

SHORT COMMUNICATION

Electrowinning of zinc from alkaline solutions at high current densities

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1. Introduction

The growing cost of industrial production and international competition give an increased importance to research in alternative zinc extraction technologies. Among the possibilities, electrowinning in alkaline solutions was presented previously as the most promising [1]. It offers the possibility of increasing productivity up to 1000 A m^{-2} and at the same time lowering energy consumption to 1.75 kWh kg^{-1} [2]. However, in Canada, where energy costs are low, higher productivity is favoured over decreased energy consumption.

To determine the maximum increase of productivity possible while keeping a specific energy consumption comparable to that in the actual industrial process, data at high current densities are necessary and these are not available in the literature. Experiments have been done at high current densities to obtain cell voltage and current efficiency data necessary for specific energy computations. The importance of the deposit morphology on the specific energy obtained, which was not previously stated clearly [1, 2], is also emphasized.

2. Experimental details

Solutions were made from twice distilled water and reagent grade chemicals with a composition of $7.5 \text{ M NaOH} + 0.92 \text{ M ZnO}$. A volume of 0.7 litres was used (except at 2000 A m^{-2} , 1.1 litres) and kept at $75 \pm 1^\circ \text{C}$ using a Haake thermostatic bath. A magnesium cathode and an NE-A-30 active anode (Electrolyser Inc.), with an apparent surface area of 9 cm^2 , were used and kept 2.5 cm apart with a Plexiglass support. Electrolysis was carried out for 1 h in a beaker using a Hewlett Packard 6266B power supply and current densities ranging from 2000 to 8000 A m^{-2} . No artificial agitation was provided. With these conditions, the decrease in zinc concentration in the solution varied from 3.3 to 13.1%. After electrolysis, the deposit was thoroughly washed with methanol and allowed to dry for 24 h before weighing.

3. Results and discussion**3.1. Nature of deposits**

The zinc structures obtained in alkaline solutions at constant current densities depend on the substrate

used as a cathode and on the time. Several possibilities can occur in succession involving several of the four different morphologies possible in unstirred solutions [2–5]: lamellar, spongy, granular and dendritic. A description of these can be found in Table 1. From a macroscopic point of view, these can be classified into two distinct categories: compact and powdery. Regardless of the type of powdery deposit, the same effect on current density and current efficiency is observed. Owing to their high specific surface area, the real current density is decreased. For example, at current densities ranging from 1000 to 5000 A m^{-2} [6], a surface area increase of 20 to 25 times was measured.

On zinc, a lamellar deposit forms first. This deposit does not increase the surface area substantially. Consequently, current density can remain constant while this deposit grows. After several minutes, depending on the experimental conditions used, this morphology always degenerates to one or several of the powdery structures. On magnesium, the lamellar deposit does not form and only a mixture of powdery structures appears, which are easily detached from the electrode surface. This is an advantage, since the process can then be automated [1, 7, 8].

Table 1 shows the range of current densities necessary to obtain the different deposits. However, it should be noted that upon obtaining these structures, the current, and consequently the evolution of morphologies, is stopped. A different result is obtained if the current is impressed further. This is because the appearance of a powdery deposit increases the real surface area and makes possible the growth of a structure obtained at a lower current density. A mixture of structures can then be seen. On magnesium, a mixture of the spongy, granular and dendritic deposits is observed. Their respective proportion varies with the applied current density. Granular and dendritic deposits become predominant as current density is increased. Hewaidy *et al.* [9] have observed that the number of smaller particles present in the mixture and the specific surface area increase with increasing current density. Based on this, it is believed that granular and dendritic structures offer a greater specific surface area than spongy ones. This is also the case with the usual blown molten zinc powder [10]. This is important in applications such as cementation, paints, battery electrodes and reduction of organic substances

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Table 1. Description of zinc deposits obtained in unstirred alkaline solutions [2–5]

Name	Description		Range of current density ($A m^{-2}$)
	Microscopic	Macroscopic	
Lamellar	Composed of ridges and layers with well-defined crystal faces	Compact, sheet-like and very thin (<0.1 mm)	200–358
Spongy	Also referred to as mossy; dull, light to dark grey, composed of very fine grains without well defined faces	Powdery with very loose grains and crystals	40–250
Granular	Also referred to as bouldery or nodular; brilliant with well defined faces	Powdery with very loose grains and crystals	200–448
Dendritic	Fern-like and brilliant with well defined faces	Powdery with very loose grains and crystals	500–1000

where high surface areas are needed to increase reaction rates.

3.2. Current efficiency

The thermodynamics of this chemical system favour hydrogen evolution over zinc crystallization [11]. However, since the hydrogen overpotential on zinc is very high and is even greater on magnesium [12], and since the zinc overpotential is comparatively low, the kinetics almost completely reverse this situation.

On a flat zinc electrode, it is possible to avoid deposition of powdery deposits if reduction is carried out for only a short time, since a compact zinc layer is formed first. Under these conditions, polarization curves show that zinc can be deposited up to the limiting current density before hydrogen begins to evolve significantly [13]. At a 0.9 M ZnO concentration and 27°C, this limiting current density is approximately $497 A m^{-2}$ in a 8.4 M KOH aqueous electrolyte [13]. In the present similar solution of 7.5 M NaOH and at 75°C, the limiting current density should be higher than that value owing to easier diffusion and natural convection at this higher temperature.

The powdery deposits which form on the magnesium cathode make it possible to use high current densities for electrolysis without significant losses of current efficiency. For example, to avoid significant hydrogen evolution at $8000 A m^{-2}$, the structures must provide an increase in surface area sufficient to decrease this applied current density to a real current density below the zinc limiting current density. Using a zinc limiting current density of $497 A m^{-2}$, the increase in surface area must be greater than 16 (i.e. $8000/497$). Zinc deposits give a surface enhancement of 20 to 25 times, which exceeds the requirement of 16. This explains why experimental zinc current efficiency remains so high (Table 2)—almost 100% at high current densities. (The values greater than 100% in Table 2 can be explained by partial oxidation of the powdery deposits obtained, and small amounts of methanol,

hydroxide and water remaining.) Hydrogen evolution is only seen for a short time when the magnesium cathode is subjected to high current densities, at the beginning of the experiments and when the deposit is removed from the cathode to avoid short-circuiting. When the real current density is high and greater than the zinc limiting value, hydrogen evolution is more favoured. After the magnesium is covered by a layer of zinc of powdery character, the real surface area increases, current density decreases below the limiting value and hydrogen evolution stops.

3.3. Cell voltage

The powdery deposits obtained during zinc electrolysis in alkaline solutions decrease considerably the real current density as a consequence of the large increase in surface area. As a result, the cathodic overpotential is also decreased. Owing to their low density, these deposits produce an outgrowth which also contributes to the decrease in the ohmic drop by occupying an important part of the volume between the electrodes.

Table 2. Characteristics of zinc electrowinning in alkaline solutions at high current densities

Current density ($A m^{-2}$)	Current efficiency (%)		Cell voltage (V)	
	Compact*	Powdery	Compact*	Powdery
700	100	—	2.26	—
1000	100	102†	2.42	2.13†
1500	100	—	2.67	—
2000	100	105	2.92	2.35
3000	—	103.6	—	2.57
5000	—	99.6	—	2.82
8000	—	99.2	—	3.00

7.5 M NaOH + 0.92 M ZnO, 75°C

* Calculated using data taken from [2].

† Data taken from [2].

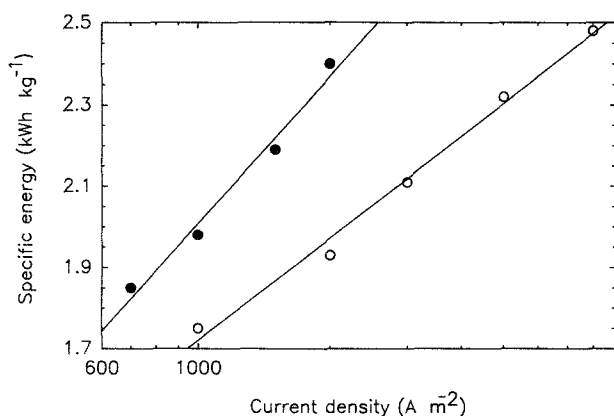


Fig. 1. Comparison of specific energy consumption as a function of current density for zinc electrowinning with the two different categories of deposit: ○ powdery deposits, unstirred solutions; ● compact deposits, stirred solutions. (7.5 M NaOH, 0.92 M ZnO, 75° C.)

In one case, this outgrowth almost reached the anode surface, so that it was necessary to remove it to avoid a short-circuit.

3.4. Specific energy

The current efficiencies and cell voltages in Table 2 were used to compute the specific energy consumptions plotted in Fig. 1. For comparison, data obtained previously [2] on compact deposits are also shown in Table 2 and in Fig. 1. The zinc polarization curve was obtained while stirring and before the appearance of a powdery deposit [2]. It shows that the limiting current was not reached even at 2000 A m⁻² because of stirring. Current efficiency is 100% and the ohmic drop was calculated as before [2]. Then, the specific energy was calculated.

Figure 1 shows the beneficial effect of powdery deposits, compared with compact ones, on the specific energy. For example, it is decreased from 2.4 to 1.93 kWh kg at 2000 A m⁻². In reality, the difference is greater than 0.47 kWh kg⁻¹, since agitation was provided for compact deposits. A part of the diffusion overpotential, which is not negligible at this high current density, was eliminated.

Furthermore, even at 8000 A m⁻², the specific energy is 2.5 kWh kg⁻¹, still lower than the typical industrial value of 3.1 kWh kg⁻¹ at 500 A m⁻² by approximately 0.6 kWh kg⁻¹. This represents a productivity increase of 16 times. At this very high current density some problems should be considered: short-circuits by dendritic growth would be more probable and an excess of heat generated by the ohmic drop in solution and overpotentials would probably have to

be eliminated by cooling. Account should also be taken of the ohmic drop in busbars.

Other factors also need to be considered in comparing the alkaline and acidic processes. Since it is possible through a mechanical operation to remove the zinc particles from the cathodes, with mechanical vibration or motor-actuated wands [7, 8] for instance, electrodes can be fixed permanently at a distance as short as 2.5 cm [7, 8, 14, 15]. Although this distance is shorter than the usual 3.5 to 4 cm used in the acidic process, reliability of the retrieval system is essential, since zinc growth is rapid at very high current densities. While our pure solutions do not allow an estimation of the purity of the end product using minerals, special high grade zinc can be obtained [7, 8, 14, 15], as with the acidic process. Extra operations are also necessary for processing and handling the zinc powder, such as washing and drying. However, these operations require only a small amount of energy which only slightly affects the total energy requirements of the process, still being lower than the acidic one [14]. These considerations, and the productivity gain which was obtained here, make this technology quite attractive for further investigations.

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