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Effects of additives on the electrodeposition of tin from an acidic Sn(II) bath

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Additive effects of formaldehyde, propionaldehyde and benzaldehyde on the deposition of tin in acidic solution of tin(II) sulfate have been investigated. The effects of these additives on cathodic polarization and a.c. impedance was measured by galvanostatic or potentiostatic methods, respectively. The reduction products of the aldehyde during the deposition and the diffusion coefficient of Sn(II) in various solutions were also determined.

1. Introduction

Tin (II) sulfate electrolytes are gradually replacing tin–lead fluoborate electrolytes in the deposition of tin in the electronics and related industries. The process is rather fast in the absence of additive agents and the deposits obtained under such conditions are mostly porous, coarse and poorly adherent. Formation of needles, whiskers and dendrites that may cause short circuits is common [1, 2]. Consequently, organic additives are necessary if smooth and dense films are to be obtained. Considerable effort has been directed to find additives which improve the tin deposit quality [2–5]. Various organic additives such as surface-active agents [2, 4–8], aromatic carbonyl compounds [4, 9, 10] and amine-aldehyde reaction products [11, 12] are used in the plating solution to modify the deposit properties and the kinetics of tin deposition. However, little attention has been focused on how the alkyl group of such carbonyl compounds influences the electrodeposition of tin.

In the present work the effects were investigated of alkyl groups of three commonly used carbonyl compounds – formaldehyde, propionaldehyde and benzaldehyde – on tin deposition by studying their polarization behaviour, a.c. impedance responses and diffusion coefficients.

2. Experimental details

A conventional three-electrode cell was used. A platinum rotating disc electrode (Pt-RDE, EG&G model 636) was used as a working electrode; this was electroplated with a layer of copper from an acidic copper sulfate solution (0.1 M) at a constant current (10 mA) for 500 s (called Cu-RDE). The Pt-RDE had a working area 0.164 cm^2, and was mounted on a variable-speed motor. A platinum wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All electrolytes were prepared with reagent grade chemicals and deionized water, and the experiments were carried out at room temperature (about 30 °C). An acidic solution of composition $SnSO_4$ (0.01 M) plus H_2SO_4 (10% by volume) was used in all experiments except for the ac impedance measurement, in which $SnSO_4$ (0.4 M) plus H_2SO_4 (10% by volume) was used. formaldehyde, propionaldehyde or benzaldehyde was used as organic additive at typically 2 mL/L or other concentrations if needed. The Pt-RDE was cleaned before each experiment with a H_2O_2/H_2SO_4 (50 : 10) solution for 30 min to strip impurities completely.

The rotational speed of the Cu-RDE electrode was set at 1000 r.p.m. and was connected to an electrochemical interface system (Schlumberger S1-1286) in the galvanostatic mode. Tin was plated at 10 mA on Cu-RDE, with electrode potential (vs SCE) continuously recorded. The electroplated tin was easily stripped with NH_4HF_2 (4 M) plus H_2O_2 (5% by volume) solution.

The diffusion coefficient of Sn(II) in an acidic Sn(II) bath was measured with a potentiostat and a rotating disc electrode (Pine RDE 4) [13]. The concentration of Sn(II) in the electrolytes was determined using an atomic absorption spectrophotometer (Varian spectrAA 30). The kinematic viscosity of the solution was measured with an Ostwald viscometer [14]. Impedance was measured with a frequency response analyser (Schlumberger S1-1255), a potentiostat (Electrochemical Interface, Schlumberger S1-1286), and a microcomputer. Inpedance diagrams in the

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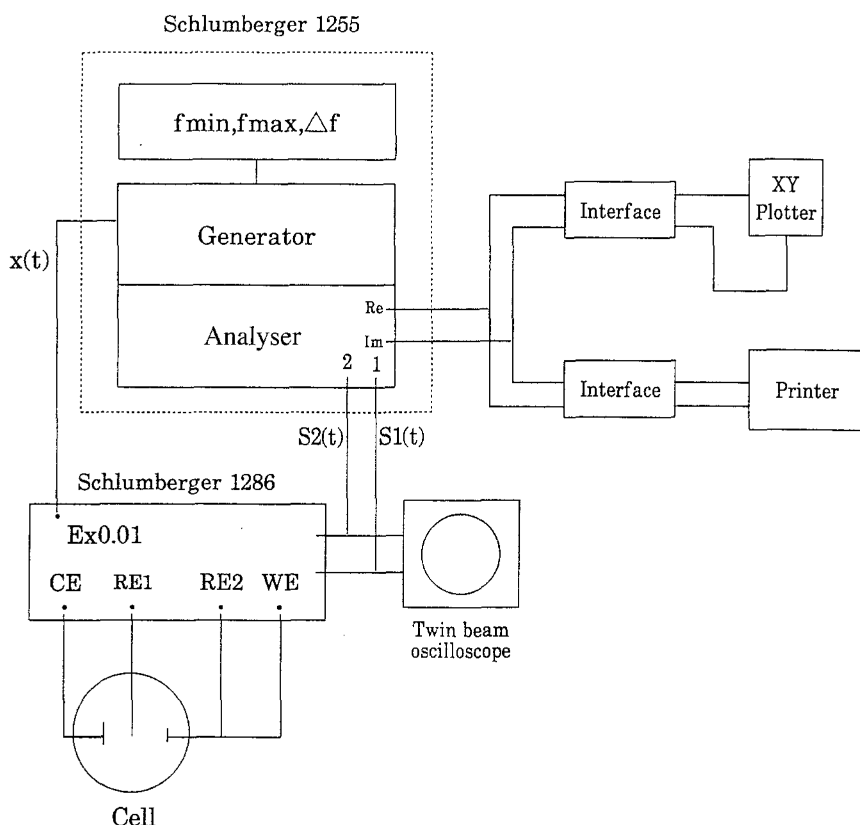


Fig. 1. Experimental arrangement for automated impedance measurement.

frequency range 0.01 Hz to 10^5 Hz were recorded on a X–Y plotter. The experimental setup is shown in Fig. 1.

Mass spectra were measured using a gas/liquid chromatograph mass spectrometer (Joel SX-102 A). The sample was introduced to the ion source by the direct inlet method and was ionized by fast atom (high energy xenon) bombardment (matrix: thioglycerol). The positive ions were detected and the mass spectra were obtained.

3. Results and discussion

3.1. *Electrode potential measurement*

Figure 2 shows a continuous recording of cathodic potential against duration of deposition of tin on the Cu-RDE for a plating solution with and without additive. The electrode potential, in every case, was almost constant throughout the deposition. The plating solution with formaldehyde or propionaldehyde additive had nearly the same cathodic potential (curves 2 and 3), about −1.05 V (vs SCE).

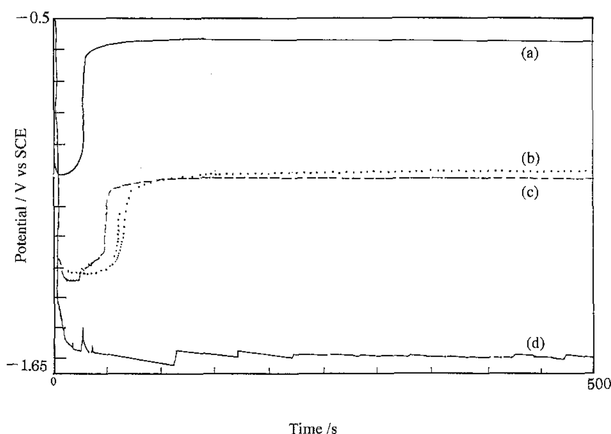


Fig. 2. Cathodic potential against time for electrodeposition of tin on Cu-RDE under the condition $i = 10\,\text{mA}$, concentration of additive = 2 mL/L. Key: (a) No additive, (b) formaldelhyde, (c) propionaldehyde, and (d) benzaldehyde.

It was previously reported [15] that the equilibrium potential of the Sn(II)–Sn couple reaction was about −0.50 V (vs SCE). Therefore the overpotential of curves 1, 2, 3 and 4 (Fig. 2) were about −0.1, −0.54, −0.55 and −1.1 V, respectively. Hence the electrode potential was most polarized in acid solution with benzaldehyde, medium polarized for formaldehyde or propionaldehyde, and least polarized for plating solution without additive.

Adsorption of organic molecules on an electrode may block the electrode surface, impede charge transfer, and thus increase the overpotential of the metal deposits [16]. Therefore, an additive of aldehyde type that has a distinct hydrophobic group, such as benzaldehyde, is more easily adsorbed on an electrode surface, resulting in a larger overpotential. This is consistent with our finding regarding the degree of polarization due to additive. Therefore, it can reasonably be predicted that a plating solution containing benzaldehyde or other hydrophobic compound as additive should produce compact, smooth and fine-grained electrodeposits of tin. Similar results were described by Puippe and Leaman [17].

3.2. *Diffusion coefficient*

The diffusion coefficient of Sn(II) in solution with and without additive was determined with a Cu-RDE system. The limiting currents for various solutions

Table 1. Diffusion coefficient of Sn(II) ($\times 10^{-6}$ cm^2 s^{-1}) *for solution with or without additive*

No additive	*Additive*		
	formaldehyde	*propionaldehyde*	*benzaldehyde*
11.7	9.78	8.53	5.05

were found to be proportional to the square root of the speed of rotation; the diffusion coefficient was then calculated from the slope of these lines according to Levich's equation [13]. The results in Table 1 show that the diffusion coefficient of Sn(II) was the largest in acidic solution of tin(II) sulfate without additive, smaller for formaldehyde and propionaldehyde and smallest for benzaldehyde.

When the solution contains more electrolyte or additive molecules, the active ions coordinate or chemically interact with these molecules, thereby resulting in a decreased diffusion rate of the active ions. Hence the diffusion coefficient of active ions decreases in magnitude. Benzaldehyde additive has the largest surface area of these three additives–formaldehyde, propionaldehyde and benzaldehyde, and it is most easily polarized with Sn(II) in an electric field. Hence, the intermolecular attraction between benzaldehyde and Sn(II) is the largest in an acidic tin(II) sulfate solution, thereby resulting in the smallest diffusion coefficient for Sn(II); the other two additives (for maldehyde and propionaldehyde) exhibit a similar effect on the diffusion coefficient for Sn(II), but are less influential than benzaldehyde. We suspect that a plating solution containing a more hydrophobic compound as additive may further decrease the diffusion coefficient of Sn(II).

3.3. *A.c. impedance measurement*

In a.c. impedance measurement, a sinusoidal a.c. voltage of small amplitude was applied to the electrode surface. The impedance diagram (or Nyquist plot) was then obtained in the complex plane from the variation of amplitude and phase of the response current. Both the charge transfer resistance and the double layer capacitance were calculated from these plots.

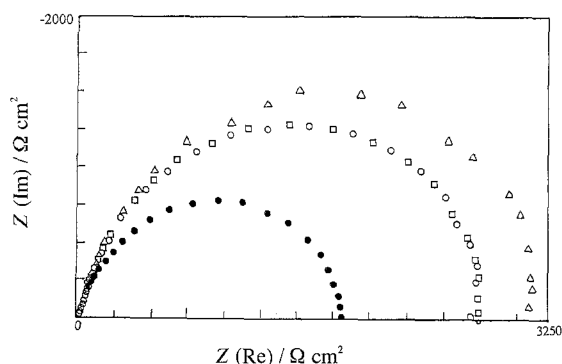


Fig. 3. Impedance diagram of an acidic tin(II) sulfate solution with additive (2 mL/L) or without additive. Key: (●) no additive, (○) formaldehyde, (□)proprionaldehyde, and (△) benzaldehyde.

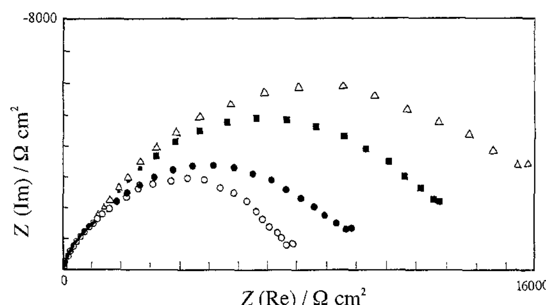


Fig. 4. Impedance diagram of an acidic tin(II) sulfate solution with various concentrations of benzaldehyde. Key: (○) no additive, (●) 250 p.p.m., (■) 750 p.p.m., and (△) 1500 p.p.m.

The Cu-RDE was controlled at 5000 r.p.m., −0.36 V vs SCE, and the frequency was swept from 0.01 Hz to 65 kHz using a 20 mV sinusoidal perturbance signal, Fig. 3 shows the impedance diagram of an acidic tin(II) sulfate solution containing formaldehyde, propionaldehyde, benzaldehyde or no additive. The charge-transfer resistance of plating solution, with or without additive, was estimated. From the capacitance semicircle, the plating solution containing benzaldehyde exhibited the largest charge-transfer resistance, formaldehyde or propionaldehyde (nearly equal) came next, and the smallest value occurred for solution without additive. These results are consistent with the overpotential measurements; that is, an aldehyde-type additive with a phenyl or a large alkyl group is easily adsorbed on the electrode surface and can increase the charge-transfer resistance significantly.

Figure 4 shows the impedance diagram of an acidic tin(II) sulfate solution containg various concentrations of benzaldehyde. The effect of benzaldehyde concentration on the charge-transfer resistance of tin electrodeposition is shown in Fig. 5. The charge transfer resistance apparently increases with increased additive concentration and probably gradually levels off at higher concentration. The reason is that the additive adsorbtion on the electrode surface gradually becomes saturated and approaches a maximum. If too much additive is added to the plating solution, the excess may contaminate the bath.

If the plating solution contains any one of these aldehyde additives, an additional capacitance semicircle is observed on the impedance diagram; for example; Fig. 6 shows the impedance diagram of an

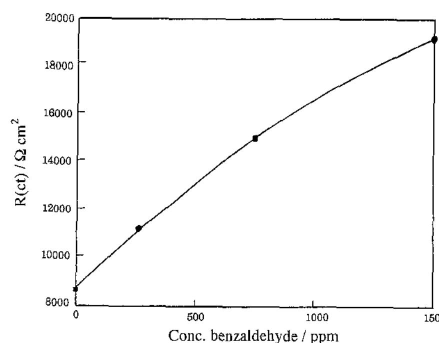


Fig. 5. Effect of benzaldehyde concentration on charge-transfer resistance of tin electrodeposition.

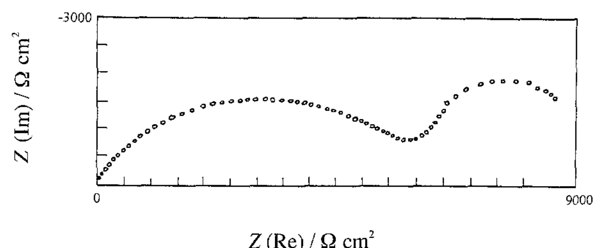
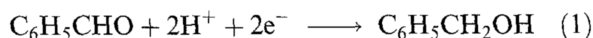


Fig. 6. Impedance diagram of an acidic tin(II) sulfate solution with 3 mL/L benzaldehyde.

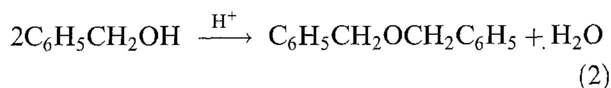
acidic tin(II) sulfate solution with 3 mL/L benzaldehyde. The secondary semicircle may indicate chemical reaction of the additives [18], which are reduced on the electrode. This assumption was confirmed by the following experiment.

Benzaldehyde (50 p.p.m.) was added to an acidic tin(II) sulfate solution (40 g/L $SnSO_4$ plus 10% by volume of H_2SO_4) as additive agent. After the deposition experiment, an unknown compound was strongly adsorbed on the working electrode surface and was analysed with GC/mass spectrometry (Fig. 7).

In the mass spectra, benzyl alcohol and dibenzyl ether were found. The reaction scheme can be described as follows:



$$C_6H_5CHO + 2H^+ + 2e^- \longrightarrow C_6H_5CH_2OH \quad (1)$$



$$2C_6H_5CH_2OH \xrightarrow{H^+} C_6H_5CH_2OCH_2C_6H_5 + H_2O \quad (2)$$

Hence, additive aldehydes were indeed reduced to alcohol during electrodeposition. These results explain why the impedance diagram of Fig. 6 has two capacitive semicircles.

To sum up, there are several effects of additives on the deposition of tin: (a) adsorption of the additive on the tin surface, which slows down the deposition rate and increases the charge transfer resistance, (b) complexation of tin by the organic molecules, which decreases the diffusion coefficient, and also causes an increase in the overpotential of Sn(II) reduction. From above discussion, the adsorption of the additive on the tin surface is probably a more significant effect during tin deposition.

4. Conclusion

The effects of formaldehyde, propionaldehyde and benzaldehyde as additives on the electrodeposition of tin from an acidic solution of tin(II) sulfate were investigated with the following conclusions.

If the plating solution contains a very hydrophobic additive such as benzaldehyde, the diffusion coefficient or the limiting current is smaller than that of a more hydrophilic additive such as formaldehyde or propionaldehyde. Hence in a steady state, benzaldehyde or other hydrophobic compounds show large overpotential for electrodeposition of tin in acidic solution of tin(II) sulfate. Therefore, these compounds should serve as good grain refiners.

Additives of aldehyde type can be reduced to alcohol during electodeposition which may affect the properties of the deposit.

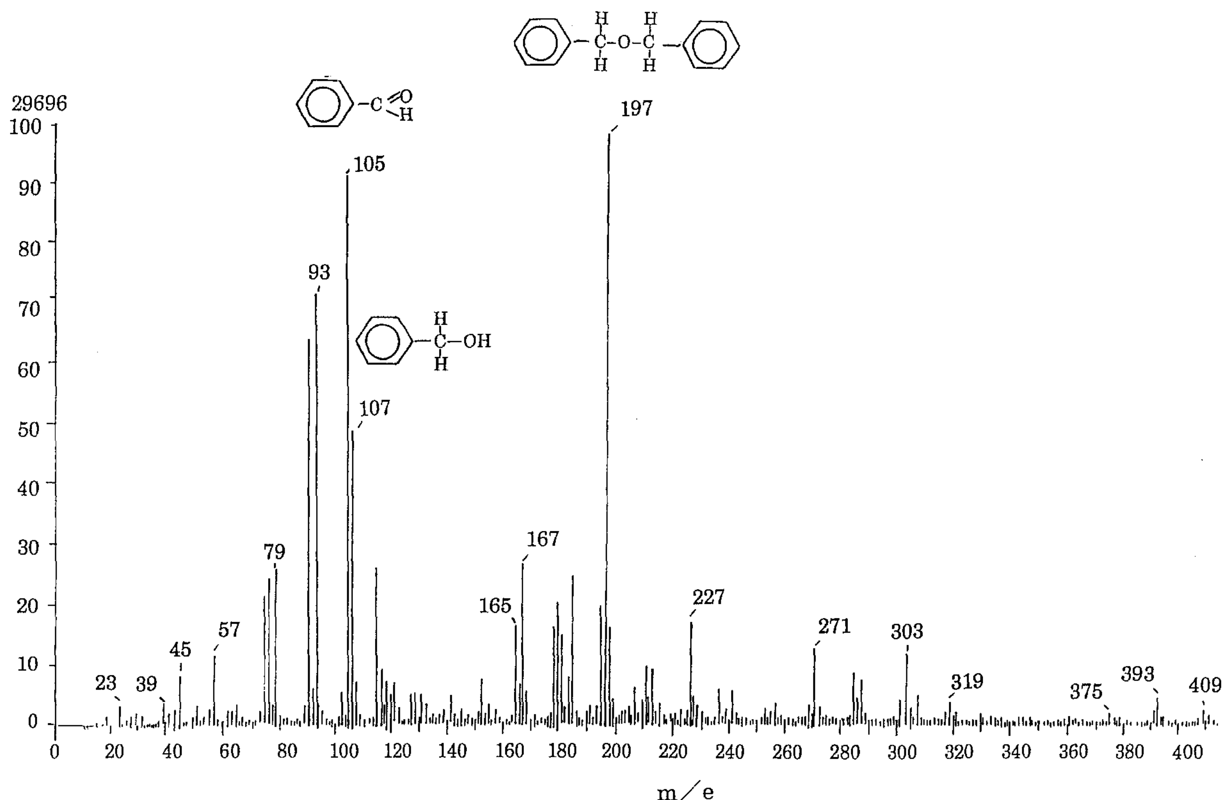


Fig. 7. Mass spectrometry of adsorped material on the working surface electrode.

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