a week and 12–16 h every 3 months which affects the stability of the anodes. However, the information of the effect of  $Mn^{2+}$  and  $MnO_4^-$  on the performance of Pb–Ag anodes during the potential decay without polarization after electrowinning is limited. In this work, the experiments of 5 h open circuit potential after electrowinning in the zinc electrolyte with permanganate ions were carried out. The purpose is to investigate the electrochemical behaviour of Pb–Ag anodes during potential decay after 5 h polarization at 60 mA/cm<sup>2</sup> by the open circuit potential measurements and electrochemical impedance spectroscopy (EIS) at the open circuit potential.

### 2 Experimental

### 2.1 Materials and sample preparation

The composition of the electrolyte used in this work was as follows:  $Zn^{2+} 60 g/L$ ;  $H_2SO_4 180 g/L$ ;  $Mn^{2+} 8 g/L$ ;  $Cl^- 250 g/L$ ; glue 3 g/L.

Zinc sulphate (ZnSO<sub>4</sub>·7H<sub>2</sub>O), manganese sulphate (MnSO<sub>4</sub>·H<sub>2</sub>O) from Sigma-Aldrich Fine Chemicals, sodium chloride and sulphuric acid from Merck KGaA were used to prepare the supporting electrolyte with double distilled water. Gelatin (glue) was product of BDH Inc. The chemicals met ACS specifications (except gelatin) and were used as received without further treatment. All concentrations of H<sub>2</sub>SO<sub>4</sub> and Zn<sup>2+</sup> stated in this paper are initial concentrations.

The anodes used in this work were made of laminated Pb-Ag and Pb-Ag-Ca alloys with surface treatment. The Anode 1 is a Pb-0.3%Ag-Ca alloy, the Anodes 2 and 3 are Pb-0.6%Ag alloy, while Anodes 4

and 5 are Pb-0.7%Ag alloys, but they have different impurities for example of Fe. Their chemical composition analyzed semi-quantitatively using X-ray fluorescence method is given in Table 1.

Table 1 Chemical composition of five Pb-Ag alloy anodes

				<u> </u>		
Anode	Chemical composition in mass fraction/%					
	Ag	Ca	Zr	Fe	Pb	
1	0.29	0.10	0.22	0.12	Bal.	
2	0.60	< 0.05	0.23	0.06	Bal.	
3	0.58	< 0.05	0.24	0.07	Bal.	
4	0.72	< 0.05	0.22	< 0.05	Bal.	
5	0.67	< 0.05	0.23	0.06	Bal.	

According to the information from the suppliers of the anodes, all of the five commercial anodes were cold-rolled. Anode 1 is a Pb-Ag-Ca alloy; Anodes 2-5 are made of Pb-Ag alloy. Anodes 4 and 5 have the same composition, but Anode 5 was treated with shot-peening method. The cathodes were made of platinum for corrosion rate measurements. The Pb-Ag alloy plates were cut into small pieces of 10 mm×10 mm×10 mm and then connected with a plastic isolated copper wire and cast in acrylic resin. The electrical contacts were made with plastic isolated copper wires and the piece was cast in acrylic resin. The exposed area surface was  $1 \text{ cm}^2$ . Before being introduced into the electrolytic cell, the working surfaces of the cathodes were ground with SiC abrasive paper (Leco Corporation) down to 600 grit, washed with double distilled water and wiped immediately with tissue paper. The working surface area was always 1 cm<sup>2</sup>. The surface preparations for the Pb-Ag anodes were divided into two kinds of situations: when the original surface (as-cast) was examined, no polishing was carried out, and the surfaces were just washed with organic solvent and distilled water; when the bulk of the anodes was examined, the original surface was removed by grinding using abrasive paper in the same manner as the surface preparation of the cathodes.

#### 2.2 Experimental setup

The electrolytic cell was a 1 L double-walled cell containing 800 mL of electrolyte heated by a flow of thermostated water in the double wall ((38±0.5) °C). The electrolyte was magnetically stirred during the experiments. The anode and cathode were mounted in a Teflon made holder and the distance between them was fixed at 2 cm. The reference electrode was mercurous sulfate electrode (MSE): Hg, Hg<sub>2</sub>SO<sub>4</sub>|sat. K<sub>2</sub>SO<sub>4</sub> (0.636 V vs SHE). A saturated K<sub>2</sub>SO<sub>4</sub> salt bridge was used to keep the reference electrode close to the anode. The experimental setup was an EG&G Princeton Applied Research 273 potentiostat/galvanostat controlled by an IBM computer. The software SoftCorr M352 was used acquisition of the polarization data. The for

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electrochemical impedance measurements at the open circuit potential were carried out using PowerSINE in Electrochemical PowerSuite of Advanced Measurement Technology, Inc. over the frequency range from 100 kHz to 100 mHz. The amplitude of the sinusoidal was 10 mV. All the experiments were duplicate or triplicate. The reproducibility for corrosion potential was  $\pm 4$  mV, and that for corrosion current was  $\pm 0.2$  µA/cm<sup>2</sup> (in passive state).

### **3** Results and discussion

### 3.1 Microstructure of anodes

Figure 1 shows the microstructure of rolled Pb–Ag and Pb–Ca–Ag alloys anodes. It is seen from Fig. 1 that Anodes 2 and 3 possess oriented structure through the rolling direction. They contain more silver than Anode 1 and the silver-containing phase is distributed rather uniformly in the alloy and alternatively with the lead-rich phase. Anodes 4 and 5 have a different structure from Anodes 2 and 3. The silver-containing phase is more

concentrated at the grain boundaries.

Figure 2 shows the microstructure of Anodes 4 and 5. It is seen that the shot-peening treatment of Anode 5 shows a certain change in the microstructure. It seems that the distribution of silver becomes more uniform.

### 3.2 Corrosion behavior of anodes at open circuit potential

3.2.1 Corrosion behavior in zinc electrolyte without permanganate ion

To examine the corrosion property of the five lead alloy anodes, the corrosion tests were conducted using polished specimens after removing the original surfaces. In these experiments, five cycles were carried out. In each cycle, the corrosion potentials of the five anodes at open circuit potential were recorded for every hour, and at the end of every hour, potentiodynamic polarizations (the potential scan range from -25 to 25 mV) were conducted to measure the corrosion rate. The potential vs time curves for the first four cycles of the five alloy anodes are presented in Fig. 3.





**Fig. 2** Backscattered electron micrographs of Anode 4 (a) and Anode 5 (b)



Fig. 3 Corrosion potential evolution of polished Anodes 1–5 in zinc electrolyte without  $MnO_4^-$  at 38 °C

It is seen from Fig. 3 that Anode 1 was in active corrosion state during the first 2 h of immersion. During the first half of the third hour of immersion, the potential rose gradually from -330 to -250 mV (increased by 80 mV) within 33 min; but from -250 to -125 mV (increased by 120 mV), it took only 2 min, and the electrode entered into passive state. After 2.5 h of immersion, the electrode kept in the passive state; the corrosion potential was 300 mV more positive than that before the passivation, and the corrosion current density dropped from 604 to 2.8  $\mu$ A/cm<sup>2</sup>. The other anodes had similar transition behavior from active to passive state, but the transition times were different. Anodes 2 and 3 began to passivate after about 2.5 h of immersion like Anode 1, while Anode 4 began to passivate after 1.5 h of immersion, and entered into complete passivation after 2 h. The corrosion current density decreased from 2210 to 3.7  $\mu$ A/cm<sup>2</sup>. Anode 5 began to passivate after 2 h of immersion and entered into the passive state after about 130 min of immersion. When the Pb-Ag anodes are immersed into the zinc electrolyte, the lead can react with  $H_2SO_4$  (Pb+ $H_2SO_4 \rightarrow PbSO_4$ ), a non-conductive

layer (PbSO<sub>4</sub>) forms on the surface of anodes. So all the five anodes entered into passivation after few hours of immersion in the zinc electrolyte.

Figure 4 shows the corrosion current density evolution of the five anodes as a function of immersion time. It is noticed that after 1 h of immersion, all the five anodes were in active corrosion state. Anode 4 had the highest corrosion current density (1499 µA/cm<sup>2</sup>), followed by Anodes 5 (1296  $\mu$ A/cm<sup>2</sup>), 3 (1140  $\mu$ A/cm<sup>2</sup>), 1 (1121  $\mu$ A/cm<sup>2</sup>) and 2 (1115  $\mu$ A/cm<sup>2</sup>). The Anode 4 entered into passive state most quickly, followed by Anodes 5, 2, 3 and 1. It is strange that Anode 5 began to passivate just at the end of the second hour, but it was not completely passivated. However, at the end of the second hour of immersion, the corrosion current density of Anode 5 was 52  $\mu$ A/cm<sup>2</sup>, while those of Anodes 1, 2, 3 and 4 were 554, 1072, 181 and 61  $\mu$ A/cm<sup>2</sup>, respectively. When all the five anodes were in passive state, the difference between their corrosion current density was not remarkable. For example, after 5 h of immersion, the corrosion current densities of the five anodes were all around 1  $\mu$ A/cm<sup>2</sup>. It can be concluded that all the five



Fig. 4 Comparison of corrosion current density for five polished anodes in zinc electrolyte without permanganate ion at  $38 \text{ }^{\circ}\text{C}$ 

anodes have low corrosion rates for a long term of immersion in the zinc electrolyte without permanganate ions. It can be found that all the five anodes entered into passivation after few hours of immersion in the zinc electrolyte without permanganate ions since passivation of Pb–Ag anodes can result in low corrosion rates of the anodes.

Figure 5 shows the corrosion potential evolution of the five anodes during 5 h of immersion in the zinc electrolyte without  $MnO_4^-$ . It is seen that Anode 4 was still passivated most quickly, followed by Anodes 2, 5, 1 and 3. However, the passivation of the five anodes took place later than that in the case of immersion with inserted linear polarization experiments of every hour. This means that the linear polarization accelerated the passivation because of the anodic polarization of 25 mV vs open circuit potential. The corrosion current densities of all the five anodes at the end of 5 h immersion test were around 1  $\mu$ A/cm<sup>2</sup>. It was almost the same as that in the case of immersion with linear polarization of every hour. It is observed that Anodes 4 and 5 had a similar corrosion current change manner. This is probably due to the same composition and similar microstructure in the bulk.



Fig. 5 Corrosion potential evolution of five anodes (polished) during 5 h of continuous immersion in zinc electrolyte without  $MnO_4^-$  at 38 °C

3.2.2 Corrosion behavior in zinc electrolyte with permanganate ion

After 5 h of polarization at 60 mA/cm<sup>2</sup> in the zinc electrolyte containing permanganate ions (MnO<sub>4</sub><sup>-</sup>), the potential vs time curves (Fig. 6) of the five anodes are very different from those obtained in the solution without  $MnO_4^-$  (Fig. 5). It is seen that all the five anodes were passivated within a few minutes at the beginning of the immersion experiments. The corrosion potentials rose from about -300 mV (vs SHE) to 0 (vs SHE) immediately when the anodes were immersed into the solution. In this case, the corrosion current density of the five anodes at the end of 5 h immersion were 28, 36, 35, 31 and 25  $\mu$ A/cm<sup>2</sup>, respectively. Comparing these corrosion current density with those obtained in the electrolyte without MnO<sub>4</sub><sup>-</sup> ions (around 1  $\mu$ A/cm<sup>2</sup>), it can be concluded that though the MnO<sub>4</sub><sup>-</sup> ions accelerated the potential jump (passivation), the corrosion current density of the five anodes in the electrolyte with MnO<sub>4</sub><sup>-</sup> ions were higher than those in the zinc electrolyte without MnO<sub>4</sub><sup>-</sup> ions. It can be observed that the permanganate ions in the zinc electrolyte accelerated the corrosion rates of the Pb–Ag alloy anodes.



Fig. 6 Corrosion potential evolution of five anodes (polished) during 5 h of continuous immersion in zinc electrolyte with  $MnO_4^-$  at 38 °C

The polarization resistances of five Pb–Ag alloy anodes were studied by electrochemical impedance spectroscopy (EIS) measurements at the open circuit potential in the zinc electrolyte with  $MnO_4^-$  ions at 38 °C as shown in Fig. 7.

It can be observed from Fig. 7 that Anode 4 had the highest polarization resistance in zinc electrolyte with  $MnO_4^-$ , followed by Anodes 5, 2, 3 and 1. It means that higher silver content causes higher corrosion resistance for the Pb–Ag anodes.

3.2.3 Effect of  $MnO_4^-$  ion and surface state on corrosion of anode

It was noticed that when the five anodes were immersed in the zinc electrolyte containing  $MnO_4^-$  ions, the anode had different potential vs time curve from that obtained in the zinc electrolyte without  $MnO_4^-$  ion as shown in Fig. 8. The potential curve was up immediately when the anode was immersed in the solution with  $MnO_4^-$  ions. The jump of the potential means the passivation of the anode. The lead anodes were passivated much more quickly in  $MnO_4^-$  ion contained solution than in  $MnO_4^-$  ion free solution. This is probably due to the high oxidation capacity of the  $MnO_4^$ ion. In the solution containing  $MnO_4^-$  ion, the permanganate could accelerate the anode surface to be passivated quickly. However, even if the potential of the anode in the solution containing  $MnO_4^-$  ions was higher than that in the solution without  $MnO_4^-$  ion (Fig. 8), the corrosion rate in the former solution was higher than that in the latter solution. For example, after 5 h of immersion, the corrosion rate of the polished Anode 5 in the solution with  $MnO_4^-$  ions was 55.4 µm/a; while that in the solution without  $MnO_4^-$  ion was only 22.1 µm/a.



Fig. 7 Polarization resistance of polished Anodes 1–5 measured by EIS in zinc electrolyte with  $MnO_4^-$  ions at 38 °C



**Fig. 8** Evolution of corrosion potential of polished Anode 5 in zinc electrolyte at 38 °C

It was also noticed that the anode with original surface was passivated more quickly than the anode with polished surface as shown in Fig. 9. This means that the original surface was helpful for the passivation of the anode because of the existing oxide film formed during the fabrication of the anodes. However, it could be also observed that after 3 h of immersion the passivation of the polished surface gave more noble potentials than that of the original surface, and this may show finally a better quality of passivation. Indeed, after 5 h of immersion, the polished Anodes 5 had a corrosion current of  $0.9 \,\mu\text{A/cm}^2$ , while the corrosion current for the Anode 5 with original surface was  $3.3 \,\mu\text{A/cm}^2$ .



Fig. 9 Evolution of corrosion potential of original and polished Anode 5 in zinc electrolyte without  $MnO_4^-$  at 38 °C

### 4 Conclusions

Pb-0.6%Ag and Pb-0.58%Ag alloy anodes possess expressed oriented structure through the rolling direction. When the five anodes were immersed into acid zinc  $MnO_4^$ sulphate electrolyte without ions. the Pb-0.72%Ag anode entered complete passivation state in the shortest time among the five anodes, followed by Pb-0.67%Ag, Pb-0.60%Ag, Pb-0.58%Ag and Pb-0.29%Ag-0.1%Ca by measurement of open circuit potential. After 1 h of immersion in electrolyte without permanganate ion, the anode Pb-0.72%Ag had the highest corrosion current density (1499  $\mu$ A/cm<sup>2</sup>), followed by Pb-0.67%Ag (1296 µA/cm<sup>2</sup>), Pb-0.58%Ag (1140 µA/cm<sup>2</sup>), Pb-0.29Ag-0.1%Ca (1121 µA/cm<sup>2</sup>) and Pb-0.60%Ag (1115  $\mu$ A/cm<sup>2</sup>). At the end of 5 h immersion, the corrosion current densities of the five anodes were all around 1  $\mu$ A/cm<sup>2</sup>. Also, MnO<sub>4</sub><sup>-</sup> ions accelerated the passivation and increased the corrosion current density of the five anodes during the 5 h immersion of the five anodes. In addition, after 3 h of immersion the passivation of the polished surface gave more noble potentials than that of the original surface. Moreover, after 14 h of immersion of the five anodes in zinc electrolyte with MnO<sub>4</sub><sup>-</sup>, the anode Pb-0.72%Ag had the best corrosion resistance, followed by anodes Pb-0.67%Ag, Pb-0.60%Ag, then the anodes Pb-0.58%Ag Pb-0.29Ag-0.1%Ca the and by electrochemical impedance spectroscopy (EIS). It means that a higher silver content caused a higher corrosion resistance for the Pb-Ag anodes.

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### MnO<sub>4</sub><sup>-</sup>和银含量对铅银合金阳极 电位衰减期电化学行为的影响

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摘 要:研究在电位衰变期间在酸性硫酸锌电解液中,MnO<sub>4</sub><sup>-</sup>和银的含量对 5个通用铅银合金阳极电化学行为的 影响。当阳极浸入不含 MnO<sub>4</sub><sup>-</sup>的酸性硫酸锌电解液中时,通过开路电位测定,发现 Pb-0.72%Ag 进入完全钝化状 态所用的时间最短,紧接着的是阳极 Pb-0.67%Ag、Pb-0.60%Ag、Pb-0.58%Ag 和 Pb-0.29%Ag-0.1%Ca。在 5 h 的 浸入期间,MnO<sub>4</sub><sup>-</sup>离子能加速钝化和增加阳极的腐蚀电流密度。通过交流阻抗法测定,发现在含有 MnO<sub>4</sub><sup>-</sup>的电解 液中,阳极 Pb-0.72%Ag 具有最好的耐蚀性,紧接着的是阳极 Pb-0.67%Ag、Pb-0.60%Ag,然后是阳极 Pb-0.58%Ag 和 Pb-0.29%Ag-0.1%Ca。

关键词: 电化学行为; 铅银阳极; 高锰酸根离子; 电位衰减期; 硫酸锌电解液

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