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Influence of S-dodecylmercaptobenzimidazole as organic additive on electrodeposition of tin

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ABSTRACT

Electrodeposition of tin from acidic baths was investigated using S-dodecylmercaptobenzimidazole (DMBI). Cyclic voltammetry measurements indicated that this compound isn't electroactive and changed the electrodeposition mechanism. It is found also that the reduction of Sn^{2+} ions run under diffusion control and the hydrogen evolution was affected by the nature of the working electrode. In addition, the averages of the effective diffusion coefficients of metal species were determined. Indeed, it is shown that the transfer coefficient, tin diffusion coefficient and electron transfer number depend with the potential. The morphology of electrodeposition of tin was also presented. So, the deposit became more uniform and smooth with the DMBI addition. It is found that the electrodeposition rate of tin and the cathodic current efficiency (P) increased with DMBI.

1. Introduction

The electrodeposition of tin has been known since the mid-nineteenth century. The process still has a great interest and its development continuation was observed. This is due to its high corrosion resistance, non-toxicity and good soldering properties of tin coatings used mainly in the food and electrotechnical industries [1–5]. Recently, the nano-whiskers electroplated [6] and the porous alloys of tin [7,8] were found very efficient for the rechargeable lithium-ion batteries.

Generally, two types of baths were used for the electroplating of tin. These are acidic stannous (tin (II)) and alkaline stannic (tin (IV)) solutions [4]. The non-corrosive alkaline stannic baths worked at high temperatures (usually above 65 °C) and showed good throwing power. But, they have to be protected from the presence of Sn(II) ions in the solution due to deterioration in the quality of the cathodic deposits. So, the acidic stannous baths worked at ambient temperature and they are easy in operation. In this case, the uniform coatings were obtained only when the organic compounds were added to the electrolyte [9]. In addition, for the tinning baths free of organic additives; the tin was strongly deposited at low over-potential [10] and the obtained deposit was porous and dendritic [11].

For this, the addition of organic additive to the tinning baths was necessary to improve the deposit quality [12–15]. In addition, to decrease the deposition rate, various organic compounds have been used such as aromatic carbonyl [15–17], amine-aldehyde [18,19], and alkyl polyglucosides [20].

In the literature, little attention has been given to the action mechanism of the organic additives on the deposition process. In this study, we investigated the effect of S-dodecylmercaptobenzimidazole (DMBI) [21] on the electrodeposition mechanism of tin from acidic bath using cyclic voltammetry and scanning electron microscopy measurements.

2. Experimental procedures

All solutions used throughout these experiments were freshly prepared from analytical grade reagents and distilled water. The composition and operating conditions of each bath of the plating are listed in Table 1. The pH was fixed at 2 ± 0.1 with H_2SO_4 addition and the temperature was held at 25 ± 2 °C.

However, the S-dodecylmercaptobenzimidazole which its structure was presented in Fig. 1, was synthesized in the laboratory by condensation of 2-mercaptobenzimidazole with the bromododecene. It occurred under the conditions of phase transfer catalysis (PTC) liquid–solid in the presence of tetra-n-butylammonium bromide as catalyzer at room temperature [21].

The electrolysis cell was a borosilicate glass (Pyrex®) cylinder closed by cap with five apertures. Three of them were used for the electrodes. So, for the cyclic voltammetry measurements, copper disk, with surface area of 0.28 cm^2, as working electrode, Pt plate as the counter while a saturated calomel electrode (SCE) was used as the reference electrode. All potentials are referred with respect to this last electrode. Prior to

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Table 1
Composition of the electroplating bath.

Electrolytes	$SnSO_4$ (M)	H_2SO_4 (M)	C_2H_5OH (% by volume)	DMBI concentration (M)
a	0.14	0.56	0	0
b	0.14	0.56	20	0
c	0.14	0.56	20	1.56×10^{-4}
d	0	0.56	0	0
e	0	0.56	20	0
f	0	0.56	20	1.56×10^{-4}
g	0	0	20	1.56×10^{-4}

immersion test, the substrate was abraded with 1.0, 0.3, and 0.05 mm alumina slurries (Fischer), cleaned ultrasonically and washed with distilled water, and finally dried by purging with N_2.

The cyclic voltammetry curves were recorded by polarization with a different sweep rate. These measurements were carried out using Potentiostat/Galvanostat/Voltalab PGZ 100 monitored by a personal computer.

The morphology of the formed deposits was examined by scanning electron microscopy using LEO 1530 FEG Scanning Electron Microscope. For this, a tin plate, with an area of 1.34 cm^2, was used.

3. Results and discussion

3.1. Characteristic of electrodeposition bath

Fig. 2 shows the obtained cyclic voltammogram from the electrolyte (g) (Table 1). It is noted that no peak of tin was observed. This result indicates that the organic additive wasn't an electroactive species.

Fig. 3 shows the cyclic voltammogram obtained from the electrolyte (a). The forward scan exhibited a peak of tin reduction at around −520 mV/SCE followed by hydrogen evolution at more cathodic potential (−610 mV/SCE). In the anodic range, the observed peak at around −355 mV/SCE was attributed to the oxidation of the formed tin during the cathodic scan.

Fig. 4 shows the obtained cyclic voltammogram from the electrolyte (b). It is noted that with alcohol addition, the reduction of H^+ was shifted to a more cathodic potential (−900 mV/SCE) compared to that in its absence (electrolyte (a)). It is also remarkable that the current densities are lower in the presence of ethanol. This can be explained by the decrease in the diffusion coefficient of the stannous ions in the presence of alcohol [21–23].

However, in both electrolytes (a) and (b), the forward scan shows a single cathodic peak corresponding to two electron step reduction:

$$Sn^{2+} + 2e^- \leftrightarrow Sn. \quad (1)$$

In the reverse potential sweep, one peak recording confirms the two electron oxidation of deposit [24,25]:

$$Sn \leftrightarrow Sn^{2+} + 2e^-. \quad (2)$$

In addition, to take an idea about the additive effect on the cyclic voltammogram aspect and its action in the electrodeposition process

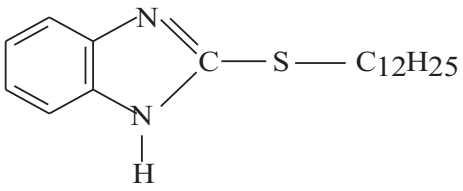

Fig. 1. Molecular structure of S-dodecylmercaptobenzimidazole (DMBI).

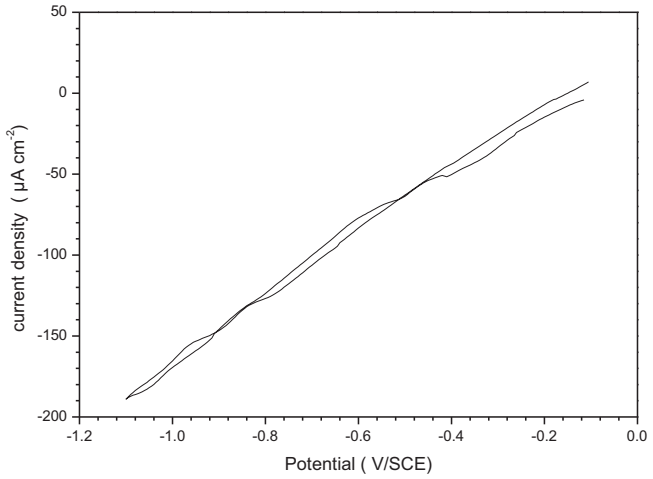

Fig. 2. Cyclic voltammogram for copper electrode from electrolyte (g) (T = 25 °C; ν = 10 mV s^{-1}). Electrolyte (g): 20% by Volume C_2H_5OH and 1.56×10^{-4} M DMBI.

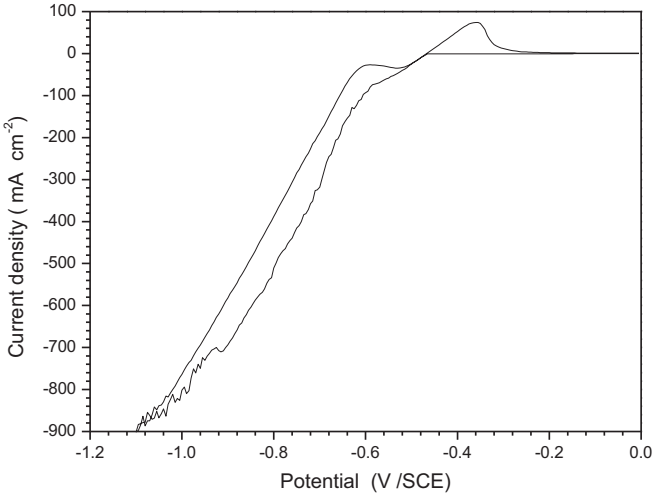

Fig. 3. Cyclic voltammogram for copper electrode from electrolyte (a) (T = 25 °C; ν = 10 mV s^{-1}). Electrolyte (a): 0.14 M $SnSO_4$ and 0.56 M H_2SO_4.

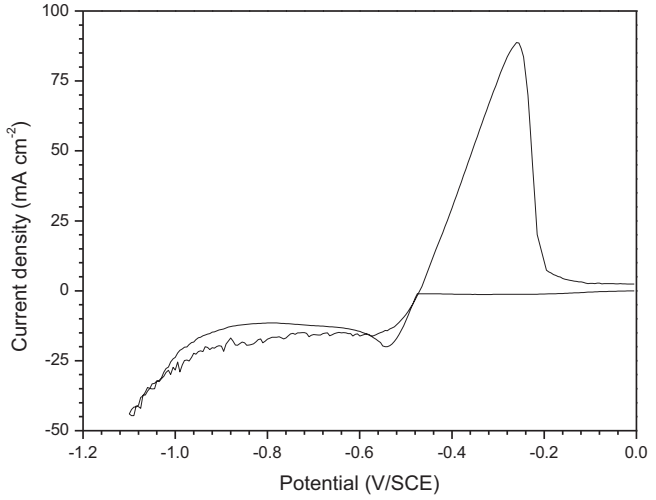

Fig. 4. Cyclic voltammogram for copper electrode from electrolyte (b) (T = 25 °C; ν = 10 mV s^{-1}). Electrolyte (b): 0.14 M $SnSO_4$, 0.56 M H_2SO_4 and 20% by Volume C_2H_5OH.