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The effect of additives on the morphology of zinc electrodeposited from a zinc chloride electrolyte at high current densities

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There are advantages if zinc can be deposited electrochemically at high current densities. In order to improve the deposit at current densities exceeding 2000 A m^{-2}, various additions were made to the electrolyte. It was found that proteinous additives produced planar deposits with a (10.2) (10.3) orientation and a current efficiency of around 85% in a small laboratory cell.

1. Introduction

There has been recent interest in the recovery of zinc using chloride solutions by chemical and electrochemical means. Amongst the reported work have been the papers by Thomas and Fray [1] on the leaching of zinc ferrites and low-grade oxidic ores and residues, and by Parsons and Ritcey [2] on complex sulphidic ores. Subsequent recovery of the metal from the chloride solution has hardly been exploited at all, solvent extraction to the sulphate more usually being practised. This is surprising considering the ease of purification of zinc chloride, especially with respect to iron, as described by Monk and Fray [3].

The electrowinning of zinc from zinc chloride was investigated by Hoepfner at the turn of the century [4], who actually commenced commercial production without success, and by Stender in 1957 [5]. They were unable however to work satisfactorily above 100 A m^{-2} without considerable hydrogen codeposition and serious degradation of the deposit quality. The most recent study has been by Mackinnon *et al.* [6, 7] who characterized deposit morphologies and orientations from a chloride electrolyte as part of a feasibility study of chloride electrowinning.

In a laboratory cell they found that one-hour deposits from the additive-free electrolyte consisted largely of clusters of platelets with an (00.2) (10.3) (10.5) orientation. Current efficiencies averaged 80%. The majority of their work was done in solutions containing 50 g dm^{-3} Zn^{2+} as ZnCl$_2$ and within the current density range 269–807 A m^{-2}. Morphology, they found, varied little within this range, although at the higher values there was a greater tendency to edgewise dendrite growth. In a similar electrolyte, but at much lower pH, Stender [5] reported that deposits were completely dendritic, although this appears to have been due in part to a lack of electrolyte agitation.

Mackinnon *et al.* [6, 7] found also that a number of additives, which increased the cathodic polarization, substantially altered deposit morphologies giving plates inclined to the cathode, corresponding to the perpendicular (10.1) (11.0) orientation, and increasing cathodic current efficiencies to >90%. The most successful additive was tetrabutylammonium chloride (TBACL) which, in a 15 g dm^{-3} Zn^{2+} electrolyte gave >96% efficiencies at 323 A m^{-2}. The same authors reported similar results in larger-scale experiments lasting 24 hours where they utilized the concept of air-sparging over the cathode face with success. This technique has been used before in copper sulphate electrowinning cells at > 5000 A m^{-2} and in zinc sulphate electrowinning cells at 700 A m^{-2} [9].

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The overall aim of this present work was to examine the feasibility of electrowinning zinc from zinc chloride using cathodic current densities exceeding 1000 A m^{-2} and solutions containing $>$50 g dm^{-3} Zn^{2+} as $ZnCl_2$. The high solubility of zinc chloride in water and the high conductivity (10 Ω^{-1} m^{-1} at $\sim$80 g dm^{-3} Zn^{2+} as $ZnCl_2$ at 298 K [10, 11]) of the solutions makes this method promising for use at these high current densities. The special problems created by elevated current density operation are associated mainly with increasing concentration polarization causing deposit degradation and hydrogen evolution.

2. Experimental procedure

2.1. *Electrolyte solution and additives*

Zinc chloride solutions were prepared from granulated, general purpose $ZnCl_2$ (BDH) containing 0.07%Fe, 0.01%Pb and 4%ZnO as major impurities, with some insoluble organic matter. Purification was effected by prolonged boiling with AnalaR (BDH) zinc giving a solution containing $<$0.4 mg dm^{-3} Fe, $<$0.1 mg dm^{-3} Sb, $<$0.1 mg dm^{-3} Pb and other impurities $<$0.1 mg dm^{-3}. In all experiments electrolyte pH was adjusted to pH 3 using AnalaR (BDH) HCl.

The additives used included a selection of gums, glues, and a number of other proteinous and active chemicals, as shown in Table 1. The molecular weights quoted are those stated by the manufacturers. In all cases additives were added from freshly prepared solutions.

2.2. *Electrolytic cell*

The cell, containing 15 dm^{-3} of electrolyte, was constructed from 1 cm thick Perspex sheet, and is described more fully elsewhere [1]. The cathodes were aluminium sheets and the anodes either fabricated from graphite or DSA anodes (IMI Titanium, Birmingham). The cathodic area was 100 cm^2. Directly below the cathode a gas-sparging unit was positioned, made of Perspex, which impinged a curtain of compressed gas (air or inert) over the whole cathode face.

2.3. *Electrolysis conditions*

All electrowinning experiments lasted one hour. Current densities were varied from 400 to 3100 A m^{-2} with the most frequently used range being 2300–2500 A m^{-2}. The electrolyte contained 70 g dm^{-3} Zn^{2+} as $ZnCl_2$ and was maintained at 294 ± 1 K. During each experiment fresh electrolyte additions were made and portions of stale electrolyte removed every 10 minutes. The gas-sparging facility was operated at 10 dm^{-3} min^{-1}.

2.4. *Deposit examination*

Cathodic current efficiencies were determined by direct weighing. Deposits could be simply

Table 1. Effects of additives upon orientation and current efficiency of deposits at 2500 A m^{-2} in an electrolyte containing 70 g dm^{-3} Zn^{2+} at 294 K. Included also are the effects upon zinc deposition potential at a current density of 800 A m^{-2}.

Additive	*Molecular weight*	*Orientation of one-hour deposits*	*Current efficiency (%)*	*mV versus SCE AE 800 A m^{-2}*	*Deposit type*
None	–	(00.2)	50.1	−1022	Dendritic
Arabic	2.4×10^5	(10.1) (10.2) (10.3)	69.0	−1101	Semi-plate
Tragacanth	2.4×10^5	(00.2) (10.2) (10.3)	55.0	−1041	Block
Ghatti	2.4×10^5	(11.2) (11.4) (10.2) (10.3)	75.0	−1068	
Dammer	3×10^5	–	51.4	−1048	
Croda K5V	5×10^4	(10.3) (11.2)	82.1	−1115	Fully developed plate
Croda K1V	4.7×10^4	(11.2) (10.2) (10.3)	89.6	−1093	
Pearl	5×10^4	(10.1) (10.2) (10.3)	85.3	−1132	
Pepsine	3.4×10^4	(10.2) (10.3) (11.2)	70.8	−1061	Semi-plate
Thiourea	76	(10.2) (10.3) (11.2) (11.4)	71.0	−1075	
Glycine	75	(10.2) (10.3)	58.0	−1034	Plate

Table 2. Deposit types from an additive-free 23 wt% $ZnCl_2$ electrolyte, pH 3.

Current density ($A\,m^{-2}$)	*Deposit orientation*	*Cathodic current efficiencies*	*Morphology type*
269–807†	(00.2) (10.3) (10.5)	80	Platelet clusters
413	(00.2) (10.0) (10.2) (10.3)	70–80	Platelet clusters
1030	(00.2)	60	Dendritic
1860	(00.2)	60	Grossly dendritic
3100	(00.2) (10.3)	<40	Powder

† Mackinnon *et al.* [6], 10 wt% $ZnCl_2$.

detached from the cathode and examined using a Cambridge Instruments SEM. Orientations were measured using a Phillips PW1050 vertical diffractometer and PW1011 generator producing CuKα radiation. Intensity measurements were made on the major $h\,k\,l$ reflexions up to 144° (2θ) and compared with intensities from a random ASTMS zinc powder sample.

2.5. *Polarization measurements*

Current–potential curves for zinc deposition were measured with an AMEL potentiostat–galvanostat 551/5 V operated in the potentiostatic mode. The scan rate was $1.66\,mV\,s^{-1}$. The cathode was prepared from AnalaR (99.9%) zinc and hot mounted in Perspex. The surface was polished to 1 μm, washed and dried with acetone, and stored in a dessicator. The deposition area of each cathode was approximately $2.5 \times 10^{-4}\,m^2$, measured accurately using the Quantimet. Contact with the cathode was made by drilling a hole into the metal through the mounting block, and setting in this a copper wire. A clean, polished electrode was used in each experiment. The counter electrode was graphite. The reference was a saturated calomel electrode, separated from the test cell with a $KCl–ZnCl_2–H_2O$ bridge. The latter terminated in a Luggin probe which was positioned very close to the working electrode. The *IR* drop was thus minimized because of the high electrolyte conductivity and small distance between the tip of the Luggin capillary and the electrode.

The effects of a number of additives (Table 1)

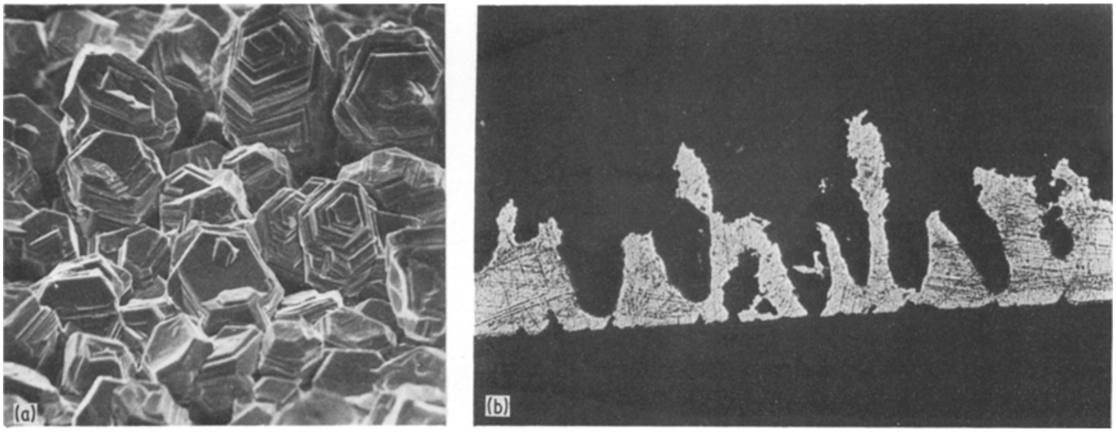

Fig. 1. (a) SEM photomicrograph (× 775) showing discrete dendritic growths from an additive-free electrolyte. (b) Profile showing extent of profile degradation (× 113). The electrolyte contained $70\,g\,dm^{-3}$ Zn^{2+} as $ZnCl_2$ at 294 K and the current density was $2100\,A\,m^{-2}$. These conditions apply to all the photomicrographs of the deposits.

Fig. 2. SEM photomicrograph (X 960) showing the block morphology obtained with the addition of 40 mg dm^{-3} Gum Tragacanth.

on the *i–V* curves for zinc deposition were measured from −900 to −1300 mV versus a saturated calomel reference electrode. Measurements were made on an electrolyte of exactly similar composition to that used in electrowinning experiments.

3. Results and discussion

3.1. *Additive-free electrolyte*

At conventional cathodic current densities ($< 1000\ A\ m^{-2}$) deposit morphologies and orientations from the additive-free electrolyte were similar to those recently reported by Mackinnon *et al.* [6] whilst working at 540 A m^{-2}. They found mainly deposits with (00.2)(10.3) orientation, corresponding to hexagonal plates of zinc parallel to the cathode (Table 2).

At higher current densities ($> 1800\ A\ m^{-2}$) the deposit orientation becomes strongly (00.2) consisting of discrete dendritic growths of hexagonal plates (Figs. 1a and b). Current efficiencies were found to be in the range 70–80%. At very high values ($> 3000\ A\ m^{-2}$) the deposits lose coherency being still strongly (00.2) but now with some (10.3) orientation. Hydrogen codeposition was extensive with the current efficiencies falling to around 40%. Under these conditions of high cathodic current density and low deposition overpotential the Bravais law of crystal growth predicts that the lateral (00.2) growth mode dominates for zinc, as in this case.

3.2. *Effect of additions*

The additives used are listed in Table 1 with the orientation of the corresponding one-hour deposits. Each additive significantly altered the deposit morphology and orientation (Table 1). In all cases the trend was towards a (10.2)(10.3) type of deposit representing a morphology of platelets of zinc inclined to the cathode rather than parallel with it. This can clearly be seen in Figs. 2 and 3a. The increased overpotential arising from the presence of the additives leads to a change from

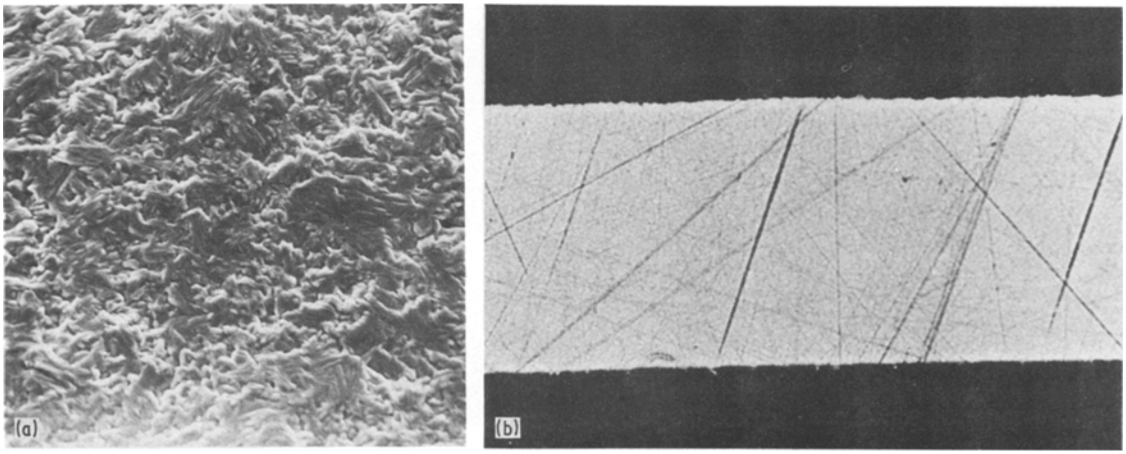

Fig. 3. (a) SEM photomicrograph (X 350) obtained with 40 mg dm^{-3} Pearl Gum. (b) Profile of deposit shown in Fig. 3a (X 50).

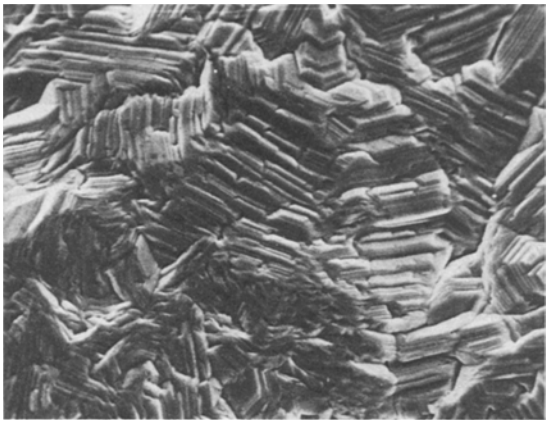

Fig. 4. SEM photomicrograph (X 350) obtained by adding 40 mg dm^{-3} glycine.

the lateral growth mode to the outward mode. In the pure outward mode the deposit orientation is (11.0) and (10.0) and is comprised of zinc platelets parallel to the current flow. Such deposits were achieved by Mackinnon *et al.* at 540 A m^{-2} using tetrabutylammonium chloride additive (TBACL) [6]. At the high current densities used by us this type was not achieved; rather, intermediate types prevailed of (10.2) (10.3) orientation.

At 2500 A m^{-2} we could identify two broad types of morphology. Firstly, a block morphology (Fig. 2) associated with Gum Tragacanth and sucrose additions. This is primarily (10.2) and (10.3) orientation, but with some retained (00.2) basal orientation. The blocks are composed of sheaths of tightly packed zinc plates. According to Sato [12], if adjacent blocks are positioned such that twinning occurs on the (10.2) planes a block structure develops.

The second type is the plate morphology (Figs. 3a, b and 4), developed to varying degrees with different additives. It is associated with a lack of (00.2) orientation and increasing (11.2)(11.4) (10.2)(10.3) orientations. Typical are Pearl Glue (Fig. 3a) and glycine (Fig. 4). In general, current efficiencies are higher when the plate morphology is fully developed (e.g. Pearl additive against glycine, Table 1). In each case the use of an excess of additive ($>$ 150 mg dm^{-3}) promoted a nodular morphology, strongly (10.2) and (10.3) oriented (Figs. 5a and b).

3.3. *Polarization measurements*

The potentiodynamic scan curves are shown in Fig. 6 and by plotting the cathodic potential (in mV versus SCE) at a current density of 800 A m^{-2} against current efficiencies for each additive, Fig. 7 is obtained. The excellent correlation implies that the greater the polarizing effect of an additive the higher the current efficiency. Additives such as Pearl Glue which polarize strongly give highest efficiencies and the most developed plate morphology (Table 1). As the (00.2) basal orientation increases, efficiencies fall (e.g. pure solution and Gum Tragacanth) because of increased dendritic growth.

The link between the structure of the additive and its effect upon polarization is not clear. From Table 1, animal glues with a medium molecular weight (5 x 10^4) give highest efficiencies and polarization. Small or very large molecules are not

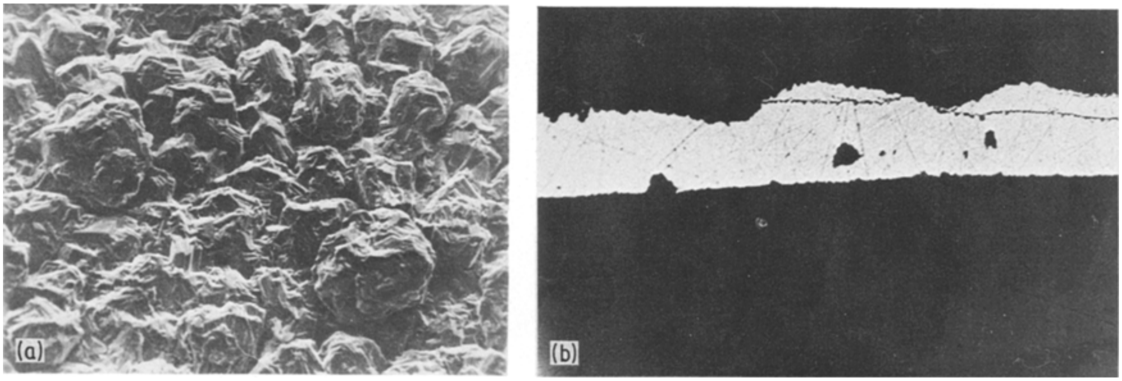

Fig. 5. (a) SEM photomicrograph (X 276) of a deposit overtreated with 1500 mg dm^{-3} Gum Arabic. (b) The profile of the deposit in Fig. 5a showing the development of a nodular morphology.

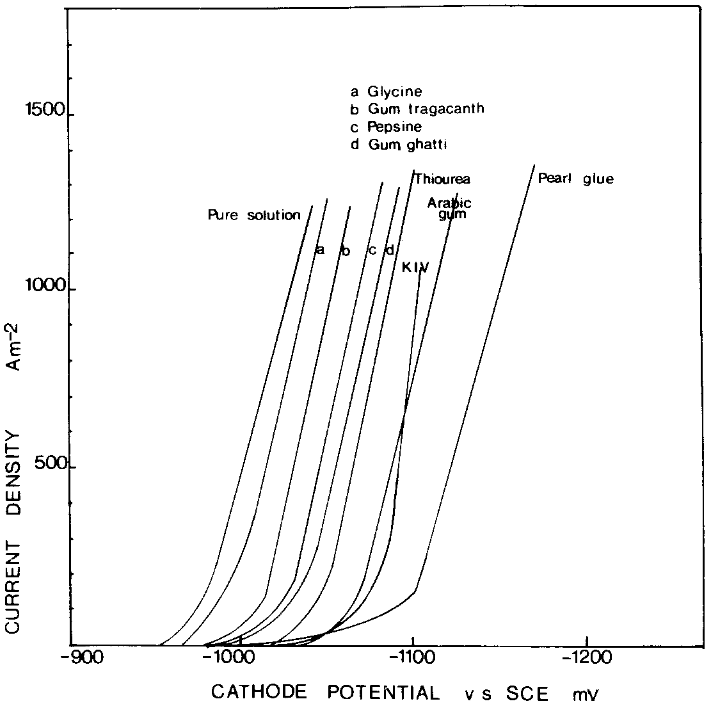

Fig. 6. Potentiodynamic scan curves (100 mV min^{-1}) in a 20 wt% $ZnCl_2$ electrolyte at 294 K containing 10 mg dm^{-3} of a number of additives.

as efficient. In addition, we found glue and gum additives were hydrolysed in the electrolyte resulting in lower efficiencies by up to 10%. Similar results were attained with the protein additives and potentiodynamic scan curves, shown in Fig. 8, demonstrate the effect of hydrolysis.

4. Conclusions

It has been possible to electrowin planar zinc from a zinc chloride electrolyte at current densities exceeding 2000 A m^{-2}. From the additive-free zinc chloride electrolyte, a lateral growth mode (00.2) orientation has been observed at current densities exceeding 1800 A m^{-2}, composed of dendritic growths of hexagonal plates parallel to the cathode.

Broadly speaking, the use of proteinous

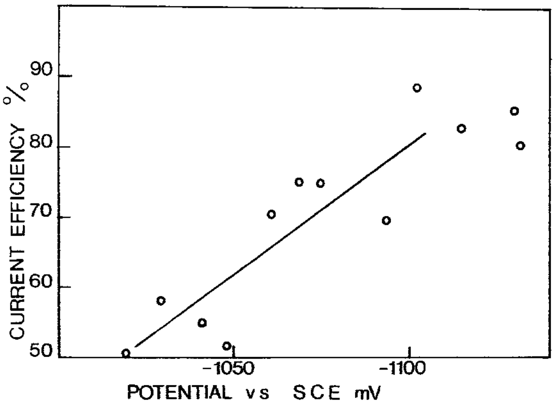

Fig. 7. Variation of cathodic current efficiency measured in one-hour experiments with the cathodic overpotential (mV versus SCE) at 800 A m^{-2} for a series of additives. The electrolyte in each case contained 70 g dm^{-3} Zn^{2+} as $ZnCl_2$ and 40 mg dm^{-3} of additive at 294 K.

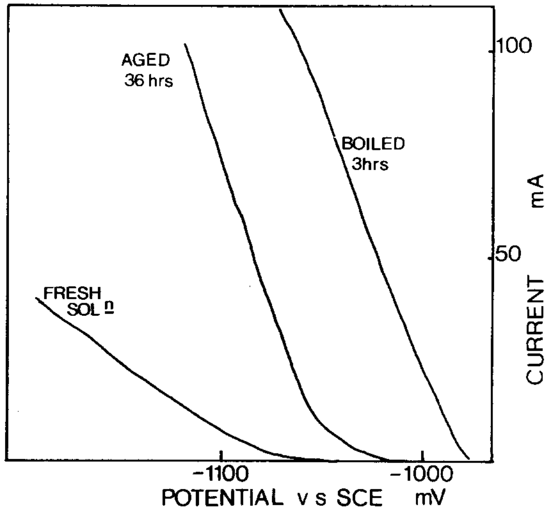

Fig. 8. Potentiodynamic scan curves (100 mV min^{-1}) showing effects of hydrolysis of proteinous material.

additives changes the deposit type to zinc platelets inclined to the cathode with a (10.2)(10.3) orientation. In such cases the deposited metal is planar and current efficiencies higher (up to 85%). Depending upon the additive, we have identified two general morphological types: block morphology and plate morphology, the latter associated with the higher efficiencies.

There is good correlation between the polarizing effect of the additions and the cathodic current efficiencies. Mackinnon and Brannen [7] reported that strongly polarizing TBACL was the best addition at low current densities, and it would seem likely that the use of this additive might further improve on efficiencies at higher current densities.

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