



The electrowinning of zinc from sodium hydroxide solutions



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ABSTRACT

Electrodeposition of zinc in the sodium hydroxide solutions on a stainless steel cathode was systematically investigated by means of cyclic voltammetry, chronoamperometry and chronopotentiometry in this paper. It was revealed that the deposition process was controlled by mass transport, and the diffusion coefficient of $\text{Zn}(\text{OH})_4^{2-}$ ions was $3.22 \times 10^{-6} \text{ cm}^2/\text{s}$. Meanwhile, the cathode process was studied at different potentials as well. It was the charging process of electrochemical double layers at potential in a range from -1.1 V to -1.4 V (vs. SCE). However, nucleation and diffusion of $\text{Zn}(\text{OH})_4^{2-}$ ions were the dominating processes at potential from -1.47 V to -1.56 V (vs. SCE). The nucleation process was promoted, and the steady diffusion current improved with the increasing potential. Remarkably, the hydrogen ions were reduced fiercely on cathode at -1.7 V and -1.8 V (vs. SCE). Furthermore, the current efficiency was also discussed at different electrowinning times and current densities. An energy waste period was found at the beginning of electrowinning, which was caused by hydrogen evolution, and the current efficiency increased to the maximum (*current efficiency peak*) slowly at 500 A/m^2 . Nevertheless, the results showed that the current efficiency peak was highest and it was fastest to reach the peak when the applied current density was near the limiting diffusion current density, 95.7 A/m^2 .

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1. Introduction

There is a huge demand for zinc due to its wide application in the fields of automobile, construction, marine, battery and light industry, so any effective progress will bring great economic profit. Generally, there are two main kinds of sources for zinc industry. Zinc sulfide ore can be easily separated from gangue and upgraded by flotation, whereas its reserve is now on the edge of depletion. As the secondary mineral, zinc oxide ore has been paid close attention and extensive works have been done to deal with this low-grade ore. For example, it can be upgraded effectively by volatilization, but the heavy pollution and high capital investment problems are associated with this process (Chen and Qu, 1998; Choi et al., 1993). In principle, sulfuric acid can be employed to leach Zn from oxide ore, while with large acid consumption and complex purification process (Bodas, 1996).

In the last few years, many researchers tried to seek an efficient leaching agent, and alkaline solution (sodium hydroxide) was considered to be a viable option (Chen et al., 2009; Feng and Yang, 2007; Frenay, 1985; Zhao and Stanforth, 2000). In our previous study, the Zn leaching rate could be reached as high as 92% in 20% (6.25 mol/L) sodium hydroxide solution with a phase ratio of 80:1 at $100 \text{ }^\circ\text{C}$ for 4 h (Zhang et al., 2013). In fact, most of Pb dissolved along with Zn during the alkaline leaching process. Nevertheless, those dissolved Pb can be

quantitatively removed from the leaching solution by adding sodium sulfide (Zhao and Stanforth, 2000).

Currently, more than 80% amounts of zinc are produced by electrowinning, which is one of the key processes to maximize the factory benefit. It has been reported that the best specific energy can be 1.75 kWh/kg with 1000 A/m^2 in the alkaline electrowinning (St-Pierre and Piron, 1986). Compared to the 3.3 kWh/kg with 500 A/m^2 in the classical industrial process, large energy can be saved. However, the current efficiency is always below 100%, which depends on the local current density. As the mass of zinc deposited on the cathode can give the mean current efficiency and the mean partial current density, the reasonable primary current density should be between the following two extreme situations: (1) the local current efficiency equals the mean current efficiency, and (2) the partial current density for hydrogen evolution is constant with the cathode (Degrez et al., 1993). Moreover, the influence of electrolysis conditions on the zinc deposits morphology has been investigated in some laboratory-scale experiments (Gurmen and Emre, 2003). Zinc can deposit on cathode in a compact form during the first few minutes of electrowinning. But it will become spongy in the following process, owing to the hydrogen gas evolution at the electrode surface. Because of the large improvement in the surface area, powdery zinc deposits make it possible to use high current density for electrolysis (St-Pierre and Piron, 1990).

In the present work, we investigated the electrodeposition behavior of zinc in sodium hydroxide solutions on the stainless steel cathode by means of cyclic voltammetry, chronoamperometry and chronopotentiometry. In order to optimize the electrowinning

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conditions, a series of experiments were carried out with different operating parameters. Besides, some detailed discussions on the cathode process and current efficiency were also included in this study. The present work could give guidance on the practical zinc electrowinning from alkaline solution.

2. Experimental

2.1. Materials

All chemicals used in this research were analytical reagent grade. The solutions were prepared with deionized water. The cathode products were washed by ethyl alcohol. The zinc oxide ore (purchased from Lanping town in Yunnan province of China) was ground to less than 150 μm particles for the following experiment.

2.2. Experimental procedure

In order to research the zinc electrodeposition behavior, electrolyte was prepared according to the experimental design and a three-electrode system was employed. The stainless steel working electrode with an area of 1 cm^2 was polished using SiC paper and then cleaned with deionized water and ethanol in sequence. A larger graphite plate was used as the counter electrode. The reference electrode was saturated calomel electrode (SCE). All the electrochemical measurements were carried out with an electrochemical workstation (solartron SI 1287).

In the electrowinning procedure, the ore was calcined in a muffle furnace at 400 $^\circ\text{C}$ for 2 h, and then leached in 20% (6.25 mol/L) sodium hydroxide solution with a phase ratio of 80:1 at 100 $^\circ\text{C}$ for 4 h. A certain amount of sodium sulfide was added to the leaching solution based on the amount of Pb. The solution could be used as the electrolyte after the solid–liquid separation process.

The current efficiency was calculated according to the following formula:

$$\eta_{\text{Zn}} = \frac{m_i - m_0}{1.22 \times I \cdot t} \times 100\% \quad (1)$$

where η_{Zn} (%) is the current efficiency of Zn, 1.22 the electrochemical equivalent of Zn, I (A) the current, t (h) the electrowinning time, m_0 (g) the mass of pure cathode, and m_i (g) the total mass of cathode when electrolysed for t hour. The total mass was measured every 10 min, so, $t = 10 \cdot i/60$.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 shows the cyclic voltammogram of $\text{Zn}(\text{OH})_4^{2-}$ ions using a stainless steel electrode at 20 mV/s potential sweep rate in an alkaline electrolyte containing 10 g/L Zn and 20% (wt.) sodium hydroxide at 298 K. The potential was firstly swept from -1.3 V to -1.8 V (vs. SCE). A sharp increasing current emerged at the nucleation potential ca. -1.56 V (vs. SCE). It is a reduction current caused by the nucleation and growth of zinc on cathode. This is different from the acid media, in which the current increase occurs at ca. -1.2 V (vs. SCE) (Leung et al., 2011; Yu et al., 2002). The current peak appeared at ca. -1.62 V (vs. SCE), indicating that the $\text{Zn}(\text{OH})_4^{2-}$ ions near the cathode were being consumed. After the peak, there was no obvious decreasing current, because $\text{Zn}(\text{OH})_4^{2-}$ ions diffused to the cathode surface to supply the reaction under this experiment condition. When the potential shifted more negative than the overpotential for hydrogen evolution, there was another increasing current due to the reduction of hydrogen ions on cathode. In the electrowinning process, hydrogen evolution which consumes a part of energy should be avoided.

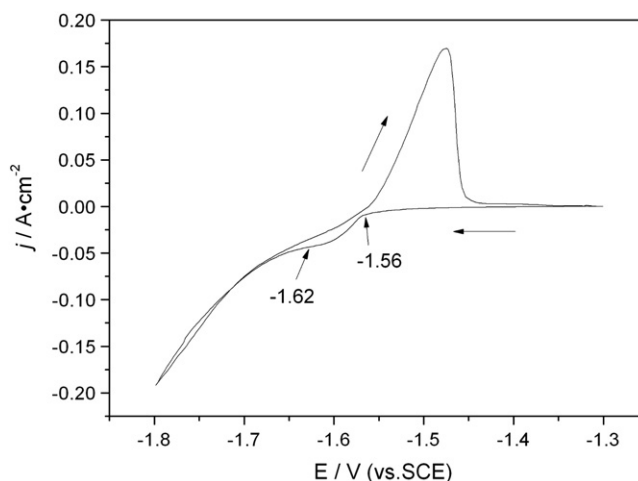


Fig. 1. Cyclic voltammogram for stainless steel cathode in alkaline Zn solution. Electrolyte: 10 g/L Zn and 20% (wt.) sodium hydroxide at 298 K. Scan rate 20 mV/s.

When the potential was swept towards the positive direction before the crossover potential at ca. -1.55 V (vs. SCE), $\text{Zn}(\text{OH})_4^{2-}$ ions were still being reduced on cathode, and there was a decreasing reduction current. But the cathode reaction switched to the oxidation of metal zinc after the crossover potential and an oxidation current emerged. It is worth mentioning that in some reports (Leung et al., 2011), the forward and reverse scans can form a nucleation loop. The difference between the nucleation potential and crossover one named nucleation overpotential (NOP) can be obtained from the loop. However, in this study, the nucleation loop could not be found (Fig. 1). It could be inferred that the overpotential of $\text{Zn}(\text{OH})_4^{2-}$ ion electrodeposition on the stainless steel cathode was very small in the sodium hydroxide solutions. Meanwhile, the obvious oxidation current shows that the zinc on the cathode will be oxidized easily after the crossover potential. So the potential should be strictly controlled in the electrowinning process.

The cyclic voltammogram tests were carried out at different sweep rates of 10, 30, 50, 70 and 90 mV/s, respectively (Fig. 2(a)). It can be found that the reduction current peak elevated with increasing potential sweep rate. This is because higher sweep rate leads to more $\text{Zn}(\text{OH})_4^{2-}$ ion reaction. However, the influence of $\text{Zn}(\text{OH})_4^{2-}$ ion diffusion on the ion reaction also becomes more significant. If the ion diffusion cannot compensate the consumption, the reduction current will decrease due to lack of $\text{Zn}(\text{OH})_4^{2-}$ ions near the cathodic surface. Therefore, the improvement of current peak exhibited a decreasing range and the current declined less obviously after the peak when the sweep rate increased from 10 mV/s to 90 mV/s. Fig. 2(b) shows a plot of reduction current peak vs. the square root of potential sweep rate. The linear property of the peak current as function of the square root of potential sweep rate indicates that it is a mass transport controlled reaction.

3.2. The nucleation potential

Zinc ions exist in the form of $\text{Zn}(\text{OH})_4^{2-}$ in alkaline solution, but $\text{Zn}(\text{OH})_2$ (aq) is the species directly discharged on the cathodic surface. In the electrodeposition process, $\text{Zn}(\text{OH})_4^{2-}$ transforms into $\text{Zn}(\text{OH})_2$ (aq) (Brenner, 1963). As the nucleation potential of Zn ions is ca. -1.56 V (vs. SCE) from Fig. 1, a potential range from -1.1 V to -1.8 V (vs. SCE) was selected to analyze the nucleation process by means of chronoamperometry with the interval of 0.1 V. From the chronoamperogram, the information could be summarized in three stages as the charging of electrochemical double layers, the ion nucleation on the cathode and the ion diffusion from bulk to cathodic surface. At the potential from -1.1 V to -1.4 V (vs. SCE), the electrochemical double layers were charging and the steady charging current improved, but in a small magnitude

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