CATHODE ELECTRODEPOSITION OF LEAD IN Pb^{2+}-OH^--$C_4H_4O_6^{2-}$ SYSTEM[①]

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ABSTRACT By using dynamic potential method, the influence of technical parameters was studied on the cathode process of electrowinning Pb in Pb^{2+}-OH^--$C_4H_4O_6^{2-}$ electrolytic system, and the methods for improving lead electrodeposition efficiency were put forward. The results showed that higher Pb(Ⅱ) content is due to the cooperative effect of $[OH]^-$ with $[C_4H_4O_6]^{2-}$ ligands in the electrolyte. The content of NaOH and $KNaC_4H_4O_6$ in the electrolyte together with mixing ratio between them decide the existing forms of Pb(Ⅱ) and the relative content of its complex compounds. Under proper conditions, higher electrodeposition efficiency can be achieved.

Key words lead NaOH $KNaC_4H_4O_6$ electrochemistry cathode polarization

1 INTRODUCTION

In the wet treatments, alkali electrolytic method is chiefly characterized by stable electrolysis process and excellent electrolyte cycling utilization. However, the present direct slurry electrolytic method is of low current efficiency (75% ~ 80%)[1], because the electrolyte contains low lead content (around 20 g/L) as sludge is directly leached with single NaOH solution as electrolyte. In the new basic electrolytic method which we developed, lead powder of 99.99% Pb was obtained by electrodeposition with NaOH-$KNaC_4H_4O_6$ solution as electrolyte which contains high Pb content (> 150 g/L), and with current efficiency ⩾98%. This paper investigates the electrochemical process of electrodepositing Pb in Pb^{2+}-OH^--$C_4H_4O_6^{2-}$ electrolytic system, and presents theoretical basis for improving the process.

2 TECHNICAL PRINCIPLE

Sludge from scrap batteries was desulfurized with NaOH and converted with the reduction-convertion agent we developed[2] to produce the $Pb(OH)_2$ solid. The Pb^{2+}-OH^--$C_4H_4O_6^{2-}$ electrolyte was obtained by dissolving $Pb(OH)_2$ with NaOH-$KNaC_4H_4O_6$ solution in a proper ratio. Pure lead powder was obtained by electrodeposition. The sludge mainly contains $PbSO_4$, PbO_2, PbO and Pb powder. Following chemical reation equations indicate the technical principle concerned.

(1) Desulphurization and Reduction-Convertion

$$PbO_2 + 2Fe^{2+} + SO_4^{2-} + 4H^+ = PbSO_4\downarrow + 2Fe^{3+} + 2H_2O \quad (1)$$

$$Pb + 2Fe^{3+} + SO_4^{2-} \xrightarrow{H^+} PbSO_4\downarrow + 2Fe^{2+} \quad (2)$$

$$PbSO_4 + 2OH^- = Pb(OH)_2\downarrow + SO_4^{2-} \quad (3)$$

$$PbO + H_2O = Pb(OH)_2\downarrow \quad (4)$$

(2) Dissolution

$$C_4H_4O_6^{2-} + 2H_2O = H_2C_4H_4O_6 + 2OH^- \quad (5)$$

$$2Pb(OH)_2 + 2H_2C_4H_4O_6 = Pb_2(C_4H_4O_6)_2 + 4H_2O \quad (6)$$

$$Pb_2(C_4H_4O_6)_2 + C_4H_4O_6^{2-} =$$

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$$[Pb_2(C_4H_4O_6)_3]^{2-} \quad (7)$$

$$Pb(OH)_2 + OH^- = [Pb(OH)_3]^- \quad (8)$$

(3) Electrodeposition

$$[Pb_2(C_4H_4O_6)_3]^{2-} + 4e \longrightarrow 2Pb\downarrow + 3C_4H_4O_6^{2-} \quad (9)$$

$$[Pb(OH)_3]^- + 2e \longrightarrow Pb\downarrow + 3OH^- \quad (10)$$

$$4OH^- - 4e \longrightarrow O_2\uparrow + 2H_2O \quad (11)$$

$$Pb^{2+} + 4OH^- - 2e \longrightarrow PbO_2\downarrow + 2H_2O \quad (12)$$

A separate desulfurizing operation and cooperative effect of NaOH with $KNaC_4H_4O_6$ greatly increase the Pb content in the electrolyte, which is very favorable to the electrodeposition process.

3 RESULTS AND DISCUSSION

The cathode polarization curves were drawn by measuring the Pb electrodeposition process with dynamic potential method. Lead-plated copper electrode was used as working electrode (cathode), with 217 type (saturated) calomel electrode as reference electrode and graphite electrode as auxiliary anode.

3.1 Effect of principle salt content on cathode polarization

Effect of Pb content in the electrolyte on cathode polarization is given in Fig. 1.

It shows that curves 1~5 are all straight lines and lines 2~4 are approximately paralell as

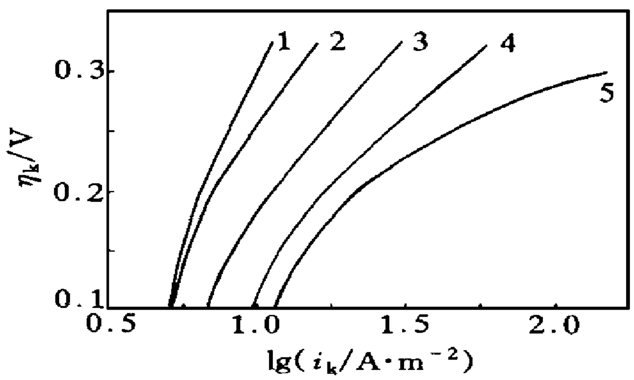

Fig. 1 Effect of lead content on cathode polarization

(NaOH: 3.75 mol/L; $KNaC_4H_4O_6$: 0.49 mol/L; gelatin: 4.0 g/L)
1—0.04 mol/L; 2—0.08 mol/L; 3—0.16 mol/L; 4—0.32 mol/L; 5—0.40 mol/L

$\eta_k > 0.2$ V, while they all assume parabola shape as $\eta_k < 0.2$ V. The cathode overpotential η_k is linearly dependent on the cathode current density i_k if $\eta_k - i_k$ figure is made. They all indicate the occurrence of electrochemical polarization in cathode under the experiment conditions. With increasing Pb content, the cathode exchange current increases and the curve removes levelly to the right. According to Tafel formula $\eta_k = a + b_k \lg i_k$, the calculated value of slope b_k decreases, which indicates that it is easy for the cathode to discharge. When Pb content increases further, degree of electrochemical polarization declines with the curve bending downward until the polarization curve characterized by diffusion control appears. At the same time, raising the Pb(II) concentration in electrolyte is of advantage for the balance potential in cathode turning positive[3]. The adoption of complex electrolyte of NaOH-$KNaC_4H_4O_6$ can greatly increase Pb content, and is beneficial to raising electrodeposition efficiency and reducing energy consumption. In addition, the discharge of single Pb^{2+} is barely found in this case, indicating that Pb exists in the electrolyte in the form of complex compounds.

3.2 Effect of NaOH content on cathode polarization

Effect of NaOH content in the electrolyte on cathode polarization is given in Fig. 2.

Fig. 2 shows that curve 1 is a straight line while $\eta_k = 0.10 \sim 0.25$ V, and starts to bend to the right while $\eta_k > 0.25$ V.

While $\eta_k = 0.10 \sim 0.35$ V, curves 2~4 are straight lines, and the linear parts of curves 1~4 are paralell to each other, which indicates the occurrence of electrochemical polarization in the cathode and basically the same discharge mechanism. With increasing NaOH content, the curve levelly removes to the right. The literature[4] mentioned that, with increasing pH value, ligand $[C_4H_4O_6]^{2-}$ is combined to ligand $[OH]^-$ and high valence metal ion as Pb(II) and so on to form some mixed-ligand complex compounds. The given concentrations of $KNaC_4H_4O_6$ and NaOH with a proper mixing

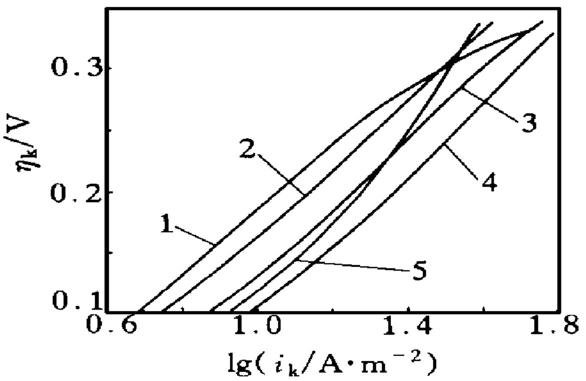

Fig. 2 Effect of NaOH content on cathode polarization

(Pb(Ⅱ): 0.32 mol/L; $KNaC_4H_4O_6$: 0.49 mol/L; gelatin: 4.0 g/L)
1 —0.23 mol/L; 2 —0.45 mol/L; —0.90 mol/L; 4 —1.80 mol/L; 5 —3.75 mol/L

ratio between them is benefitial to the formation of mixed-ligand complex compounds. Since $[C_4H_4O_6]^{2-}$ is a multi-element ligand, the obtained complex compounds are generally stable, large-volumed, with small discharge coefficient and large electronegativity, being difficult to discharge on cathode.

Complex compound $[Pb(OH)_3]^-$ easily formed at higher pH value with small electronegativity and volume, however, is easy to discharge on cathode, therefore it is preferential to discharge on cathode. When NaOH in electrolyte is lower, as curve 1 shows, $[Pb(OH)_3]^-$ content is relatively low and Pb(Ⅱ) mainly exists in the electrolyte in the form of mixed-ligand complex compounds. $[Pb(OH)_3]^-$ preferentially discharges while η_k is lower, and when η_k reaches a certain value, the mixed-ligand complex compounds start to discharge on cathode with cathode current density i_k increasing rapidly and the curve bending to the right. The relative content of $[Pb(OH)_3]^-$ in the electrolyte increases and the exchange current rises with increasing NaOH content, hence, the curve levelly removes to the right. When NaOH content is excessive in the electrolyte, as curve 5 shows, there will be excessive free $[OH]^-$ ligands, large quantities of which will form negative ions layers adsorbed on the surface of lead electrode, which is harmful to $[Pb(OH)_3]^-$ reducing-discharging on cathode. In this case, all curves levelly remove a little to the left, and the curve slope b_k rises a bit. Therefore under given electrodeposition condition, NaOH content should be controlled within a proper range.

3.3 Effect of $KNaC_4H_4O_6$ content on cathode polarization

Effect of $KNaC_4H_4O_6$ content in the electrolyte on cathode polarization is given in Fig. 3.

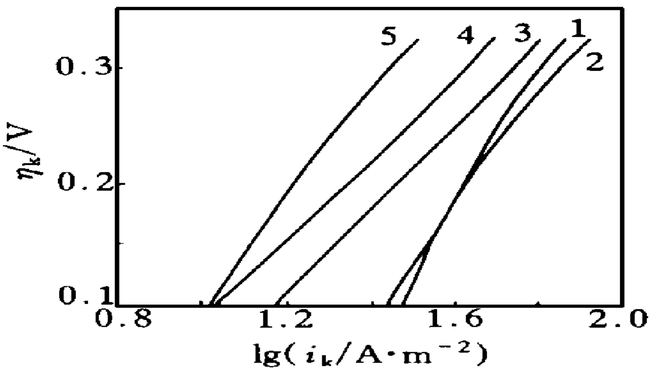

Fig. 3 Effect of $KNaC_4H_4O_6$ content on cathode polarization

(Pb(Ⅱ): 0.32 mol/L; NaOH: 3.75 mol/L; gelatin: 4.0 g/L)
1 —0.03 mol/L; 2 —0.06 mol/L; 3 —0.12 mol/L; 4 —0.24 mol/L; 5 —0.49 mol/L

It can be seen that with increasing $KNaC_4H_4O_6$ content, the cathode polarization curves move levelly to the left, and are approximately straight lines paralell to each other. This indicates that electrochemical polarization occurs and discharge mechanism are basically the same. Contrary to the increase of NaOH content, raising $KNaC_4H_4O_6$ content in the electrolyte would increase the relative amount of mixed-ligand complex compounds, reduce the relative amount of $[Pb(OH)_3]^-$ and increase the amount of free $[OH]^-$ ligands, therefore the polarization curves remove to the left levelly.

3.4 Effect of content ratio of NaOH to $KNaC_4H_4O_6$ on cathode current density

Based on the data of Fig. 2 and Fig. 3, lg[$NaOH/KNaC_4H_4O_6$] *vs* lgi_k was obtained as shown in Fig. 4.

It can be seen that, with the increase of R, the ratio of NaOH to $KNaC_4H_4O_6$, cathode current density i_k increases and reaches its extreme value at points *B* and *C*. At point *C*, contents of both NaOH and $KNaC_4H_4O_6$ are of the maximum value under the experiment condition. The appearance of the low valley points in the curves results from the cooperative effect of both increase of i_k value with increasing relative content of $[Pb(OH)_3]^-$ in the electrolyte, and decrease of i_k value with increasing negative ion adsorption of free ligands $[OH]^-$ on cathode surface.

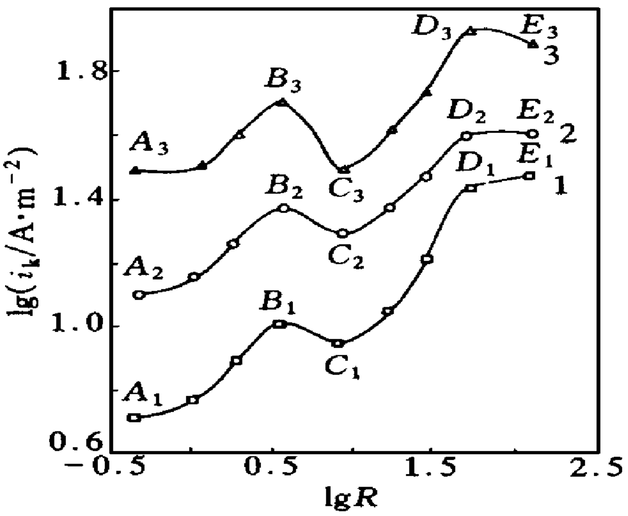

Fig. 4 Effect of the content ratio of NaOH to $KNaC_4H_4O_6$ on cathode current density

(*A* ~ *C*: $KNaC_4H_4O_6$ = 0.49 mol/L;
C ~ *E*: NaOH = 3.75 mol/L; Pb(Ⅱ): 0.32 mol/L;
gelatin: 4.0 g/L)
1 — η_k = 0.10 V; 2 — η_k = 0.20 V;
3 — η_k = 0.30 V

According to the results in Figs. 1~ 4, under the condition of the given Pb(Ⅱ) content, when NaOH content rising whithin certain range, the value of cathode current density i_k increases, and electrodeposition efficiency rises as well. On the contrary, when $KNaC_4H_4O_6$ content rising in certain range, the i_k value decreases and electrodeposition efficiency goes down. However, the rise of Pb(Ⅱ) content most notably enlarges the i_k value. Hence, under the conditions of maintaining the content level of NaOH and $KNaC_4H_4O_6$ in the electrolyte, and obtaining Pb(Ⅱ) content higher than that in single NaOH system through cooperative effect of ligands $[OH]^-$ and $[C_4H_4O_6]^{2-}$, controlling the mixing ratio of NaOH to $KNaC_4H_4O_6$ is very important for raising electrowinning efficiency to a maximum. Proper amount of gelatin added to the electrolyte is mainly used to improve the surface quality of electrodeposited lead on cathode, that is, to obtain uniform, compact and fine-grained deposit layer of lead.

4 CONCLUSIONS

(1) In comparison with the single NaOH system, the cooperative effect of $[OH]^-$ and $[C_4H_4O_6]^{2-}$ ligands in NaOH-$KNaC_4H_4O_6$ electrolyte system raises the Pb(Ⅱ) content to a large extent.

(2) NaOH and $KNaC_4H_4O_6$ content together with the ratio between them in electrolyte decides the existing form of Pb(Ⅱ) and the relative content of its complex compounds. By controlling proper conditions for obtaining high Pb(Ⅱ) content, large relative amount of $[Pb(OH)_3]^-$ complex compound and less free $[OH]^-$ ligand in the electrolyte, higher electrodeposition efficiency can be achieved.

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