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INFLUENCE OF Pb^{2+} IONS ON ZINC ELECTROWINNING FROM SULFATE SOLUTIONS

LIANA MUREŞAN, OLIMPIA ONAC

"Babeş-Bolyai" University, Faculty of Chemistry and Chemical Engineering, Department of Physical Chemistry, 3400 Cluj-Napoca, Romania

ABSTRACT. The effect of trace lead on zinc electrodeposition from sulfate electrolyte has been investigated in terms of cathodic deposit morphology and cyclic voltammetry.

The results indicated that Pb^{2+} ion has a deleterious effect on zinc electrodeposition from sulfate electrolyte. In presence of increasing Pb^{2+} concentrations, the morphology of zinc deposits was observed to change from smooth to dendritic, less adherent and the color changed from silver to a dark gray, proving a grain refining related to an inhibition effect. Pb^{2+} also affects the zinc deposition cyclic voltammograms. It increases the nucleation overpotential and diminishes the area of cathodic and anodic peaks, proving the inhibition of both the cathodic and anodic reactions.

The addition of horse chestnut extract (HCE) to the Pb^{2+} containing electrolyte counteracts the detrimental effect of these ions, leading to cathodic deposits with acceptable morphology, while increasing concentrations of animal glue, at the same Pb^{2+} concentration ($3.18\ 10^{-4}$ g/l) do not improve the cathodic morphology.

INTRODUCTION

The effects of metal impurities on zinc electrowinning from acid sulfate electrolytes have been extensively analyzed in terms of current efficiency, deposit morphology, crystal orientation and cyclic voltammetry [1-7]. Impurities behavior is not well understood and many questions remain regarding the acceptable limits of impurities for an efficient operation of zinc electrodeposition.

Unfortunately, not only the absolute magnitudes of the various impurities, but also the synergistic interactions among them ultimately determine the quality of deposit [3]. The presence of trace lead in zinc tankhouse solutions is inevitable because the zinc ore contains lead and either silver-lead or pure lead anodes are employed in the electrowinning step. Estimates of lead solubility in acid zinc sulfate solutions range from 4 to 10 mg/l [4].

The effects of trace lead and the corrosion behavior of Zn-Pb alloys have been investigated with respect to applications in alkaline zinc batteries. Trace lead (~20 mg/l) suppresses the onset of zinc dendrites [2,8] and Zn-Pb compositions (Pb ≤ 1% weight percent) exhibit superior corrosion resistance compared to pure zinc [9].

In acid media, lead has been reported as having either a small positive [5] or a small negative [10] effect on current efficiency, depending on the electrolysis conditions, solution purity, form of lead added and method of current efficiency measurement. On the other hand, lead is an impurity able to impede hydrogen evolution on zinc; at the same time, adsorbed lead strongly inhibits most of the reactions taking place on the zinc electrode [2].

Since is little agreement in the existing literature on the effects of lead, particularly with regard to its influence in the presence of organic additives, the present work was undertaken to help clarify the matter.

EXPERIMENTAL

Solution preparation

A stock solution of 1M zinc sulfate was prepared by using pure reagents (Merck) and distilled water. Electrolytes with various Pb^{2+} content ($1.59 \cdot 10^{-4}$ g/l – $1.9 \cdot 10^{-3}$ g/l) were prepared using this solution and a saturated solution of $PbNO_3$, by adding appropriate volumes into a known volume of stock solution. The horse chestnut extract was prepared by an original method [11] from the seeds of Aesculus Hyppocastanum.

Electrolysis

Small-scale electrolysis was performed in the absence and in the presence of various amounts of Pb^{2+} and/or organic additives, employing a 250 dm^3 plexiglass cell equipped with one central aluminum cathode and two symmetrical lead anodes. Zinc deposited on both sides of the cathode. The current density was held constant at 500 mA cm^{-2} and the deposition time was 60 min. Morphological examination of the copper deposits was made by visual inspection.

Cyclic voltammetry

The cyclic voltammetry experiments were conducted in a glass cell with separate compartments, using an Al disk working electrode (area 0.9 cm^2), a Pt counter electrode and a saturated calomel reference electrode. The working electrode was prepared by wet polishing on 600 grit paper and then rinsing with distilled water before each experiment. The cyclic voltammograms were recorded under potentiostatic conditions using a PS 3 potentiostat (Meinsberg, Germany), a signal generator (LP 7e Praha, Czech Republic) and a X-Y recorder (Endim 620.02, Germany). The potential range was between 0.5 V vs. SCE and –1.6 V vs SCE and the scan rate was 0.75 V/min.

RESULTS AND DISCUSSIONS

Influence of Pb^{2+} in absence of organic additives

A typical voltammogram obtained for zinc electrodeposition from an additive-free electrolyte is shown in Figure 1a. A cycle starting from point A goes through a region of low current until point C where the cathodic process begins. The current increases to point D where the scan is reversed. At the point B the current becomes anodic, corresponding to zinc dissolution. The anodic peak reaches a maximum at point E and dissolution is complete on return to A.

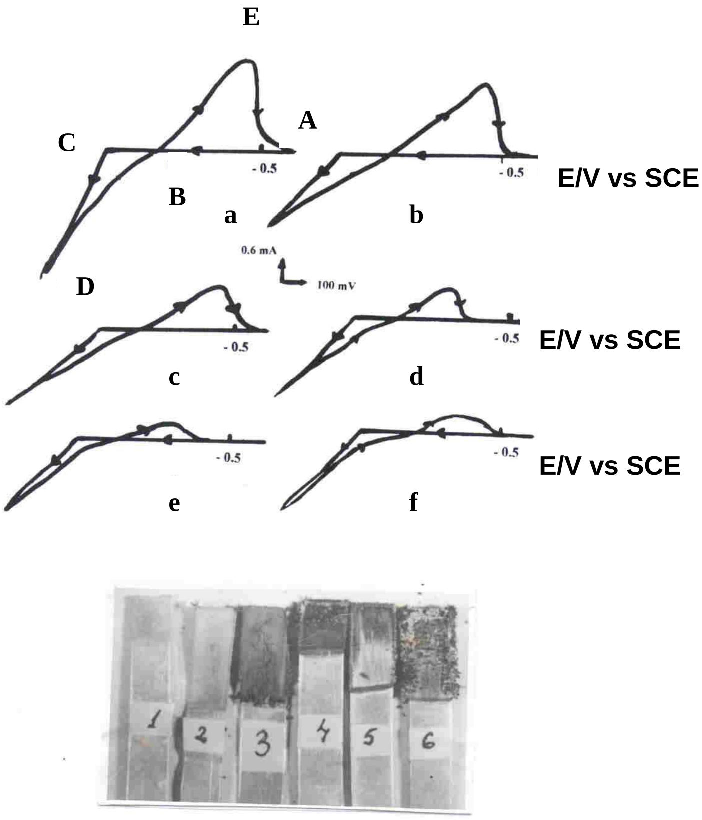

Figure 1. Cyclic voltammograms and cathodic deposits obtained in 1 M $ZnSO_4$ with increasing Pb^{2+} concentrations: a) without Pb^{2+} (electrode 1); b) $1,59.\ 10^{-4}$ g/l Pb^{2+} (electrode 2); c) $3.18.10^{-4}$ g/l Pb^{2+} (electrode 3); d) $6.37.10^{-4}$ g/l Pb^{2+} (electrode 4); e) $1.27.\ 10^{-3}$ g/l Pb^{2+} (electrode 5); f) $1.91.\ 10^{-3}$ g/l Pb^{2+} (electrode 6) Experimental conditions for voltammetry: scan rate 0.75 V/min; Experimental conditions for small-scale electrolysis: current density 500 mA/cm^2; Al cathode; Pb anodes.

The region BCD is called nucleation hysteresis loop. The point C has been used to define a nucleation overpotential [6]. The position of C shifts when certain impurities and/or additives are present in the electrolyte. The crossover potential, corresponding to B point is at or close to the reversible potential of the system.

Curves from Figure 1b until 1f represent the voltammograms recorded in presence of different Pb^{2+} concentrations. It can be observed that Pb^{2+} inhibits both cathodic and anodic reactions. The BEA region of the voltammogram, i.e. the anodic dissolution of zinc, is considerably reduced in the presence of increasing Pb^{2+} concentrations, the hight of the anodic peak (I_a) decreasing as well (Figure 2).

At the same time, the nucleation overpotential, (section BC in figure 1a) increases and the slope of CD section decreases, proving the inhibition of the cathodic process by adsorbed lead. These results are in accordance with those already reported in the literature [2], which admit that Pb^{2+} ions adsorb on the electrode, reducing the electrode coverage by ZnH_{ads}, Zn^{+}_{ads}, and active sites Zn*, species involved in the multi-step process of zinc deposition, and thus generate an inhibiting effect.

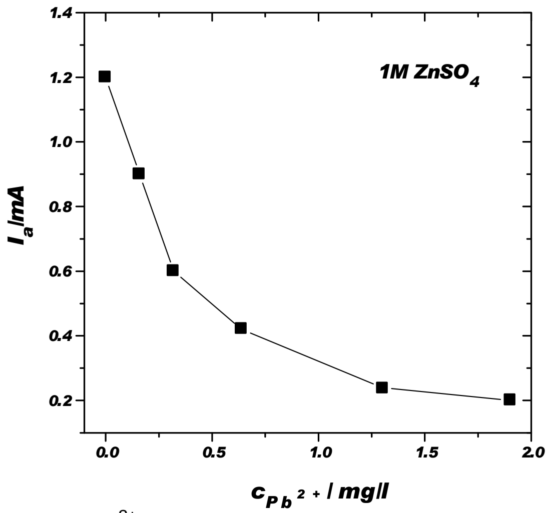

Figure 2. Influence of Pb^{2+} concentration on anodic peak current from the cyclic voltammograms recorded in 1M $ZnSO_4$ solutions; experimental conditions as in figure 1.

Moreover, hydrogen evolution on Pb_{ads} differs from hydrogen evolution on zinc, taking place with a higher overpotential. The morphology of zinc deposits was observed to be changed from smooth to dendritic, less adherent and the colour changed from silver to a dark grey, proving a grain refining related to the inhibition effect. At the same time, the deposit quality changes from acceptable to unacceptable, suggesting that Pb may be partially incorporated into the zinc lattice, as reported in the literature [4].

Influence of Pb^{2+} in presence of organic additives

Organic additives are usually added to the zinc electrolyte because they counteract the effect of impurities and thus maintain a high current efficiency [7]. They refine the deposit grain size and this results in smooth and compact deposits.

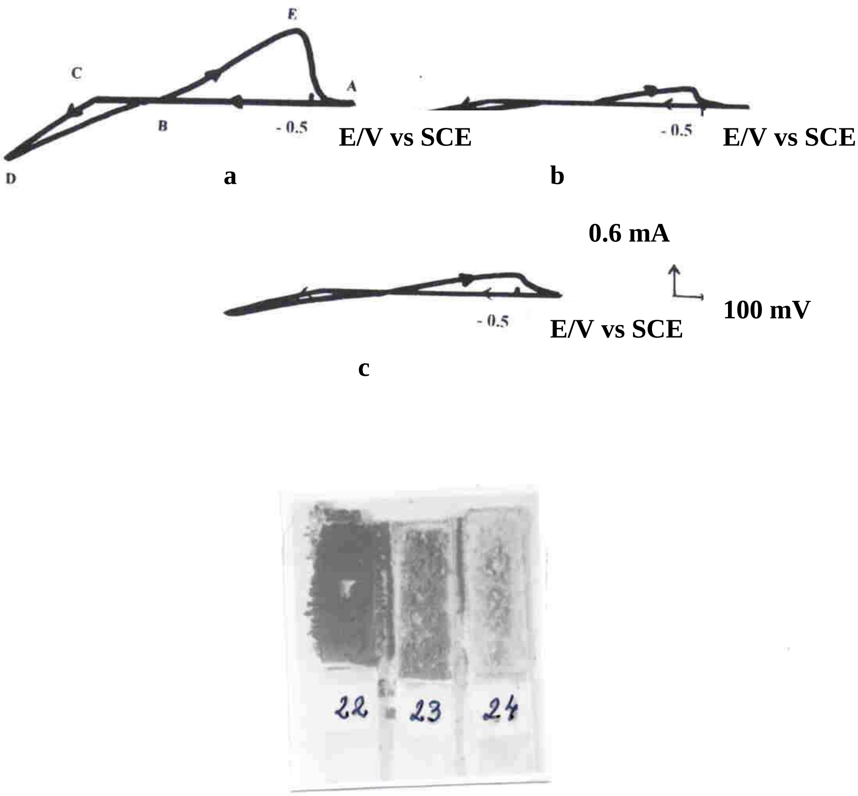

Figure 3. Cyclic voltammograms and cathodic deposits obtained in 1 M $ZnSO_4$ with fixed Pb^{2+} concentration ($3.18 \cdot 10^{-4}$ g/l) aznd increasing concentration of HCE: a) 15 mg/l HCE (electrode 22); b) 45 mg/l HCE (electrode 23); 90 mg/l HCE (electrode 24). Experimental conditions as in figure 1.

Figure 3 shows the effect of increasing HCE concentration on deposit morphology and cyclic voltammograms for electrolytes containing a fixed concentration of lead (3.18. 10^{-4} g/l). As it can be seen, increasing concentration of the organic additive has a beneficial influence on cathodic morphology. At higher HCE concentrations (Figure 3, electrode 24) the deposits become levelled and any negative influence of Pb^{2+} seems to be counteracted.

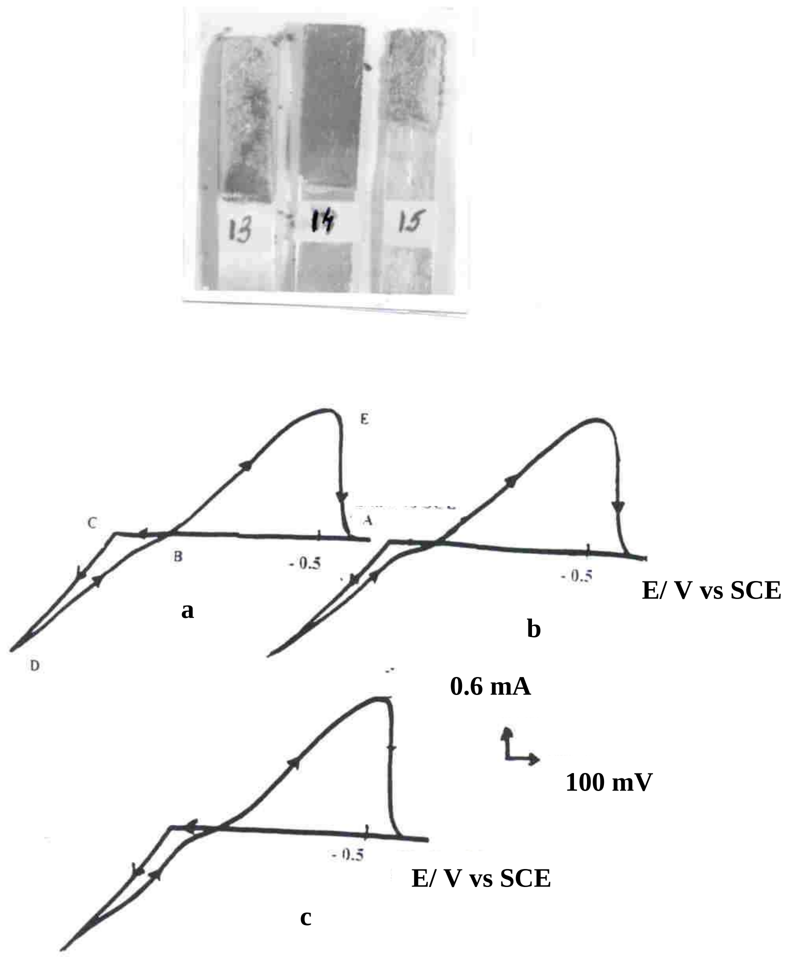

Figure 4. Cyclic voltammograms and cathodic deposits obtained in 1 M $ZnSO_4$ with fixed Pb^{2+} concentration (3.18 10^{-4} g/l) and increasing concentration of animal glue: a) 15 mg/l glue (electrode 13); b) 45 mg/l glue (electrode 14); 90 mg/l glue (electrode 15). Experimental conditions as in figure 1.

The aspect of cyclic voltammograms suffers some changes. At higher HCE concentration, they exhibit smaller anodic and cathodic peaks as in the absence of HCE, at the same Pb^{2+} concentration (Figure 1c). In all cases, the slopes of CD and BE portions decrease dramatically, showing a diminution of zinc deposition, hydrogen evolution rate and zinc corrosion, respectively. The 3D-hysteresis loop BCD diminishes its area proving a controlled nucleation.

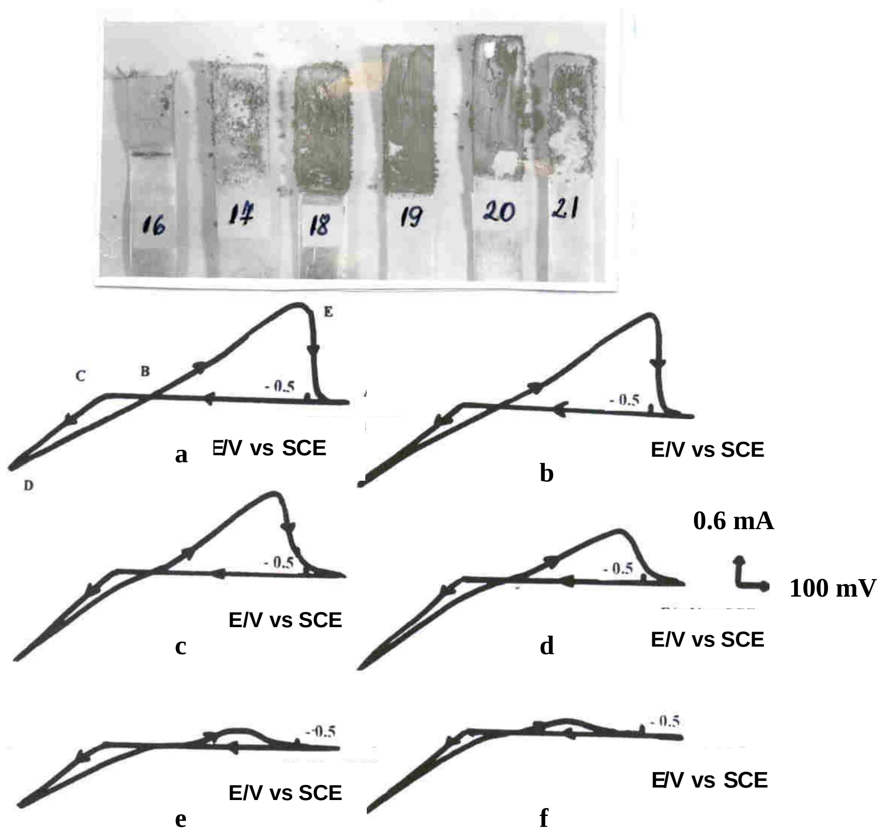

Figure 5. Cyclic voltammograms and cathodic deposits obtained in 1 M $ZnSO_4$ with fixed HCE concentration (30 mg/l) and increasing concentrations of Pb^{2+}: a) 0 g/l Pb^{2+} (electrode 16); b) 1,59. 10^{-4} g/l Pb^{2+} (electrode 17); c) 3.18·10^{-4} g/l Pb^{2+} (electrode 18); d) 6.37· 10^{-4} g/l Pb^{2+} (electrode 19); e) 1.27.10^{-3} g/l Pb^{2+} (electrode 20); f) 1.91. 10^{-3} g/l Pb^{2+} (electrode 21). Experimental conditions as in figure 1.

A different effect is put on evidence in the presence of animal glue. Increasing concentration of glue, at the same Pb^{2+} concentration (3.18 10^{-4} g/l) do not improve the cathodic morphology (Figure 4). An increase of anodic and cathodic peak area is observed and the slopes of CD and BD portions are almost unaffected. Thus, it can be concluded that the animal glue does not counteract the effect of Pb^{2+} ions.

This difference in the behavior of the two additives could be attributed to the formation of an adsorbed complex species $[Pb\ (HCE)]_{ads}$ when HCE is used, complex which exerts a beneficial inhibiting effect upon zinc electrodeposition. The above-mentioned complex species was put on evidence during lead electrodeposition and its formation is diffusion-controlled [11]. A similar complex does not appear in the case of animal glue.

The beneficial effect of HCE vanishes by increasing Pb^{2+} concentration at constant HCE (Figure 5). This leads to the idea that, as both additives act at the interface, a competition between them is possible, and Pb^{2+} adsorption prevails at higher concentration of this ion and, consequently, the result is a decrease of cathodic leveling degree.

CONCLUSIONS

The results indicated that Pb^{2+} ion has a deleterious effect on zinc electrodeposition from sulfate electrolyte. In presence of increasing Pb^{2+} concentrations, the morphology of zinc deposits was observed to change from smooth to dendritic, less adherent and the color changed from silver to a dark gray, proving a grain refining related to an inhibition effect. Pb^{2+} also affects the zinc deposition cyclic voltammograms. It increases the nucleation overpotential and diminishes the area of cathodic and anodic peaks, proving the inhibition of both the anodic and cathodic reactions.

The addition of horse chestnut extract (HCE) to the electrolyte counteracts this detrimental effect, leading to cathodic deposits with acceptable morphology, while same amount of animal glue doesn't have a similar beneficial effect. Increasing concentrations of glue, at the same Pb^{2+} concentration (3.18 10^{-4} g/l) do not improve very much the cathodic morphology.

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