

Particle Size Refinement of Zn Electrodeposits in Alkaline Zincate Solutions with Polyethylene Glycol and Tween 80

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The alkaline zinc electrowinning process can directly recover powdery Zn metal from oxidized zinc ores and industrial wastes. However, the industrial-scale practice shows that the Zn powders produced generally have a broad particle size distribution, and further milling is required prior to applications. In this study, the effects of two kinds of organic additives, polyethylene glycol (PEG) and tween 80, on the particle size refinement of Zn deposits in alkaline electrolytes were investigated for the first time. The results show that both of the additives dramatically reduced the particle size of Zn deposits and increased the weight percentage of undersized product (<150 μm) while the current efficiency remained > 98% and the Zn purity was > 99%. From results of scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), X-ray diffraction (XRD) analysis, and cyclic voltammetry (CV) experiments, the possible explanation is that the addition of tween 80 and/or PEG increased cathodic overpotential and subsequently increased the Zn nucleation rate and restrained the Zn grain growth. Eventually, an increased amount of Zn deposits with fine 3-D structure were produced, and a higher Zn deposit refinement was achieved. Orthogonal experiments were designed to investigate the co-effects of the additives and the electrolysis parameters: electrolyte temperature, current density, and electrolysis time. The optimum particle size refinement was obtained when 5 mg/L tween 80 and 100 mg/L PEG were added to the alkaline electrolyte, and the electrolysis was conducted for 10 min at 0 °C with a current density of 800 A/m²; 99.82 wt.% of <150 μm particles and 52.94 wt.% of <45 μm particles were observed.

Keywords: Polyethylene glycol; Tween 80; Particle Size Refinement; Zn powder; Alkaline

1. INTRODUCTION

Over the past few decades, more than 80% of the global Zn metal was produced from zinc sulfide concentrates using the roast-acidic leach-electrowinning process [1,2]. However, with the depletion of zinc sulfide ores, oxidized zinc ores and industrial wastes such as zinc ash, dross, and flue dusts, are important resources in zinc metal production [1,3]. Several researchers have demonstrated that the alkaline zinc electrowinning process has distinct advantages over the acidic electrowinning process [4-8]. One of the advantages is that Zn powder can be directly produced by the alkaline electrowinning process [9,10]. Zn powders with fine particles have been applied in a number of areas including cementation, paints, and the reduction of organic substances, because they have high specific surface areas and can significantly enhance reaction rates. Nevertheless, the industrial-scale alkaline zinc electrowinning practice shows that the Zn powders produced have a broad particle size distribution, and further milling is required prior to applications [11].

According to the literature, there are limited studies of the particle size refinement of Zn deposits in alkaline electrolytes while the improvement of Zn electro-deposition structure has been studied more substantially. A variety of inorganic additives such as PbO, Na₂WO₄, SnO, CdO, Pb₃O₄, and BiCl₃ has shown a beneficial effect on suppressing the dendritic growth of Zn deposits which has the potential to lead to particle size refinement [12-16]. Our previous work demonstrated that the presence of Pb (20-40 mg/L) in alkaline electrolytes affected the particle size refinement [17]. An obvious disadvantage of the above inorganic additives is the co-deposition of heavy metals in the zinc powder, and this is potentially hazardous in subsequent applications. Organic additives, however, are not incorporated into Zn during the electrodeposition process. Cetyltrimethylammonium bromide and sodium lauryl sulfate have shown positive effects on particle size refinement [18]. Finding new convenient additives remains a significant area of research.

We tested two new organic substances, polyethylene glycol (PEG) and tween 80, which have been used as surfactant additives to improve cathodic deposition structure [19,20,21]. Effects of these on particle size refinement and morphology of the Zn deposits during alkaline electrowinning were studied. In order to simulate industrial reaction conditions, the concentrations of sodium hydroxide (NaOH) and Zn²⁺ in the electrolytes was the same as the industrial practice described in the literature [11]. Further orthogonal experiments were used to study the co-effects of the additives and the electrolysis parameters (temperature, time, and current density) on the particle size refinement, since these electrolysis parameters also contribute to the cathodic deposition [9,17,22].

2. EXPERIMENTAL DETAILS

2.1 Solution Preparation

An electrolyte with 0.55 M Zn²⁺ and 5 M NaOH was selected to mimic industrial conditions. The electrolyte was prepared by dissolving 0.55 mol ZnO and 6.1 mol NaOH in distilled water. (0.55 M ZnO requires 1.1 M NaOH for dissolving.) Different amounts of additives (PEG and tween 80)

were added to the above electrolyte to prepare different concentrations of additives (from 1 mg/L to 500 mg/L) in each experiment. Distilled water was used to bring the volume of each electrolyte solution to a total of 1 L. All chemicals were of analytical grade.

2.2 Laboratory-scale electrowinning experiments

The electrowinning experiments were carried out in a 1 L cell which was made as described in the literature [17]. One magnesium cathode flanked by two stainless steel anodes was used, with a 3 cm heteropole distance and a 100 cm² active area. After electrolysis, the Zn deposits were removed from the cathode, washed thoroughly with distilled water and dried in a vacuum drying oven. The effects of particle size refinement were defined by the weight percentage of the undersized product, obtained with a 150 µm (or 45 µm) aperture screen. The weight percentage increased with decreased particle size.

The co-effects of electrolysis conditions [temperature (factor A), time (factor B), current density (factor C), and additive (factor D)] on the particle size refinement of Zn deposits were investigated through an orthogonal experimental design. An orthogonal array $L_9(3^4)$ was employed to assign the four factors with three levels. The factor level details are shown in Table 1. The values of factor D were determined by the results of the electrowinning experiments, and the values of factors A, B, and C were based on our earlier experiments.

Table 1. Factors and levels affecting the particle size refinement of Zn electrodeposits

Level	Factor			
	A (temperature, °C)	B (time, min)	C (current density, A/m ²)	D (additive, mg/L)
1	0	5	800	5 mg/L tween 80
2	25	10	1000	100 mg/L PEG
3	50	20	1200	5mg/L tween80+100mg/L PEG

2.3 Cyclic voltammetry (CV) experiments

A three-electrode Plexiglas cell was used for cyclic voltammetry experiments to study the mechanisms of particle size refinement. Pt foil was used as the counter electrode, and the Hg/HgO electrode was the reference electrode. The working electrode was a foil electrode of nickel (Alfa Aesar, 99.5%), which was masked so that an area of 1 cm² was exposed to the electrolyte. Prior to each experiment, the nickel electrode was polished with 1000 grid emery paper and then rinsed with distilled water. Cyclic voltammetry was performed for all of the samples in the potential range of -0.6 to -1.8 V vs. Hg/HgO at a scan rate of 10 mV/s. The voltammograms were measured using an electrochemical station (CHI600E, CH Instruments Ins., USA) at room temperature.

2.4 Zn electrodeposits characterization

The 150 μm and 45 μm aperture screens were used to obtain the respective undersized product. The collected undersized product was weighed, and the weight percentage was calculated. The weight percentage was used to describe the effect on particle size refinement. The Zn electrodeposits were collected for the analysis of morphology, chemical composition, crystal structure, and Zn purity. The morphology and chemical composition of the Zn electrodeposits were examined using scanning electron microscopy (SEM, SU8010, Hitachi, Japan) and energy-dispersive X-ray spectroscopy (EDS, APOLLOX, AMETEK, USA). The crystal structure was analyzed using X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with a scanning rate of $2^\circ/\text{min}$. The content of Zn in the Zn electrodeposits was analyzed by chemical titration.

3. RESULTS AND DISCUSSION

3.1 Effects of polyethylene glycol and tween 80 on the particle size refinement

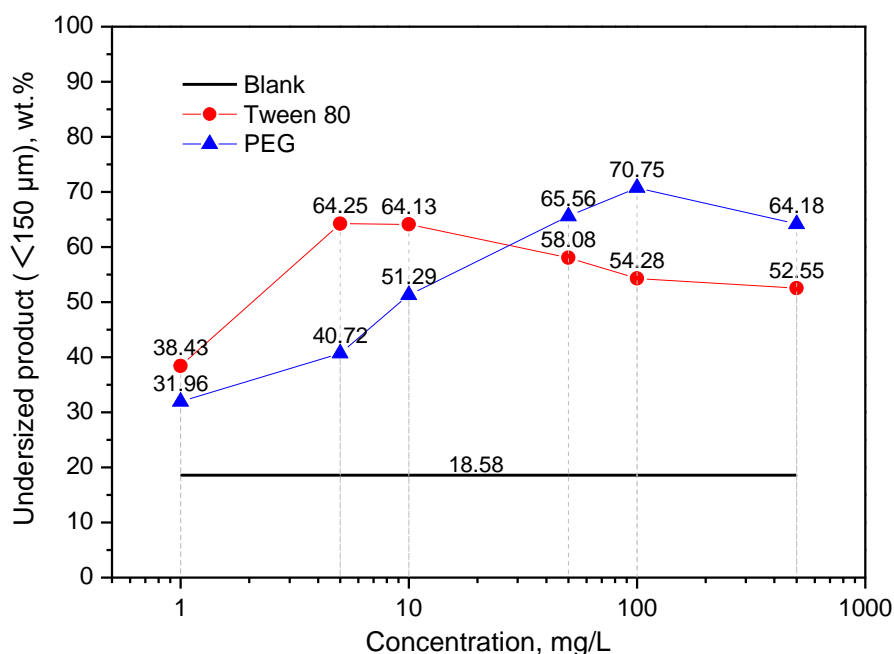


Figure 1. Effects of tween 80 and PEG on the particle size refinement of Zn electrodeposits. The electrolysis parameters were 50°C , 1000 A/m^2 , and 20 min.

After the addition of different concentrations of tween 80 and PEG, the electrolysis was carried out for 20 min at 50°C with a current density of 1000 A/m^2 . The effects of tween 80 and PEG on the particle size refinement were described by the weight percentage of undersized product. Fig. 1 shows the relationship between the different concentrations of tween 80 and PEG and the corresponding undersized product (wt.%). In the additive-free electrolyte, 18.58 wt.% of undersized product ($< 150\text{ }\mu\text{m}$) was obtained from the Zn electrodeposits. After the addition of a small amount of tween 80 (5 mg/L) and PEG (100 mg/L), the undersized product ($< 150\text{ }\mu\text{m}$) increased significantly to 64.25 wt.%

and 70.75 wt.%, respectively (Fig. 1). Moreover, the weight percentage of the undersized product increased up to 71.55 wt.% when both 5 mg/L tween 80 and 100 mg/L PEG were added to the alkaline solution. We suggested that the addition of tween 80 and/or PEG dramatically increases the percentage of undersized product, i.e., it ultimately reduces the particle size of Zn electrodeposits.

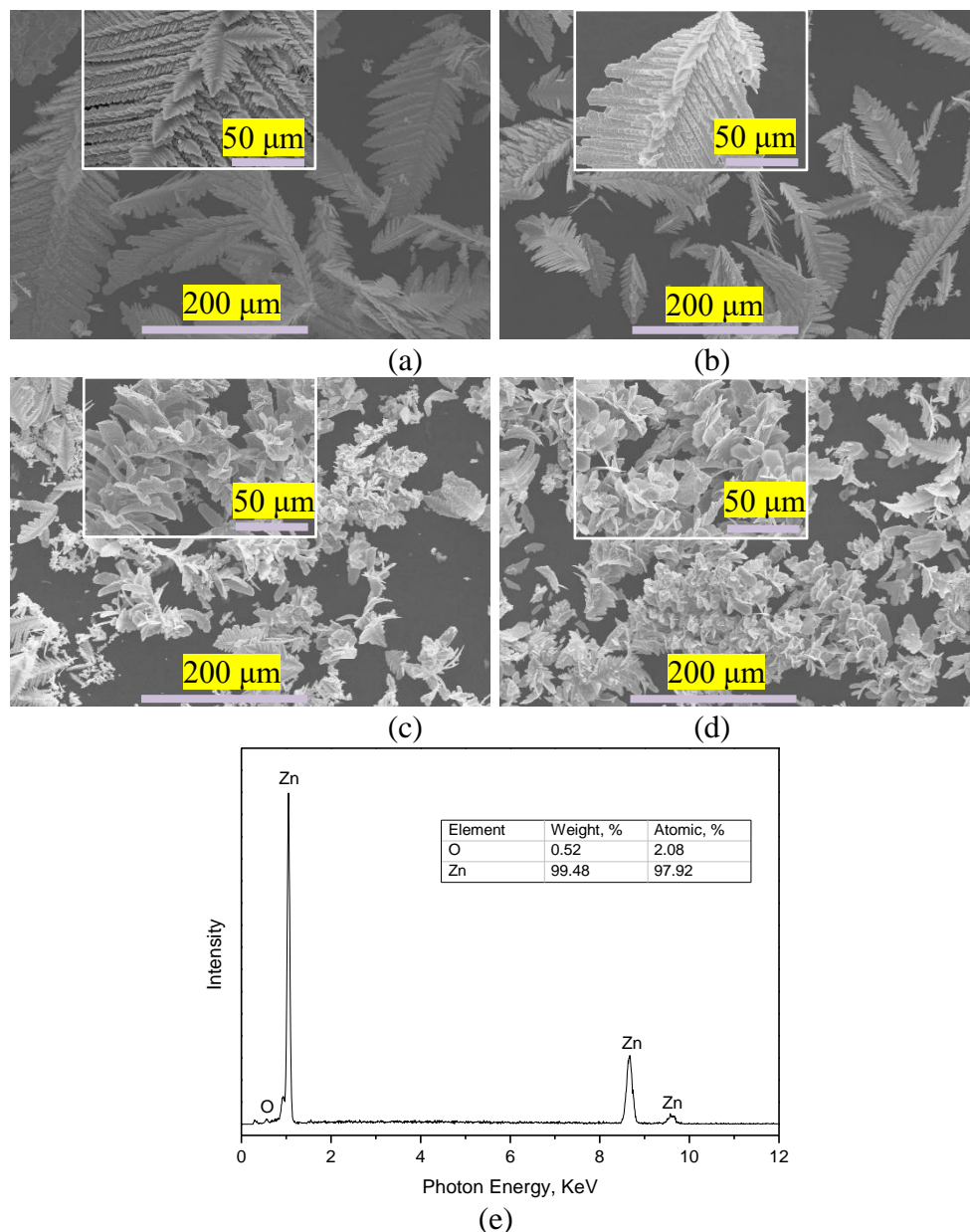


Figure 2. Microscopic images of the Zn electrodeposits prepared with different additives: (a) additive-free, (b) 5 mg/L Tween 80, (c) 100 mg/L PEG, (d) 5 mg/L Tween 80 + 100 mg/L PEG and (e) the EDS result of (d). The electrolysis parameters were 50°C, 1000 A/m², 20 min.

To further illustrate the reason of the increased proportion of fine Zn particles with additives, further microscopic images of the Zn electrodeposits were collected. Fig. 2 shows the microscopic images of the Zn electrodeposits. In the additive-free electrolyte, dendritic growth was well observed (Fig. 2a). After adding 5 mg/L tween 80, more dendrites were observed with finer stems and shorter

side branches (Fig. 2b). After the addition of 100 mg/L PEG, the dendrites were finer, and the morphology was partially changed from dendritic growth to a three-dimensional structure, consisting of many small leaves as side branches (Fig. 2c). This change was well promoted when 5 mg/L tween 80 and 100 mg/L PEG co-existed in the alkaline electrolyte. In particular, more fine dendrites and 3-D structure were observed (Fig. 2d). This may indicate that the exact mechanism of particle size refinement is different when tween 80 and PEG are added to the alkaline electrolyte individually or in combination. Nevertheless, the higher percentage of undersized product, which corresponds to Zn electrodeposits refinement, probably results from an increased production of fine 3-D structure.

The EDS spectrum and X-ray diffraction (XRD) patterns of the above Zn electrodeposits were collected to analyze the purity of the Zn electrodeposits (Fig. 2e and Fig. 3). The EDS spectrum of the Zn electrodeposits was collected from the deposits which were prepared in the presence of 5 mg/L tween 80 + 100 mg/L PEG (Fig. 2d). Both the EDS spectrum and the XRD patterns confirmed that the electrodeposits were mainly composed of metallic Zn. The result of chemical titration also showed that the Zn purity of the deposits was higher than 99%. The oxygen peaks detected (Fig. 2e) can possibly be explained by the partial oxidation of the powdery deposits. In Fig. 3, it is noted that the XRD peaks were broader after the addition of 5 mg/L tween 80 + 100 mg/L PEG, which might be a reflection of Zn grain size refinement.

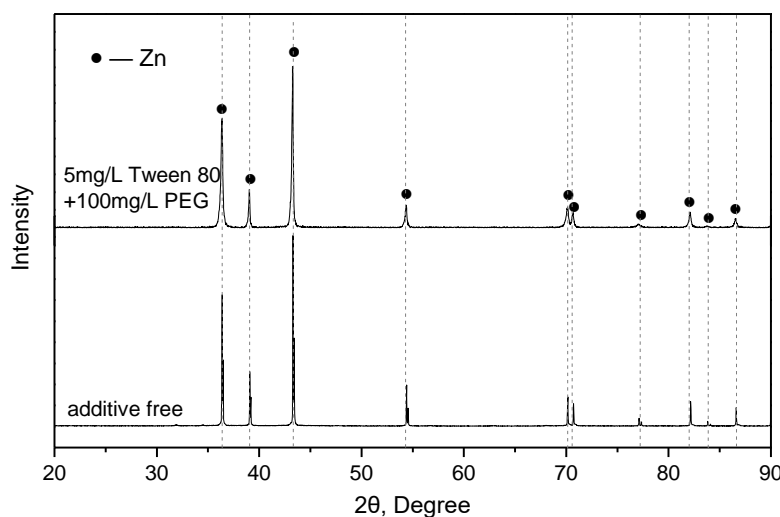


Figure 3. X-ray diffraction patterns of the samples prepared in the additive-free and 5 mg/L tween 80+100 mg/L PEG containing alkaline electrolytes. The electrolysis parameters were 50 °C, 1000 A/m², 20 min.

The mechanisms of particle size refinement were further studied by cyclic voltammetry (CV) experiments. The cyclic voltammograms with the addition of 5 mg/L tween 80, 100 mg/L PEG, 5 mg/L tween 80 + 100 mg/L PEG, and no additives were determined. The results show that the presence of 5 mg/L tween 80 remarkably increased the cathodic overpotential (Fig. 4). An even higher overpotential was obtained when the alkaline electrolyte contained 100 mg/L PEG or 5 mg/L tween 80 + 100 mg/L PEG. This suggests that the increased particle size refinement was possibly promoted by

the increased cathodic overpotential which was caused by the additives. This might be due to the specific adsorption of zincate on the additives or on the decomposition products of the additives [8]. These can decrease the zincate mass transfer rate, increase the cathodic overpotential, and increase the Zn nucleation rate, all of which subsequently restrain the Zn grain growth.

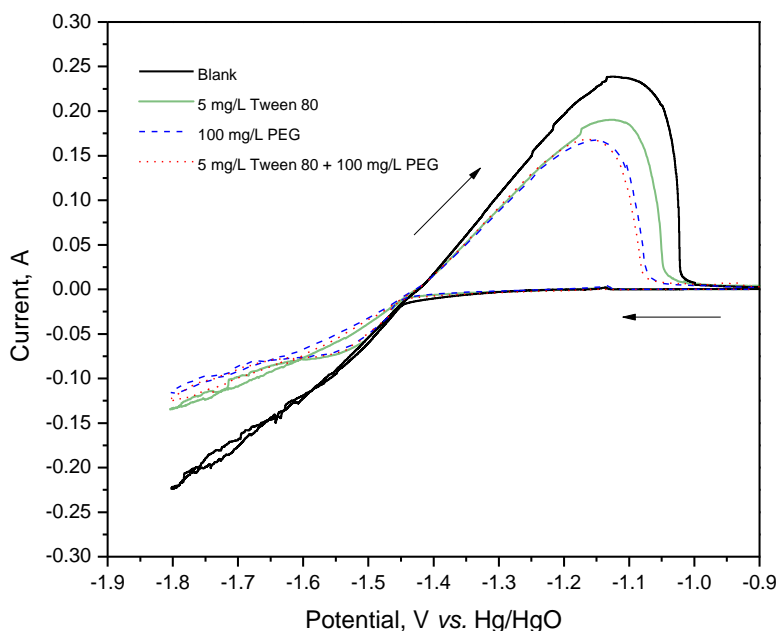


Figure 4. Cyclic voltammograms measured in the electrolytes containing different amounts of additives. Scan rate: 10 mV/s.

It was noted that the anodic current decreased in the presence of the additives (Fig. 4). This result agrees with a previous report that the anodic current decreased by adding Pb^{2+} or WO_4^{2-} to alkaline electrolytes [12]. It has also been reported that the anodic current increased when SnO was added to alkaline electrolytes [13]. The anodic current reflects the dissolution rate of metallic Zn. The decrease of the anodic current possibly indicates that the presence of the additives restrained the Zn electrodeposition reaction. However, no evident changes in the weight of the deposited Zn powder were observed, and the Zn current efficiency remained high ($>98\%$) in all of the electrowinning experiments, regardless of whether the additives were present or not. This may be because the cathode used in the electrowinning experiments was magnesium instead of nickel. Meanwhile, the electrolysis time increased from 2 min in the CV experiments to 10 or 20 min in the electrowinning experiments. Hydrogen evolution was only seen for a short time at the beginning of all of the electrowinning experiments. After the magnesium cathode was covered with a layer of zinc deposits, the hydrogen evolution stopped, and a high current efficiency was obtained [9,23].

3.2 Results based on Orthogonal experiment design

Nine more trial studies were carried out according to the orthogonal array $L_9(3^4)$ to verify the co-effects of the four factors on the particle size refinement. The experimental results and the range

analysis data are shown in Table 2. K_{ij} and R_j are the two parameters in the range analysis. The notation K_{ij} refers to the mean value of experimental results for a particular factor j (where $j = A, B, C$, or D) at a particular level i (where $i = 1, 2$, or 3). For the same factor j , a higher value of K_{ij} means that the corresponding level has a larger effect on the particle size refinement [24]. R_j is defined as the range between the maximum and minimum values of K_{ij} . R_j is used for evaluating the importance of factor j , i.e., a larger R_j means a factor is of greater importance [25]. For example, the calculations for factor A are as follows:

$$K_{1A} = \frac{71.96 + 75.73 + 85.60}{3} = 77.76$$

$$K_{2A} = \frac{60.75 + 58.72 + 65.29}{3} = 61.59$$

$$K_{3A} = \frac{46.27 + 61.13 + 40.59}{3} = 49.33$$

$$R_A = \max(K_{iA}) - \min(K_{iA}) = 77.76 - 49.33 = 28.43$$

where K_{iA} is the K value of factor A at level i . The K and R values of the other factors can be determined in the same manner.

Table 2. Results and range analysis data of the orthogonal array $L_9(3^4)$ test. i is the level with $i = 1, 2$, and 3 ; j is the factor with $j = A, B, C$, and D ; K_{ij} refers to the mean value of experimental results for factor j at level i ; R_j indicates the significant influence of the factor j .

Trial no. \ Level, i	Factor, j				Results
	A (temperature, °C)	B (time, min)	C (current density, A/m ²)	D (additive, mg/L)	Undersized product (<150 µm), wt. %
1	1	1	1	1	71.96
2	1	2	2	2	75.73
3	1	3	3	3	85.60
4	2	1	2	3	60.75
5	2	2	3	1	58.72
6	2	3	1	2	65.29
7	3	1	3	2	46.27
8	3	2	1	3	61.13
9	3	3	2	1	40.59
K_{1j}	77.76	59.66	66.13	57.09	-
K_{2j}	61.59	65.19	59.02	62.43	-
K_{3j}	49.33	63.83	63.53	69.16	-
R_j	28.43	5.53	7.10	12.07	-

A decreasing order of $R_A > R_D > R_C > R_B$ can be concluded from Table 2. As mentioned above, R_j indicates the significant influence of factor j , and a large R_j means that this factor has a more significant impact on the particle size refinement. Hence, the decreasing order means that the impact order of the factors is: temperature (28.43) > additive (12.07) > current density (7.10) > time (5.53). Of these, R_A is the largest, which means the electrolyte temperature is the most significant factor.

The mean value (K_{ij}) of each factor is shown in Fig. 5. The weight percentage of undersized product (<150 μm) decreased dramatically and regularly with electrolyte temperature, from 77.76 wt.% at 0 °C to 49.33 wt.% at 50 °C. This means more fine particles were formed at lower temperature. This trend is consistent with a previous report that the apparent density of the Zn deposits increased with decreasing temperature [8]. This may be due to the higher cathode overpotential caused by the decrease in temperature, which increases the Zn nucleation rate and restrains the grain growth [17]. The weight percentage of particles (<150 μm) increased from 59.66 wt.% to 65.19 wt.%, and then slightly decreased to 63.83%, when electrolysis time increased from 5 min to 10 min, and then further to 20 min. After increasing current density from 800 to 1000, and then to 1200 A/m^2 , the weight percentage decreased from 66.13 wt.% to 59.02 wt.%, and then increased to 63.53 wt.%. A previous report showed that the average Zn particle size decreased regularly when current density decreased in sulfuric acid electrolytes [26]. Although the best level of current density for particle refining is still the minimum value (800 A/m^2), the trend is different. This difference could be the result of the different aqueous systems employed. For the additive (factor D), the largest weight percentage (69.16 wt.%) was observed when both 5 mg/L tween 80 and 100 mg/L PEG were added to the alkaline electrolytes. This trend is consistent with the results of the electrowinning experiments in this research.

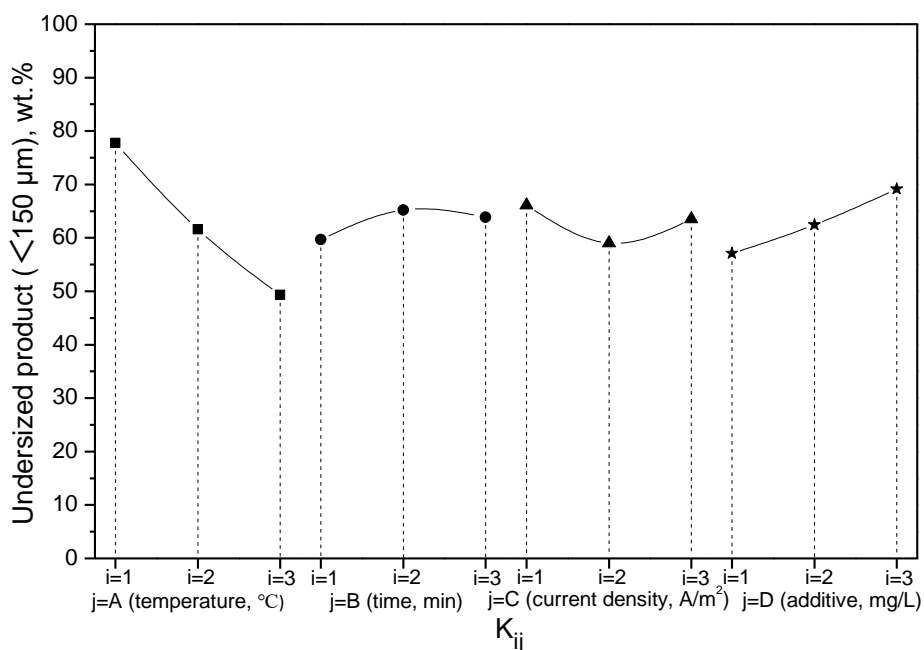


Figure 5. Relationship between the mean value (K_{ij}) of each factor and the weight percentage of undersized product (<150 μm , wt.%).

We propose that the best level for the four factors is 0 °C, 10 min, 800 A/m^2 , and 5 mg/L tween 80 + 100 mg/L PEG. At this level, Zn electrodeposits of 99.82 wt.% of <150 μm particles and 52.94

wt.% of $<45\text{ }\mu\text{m}$ particles, were obtained in the supplementary experiments. Since an electrolyte temperature of $0\text{ }^{\circ}\text{C}$ is difficult to achieve in industry, a supplementary electrowinning experiment was carried out at $25\text{ }^{\circ}\text{C}$, 10 min, 800 A/m^2 , and 5 mg/L tween 80 + 100 mg/L PEG. However, the results show that increasing the temperature from $0\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$ caused the weight percentage of the particles ($<150\text{ }\mu\text{m}$) to decrease sharply from 99.82 wt.% to 80.52 wt.%, and that the electrodeposited leaves became larger and thinner (Fig. 6). As mentioned above, the electrolyte temperature was the largest factor for particle refinement. A small change in electrolyte temperature can lead to a large change in the weight percentage of undersized product.

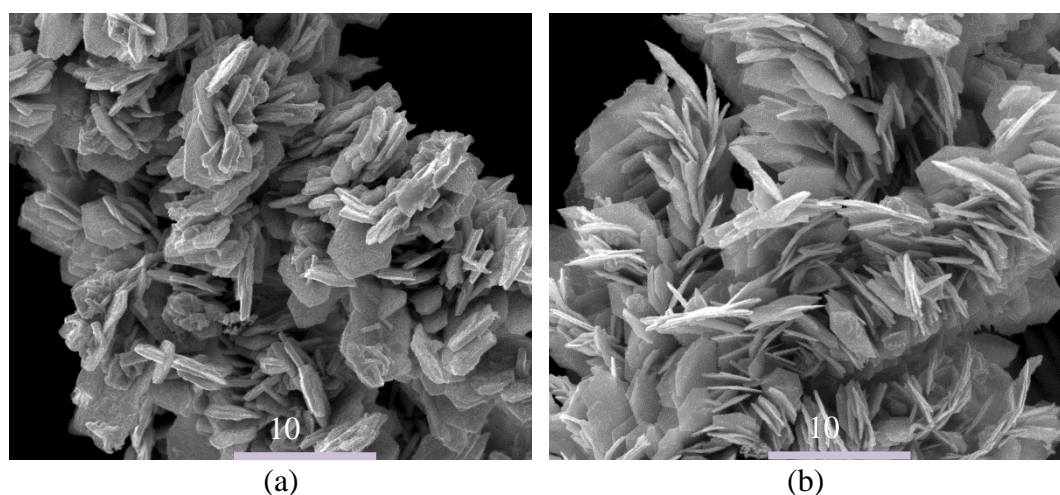


Figure 6. Microscopic images of the Zn electrodeposits prepared at a temperature of (a) $0\text{ }^{\circ}\text{C}$ and (b) $25\text{ }^{\circ}\text{C}$. The electrolysis conditions were 10 min, 800 A/m^2 , and 5 mg/L tween 80 + 100 mg/L PEG.

4. CONCLUSIONS

This study demonstrated the effects of two kinds of organic additives, polyethylene glycol and tween 80, on the particle size refinement of Zn deposits in the alkaline zinc electrowinning process. The results showed that the addition of 5 mg/L tween 80 and 100 mg/L PEG, individually or in combination, significantly increased the proportion of the fine particles ($<150\text{ }\mu\text{m}$) while the current efficiency and the Zn powder purity remained high ($>98\%$ and $>99\%$, respectively). The possible explanation is that the addition of tween 80 and/or PEG increased the cathodic overpotential, produced more fine 3-D structure, and eventually reduced the particle size of the Zn electrodeposits. More work is needed to investigate the effect of tween 80 and/or PEG on the zincate reduction and their relationship to the morphology of the Zn electrodeposits. Furthermore, low temperature is anticipated to significantly promote the particle size refinement. The optimum particle size refinement was obtained when 5 mg/L tween 80 + 100 mg/L PEG were added to the electrolyte and the electrolysis was conducted for 10 min at $0\text{ }^{\circ}\text{C}$ with a current density of 800 A/m^2 . Under these conditions, 99.82 wt.% of $<150\text{ }\mu\text{m}$ particles and 52.94 wt.% of $<45\text{ }\mu\text{m}$ particles were observed.

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