

# The Influence of Alloying Elements and Microstructure on the Properties of Lead Anodes for Zinc Electrowinning: A Review

## **Zhang Yongchun**

Department of Mechanical Engineering, Baoji University of Arts and Science, Baoji, China

### **Email address**

1040130198@qq.com

### Citation

Zhang Yongchun. The Influence of Alloying Elements and Microstructure on the Properties of Lead Anodes for Zinc Electrowinning: A Review. *American Journal of Earth Science and Engineering*. Vol. 1, No. 1, 2018, pp. 25-32.

Received: January 26, 2018; Accepted: February 26, 2018; Published: March 23, 2018

**Abstract:** In order to search for a suitable anode with lower oxygen evolution reactio (OER) potential and corrosion rate for zinc electrowinning, the influence of alloying elements and microstructure on the properties of lead anodes for Zinc electrowinning have been reviewed and summarized. The results pointed the advantages and disadvantages of the lead alloy anodes and the new type anodes used were reviewed by the preparation technology, mechanical properties, corrosion resistance, electrocatalytic activity and so on.

Keywords: Anode, Reviewed, Zinc Electrowinning

# **1. Introduction**

As lead alloy's anode has good conductivity, high economic benefits and high stability in the case of high potential and low pH value, Pb-based anode is an optimal anode material choice in the current non-ferrous metal electrolysis industry [1]. More than 80% of the zinc and 20% of the copper in the world are extracted hydrometallurgically [2, 3]. The structure and mechanical performance of anode material can improve its service life [4]. At present, during the hydrometallurgy process, zinc electrowinning energy consumption accounts for about 70% of that of the entire zinc extraction process [2], while copper electrowinning energy consumption accounts for 30% of the entire copper extraction process [4]. With the increase in energy consumption costs, it is an inevitable trend to increase the electrowinning current efficiency.

Low oxygen evolution overpotential of anode can help to reduce the cell voltage [5, 6]. By reducing the oxygen evolution overpotential, it will promote the generation of low-solubility compact and conductive oxide film on the surface of anode, thereby increasing the anode's conductivity and corrosion resistance. In the case of poor binding force of oxide film and underlying lead, the oxide film will fall off, which accelerates the anode's corrosion resistance and increases anode slime. An excellent zinc electrowinning anode shall be equipped with the following conditions [7]: a) alloy workability; b) mechanical stability; c) mass of cathode products; d) anode slime's quantity and processability; e) anode maintainability [8, 9]; f) environmental pollution [9]; g) low oxygen evolution potential.

In order to improve the performance of Pb anode, scientists have prepared binary alloys including Pb-Ag, Pb-Co, Pb-Sb and Pb-Ca, ternary alloys like Pb-Ag-Ca, Pb-Ag-Co, Pb-Ag-Sn, Pb-Ag-Mn, Pb-Ag-Ti, Pb-Ag-As, Pb-Ag-Bi, Pb-Ag-Se and Pb-Ag-Sr, and quaternary alloys such as Pb-Ag-Ca-Sr, Pb-Ag-Sn-Co and Pb-Ag-Sb-Ca. The previous studies concluded that the elements like Ag, Ca, Co, Sb, Sn, As, Ti, Bi, Se and Sr can be used to improve the electrochemical and mechanical properties of lead alloy anode to a certain extent.

During the zinc electrowinning process, Pb in the lead alloy anode will be partially dissolved, which then enters the cathode zinc in the form of particle and reduces the mass of zinc. When Pb is heated to 400-500°C, Pb steam will come out and form Pb fume. In the process of manufacturing lead powder and polar plate by lead pig, lead dust will spread and pollute the air. When the lead dust in the air accumulates to a certain concentration, it will be harmful to human bodies. Dust control units are mostly used in the industries to reduce the pollution caused by lead dust. The author considers that physical examinations shall be regularly conducted and that daily diets shall contain as many vitamins as possible. Considering the energy consumption, cathode zinc mass and environmental pollution, scientists have prepared composite electro-catalyzed Pb-based anode, electro-catalyzed Ti-based anode and Pb-based lead alloy anode.

# 2. Formation of Pb Anode Surface Film

Currently, Pb-Ag anode for industrial use generally contains 0.3-1% Ag. Before the normal anodic reaction (1) starts, the electrified uncoated anode will experience the following stages [10].

 $4OH^{-} - 4e = O_2 + 2H_2O \quad E = 0.401V \tag{1}$ 

$$Pb - 2e = Pb^{2+} \quad E = -0.126V \tag{2}$$

$$Pb + SO_4^{2-} - 2e = PbSO_4 \quad E = -0.356V \tag{3}$$

$$Pb + 2H_2O - 4e \rightarrow PbO_2 + 4H^+ \quad E = 0.655V \tag{4}$$

$$Pb^{2+} + 2H_2O - 2e \to PbO_2 + 4H^+ \quad E=1.45V$$
 (5)

First of all, Pb dissolution (2) will occur, and PbSO<sub>4</sub> will be formed, which covers the surface the anode (3); on the anode surface not covered by PbSO<sub>4</sub>, PbO<sub>2</sub> (4) will be directly generated by Pb; with the disappearance of bared Pb on the surface, PbSO<sub>4</sub> covered on the anode surface will generate PbO<sub>2</sub> (5). There is a large electric potential and current density between the non-conducting PbSO<sub>4</sub> layer and its neighboring region. Under high voltage, PbO<sub>2</sub> (6) will be generated from PbSO<sub>4</sub>. After the lead alloy anode is basically covered by PbO<sub>2</sub>, normal anodic reaction (1) will start:

$$PbSO_4 + 2H_2O - 2e \rightarrow PbO_2 + H_2SO_4 + 2H^+ \quad E = -1.685V$$
 (6)

As a result, in the  $ZnSO_4$ - $H_2SO_4$  electrolyte, the overall reaction of anode and cathode can be written as (7):

$$ZnSO_4 + H_2O \rightarrow Zn + \frac{1}{2}O_2 + H_2SO_4$$
 (7)

The growth of conductive  $PbO_2$  on the anode surface is also a process of over-oxidation [11] and dissolution [12] of the anode, as well as a positive electrode process. Pb anode has different oxidation reactions (8-10) at different potentials in the sulfate electrolyte [13].

$$Pb \rightarrow PbSO_4 , \quad -0.95V < E < -0.4V \tag{8}$$

$$PbO \rightarrow PbO_n$$
,  $-0.95V < E < -0.4V$  (9)

$$PbSO_4 \rightarrow \beta - PbO_2 \text{ or } \alpha - PbO_2, \quad E > +0.95V \quad (10)$$

The formation of oxidation film on the surface of Pb anode may be the passivation to avoid corrosion [14]. Under different conditions, due to the difference in reaction mechanisms, different oxides will be generated from Pb's oxidation reactions. PbSO<sub>4</sub> generated by Pb will continue to generate  $\alpha$ -PbO<sub>2</sub> with better conductivity, and  $\alpha$ -PbO<sub>2</sub> film's potential and current density are lower than those of PbSO<sub>4</sub>.  $\alpha$ -PbO<sub>2</sub> can be reduced to generate PbSO<sub>4</sub>, but such PbSO<sub>4</sub> can only generate  $\alpha$ -PbO<sub>2</sub> [15].

PbSO<sub>4</sub> and PbO<sub>2</sub> films are ion-selective semi-permeable films [16] in which the original oxide layer with high compactness and adhesion will easily become layered and broken off, thereby making Pb anode exposed to corrosion. Main reaction in the pores of anode surface is possibly [17]: compact thick oxidation film makes it very difficult for Pb<sup>2+</sup> to diffuse in the electrolyte, which promotes the generation of Pb<sup>4+</sup>. Pb<sup>4+</sup> further generates PbO<sub>2</sub> together with OH. Therefore, what diffuse in the electrolyte are mainly  $SO_4^{2-}$ and O<sub>2</sub>. Due to the difference in pH value of electrolyte, two kinds of PbO<sub>2</sub> will be generated during the electrochemical process on the anode surface:  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub>.  $\alpha$ -PbO<sub>2</sub> has high strength, and  $\beta$ -PbO<sub>2</sub> has low electric potential and corrosion rate [6]. a-PbO2 is mainly generated by reaction of Pb oxide and OH<sup>-</sup>, while  $\beta$ -PbO<sub>2</sub> is generally produced by reaction of Pb oxide and  $SO_4^{2-}$ . As a result, Ho [18] et al. considered that  $\alpha$ -PbO<sub>2</sub> can only be generated in alkaline or neutral solution, while  $\beta$ -PbO<sub>2</sub> is only generated by PbSO<sub>4</sub> under acidic conditions. However, Ivanov [5] et al. found that  $\alpha$ -PbO<sub>2</sub> can also be generated by PbSO<sub>4</sub>. The contradiction lies in that  $\alpha$ -PbO<sub>2</sub> can be generated in the acid solution but  $Pb^{4+}$  exists in a solution with  $H_2SO_4$  concentration higher than 15M. This contradiction is possibly caused by different absorption processes of PbO<sub>2</sub> grains on the surface of anodes with different alloy materials [7].

While the oxygen passes through the interface between Pb oxide in oxide film and sulfate electrolyte, a thin layer of  $\beta$ -PbO<sub>2</sub> will be generated. When the electric potential is higher than the equilibrium potential,  $\alpha$ -PbO<sub>2</sub> will be generated from Pb in the pores of  $\beta$ -PbO<sub>2</sub> film. The reaction goes on and the oxide film layer becomes thicker and thicker. The newly generated oxide has no sufficient oxygen, and  $\alpha$ -PbO<sub>2</sub> will become tetragonal PbO+Pb. If Pb anode proceeds with passivation and exceeds the critical point, the thickness of oxide film will go beyond the limits, and the resulting internal stress will make the oxide become layered and the oxide film break off. As a result, the ideal oxide film shall be pure thin $\beta$ -PbO<sub>2</sub> of high strength and good compactness and adhesion [19].

In industrial practices, Pb content in cathode zinc can be reduced and chemical corrosion of Pb anode can be slowed down by controlling  $Mn^{2+}$  concentration in the electrolyte. The reason lies in that  $Mn^{2+}$  is oxidized on the anode to generate  $MnO_2$  which is adhered to the surface of anode and forms a protective film to hinder the dissolution of Pb. Therefore, Reaction (10) shall be always maintained during the zinc electrowinning process. Yet,  $MnO_2$  is excessively evolved at the anode, which will not only increase the burden of leaching process, but also lead to the depletion of  $Mn^{2+}$  in the electrolyte and directly affect the mass of zinc evolution mass [10].

$$Mn^{2+} + 2H_2O - 2e = MnO_2 \downarrow + 4H^+, E = 1.25V$$
 (11)

Generally speaking, Reaction (1) and Reaction (11) are major competing reactions occurring during the zinc electrowinning anode process. Previous studies found that electrolyte acidity has a small influence on  $O_2$  and  $MnO_2$  evolution, and current density has the largest influence on  $MnO_2$  evolution. The lower the current density is, more easily will  $MnO_2$  be evolved.  $Mn^{2+}$  concentration shall be controlled around 3g/L. Thus, a compact protective film will form on the anode surface, and  $MnO_2$  will not fall off too much to cause depletion of  $Mn^{2+}$ . Since the evolution of  $MnO_2$  by  $Mn^{2+}$  at the anode is an electrochemical control process,  $MnO_2$  will be more easily evolved with the increase in temperature [20].

# 3. Impact of Modifying Elements on the Performance of Lead Alloy Anode

By adding modifying elements, Pb anode's mechanical strength, corrosion resistance and electrocatalytic activity can be improved. If the Pb anode's mechanical strength is enhanced, the anode will not easily deform during its use and the anode structure will not easily be damaged, which will be beneficial to its service life. By increasing the anode's corrosion resistance, the anode's service life can be prolonged, and the cathode zinc's quality can be improved.

### **3.1. Traditional Pb-Ag Anode**

By adding Ag to Pb, the lead alloy's strength and creep strength can be enhanced, and lead alloy's corrosion resistance in the sulfuric acid can also be improved [21]. Currently, Pb-Ag anode plate is mainly made via rolling. With the increase of Ag content in Pb-Ag alloy, the anode's electric potential will be reduced [21]. Pb-1%Ag anode's electric potential is about 280mv lower than that of pure Pb anode, and Pb-0.3%Ag anode's electric potential is about 200mv lower than that of pure Pb anode. With the increase of Ag content in Pb-Ag alloy, the anode's corrosion rate is also reduced [6]. Pb-1%Ag anode has lower oxygen evolution potential and corrosion rate than Pb-0.3%Ag anode and Pb-0.5%Ag anode, due to the high content of  $\beta$ -PbO<sub>2</sub> with lower oxygen evolution potential and smaller polarization resistance occurring in the polarization process of Pb-1%Ag anode [10]. As Ag content in Pb-Ag alloy increases, the anode's hardness will also increase, which is attributed to the increase of Pb-Ag alloy's eutectic phase [6].

Lai Yanqing and Jiang Liangxing et al. [8-9] adopted anti-gravity penetration technology to respectively design porous anode and "reverse-sandwich-structured" composite porous anode. The research results showed that, porous anodes with different pore sizes have different electrochemical behaviors in the electrolytes  $H_2SO_4$ -ZnSO<sub>4</sub> and  $H_2SO_4$ -ZnSO<sub>4</sub>-MnSO<sub>4</sub>; porous anode's oxygen evolution potential in  $H_2SO_4$ -ZnSO<sub>4</sub> declines with the increase in the electrolysis time; porous anode's oxygen evolution potential in H<sub>2</sub>SO<sub>4</sub>-ZnSO<sub>4</sub>-MnSO<sub>4</sub> rises with the increase in the electrolysis time [8]; oxygen evolution potential decreases first and then increases with the increase in pore size. The corrosion rate also decreases first and then increases with the increase in pore size, which peaks at a pore size of 1.6-2.0mm. Jiang Liangxing et al. found that when 2mm Pb-Ag alloy plate is adopted as the central reinforced metal plate for "reverse-sandwich-structured" composite porous anode, the ultimate tensile strength and average conductivity of composite porous anode with a pore size of 1.25-1.43mm are 3 times and 1.3 times of those of porous anode with the same pore size, respectively. Zhang Yongchun et al. [22] prepared Al/Pb-Ag composite anode through electro-deposition, and the results showed that under the same Ag content, Al/Pb-Ag anode has better corrosion resistance than traditional Pb-Ag alloy, which is possibly due to the finer Pb-Ag alloy grains and less segregation in the electro-deposition process, as shown in Figure 1.



*Figure 1.* Metallographic structure of conventional Pb-Ag(a) Al/Pb-Ag(b) anodes.

### 3.2. Impact of Co on Lead Alloy Anode

According to previous studies, when Co content in lead alloy reaches 0.02-0.1%, the lead anode's oxygen evolution potential and corrosion rate can be significantly reduced [23]. As Co has a very small dissolubility in lead solution, Co content in Pb-rich liquid phase at 1,550°C is only 0.33% [21]. Even if at very high temperature, it is difficult to achieve mixed casting of Co and Pb. In order to solve this problem, people have tried several methods, including Co-Sn/Sb/Bi low-temperature intermediate alloy process, and mechanic alloving process of arc-melted and rapidly-cooled Pb-Co. The results showed that among the Pb-Co alloys prepared by the abovementioned methods, Co content did not exceed 0.1%, and that the mechanical performance of Pb-Co alloy prepared through mechanical alloying process could not satisfy the industrial requirements [24]. The most commonly-used method at present is to prepare Pb-Co alloy through electro-deposition in indium sulfamate system [25]. Y. Stefanov and P. Yu [26] considered that compared to Pb-0.90%Co anode, after 48h of polarization, Pb-2.11%Co anode's oxygen evolution reaction presented minor depolarization, which was possibly due to the reduction of oxygen evolution potential [27] and the decrease of PbO<sub>2</sub> content on the surface resulting from the increase in Co content. When Co content increases to 5%, a layer of coarse porous  $\beta$ -PbO<sub>2</sub> will be adhered to the anode surface [28].

By adding  $\text{Co}^{2+}$  to the electrolyte, the anode's oxygen evolution potential and corrosion rate can be reduced [29-30]. I. Ivanov and Y. Stefanov [5] et al. considered that  $\text{Co}^{2+}$  may have the following reactions in the electrolyte:

$$Co^{2+} = Co^{3+} + e \tag{12}$$

$$Co^{3+} + OH^{-} = CoOH^{2+}$$
 (13)

$$2CoOH^{2+} = 2Co^{2+} + H_2O + O \tag{14}$$

$$O + O = O_2 \tag{15}$$

Antonov and Stepanenko [28] found that by adding a small amount of  $Co^{2+}$  to the electrolyte, the anode's polarization potential can be reduced, and the generation of  $Co^{3+}$  can promote the decomposition of water and the generation of PbO<sub>2</sub>. That is to say,  $Co^{2+}$  or  $Co^{3+}$  can improve the surface activity of lead anode. This process may be expressed as Reaction (16) and Reaction (17):

$$4Co^{3+} + 2H_2O = 4Co^{2+} + 4H^+ + O_2 \tag{16}$$

$$Co^{2+} - e = Co^{3+} \tag{17}$$

$$PbSO_{4} + 2H_{2}O - 2e = PbO_{2} + H_{2}SO_{4} + 2H^{+}$$
  

$$E(vs \cdot SCE) = +1.92V$$
(18)

$$Co^{2+} + 2e = Co \quad E(vs \cdot SCE) = -0.233V$$
 (19)

Reaction (16) and Reaction (17) are faster than Reaction (18), thereby reducing the oxygen evolution potential.

$$Pb + SO_4^{2-} - 2e = PbSO_4 \quad E(vs \cdot SCE) = +0.359V$$
(20)

$$Co - 2e = Co^{2+} E(vs \cdot SCE) = +0.233V$$
 (21)

$$Co^{3+} + e = Co^{2+} \quad E(vs \cdot SCE) = +1.83V$$
 (22)

In the process of zinc electrowinning, Reaction (20) on Pb-Ag anode's surface is inevitable; the electrochemical dissolution potential of Reaction (21) is 0.126V lower than that of Reaction (20); Reaction (22) will happen eventually in the anode reaction process. Antonov and Stepanenko concluded that by adding a small amount of  $Co^{2+}$  to the electrolyte, Reaction (16) or Reaction (17) may be the process that reduces the lead anode's polarization potential. Consequently, it is deduced that Co's oxidation process in the zinc electrowinning is also its catalytic process:  $Co \rightarrow Co^{2+} \rightarrow Co^{3+}$ .

### 3.3. Impact of Other Elements on Lead Alloy Anode

By adding Sn and Co to the Pb-Ag alloy with the same Ag content, its anode potential is significantly reduced; when the current density is 1,000A/m<sup>2</sup>, its oxygen evolution potential also decreases by about 60mv. Besides, the corrosion rate is also significantly reduced. After 672h of electrolysis, Pb-1%Ag anode's weight loss is 190g/m<sup>2</sup>, while Pb-1%Ag-0.3Sn%-0.02%Co anode's weight gain is only 24g/m<sup>2</sup>, which is possibly due to better adhesion of PbO<sub>2</sub> on Pb-1%Ag-0.3Sn%-0.02%Co anode than that on Pb-1%Ag anode. After 168h of electrolysis, cathode zinc product obtained by Pb-1%Ag anode contains 0.02% Pb, while cathode zinc product of Pb-1%Ag-0.3Sn%-0.02%Co anode only has 0.004% Pb [31]. This suggests that Sn and Co may reduce the anode's oxygen evolution potential and corrosion rate.

Zhong Shuiping and Lai Yanqing et al. [32, 33] prepared a new Pb-0.8%Ag-0~5.0%Bi anode for zinc electrowinning, and compared the electrochemical properties of this ternary alloy anode and Pb-0.8%Ag anode for industrial use. The potential-time curve showed that, the anode's over-potential decreases with the increase in Bi content in the alloy; when Bi content reaches 1.0% and 5.0%, its over-potential is 40-50mV and 60-80mV lower than that of Pb-0.8%Ag anode, respectively. The surface oxide films of these two anodes are mainly composed by  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub>, but they have different structures. Compared to Pb-0.8%Ag anode, Pb-0.8%Ag-0~5.0%Bi anode has more regular and compact surface oxide film structure, but Pb-0.8%Ag-0~5.0%Bi anode's surface film is not closely bound with the base and presents loose fragmental structure [33]. The corrosion rate goes up with the increase in Bi content, but when Bi content is less than 0.8%, Pb-Ag-Bi anode's corrosion rate is smaller than that of Pb-Ag anode [34], which is possibly attributed to the growth of Pb grains under the role of Bi.

Petrova and Rashkov [35] found from potential-time curve and cyclic voltammetric curve that Ca can help to reduce the electric potential and corrosion rate of the anode. When Ca content is 0.05%, 0.08% and 0.11%, respectively, the electric potential of Pb anode goes down with the increase in Ca content [36, 37], and its corrosion rate reaches a minimum value when Ca content is 0.08% [38]. Takasaki Y [37] and Liu Song [38] et al. considered that this is the result of more compact PbO<sub>2</sub> film produced on the anode surface by adding a small amount of Ca to Pb anode.

Metikos-Hukovic [39] and T. Laitinen [40] found that Sb could help to reduce Pb anode's oxygen evolution potential, which was possibly due to the reason that Sb could promote the generation of  $PbO_2$  film on the anode surface. The electric potential for  $PbSO_4$  to convert into  $PbO_2$  is 200-300mv lower than that of pure lead [41]. However, with the continuous increase of Sb content in Pb-Sb alloy, Pb-Sb alloy anode's corrosion resistance will be reduced, and the reason lies in that grain boundary corrosion will occur during the electrolysis process since Sb is largely evolved in the grain boundary of Pb-Sb alloy, as shown in Figure 2 [23].

# Pb-Sb 50 μ m.

Figure 2. Metallographic structure of Pb-Sb alloy.

By adding a small amount of As to Pb-Ag anode, Pb-Ag anode's corrosion resistance in the sulfuric acid solution can also be significantly improved [42]. This is possibly due to the fact that the addition of As helps to reduce the contraction at the time of solidification, reduce the occurrence of pinholes and improve the hardness of Pb [21]. Sr alloy may reinforce the strength of lead base through deposition [17]. When Ag content in Pb alloy reaches 1%, the corrosion resistance and oxygen evolution potential of Pb alloy anode can be improved by adding Sr [42]. After adding a small amount of Pr, the tensile strength and electric potential of Pb alloy anode can be increased [43].

### 4. New Composite Anode

### 4.1. Pb-based Pb-MnO<sub>2</sub> Composite Anode

With pure lead as the base, Pb-based Pb-MnO<sub>2</sub> composite anode has a layer of Pb-MnO<sub>2</sub> alloy on its surface for composite electro-deposition [44-45]. The research results showed that MnO<sub>2</sub> can be used to reduce the oxygen evolution potential of lead alloy anode due to its good catalytic activity. The industrial experiments suggested that, with Pb/Pb-MnO<sub>2</sub> composite material as the anode, its cell voltage decreased by about 120mV compared to the traditional Pb-1%Ag alloy in 150g/L H<sub>2</sub>SO<sub>4</sub> under normal current density for zinc electrowinning. By using such anode, not only the costs are reduced, but also the precious metal consumption is decreased. However, during the process of zinc electrowinning, the anode's grain boundary corrosion is serious, which will easily fall off and lead to shorter service life.

### 4.2. Ti-based DSA Anode

Ti-based DSA anodes mainly include thin-coated and thick-coated Ti-based anodes. In terms of thin-coated Ti-based DSA anodes, Ti is generally covered by oxides like IrO<sub>2</sub>, RuO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>, through which the anode with excellent electrochemical performance can be acquired. Kwang-Wook [46] et al. considered that Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> composite anode has excellent electrochemical stability and electro-catalytic activity. However, Ti-based DSA anode is plagued with short service life and expensive price, which restrict its industrial applications. Thick-coated Ti-based DSA anodes are mostly Ti/MnO<sub>2</sub> [47] and Ti/PbO<sub>2</sub> [48]. According to the industrial electrolytic zinc experiments of Ti/MnO<sub>2</sub> anodes prepared by Zhang Zhaoxian [49], it was found that the lead content in its cathode zinc is less than 0.00057%, which is lower than the national Level-I zinc standard 0.005%. Ti/PbO2 anode has a good corrosion resistance to chlorine and higher current efficiency; besides, it will not produce Mn slag. Ti-based coated anode prepared by Li Naijun [50] et al. has 0,156V over-potential under the zinc electrowinning conditions, which reduced by about 1V compared to Pb-1%Ag anode; an accelerated life test on the anode's service life showed that, under a current density of  $20,000 \text{ A/m}^2$ , the anode has a service life of 113.3h. However, due to weak strength and fragility of  $\beta$ -PbO<sub>2</sub>, Ti/PbO<sub>2</sub> anode's applications in the zinc electrowinning industry are restricted.

Table 1. A comparison of zinc electrowinning results of Pb-Ag anode and Ti-based DSA anode [51].

No.	Anode Name	Electrowinning Time (h)	Average Cell Voltage (v)	DC Power Consumption (kW·h/t)	Pb% in zinc
1	А	5	2.99	2648.48	0.0043 (Zn99.99)
2	В	5	2.91	2598.10	0.0014 (Zn99.995)
3	А	5.67	3.09	2693.71	
4	В	6	2.92	2610.15	
5	А	3	3.08	2651.00	

No.	Anode Name	Electrowinning Time (h)	Average Cell Voltage (v)	DC Power Consumption (kW·h/t)	Pb% in zinc
6	В	3	2.89	2571.16	
7	А	3	3.11	2701.65	
8	В	3	2.89	2542.60	
9	А	3	3.11	2673.40	
10	В	2.17	2.88	2506.64	
11	А	3	3.09	2670.70	
12	В	3	2.90	2620.70	

Note: A and B represent Pb-Ag anode and Ti-based DSA anode, respectively.

As shown in Table 1 [51], Ti-based DSA anode's oxygen evolution potential is about 0.17V lower than that of Pb-Ag anode, and its DC power consumption reduces by about 98.27kW·h/t·Zn. In the case that no SrCO<sub>3</sub> is added, Pb% in evolved zinc reduces to 0.0014% from 0.0043%, meeting the standard requirements of Zn 99.995.

### 4.3. Pb-based Composite Lead Alloy Anode

Sun Yong [52] et al. studied the Al-Pb layered composite material. The first method is to adopt 3003 aluminum plate with a thickness of 1.2mm for industrial use. The aluminum plate is cut into 30mm×90 mm rectangular aluminum strips, which are then cleansed with ethyl alcohol and acetone for deoiling and degreasing; then, these strips are put into alkali liquor with 10 wt% NaOH and a temperature of 65°C to remove the oxide layer on the aluminum surface; take the strips out and put them into 350°C Sn or Bi plating tank for 15-20min of dip plating. The aluminum stripes are then coated with a layer of Sn or Bi with a thickness of 30-70 micrometer. Then, the Sn-coated or Bi-coated aluminum strips are placed in the central parts of coated steel at 200°C to get a solid-liquid coating for lead alloy (Pb-0.1%Ca-1%Ag). When the temperature of lead alloy solution is controlled at 370°C, pour it into the steel mould. After the steel mould gets cooled naturally, the sandwich-structured Al-coated composite aluminum alloy anode material can be obtained. The advantages of this method lie in that the anode has good conductivity and mechanical strength like aluminum, and that its weight can be reduced by 15% or so. However, it also has some disadvantages: the cast lead alloy has some pore gaps, and the cast alloy's metallographic structure has large crystallized grains and poor corrosion resistance, so the electrolyte will penetrate into the pore gaps of the electrode material during the use process to dissolve the aluminum base, thereby losing its functions.

Another method is to get lead alloy coat on the aluminum alloy base through electro-deposition [53-55]. The preprocessing method for aluminum alloy base is basically the same with that of the first method: polishing, deoiling, alkaline cleaning, acid cleaning, zinc immersion, acid cleaning, double zinc dip plating, transition layer and composite electrowinning. Thus, we can get a layer of lead alloy coating which has uniformly distributed alloy elements and small grains.

### 5. Conclusions

At present, Pb alloy anodes used in zinc electrowinning

industry are mostly binary alloy anodes such as Pb-(0.7-1)%Ag prepared through rolling, ternary alloy anodes like Pb-(0.3-0.5)%Ag-(0.05-0.11)%Ca, and quaternary alloy anodes like Pb-Ag-Ca-Sr. Ca and Sr can both be used to improve the electrochemical and mechanical performance of Pb-Ag alloy anodes.

In addition to the abovementioned anodes, other Pb alloy anodes also have some advantages in the zinc electrowinning experiments. Yet, in consideration of the preparation process, the electrolyte purification (such as Pb-Co alloy), the processing of anode slime and the potential safety hazards (such as Pb-As alloy), the application of the preparation process in the zinc electrowinning industry has to be further explored.

### References

- Tunnicliffe M, Mohammadi F, Alfantazi A. Polarization behavior of lead-silver anodes in zinc electrowinning [J]. Journal of Electrochemical Society, 2012, 159 (4): c170-c180.
- [2] Moats M, Freem M. A bright future for copper electrowinning [C]. JOM, 2007, 34-35.
- [3] Zhou J, Xu R, Chen B. Study on Electrochemical Properties of Al/Pb-PANI-WC Inert Anodes. Advanced Material Letter, 2011, 4 (3): 1255-1229.
- [4] Schlesingeer M E, King M J, Sole K C, et al. Extractive Metallurgy of Copper [M]. 5<sup>th</sup> E. The Netherlands, 2011, 360-369.
- [5] Ivanov I, Stefanov Y, Noncheva Z, et al. Insoluble anodes used in hydrometallurgy PartΠ. Anodic behaviour of lead and lead-alloy anodes [J]. Hydrometallurgy, 2000, 57 (2), 109-124.
- [6] Zhang W, Houlachi G. Electrochemical studies of the performance of different Pb-Ag anodes during and after zinc-electrowinning, Hydrometallurgy, 2010, 104 (2), 129-135.
- [7] Clanay M, Bettles C J, Stuart A, et al. The influence of alloying elements on the electrochemistry of lead anodes for electrowinning of metals: A review [J]. Hydrometallurgy, 2012, 131 (1), 144-157.
- [8] Lai Y Q, Jiang L X, Li J, et al. A novel porous Pb-Ag anodes for energy-saving in zinc electrowinning: PartII: Preparation and pilot plant tests of large size anode [J]. Hydrometallurgy, 2010, 102 (1), 81-86.
- [9] Lai Y Q, Jiang L X, Li J, et al. A novel porous Pb-Ag anodes for energy-saving in zinc electrowinning: PartI: Preparation and pilot plant tests of large size anode [J]. Hydrometallurgy, 2010, 102 (1), 73-80.

- [10] Cachat C, Rerolle C. Kinetics of oxygen evolution on Pb and Pb-Ag anodes during zinc electrowinning [J]. Electrochimica Acta, 1996, 41 (7): 1063-1069.
- [11] Pregaman R D. The metallurgy of lead alloys for electrowinning anodes [M]. Proceeding of the AIME Annual Meeting. The Metallurgical Society of AIME, Warradale, Pennsylvania, 1984.
- [12] Shervadani R K, Isfhani A Z, Khodavisy R, et al. Electrochemical investigations of the anodic corrosion of Pb-Ca-Sn-Li grid alloy in H<sub>2</sub>SO<sub>4</sub> solution [J]. Journal of Power Sources, 2007, 164 (2): 890-895.
- [13] Hrussanova A, Mirkova L, Dobrev Ts. Anodic behaviour of the Pb-Co<sub>3</sub>O<sub>4</sub> composite coating in copper electrowinning [J]. Hydrometallurgy, 2001, 60 (3): 199-213.
- [14] Nikoloski A, Nicol M, Stuart A. Managing the passivation layer on lead alloy anodes in copper electrowinning [A]. Proceedings of copper, Hamburg, Germany, 2010, 4: 1559-1568.
- [15] Cui C, Ma X, Kong D, et al. A comparative study of charge-discharge behaviors of  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub> cathodes. Journal of Electrochemistry, 2013, 19 (1): 43-52.
- [16] Slavkov D, Haran B S, Popov B N, et al. Effect of Sn and Ca doping on the corrosion of Pb anodes in lead acid batteries [J]. Journal of Power Sources, 2002, 112 (1): 199-208.
- [17] Ivanov I, Stefanov Y, Noncheva Z, et al. Insoluble anodes used in hydrometallurgy: PartI. Corrosion resistance of lead and lead alloy anodes [J]. Hydrometallurgy, 2000, 57 (2): 109-124.
- [18] Ho J K C, Filho G T, Simpraga R, et al. Structure influence on electrocatalysis and adsorption of intermediates in the anodic O<sub>2</sub> evolution at dimorphic α- and β-PbO<sub>2</sub>, Journal of Electroanalytic Chemistry [J]. 1994, 366 (1): 147-162.
- [19] Prengaman R D, Ellis T W, Mirza A H. New lead anode for copper electrowinning [J]. Hydroprocess. Gecamin, 2010.
- [20] Yang H, Chen B, Liu H, et al. Effects of manganese nitrate concentration on the performance of an aluminum substrate  $\beta$ -PbO<sub>2</sub>-MnO<sub>2</sub> -WC-ZrO<sub>2</sub>, composite electrode material [J]. International Journal of Hydrogen Energy, 2014, 39 (7): 3087-3099.
- [21] Li R. Lead and Lead alloys. Chang sha, 1996.
- [22] Zhang Y, Chen B, Guo Z, et al. Corrosion resistance of electrodeposited Al/Pb-Ag anode during zinc electrowinnig. Chinese journal of applied chemistry, 2013, 30 (4): 458-462.
- [23] Rashkov St, Dobrev Ts, Nonchev Z, et al. Lead-cobalt anodes for electrowinning of zinc from sulphate electrolytes [J]. Hydrometallurgy, 1999, 52 (3): 223-230.
- [24] Maryam J B, Aleksandar N N. Electrodeposition of lead-cobalt composite coatings electrocatalytic for oxygen evolution and the properties of composite coated anodes for copper electrowinning [J]. Hydrometallurgy, 2012, 129 (11): 59-66.
- [25] Stefanov Y, Dobrev Ts. Potentiodynamic and eletronmicroscopy investigations of lead-cobalt alloy coated lead composited anodes for zinc electrowinning [J]. Transaction of Institution Metal Finishing, 2005, 83 (6): 296-299.

- [26] Alamdari E K, Darvishi D, Koshkhoo M S, et al. On the way to develop co-containing lead anodes for zinc eletrowinning [J]. Hydrometallurgy, 2012, 119-120: 77-86.
- [27] Antonov S P, Stepanenko V G. Anodic behaviour Pb in the presence of Co ions [J]. Ukrainskii Khimicheskii Zhurnal, 1972, 38 (9): 935-937.
- [28] Huang H, Zhou J Y, Guo Z C. Effect of added cobalt ion on copper electrowinning from sulfate bath using doped polyaniline and Pb-Ag anode [J]. Tansactions of Nonferrous Metals Society of China, 2010, 20: s55-s59.
- [29] Cachet C, Rerolle C, Wiart R. Influence of Co<sup>2+</sup> and Mn<sup>2+</sup> ions on the kinetics of lead anodes for zinc electrowinning [J]. Journal of Applied Electrochemistry, 1999, 29: 811-818.
- [30] Zhong S, Lai Y, Jiang L, et al. Electrochemical behavior of Pb-Ag-Bi alloys as anode in zinc electrowinning [J]. Chinese Journal of Process Engineering, 2008, 8: 289-293.
- [31] Kiryakov G Z, Stender V V. Stability of anodes of lead and its alloys in the electrolysis of sulfate solutions [J]. Zhurnal Prilkadnoi Khimii, 1951, 24: 1429-1439.
- [32] Zhong S P, Lai Y Q, Jiang L X, et al. Effect of doping Bi on oxygen evolution potential and corrosion behavior of Pb-based anode in zinc electrowinning [J]. Journal of Centre South University Technology, 2009, 16 (2), 236-241.
- [33] Chen W M, Guo B K, Hein K. Study on kinetics of oxygen evolution on lead alloy anodes [J]. Journal of Centre South University Technology, 1997, 4 (1): 69-72.
- [34] Rashkov St, Dobrev Ts, Nonchev Z, et al. Lead-cobalt anodes for electrowinning of zinc from sulphate electrolytes [J]. Hydrometallurgy, 1999, 52 (3): 223-230.
- [35] Hein K, Schierle T. Oxygen overvoltage at insoluble anodes in the system Pb-Ag-Ca [J]. Erzmetall, 1991, 44 (9), 447-451.
- [36] Felder A, Prengaman R D. Lead alloys for permanent anodes in the nonferrous metals industry [A]. JOM, 2006, 58 (10): 28-31.
- [37] Takasaki Y, Watanabe H, Kamada S, et al. Mechanical Properties and Electrolytic Behavior of Pb-Ag-Ca Alloy for Insoluble Electrode of Zinc Electrowinning [J]. Shigen-to-Sozai, 2003, 119 (8): 477-483.
- [38] Liu S, Ma R, Liu L. Anodic behavior of Pb-Ag-Ca anode. Nonferrous Metals, 1995, 47 (3): 61-63.
- [39] Laitinen T, Salmi K, Sundholm G, et al. The effect of antimony on the anodic behaviour of lead in sulphuric acid solutions—I. Voltammetric measurements [J]. Electrochimica Acta, 1991, 36 (3-4): 605-614.
- [40] Metikos-Hukovic M, Babic R, Brinic S. Influence of antimony on the properties of the anodic oxide layer formed on Pb-Sb alloys [J]. Journal of Power Source, 1997, 64 (1), 13-19.
- [41] Monahov B, Pavlov D. Influence of antimony on the structure and the degree of hydration of the anodic PbO<sub>2</sub> layer formed on Pb-Sb electrode [J]. Journal of Electrochemical Society, 1994, 141 (9): 2316-2326.
- [42] Zhong S P, Lai Y Q, Jiang L X, et al. Anodization behavior on Pb-Ag-Ca-Sr alloy during zinc electrowinning [J]. Chinese Journal of Nonferrous Metals, 2008, 18 (7): 1342-1346.

- [43] Dai B, Yu J, Zhou X, et al. Influence of Pr on Pb-Ag alloy anode for zinc electrowinning [J]. Gongneng Cailiao/journal of Functional Materials, 2017, 48 (8): 08113-08116.
- [44] Ma R, Cheng S, Zhang X, et al. Oxygen evolution and corrosion behavior of low-MnO<sub>2</sub> -content Pb-MnO<sub>2</sub>, composite anodes for metal electrowinning [J]. Hydrometallurgy, 2016, 159: 6-11.
- [45] Kiryakov G Z, Stender V V. The stability of lead and its alloys during the electrolysis of sulfuric acid solutions. II, Anode potentials of lead and its alloys. III. Binary electrochemical systems composed of lead and its alloying ingredients [J]. Zhurnal Prilkadnoi Khimii, 1952, 25: 25-31.
- [46] Li Y, Jiang L X, Lv X J, et al. Oxygen evolution and corrosion behaviors of co-deposited Pb/Pb-MnO<sub>2</sub> composite anode for electrowinning nonferrous metals [J]. Hydrometallurgy, 2012, 109: 252-257.
- [47] Kwang K, Eil L, Jung K, et al. A study on performance improvement of Ir oxide-coated titanium electrode for organic destruction [J]. Electrochimica Acta, 2002, 47 (15): 2525-2531.
- [48] Hu J M, Zhang J Q, Cao C N. Oxygen evolution reaction on IrO<sub>2</sub>-based DSA type electrodes: kinetics analysis of Tafel

lines and EIS [J]. International Journal of Hydrogen Energy, 2004, 29 (8): 791-797.

- [49] Zhang Z. Titanium electrode technology, 2th. metallurgical industry press, Beijing, 2003.
- [50] Li N, Liao J, Liu X. Research on the Sintering titanium anode for zinc electrowinning. Nonferrous Metals, 1989, 5: 16-18.
- [51] Fu Y. Application of Ti-matrix DSA anode for zinc electrowinning. Nonferrous Metals, 2004, 3: 19-20.
- [52] Sun Y, Zhu X. A method of Al-Pb composite electrode material. Chinese, CN101092707A, 2007.
- [53] Zhou S, Chen B, Guo Z, et al. Electrochemical performances of Al/Pb-Ag-Sn anode for zinc electrowinning [J]. Materials Science & Technology, 2015, 23 (1): 108-114.
- [54] Zhang Y, Guo Z. Anodic behavior and microstructure of Pb-Ca-0.6%Sn, Pb-Co<sub>3</sub>O<sub>4</sub>, and Pb-WC composite anodes during Cu electrowinning [J]. Journal of Alloys & Compounds, 2017, 103-111.
- [55] Song H, Huang H, Tan N, et al. Electrochemical Behavior of Al/Pb-0.2%Ag Anode in Fluoride Ion and Sulfuric Acid [J]. Chinese Journal of Applied Chemistry, 2016, 33 (12): 1455-1461.