

Use of impedance measurements for the control of the dendritic growth of zinc electrodeposits

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It is shown that the inhibiting effect of an additive (lead acetate) on the irregular growth of zinc electrodeposits is connected with a change in the kinetics of the reaction. In both alkaline and acid electrolytes, the range of current densities leading to compact deposits is widened by the additive. Simultaneously a shift of the current–potential curves towards more cathodic voltages is observed, and this inhibition rises with an increase of the additive concentration. In addition, the disappearance of the multiple steady states and the change observed at low frequencies in the impedance diagrams prove that the additive modifies the rates of some of the elementary reactions taking place at the interface and seems to decrease the importance of the autocatalytic step in the reaction mechanism.

1. Introduction

Zinc electrodeposition in both alkaline and acid media gives successively spongy, compact and dendritic deposits when the current density increases. This property is due to an autocatalytic step in the reaction mechanism which leads to multiple steady states [1] and to local overintensities able to give rise to an irregular growth of the deposits [2]. It is known that small amounts of certain additives such as lead acetate in an electrolyte are able to prevent the heterogeneous growth of zinc electrodeposits [3–8]. The aim of this paper is to show that the inhibiting effect of the additives on irregular growth is connected with a change in the kinetics of the reaction. In order to get new data on the mechanism of this inhibition, the morphology of the deposits, the steady state polarization curves and the low frequency cathode impedance have been analysed.

2. Experimental

2.1. *Electrolytic solutions and electrolysis cell*

Two types of electrolyte commonly used in the zinc industry were studied: (a) the Leclanché cell electrolyte: NH_4Cl 2.67 M, ZnCl_2 0.72 M pH

adjusted to 5.2 with small amounts of NH_4OH and (b) an alkaline electrolyte: KOH 7 M, ZnO 0.5 M used in accumulators. The chosen additive was lead acetate. All the solutions were prepared with twice ion-exchanged water and 'MERCK' compounds of analytical purity. During the electrolysis, the electrolyte was maintained at $26 \pm 0.5^\circ\text{C}$ and an inert cell atmosphere maintained by argon bubbling. The anode was a zinc cylinder of high purity (99.999%). In acid media, the reference electrode (a saturated calomel electrode SCE) was in contact with the electrolyte through an intermediate compartment filled with a KCl saturated solution; in alkaline media another intermediate compartment filled with the electrolyte was necessary so as not to pollute the reference electrode.

Metal deposition was performed on the cross-section of a zinc cylinder the area of which was 0.28 cm^2 . The wall of the cylinder was insulated from the electrolyte with a coat of 'Specifix' type resin. The speed of the rotating disc electrode could range between 0 and 5000 rev min^{-1} . Using such a device, zinc electrodeposits were prepared under well-controlled hydrodynamic conditions [9].

In order to obtain reproducible plots of the current–potential curves, the electrode surface was polished by emery paper (grade 600), then

immersed into a nearly 50% HCl solution for a few seconds and rinsed with twice ion-exchanged water before each deposition.

2.2. Preparation of the deposits

For morphology studies, the deposits were galvanostatically prepared on a Johnson Matthey (99.999%) copper disc. They are thick enough ($10\ \mu\text{m}$ at low current densities and $20\ \mu\text{m}$ at high current densities) so that their morphologies were independent of the thickness. In order to facilitate the adherence of the spongy deposits obtained at low current densities, it was often necessary to perform a compact ground coating at a higher current density ($36\ \text{mA cm}^{-2}$) for a few minutes. After each electrolysis, the deposit was washed, dried and then observed through a scanning electron microscope.

2.3. Plotting of the current-potential curve and measurements of the impedance

As, during the electrocrystallization of zinc, the current is varying very rapidly with the cathodic polarization [1, 10], the plotting of the $I(V)$ current-potential curve and the measurements of the impedance have been performed under galvanostatic conditions. Provided that the applied electrolysis current remains sufficiently low, the dendritic growth of zinc is avoided and steady-state conditions for the electrocrystallization can be maintained. As a matter of fact, the recording of the electrode potential as a function of time reveals, after a short time transient response, a plateau which defines the steady-state potential U : the lower the current, the more extended this plateau. In order to obtain the potential V , the steady-state potential U was measured and corrected for the ohmic drop which has been determined using an interruptor method [11] and, also, from the high frequency limit of the impedance. Each steady-state curve, which has been recorded both with decreasing and increasing values of current density, shows no hysteresis effect.

In the range of high current densities, steady-state conditions cannot be maintained any more. That is the reason why the polarization curves were studied by using a current sweep method, the galvanostat being supplied with a triangular wave

signal. The linear sweep rate ($13\ \text{mA s}^{-1}$) was chosen to be high enough to avoid an electrode area increase with time and thus to allow reproducible recordings of the curves up to current densities of approximately $500\ \text{mA cm}^{-2}$. The ohmic drop was compensated by using a method perfected in our laboratory [13] and the polarization curves were automatically drawn on a X - Y recorder.

The electrode impedance was obtained under steady-state conditions by superimposing on the direct current a sine current of small amplitude. Measurements were performed with a correlation transfer function analyser: SOLARTRON JM1600 + JX1639, connected to a wide band galvanostat built in our laboratory [12]. Such a device allows an easy measurement of the electrochemical impedance between 10^{-3} Hz and 70 kHz. In order to measure the faradaic impedance with a sufficient accuracy over the whole useful frequency range, the electrolyte resistance (R_e) was partially or totally compensated [13].

3. Results and discussion

3.1. Deposit morphology

The morphology of zinc electrodeposits is changed by the addition of small amounts of lead acetate to the electrolyte. The main effect of this additive is to increase markedly the range of current densities which lead to compact deposits.

As an example, Fig. 1 shows the influence of the addition of lead acetate on the deposit at low current densities in a Leclanché cell electrolyte. Without any inhibitor, the deposit consists of some packs of spongy deposit distributed on the electrode: the aspect of such a spongy deposit can be seen on Fig. 1(a). Under the same conditions and with an addition of 10^{-4} M lead acetate, the deposit has become compact (Fig. 1(b)). At high current densities, zinc deposits are dendritic and the dendritic growth is favoured by low rotation speeds of the electrode. A deposit prepared under such conditions and without inhibitor is shown in Fig. 2(a). With the addition of 5×10^{-5} M lead acetate, the dendritic growth is inhibited and instead of dendrites a compact coarse-grained deposit is obtained [Fig. 2(b)]. It has to be noted that to achieve such an inhibition of the dendritic growth, optimal conditions have to be fulfilled

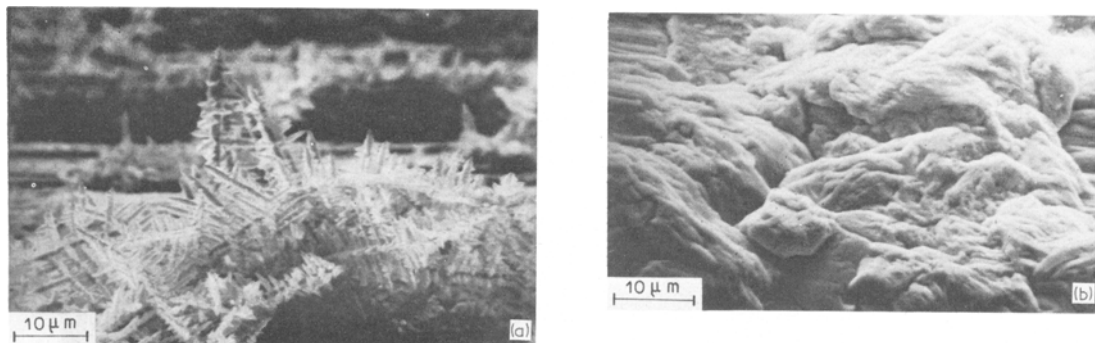


Fig. 1. Zinc deposits prepared in a Leclanché cell electrolyte at low current density (3.5 mA cm^{-2}). Rotation speed of the electrode $1200 \text{ rev min}^{-1}$. (a) Without any inhibitor; (b) with 10^{-4} M lead acetate.

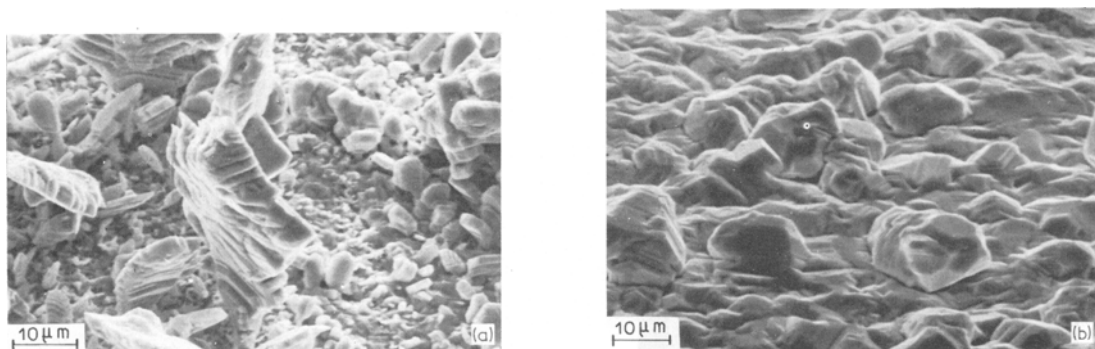


Fig. 2. Zinc deposits prepared in a Leclanché cell electrolyte at high current density (350 mA cm^{-2}). Rotation speed of the electrode 500 rev min^{-1} . (a) Without any inhibitor; (b) with $5 \times 10^{-5} \text{ M}$ lead acetate.

concerning the additive concentration and the electrode rotation speed. It should be noted that the dendrites were no longer inhibited when the concentration of lead acetate or the rotation speed of the electrode were too high.

In alkaline electrolytes, lead acetate has a similar effect on the deposit [3–8].

3.2. Current–potential curves

The influence of the additive on the kinetics of zinc electrocrystallization has been studied both in alkaline and acid media.

Without any inhibitor in the Leclanché cell electrolyte, the polarization curve plotted under steady-state conditions (Fig. 3, curve 1) is S-shaped, thus revealing the existence of multiple steady states. From the other curves of Fig. 3 it can be seen that the addition of small amounts of lead acetate gives rise to a shift of the polarization curves towards more cathodic voltages and this

inhibiting effect is an increasing function of the additive concentration. In addition, the multiple steady states are cancelled out by the additive.

At high current densities where steady-state conditions cannot be maintained because of the dendritic growth, the influence of mass transport on the polarization curves was not eliminated at the rotation speed used. However, as shown in Fig. 4, it is clear that the inhibiting effect still occurs up to high current densities. Consequently these results indicate that the kinetics of zinc electrodeposition are modified by the additive which seems to decrease in particular the importance of the autocatalytic step in the reaction mechanism.

In alkaline media, the influence of the additive on the polarization curves (Fig. 5) is similar to that observed in acid media. Without any inhibitor, the polarization curve (curve 1) is single-valued at the concentration of zincate we used. The additive increases the cathodic polarization and this inhibiting effect which has been mentioned

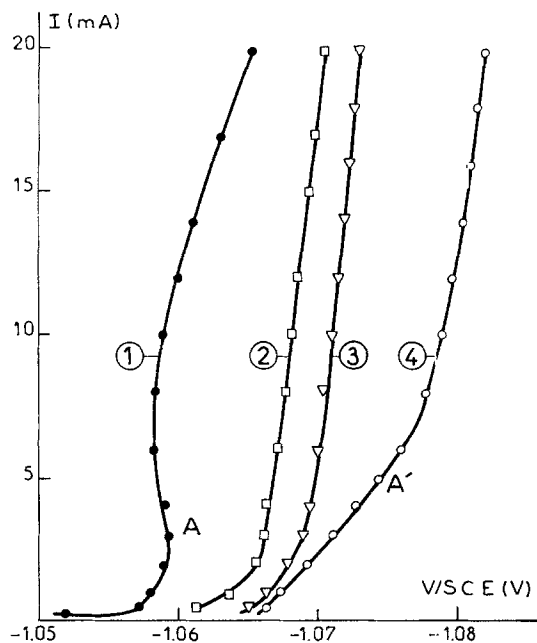


Fig. 3. Steady-state current-potential curves plotted for the Leclanché cell electrolyte with a rotating disc electrode ($1000 \text{ rev min}^{-1}$, area 0.28 cm^2). Concentrations of lead acetate: 0 (curve 1), 5×10^{-5} (curve 2), 10^{-4} (curve 3) and $3 \times 10^{-4} \text{ M}$ (curve 4).

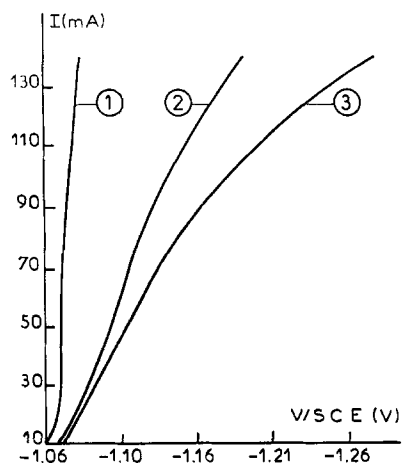


Fig. 4. Non steady-state current-potential curves recorded with increasing values of current; Leclanché cell electrolyte; rotating disc electrode ($2000 \text{ rev min}^{-1}$, area 0.28 cm^2); current sweep rate 13 mA s^{-1} . Concentrations of lead acetate: 0 (curve 1), 5×10^{-5} (curve 2) and 10^{-4} (curve 3).

previously [14] is confirmed in Fig. 5 to be an increasing function of the additive concentration.

So in alkaline media as well as in acid media, the kinetics of zinc electrodeposition are changed by

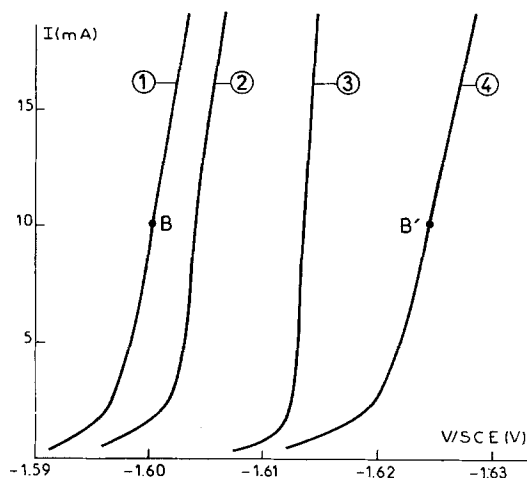


Fig. 5. Steady-state current-potential curves recorded for the alkaline zincate electrolyte with a rotating disc electrode ($1500 \text{ rev min}^{-1}$, area 0.28 cm^2). Concentrations of lead acetate: 0 (curve 1), 10^{-5} (curve 2), 3×10^{-5} (curve 3) and 10^{-4} (curve 4).

the presence of the additive which decreases the rate of the overall process at a given potential.

3.3. Impedance

Measurements of the electrode impedance allow us to be more specific concerning the change of the kinetics of electrocrystallization resulting from an addition of lead acetate. An example of an impedance diagram obtained without any inhibitor in the Leclanché cell electrolyte is shown in Fig. 6(A). Between 30 kHz and 200 Hz the diagram exhibits a capacitive loop corresponding to the transfer resistance in parallel with the double layer capacity (about $50 \mu\text{F cm}^{-2}$). At low frequencies three inductive loops are observed. Two of them correspond to the relaxation of the partial coverages of the electrode by the two adsorbed species: H_{ads} and Zn_{ads}^+ [2]. The third one can be ascribed to a slow relaxation of the surface concentration of growth sites [15]. The polarization resistance R_p associated with the slope of the current potential curve is negative.

Fig. 6(A') shows a typical diagram plotted in the presence of lead acetate. Such diagrams have been observed from 5×10^{-5} to $3 \times 10^{-4} \text{ M}$ lead acetate and for currents between 3 and 15 mA. At frequencies higher than 800 Hz, the diagram is close to a semi-circle and this allows us to evaluate the double layer capacity (this is 3 or 4 times

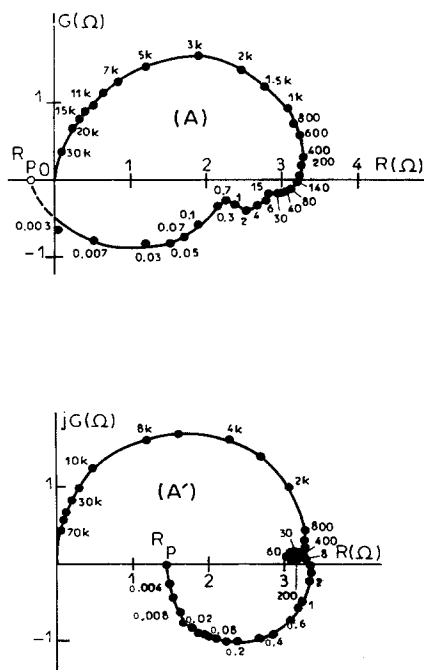


Fig. 6. Complex impedance diagram $Z = R - jG$ corresponding to points A and A' in Fig. 3 (frequency in Hz).

lower in the presence of lead acetate). At low frequencies, it can be seen that the diagram is characterized by a capacitive loop between two inductive loops, and it is therefore markedly different from the diagram [Fig. 6(A)] obtained without any inhibitor.

In alkaline media, the change in the low frequency impedance produced by the additive is similar to the change observed in acid solution: a capacitive loop between two inductive loops is still clearly exhibited [see Fig. 7(B')]. However, the reaction mechanism appears to be more complicated in alkaline media than in acid media, since the impedance often reveals, at low frequencies, four relaxation processes corresponding, for example, to the four inductive loops observed in Fig. 7(B).

This major change occurring in impedance diagrams at low frequencies means that some of the elementary reactions taking place at the interface are more slowed down than others [15, 16]. Particularly with a preferred decrease of the rate of the autocatalytic step, the local overintensities which lead to irregular growth become less probable and the deposit remains compact. There-

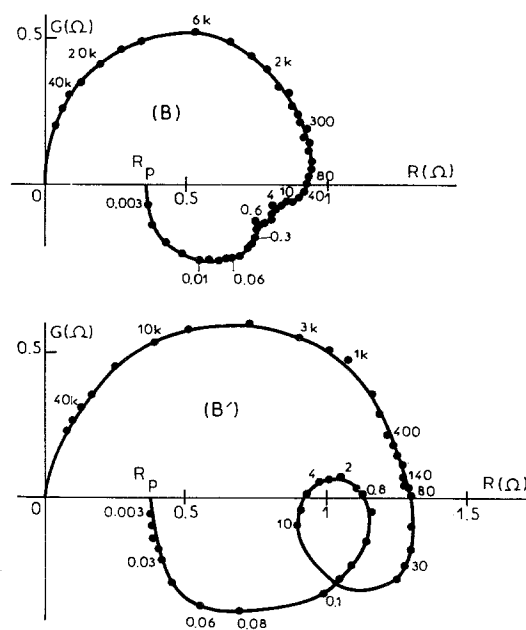


Fig. 7. Complex impedance diagram $Z = R - jG$ corresponding to points B and B' in Fig. 5 (frequency in Hz).

fore, the inhibition of the irregular growth is shown to be connected to the preferred inhibition of certain interfacial reactions.

4. Conclusion

In both alkaline and acid media, lead acetate increases the range of current densities which lead to compact deposits. In addition, this inhibitor cancels out the multiple steady states. This corroborates the relation between the S-shape of the $I(V)$ curve and the succession of three different morphologies of the deposit: spongy, compact and dendritic with increasing current density. The disappearance of the multiple steady states is connected with the existence of compact deposits over a larger range of current densities. This influence of lead acetate on the polarization curves and the major change observed at low frequencies in the impedance diagrams show that the additive alters the rates of the elementary reactions taking place at the interface and seems to decrease the importance of the autocatalytic step in the reaction mechanism. A recent improvement of the model [15] allows a better understanding of the different time constants observed at low frequencies.

This will probably enable us to determine more precisely how and to what extent the interfacial steps are inhibited by the presence of the additive in the electrolyte.

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