

## Particle Size Refinement of Zn Electrodeposits in Alkaline Zincate Solutions with Poly (ethylene glycol ) (12) Tridecyl Ether. Part II

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Electrowinning of zinc from alkaline solutions is a promising technology which can directly produce metallic zinc powder from the treatment of zinc-containing ores and wastes. Fine zinc powder is of great interest in a variety of industries, such as paints, battery electrodes and cementation. This study investigated the effect of Poly (ethylene glycol) (12) tridecyl ether (PTE) on the dendritic growth and the particle size distribution of Zn electrodeposits in alkaline solutions that have similar content as used in industry. The dendritic growth of Zn electrodeposits was studied using current-time technique and scanning electron microscopy (SEM) while the purity was analyzed by energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The particle size distribution was investigated by sieve analysis, laser particle size analyzer and cathodic potentiodynamic polarization, respectively. The results suggest that the presence of PTE can effectively inhibit the dendritic growth of Zn electrodeposits, where small, flat and layer-less dendrites with high Zn purity (99.34 wt.%) were electrodeposited. The data from the sieve analysis shows that 77.16 wt.% of electrodeposits can pass the sieve up to 150  $\mu\text{m}$  in size after the addition of PTE. This was significantly higher than from the additive-free electrolyte (19.21 wt.%). The cathodic polarization curves suggest that, after the addition of PTE, more negative overpotential of Zn electrodeposition was observed, which increased the nucleation rate of Zn nuclei and more fine zinc particles were produced. These results indicate that PTE is an effective additive for the particle size refinement of Zn electrodeposits in alkaline zincate solutions.

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**Keywords:** Poly (ethylene glycol) (12) Tridecyl Ether; Particle Size Refinement; Alkaline; Electrowinning; Zinc

## 1. INTRODUCTION

Electrowinning of zinc from alkaline solutions is a promising technology for the treatment of low-grade zinc ores and industrial wastes which are not amenable to the typical acid electrolysis process [1,2]. It offers significant energy savings and high productivity as compared to the acid process [3,4]. Moreover [5,6], the alkaline electrowinning can directly produce zinc metal in a powdery form, i.e. zinc powder, which is widely used in a variety of industries.

The alkaline electrolysis process has been successfully applied at a scale used in commercial production [7]. The zinc powder deposited on the cathode has a wide range of particle size distribution, mainly from 28  $\mu\text{m}$  to 250  $\mu\text{m}$  or even larger. Some industries, such as paints, battery electrodes and cementation, however, prefer fine to large zinc powder since high surface areas are required to increase reaction rates. A further crushing and screening process is thus required for such purposes which leads to increased capital investment, energy costs and even the risk of oxidization of metallic zinc during the crushing process [8]. Hence, it is of great significance to find suitable methods to electrodeposit fine zinc powder directly in alkaline zincate solutions.

It is found that changing the electrolysis conditions, including the cathode material, current density, temperature and alkaline concentration, etc., may lead to the refinement of electrodeposited Zn particles [4,6,9,10]. However, the electrolysis parameters have been already optimized with a synthetic consideration of particle size, current efficiency, productivity and raw-leaching efficiency (involving alkaline concentration). The change is scrupulous and not even allowed in commercial production, since some unexpected problems may occur. For example, with the increase of the current density, smaller particles can be observed, while a higher specific energy consumption is also attained [4].

The addition of surfactants seems a feasible method for the particle size refinement of Zn electrodeposits. It is reported that Zn electrodeposits obtained from the commercial production, in the main, have a dendritic structure [7]. Our previous study found that such dendritic growth could be inhibited and subsequently more and finer zinc powder obtained with the presence of surfactants Tween 80 and Polyethylene Glycol [11]. Chang et al. [12] reported that the surfactant, Poly (ethylene glycol) (12) tridecyl ether (PTE) could be used as a crystal growth capping agent for Au deposition on Al foil. The surfactant was adsorbed by certain metallic Au crystal facets and thus suppressed the crystal facets growth. It is anticipated that PTE maybe capable of suppressing the dendritic growth of Zn electrodeposits. However, to the best of our knowledge, the surfactant PTE has not being studied and used in Zn electrodeposition. In this paper, we aimed to test the effect of PTE on the particle size refinement of Zn electrodeposits in alkaline zincate solutions. The effect of PTE on dendritic growth and particle size distribution was studied and the possible driving mechanism is discussed.

## 2. EXPERIMENTAL

### 2.1 Materials

Electrolyte composition of 35 g/L  $\text{Zn}^{2+}$  and 200 g/L NaOH was utilized to mimic the electrolyte used in commercial production. Deionized water, ZnO and NaOH (Chemical pure, Sinopharm Chemical Reagent Co., Ltd.) were used to prepare the electrolyte. Different amounts of

PTE ( $C_{13}H_{27}(OCH_2CH_2)_nOH$ ,  $n \sim 12$ , Aldrich) were added to prepare electrolytes with different PTE concentrations.

## 2.2 Electrochemical test

A three-electrode system was used for the electrochemical test. A platinum foil served as a counter-electrode and a Hg/HgO electrode served as the reference, and a nickel foil (Alfa Aesar, 99.5%) with an exposed area of  $1 \text{ cm}^2$  served as the working electrode. Prior to the electrochemical testing experiments, the working electrode was polished with emery paper (1000 grid) and rinsed with distilled water.

Electrochemical testing experiments were carried out with an electrochemical station (CHI600E, CH Instruments Ins., USA) at room temperature. The current-time curves were measured at a pre-determined cathodic potential and the cathode polarization curves were obtained by the potentiodynamic method with a scan rate of 5 mV/s.

## 2.3 Zinc electrowinning experiment

A 1000 mL volume apparatus was used for the zinc electrowinning experiments. More details about the apparatus settings were described in our earlier study [9]. One magnesium cathode flanked by two stainless steel was used with a 30 mm heteropole distance and  $70 \times 70$  mm dimensions.

To mimic the real conditions of commercial production, the zinc electrowinning experiments were performed with a current density of  $1000 \text{ A/m}^2$  at  $50 \text{ }^\circ\text{C}$ . After electrolysis, the electrodeposits were removed from the cathode, washed with deionized water and dried in a vacuum drying oven.

## 2.4 Electrodeposits characterization

The particle size distribution of Zn electrodeposits was examined from a laser particle size analyzer (S3500, Microtrac, USA) and sieve analysis (Sinopharm Chemical Reagent Co., Ltd.). The specific surface area was measured on the surface area and porosimetry analyzer (ASAP2460, Micromeritics, USA). The morphology was observed by a scanning electron microscopy (SEM, SU 8010, Hitachi, Japan) while the chemical composition was analyzed with an energy-dispersive X-ray spectroscopy (EDS, APOLLOX, AMETEK, USA). The crystal structure was investigated by X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with a scan rate of  $2^\circ/\text{min}$ .

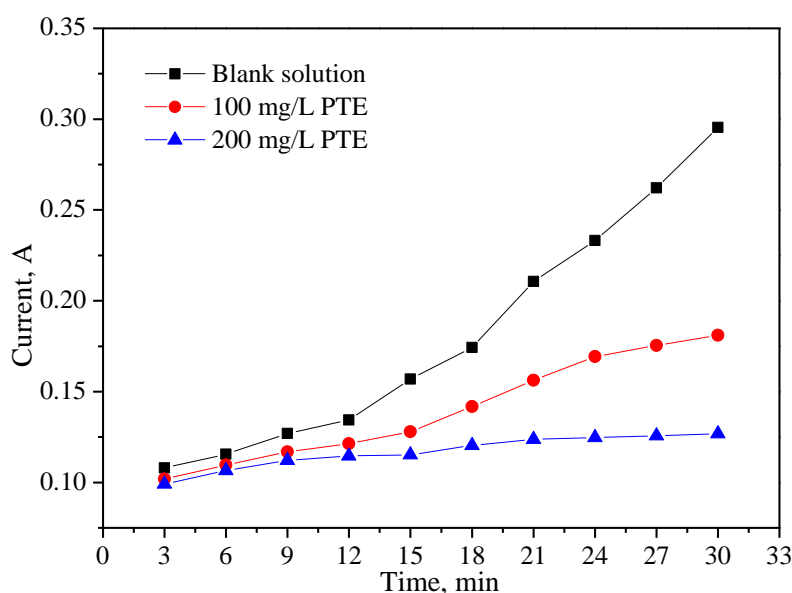
# 3. RESULTS AND DISCUSSION

## 3.1 The effect of PTE on the dendritic growth of Zn electrodeposits

The current-time curves of zinc electrodeposition in the alkaline solutions with and without PTE at a cathodic potential of  $-1.6 \text{ V}$  are shown in Figure 1. At this potential zinc electrodeposition is the main reaction on the cathode. Since the zinc electrodeposition is controlled by mass transfer, any

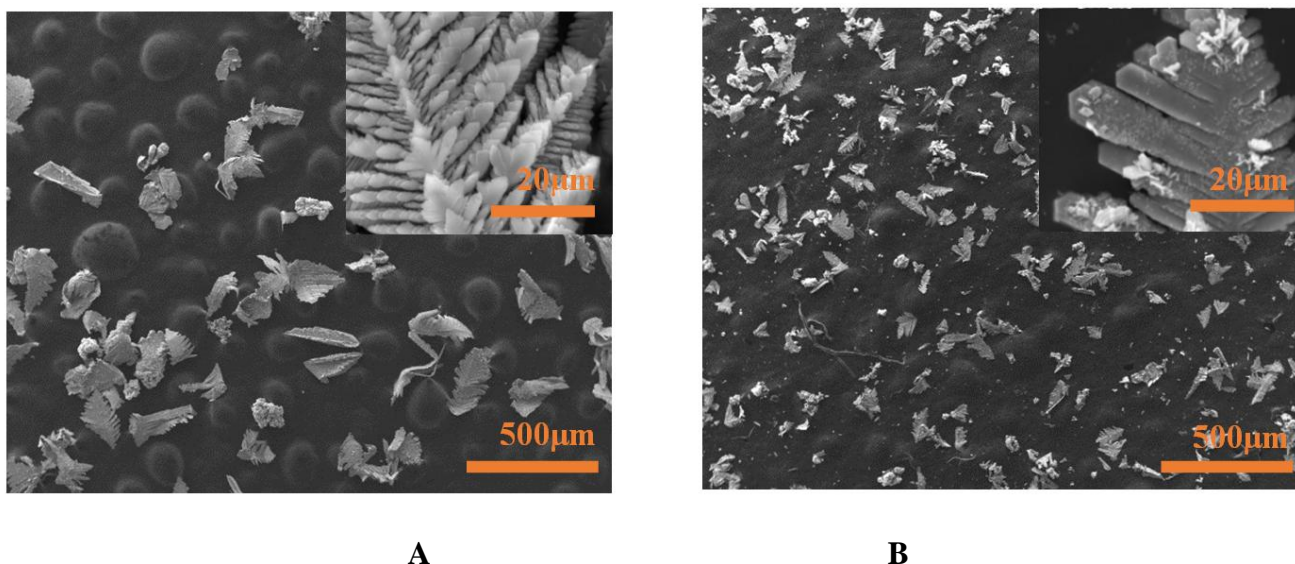
rise in cathodic current during a potential-controlled electrodeposition can be attributed to the true electrode surface area increasing (often dendritic growth) [13]. On the contrary, a flatter current-time curve indicates the decline of the increased true electrode surface area and the inhibition of dendritic growth. Hence, the effect of PTE on the dendritic growth of Zn electrodeposits can be assessed by its effect on the current.

Figure 1 shows that the cathodic current in the blank solution rises about 0.19 A (from 0.11 A to 0.30 A) during the test. It indicates that many Zn dendrites were produced on the electrode surface. However, flatter current-time curves were obtained after the addition of PTE (Figure 1). Along with the increase of PTE concentration from 100 mg/L to 200 mg/L, the rise of cathodic current significantly decreased from 0.08 A to 0.03 A. The results suggest that the presence of PTE leads to a decline of the increased true electrode surface area and effectively inhibits the dendritic growth of Zn electrodeposits.



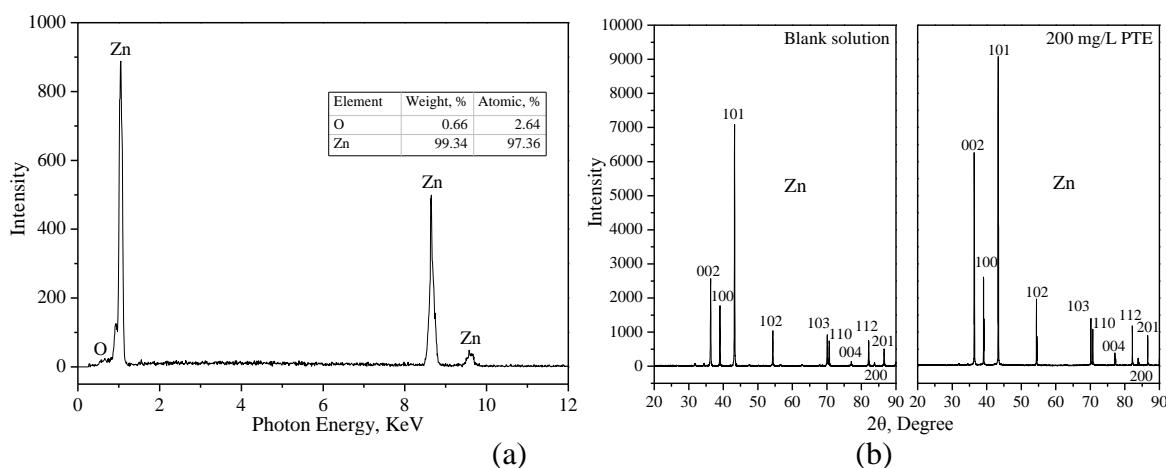
**Figure 1.** Current-time curves of zinc electrodeposition in electrolytes with different amounts of PTE at a cathodic potential -1.6 V. Blank solution: 35 g/L  $Zn^{2+}$ , 200 g/L NaOH.

Both visual observation and SEM images further confirm the inhibition of dendritic growth after the addition of PTE. Visual observation found loose and large dendritic deposits on the electrode surface in the blank solution while dense and small deposits were observed in the electrolyte containing 200 mg/L PTE. Selected SEM images show that the electrodeposits were all in dendritic form. However, in comparison with the SEM images of electrodeposits obtained in additive-free electrolyte (Figure 2A), the dendrites became small, flat and layer-less after the addition of 200 mg/L PTE (Figure 2B)



**Figure 2.** Microscopic images of Zn electrodeposits obtained from electrolytes with different amounts of PTE: (A) Blank solution; (B) 200 mg/L PTE. Blank solution: 35 g/L Zn<sup>2+</sup>, 200 g/L NaOH. The Zn electrowinning experiments were conducted with a current density of 1000 A/m<sup>2</sup> at 50 °C for 1 h.

The purity and crystal structure of the electrodeposits obtained in the electrolyte with 200 mg/L PTE were analyzed by EDS and XRD. EDS analysis shows that the electrodeposits were mainly composed of Zn (99.34 wt.%) after the addition of 200 mg/L PTE (Figure 3a). The presence of PTE had no obvious influence on the purity of Zn electrodeposits. The existence of minimal oxygen (0.66 wt.%) was possibly due to the partial oxidation of Zn during the washing and drying process. XRD patterns further confirmed that the electrodeposits were metallic Zn no matter with or without PTE (Figure 3b). The presence of 200 mg/L PTE obviously promoted the growth of (101) and (002) crystal plane. A similar result was found by Li et al. [14] where the growth of (101), (002) and (100) crystal plane was observed while more fine Zn particles were produced.



**Figure 3.** EDS analysis and XRD patterns of Zn electrodeposits obtained in the electrolyte with 200 mg/L PTE. Blank solution: 35 g/L Zn<sup>2+</sup>, 200 g/L NaOH. The Zn electrowinning experiments were conducted with a current density of 1000 A/m<sup>2</sup> at 50 °C for 1 h.

Overall, all data from current-time curves tests, visual observation, SEM imaging, EDS and XRD analysis confirmed that the dendritic growth of Zn electrodeposits was obviously suppressed and more fine zinc particles with high purity were electrodeposited in the presence of PTE, especially at the high concentration of 200 mg/L.

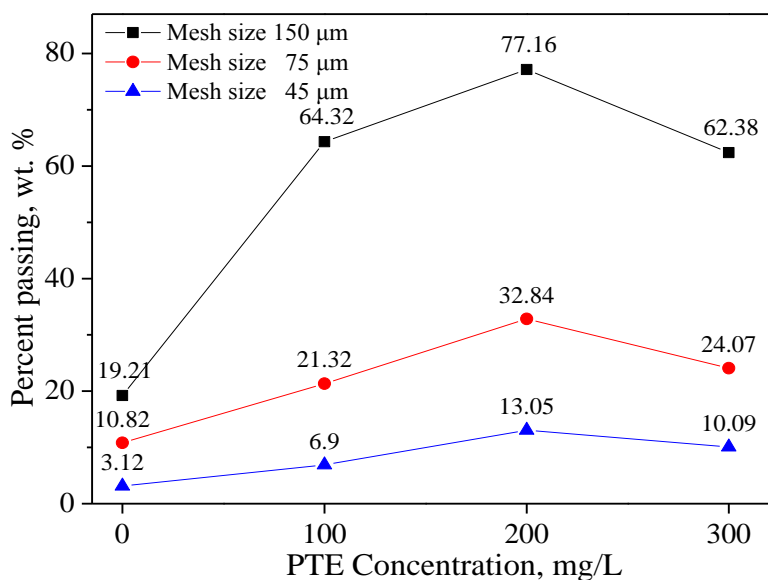
### 3.2 The effect of PTE on the particle size refinement of Zn electrodeposits

To investigate the effect of PTE on the particle size refinement of Zn electrodeposits, further zinc electrowinning experiments were carried out and the particle size distribution of the electrodeposited zinc particles was analyzed. Results from sieve analysis are shown in Figure 4 while the data from the laser particle size analyzer is shown in Figure 5 and Table 1.

Figure 4 shows the relationship between the percent passing (wt.%) of Zn electrodeposits and the PTE concentration changings. The percent passing (PP) was calculated by the following equation:

$$PP = \frac{W_{Below}}{W_{Total}} \times 100\%$$

where:  $W_{Below}$  is the total mass of the Zn electrodeposits within the sieves below the current sieve, not including the current sieve's Zn electrodeposits; and  $W_{Total}$  is the total mass of all of the Zn electrodeposits in the sample. The mesh size of 150  $\mu\text{m}$ , 75  $\mu\text{m}$  and 45  $\mu\text{m}$  were employed and the corresponding PP result was marked as PP150, PP75 and PP45, respectively.

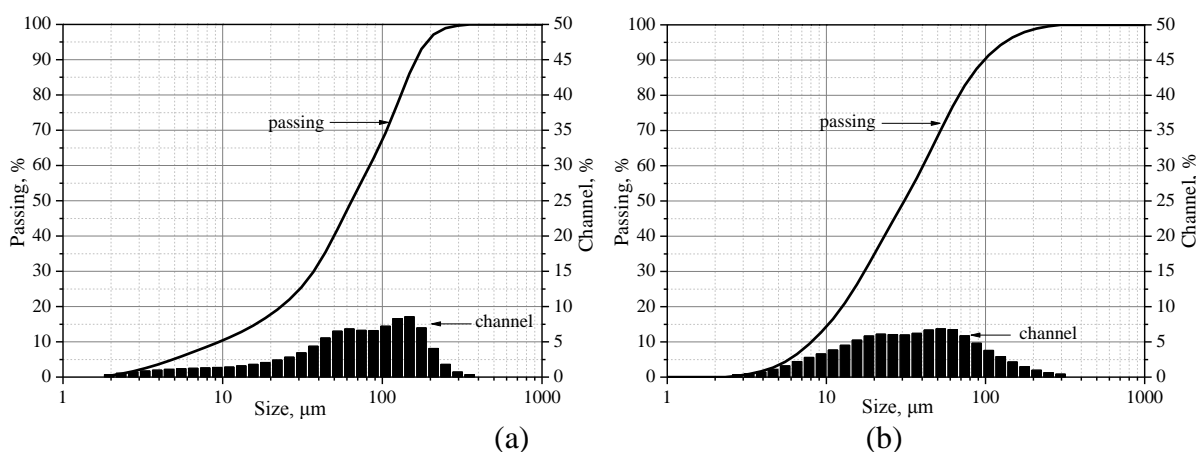


**Figure 4.** Percent passing of the zinc electrodeposits obtained from electrolytes with different amount of PTE. The Zn electrowinning experiments were conducted with a current density of 1000  $\text{A}/\text{m}^2$  at 50  $^\circ\text{C}$  for 1 h.

Figure 4 indicates that in the additive-free electrolyte, the PP150 was 19.21 wt.%. The PP150 significantly increased to 64.32 wt.% and further to 77.16 wt.% after increasing the PTE concentration to 100 mg/L and 200 mg/L, respectively. The peak PP150 was much higher than in our previous work, where the PP150 was 71.55 wt.% after the addition of Tween 80 and Polyethylene Glycol together

[11]. Therefore, the surfactant PTE seems have a more positive effect on the particle size refinement than Tween 80 and Polyethylene Glycol. Similar trends were observed with PP75 and PP45 where the percent passing constantly increased after the addition of 100 mg/L and 200 mg/L PTE. These results mean a constant increase percent of fine particles in Zn electrodeposits after the addition of PTE up to 200 mg/L. However, it was found that the PP150 decreased to 62.38 wt.% from 77.16% once the PTE concentration further increased to 300 mg/L from 200 mg/L. Similar trends were also observed with PP75 and PP45. It indicates that the decline of the particle refinement occurred at the higher PTE concentration of 300 mg/L.

Figure 5 indicates that the Zn electrodeposits had more fine particles after adding 200 mg/L PTE, where the channels of fine particles (e.g. 3 μm - 70 μm) dramatically increased. Table 1 shows that half the number of the electrodeposited Zn particles were < 30.85 μm (D50) with the presence of 200 mg/L PTE, while the D50 of the Zn particles, electrodeposited without PTE was 64.31 μm. Similar trends were found in other size analysis parameters, such as D90, D (4, 3) and D (3, 2), where the respective size of Zn particles with PTE was lower than the ones without PTE. The data from Table 1 also confirmed that more fine Zn particles were electrodeposited after the addition of 200 mg/L PTE.

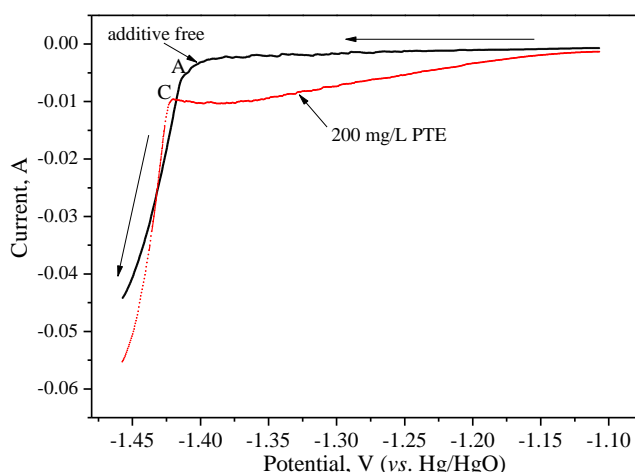


**Figure 5.** Graphs of Zn electrodeposits passing and channel versus the logarithmic size in (a) the blank solution and (b) 200 mg/L PTE. Blank solution: 35 g/L Zn<sup>2+</sup>, 200 g/L NaOH. The Zn electrowinning experiments were conducted with a current density of 1000 A/m<sup>2</sup> at 50 °C for 1 h.

**Table 1.** Mean diameter of the Zn electrodeposits obtained from electrolytes with different amount of PTE. Notes: The Zn electrowinning experiments were conducted with a current density of 1000 A/m<sup>2</sup> at 50 °C for 1 h. D (3, 2): mean diameter by area. D (4, 3): mean diameter by volume. D (50): diameter for 50 % passing. D (90): diameter for 90 % passing.

PTE concentration, mg/L	Mean diameter, μm			
	D (3, 2)	D (4, 3)	D50	D90
0	23.49	78.44	64.31	162
200	18.71	44.54	30.85	97.97

The cathodic potentiodynamic polarization curves of zinc in electrolytes with and without PTE are described in Figure 6. The beginning of the rapid current increase in the additive-free solution was observed at point A (-1.37 V) while the beginning of the rapid current increase in the 200 mg/L PTE electrolyte was observed at point B (-1.43 V). The overpotential of Zn electrodeposition in the presence of PTE became more negative than in the blank solution. This can possibly be attributed to the decreased mass transfer rate of the zinc ion by the PTE adsorption. Such rapid increase in current normally reflects the Zn reduction reaction which leads to the Zn electrodeposition. Furthermore, the size of the particles that form during crystallization is dependent on the ratio of nucleation rates of nuclei and their further growth [15]. After the addition of PTE, more negative overpotential was obtained which increased the nucleation rate of the nuclei [9] and, consequently, more fine Zn particles were electrodeposited.



**Figure 6.** Cathodic polarization curves of zinc in alkaline solutions with different amount of PTE. Scan rate: 5 mv/s. Temperature: 25 °C.

In addition, the specific surface area of electrodeposits, current efficiency and cell voltage during the zinc electrowinning experiments were also studied. We found that the specific surface area of Zn electrodeposits significantly increased from 0.52 m<sup>2</sup>/g to 1.74 m<sup>2</sup>/g after adding 200 mg/L PTE, indicating that more fine particles were produced. The current efficiency decreased a little from almost 100 % to 97.6% after adding 200 mg/L PTE while the cell voltage always fluctuated over a similar range (2.5 V – 2.7 V).

#### 4. CONCLUSIONS

This study investigated the effect of PTE on the dendritic growth and particle size refinement of Zn electrodeposits in alkaline zincate solutions. The results indicated that the presence of PTE effectively inhibited the dendritic growth of Zn electrodeposits by decreasing the mass transfer rate of zinc ion via the PTE adsorption. As a result, the percent of Zn particles passing the mesh size of 150



$\mu\text{m}$  (PP150) significantly increased from 19.21 wt.% in additive-free electrolyte to 77.16 wt.% after the addition of 200 mg/L PTE while the purity of Zn electrodeposits was as high as 99.34 wt.%. Meanwhile, the current efficiency remained at a high level (97.6 %) and the cell voltage always fluctuated over a similar range. We believe that PTE is a valuable addition to the current additive "library" which can enhance the particle size refinement of Zn electrodeposits during the electrowinning of zinc from alkaline solutions. It also suggests that the stability of PTE in alkaline zincate solutions, the effect of PTE on the impurities removal and raw-leaching efficiency should be studied further.

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