SHORT COMMUNICATION

Electrowinning of zinc at high current density in the presence of some surfactants

M. KARAVASTEVA*, St. KARAIVANOV

Faculty of Chemistry, Sofia University, 1 James Bourcher Avenue, Sofia 1126, Bulgaria

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1. Introduction

Zinc electrowinning is usually carried out at current densities in the range 300 to 700 A m^{-2} [1]. High current density (1000 A m^{-2}) was used at the Sullivan Mining Co., Kellog, Idaho (USA), where stringent purification of zinc sulphate solutions was performed [2]. The cost of electric power is usually more expensive during the day, thus it would be more economical for zinc electrowinning at high current density to be done at night. Combination between the low current density during the day with the high current density at night suggests a possibility for decreasing the costs of production.

Detailed laboratory investigations on zinc electrowinning at a current density of 1000 A m^{-2} in the presence of some surfactants, varying the temperature, electrolyte composition and additive concentration [3–5] have shown that the current efficiency is increased and the zinc cathode quality is improved by using a combination of the following surfactants: nonylphenolpolyethylene glycol (D1), dinaphthylmethane-4,4′-disulphonic acid (D2) and polyethylene glycol with molecular weight 400 (D3).

The aim of the present study is to investigate the effect of these surfactants on the structure of cathodic zinc, current efficiency, cell voltage, specific energy consumption and the purity of zinc metal electrowon at high current density under simulated industrial conditions.

2. Experimental details

The experiments were carried out for 8 h at a current density of 1000 A m^{-2} with and without surfactants D1, D2 and D3. During electrolysis the temperature was kept in the range 36–38 °C. The cell of 20 dm^3 volume was equipped with four Pb–Ag (1% Ag) anodes and three aluminium cathodes having an overall surface of 1200 cm^2; the electrode spacing was 35 mm. Two sets of Pb–Ag anodes were used, one for the experiments in the presence of surfactants and the other for the experiments without additives. Electrolytes were prepared by using the industrial zinc sulphate solutions from zinc plant in Plovdiv (Bulgaria) containing high impurity concentrations (Sb, Ni and Ge) typical for this plant. Concentration of base ingredients varied in the range 76–79 g dm^{-3} Zn and 73–79 g dm^{-3} H_2SO_4. Concentration of surfactants varied (in mg dm^{-3}) as follows: D1 14–150, D2 14–150 and D3 5–50. D1 and D2 were added in equal concentrations.

The cell was connected to a storage reservoir so that the overall volume of the electrolyte for each experiment was about 70 dm^3. The concentration of zinc and H_2SO_4 in the cell at the beginning of the tests and in the spent solution leaving the cell during the electrolysis was kept in the range 45–49 g dm^{-3} Zn and 115–120 g dm^{-3} H_2SO_4. Zinc and acid concentrations were, respectively, 10 and 20 g dm^{-3} lower than usually used in the above mentioned zinc plant. Zinc deposits were throroughly washed with water and ethanol and dried for 24 h. Current efficiency was determined by weighing the deposits after drying at 105 °C for an hour.

The influence of surfactants on the structure of cathodic zinc was determined for deposits obtained at different conditions. The deposit thickness was in the range 0.95–1.3 mm. Specimens were cut from the deposits, mounted in Araldite, polished and etched with 5% nitric acid in ethanol prior to microscopic observations.

3. Results and discussion

The most interesting results obtained for zinc electrowinning at current density 1000 A m^{-2} are given in Table 1. Comparison between the experimental data obtained with and without surfactants shows the difference in the values of electrolysis characteristics. The current efficiency depends on both the purity of the solutions (Tests 1 and 2; Tests 5 and 6–8) and the addition of surfactants (Tests 1 and 3–8). The addition of the combinations D1 + D2 and D1 + D2 + D3 to the electrolytes increases the current efficiency by 10–15%. However, in the presence of D1 + D2, the value of the current efficiency is slightly higher (Test 3) than in the presence of D1 + D2 + D3 (Tests 4 and 5). The experiments at high concentration of some metal impurities with and without surfactants (Tests 2 and 5–8) show that the negative effect of the impurities on the current efficiency is decreased by using a combination D1 + D2 + D3. These additives also increase the cell voltage. However, for the combination D1 + D2 + D3 the cell voltage is lower than that without D3, compare Tests 4 and 5 with 3. The specific energy consumption depends on both the current efficiency and cell voltage. The lowest values (3200–

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* Author to whom all correspondence should be addressed.

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Table 1. Characteristics of zinc electrowinning at high current density

Test no.	*Electrolyte impurities* /mg dm^{-3}						*Surfactants* /mg dm^{-3}		*Current efficiency* /%	*Cell voltage* /V	*Energy consumption* /kWh t^{-1}
	Cu	Sb	Ni	Co	Ge	As	D1 = D2	D3			
1	0.04	0.05	0.6	0.25	0.03	0.08	–	–	75.9	3.45	3726
2	0.10	0.05	4.2	0.60	0.03	0.10	–	–	70.3	3.42	3988
3	0.13	0.05	1.0	0.20	0.03	0.10	14.5	–	88.1	3.59	3340
4	0.13	0.05	0.8	0.30	0.05	0.06	14.5	5	87.5	3.51	3288
5	0.04	0.10	1.0	0.30	0.03	0.05	15	10	87.9	3.50	3264
6	0.03	0.07	4.1	0.15	0.08	0.08	50	10	82.9	3.60	3559
7	0.05	0.10	3.4	0.30	0.05	0.10	30	5	86.9	3.61	3405
8	0.02	0.13	2.8	0.05	0.05	0.05	150	50	79.2	3.49	3612

3300 kWh t^{-1}) of the energy consumption are obtained when using a combination D1 + D2 + D3 (Tests 4 and 5).

The concentrations of impurities in the cathodic zinc obtained during the experiments are given in Table 2. The results indicate that despite the high concentration of some impurities in the solutions, the deposits meet the ASTM specification for high grade zinc.

The structure and the surface of cathodic zinc are also important characteristics of the zinc electrowinning process. The photomicrographs of zinc deposits obtained without (Test 1) and with surfactants (Tests 3 and 4) are shown in Figs 1 and 2. Cathodic zinc obtained without the additives (Figs 1(a) and 2(a)) is very porous with many holes, cracks and pits. Its crystallites are considerably larger than those formed in the presence of surfactants. The results show that

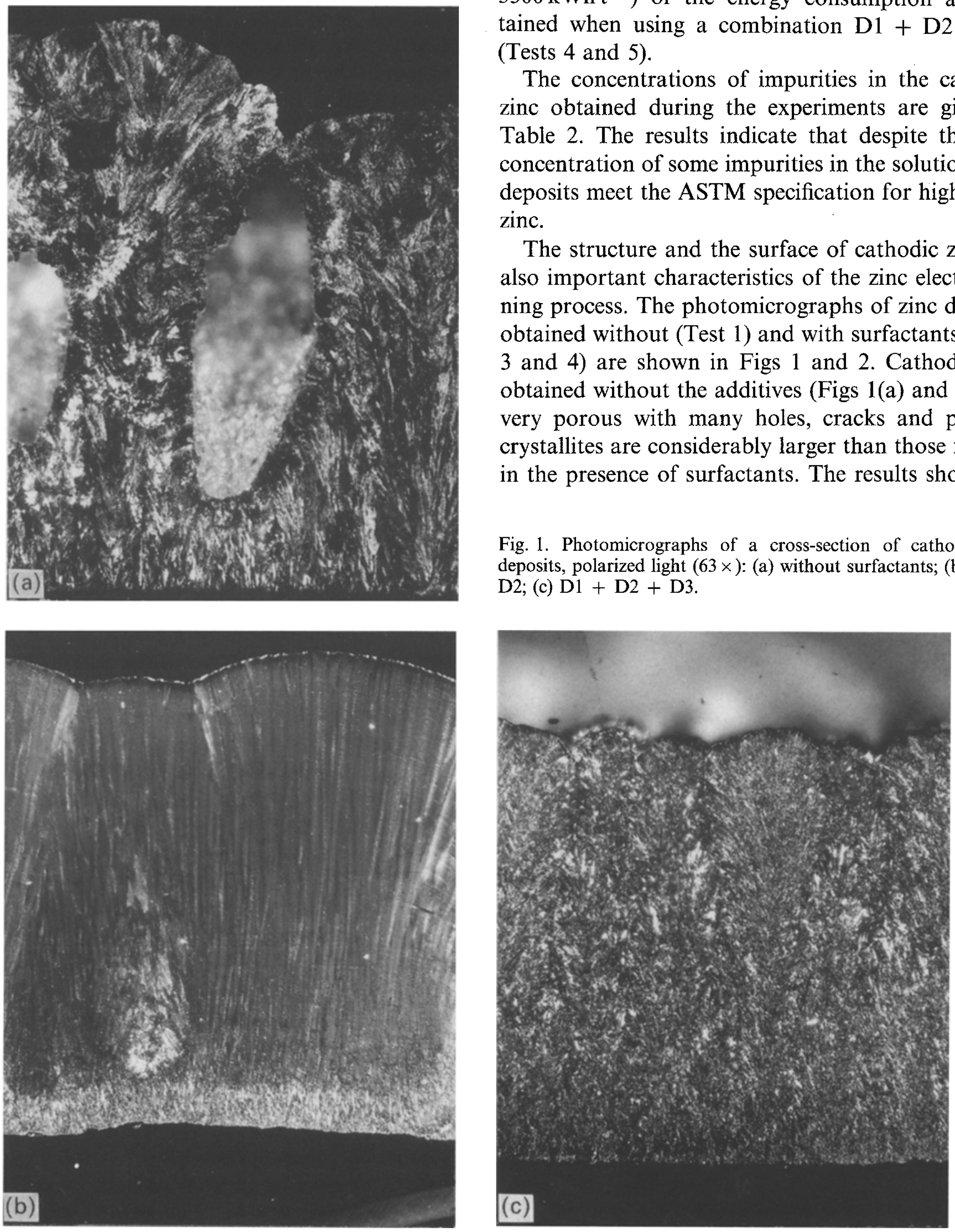

Fig. 1. Photomicrographs of a cross-section of cathodic zinc deposits, polarized light (63 ×): (a) without surfactants; (b) D1 + D2; (c) D1 + D2 + D3.

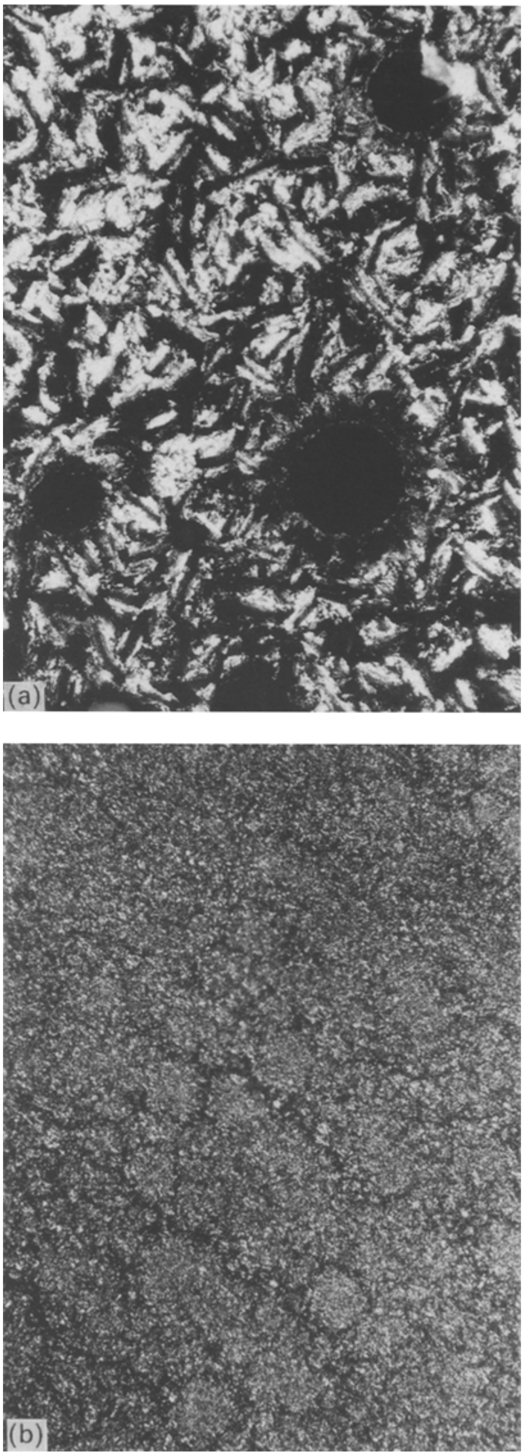

Fig. 2. Photomicrographs of a surface of cathodic zinc deposits, polarized light (63 x): (a) without surfactants; (b) D1 + D2 + D3.

Table 2. Impurity content of zinc deposits electrowon at high current dentisty

Impurity	*Concentration* /ppm
Pb	110–170
Cd	23–60
Cu	2–6
Ni (tests 2, 6–8)	5
Ni (tests 1, 3–5)	1
Co, Sb, As, Ge	1

the deposits obtained without the additives include a large quantity (about 10–15%) of electrolyte. In the presence of surfactants the zinc surface is fine-grained and without dendrites (Figs 1(b), (c) and 2(b)). Figure 1(b) and (c) illustrate the structure of zinc obtained in the presence of both D1 + D2 and D1 + D2 + D3. It is evident that the deposits are pore-free. Comparison between Fig. 1(b) and (c) shows that the influence of D1 + D2 on the structure of zinc is different from that of D1 + D2 + D3. In the presence of D1 + D2 + D3 the deposits are quite fine-grained.

5. Conclusion

At high current density (1000 A m^{-2}) a pore-free and fine-grained zinc deposit can be obtained only in the presence of suitable additives. A combination of the surfactants nonylphenolpolyethylene glycol (D1), dinaphthylmethane-4,4′-disulphonic acid (D2) and polyethylene glycol with molecular weight 400 (D3) decrease the negative effect of metal impurities on both the current efficiency and the structure of zinc deposits. As a result, the use of electrolytes with higher concentrations of impurities appears to be possible in zinc electrowinning. The best current efficiency (88–89%) and specific energy consumption (3200–3300 kWh t^{-1}) were obtained under simulated industrial conditions in the presence of the following optimal concentrations of surfactants (in mg dm^{-3}): D1 14–50; D2 14–50; D3 5–10.

References

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