Effects of Additive Agents on the Kinetics Of Tin Electrodeposition from An Acidic Solution of Tin(II) Sulfate

By G.-S. Tzeng

The effects of benzaldehyde, acetophenone and 4-methyl 2-pentanone additives on deposition of tin in acidic solution of tin(II) sulfate were investigated. The solution containing the first two additives produced greater cathodic polarization than that of the other ketone, according to galvanostatic experiments. The kinetics of deposition of tin, with or without additives, were investigated with cyclic voltammetry and Tafel plots. Based on these results, a mechanism is proposed for the deposition process. The correlation of overpotential with the diffusion coefficient of Sn(II) in various solutions was also investigated.

Stannous sulfate electrolytes are widely used for deposition of tin in electronics and related industries, but tin is electrodeposited with little activation polarization from acidic solutions of stannous sulfate in the absence of added agents. The deposits obtained under such conditions are porous, coarse and poorly adherent, with formation of needles, whiskers and dendrites that cause short circuits between anode and cathode.^{1,2} Many authors have suggested addition of organic compounds to ensure fine-grained, smooth and compact deposits.2-6 Various organic additives, such as surface agents,2.7 aromatic carbonyl compounds,4,8 and amine-aldehyde reaction products^{9,10} are used in plating solutions. Although considerable efforts are directed to finding additive agents for tin plating and to examine the effects of these agents on structural properties of deposits, little attention has been focused on establishing the way in which such organic additives influence the kinetics of electrodeposition.

In this study, the effects of three compounds—benzaldehyde, acetophenone and 4-methyl 2-pentanone, which represent organic additives used in plating solutions—on the polarization behavior and kinetic parameters of the electrode reaction in acidic solutions of stannous sulfate were investigated. More information about electrodeposition of tin from these solutions, with and without additives, resulted from use of cyclic voltammetry. Finally, the correlation of overpotential with the diffusion coefficient of Sn(II) in acidic solutions of Sn(II) sulfate containing varied organic additives was also assessed.

Experimental Procedure

A conventional three-electrode cell was used throughout. The working electrode, a platinum rotating disk (Pt-RDE), was electroplated with a layer of copper at a constant current (10 mA) for 500 sec (referred to as Cu-RDE), or electroplated with tin under the same conditions, except using acidic Sn(II) sulfate as the plating solution (referred to as Sn-RDE), and used as cathode, except as explained otherwise. The Pt-RDE has a working area of 0.164 cm², and was mounted on a variable speed motor. 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 at room temperature. An acidic solution of $SnSO_4$ (0.01 M) and H_2SO_4 (10% by volume) was used in all experiments except for cyclic voltammetry measurement, where $SnSO_4(0.01 \text{ M})$ and H₂SO₄ (3% by volume) was substituted. Benzaldehyde, acetophenone or 4- methyl 2-pentanone was used as a representative organic additive at 1 or 2 mL/L. The Pt-RDE was cleaned before each experiment with a H_2O_2/H_2SO_4 (5:1) solution for 30 min,

to strip impurities completely.



Fig. 1—Cathodic potential vs. time of deposition of tin on Pt-RDE or Cu-RDE (i = 5 mA; conc. of additive, 1 mL/L); (1) no additive, Cu-RDE; (2) no additive, Pt-RDE; (3) 4-methyl 2-pentanone, Cu-RDE; (4) benzaldehyde, Cu-RDE; (5) acetophenone, Cu-RDE.



Fig. 2—Tafel plots of tin plate electrode in solution with 1 mL/L additive: (1) no additive; (2) benzaldehyde; (3) acetophenone; (4) 4-methyl 2-pentanone.



Fig. 3—Cyclic voltammograms of Pt-RDE in acidic solution of tin(II) sulfate at various scanning rates: (1) 50 mV/sec; (2) 100 mV/sec; (3) 2 mV/sec (X 2.5).

The rotational speed of the Cu-RDE electrode was set at 1000 rpm, connected to an electrochemical interface system in the galvanostat mode. Tin was plated at a constant current of 5 mA on the Cu-RDE, with electrode potential (vs. SCE) recorded against time. Data obtained from electrolytes, with or without additives, were transferred to a microcomputer for storage and analysis. The electroplated tin was easily stripped with NH₄HF₂ (4 M) plus H₂O₂ (5% by volume) solution.

Tafel plots were made in the same way as electrode potential measurements, but in a potentiodynamic mode.¹¹ Experiments were made in a static solution with and without organic additives. Pure tin plate was used as a working electrode. The Tafel plot of a given solution was obtained from an initial potential of about -0.6 V (vs. SCE) and scanning anodically at a rate of 2 mV/sec, to the final potential of -0.3 V. Because surface conditions affect Tafel plots, all plots were made without prescan.

The cyclic voltammograms were measured with a potentiostat/galvanostat, connected to an X-Y recorder. The working electrode was either the Cu-RDE or Sn-RDE. Experiments were carried out in a static solution with or without organic additives. Cyclic voltammograms were measured with potential scan starting at -0.3 V (vs. SCE) and scanning cathodically; finally, scanning was reversed at -0.8 V. All voltammograms were measured without prescan.

The diffusion coefficient of Sn(II) in the acidic solution, with or without additives, was measured with a potentiostat and a rotating disc electrode.¹² The concentration of Sn(II) in the electrolytes was determined with an atomic absorption spectrophotometer. The kinematic viscosity of solutions was measured with an Ostwald viscometer.¹³

Results and Discussion

Polarization Measurement

Figure 1 shows a continuous recording of cathodic potential against duration of deposition of tin on Pt-RDE or Cu-RDE, at 1000 rpm and constant current of 5 mA, for a plating

Table 1
Kinetic Parameters of Tin Deposition for Different Additives*

Additive	b _a	b _c	α_{a}	α_{c}	$\alpha_a + \alpha_c$
None	52.2	105.2	1.13	0.56	1.69
benzaldehyde	48.8	107.5	1.21	0.55	1.76
acetophenone	52.5	108.1	1.12	0.55	1.67
4-methyl					
2-pentanone	48.8	103.7	1.21	0.57	1.78

*Units of b are mV/decade; subscripts a and c denote the anodic and cathodic values, respectively.

solution containing benzaldehyde, acetophenone or 4-methyl 2-pentanone, or without additive. According to Fig. 1, in the nonsteady state (the first 100 to 150 sec), tin is deposited on the Pt or Cu substrate with high overpotential whether the plating solution has additives (4-methyl 2-pentanone, plating on Cu-RDE) or not. Once the substrate is covered with some Sn, the overpotential decreases (curves 1-3) and, at the steady state, Sn is deposited on the substrate overpotential. In the steady state, all three plating solutions had nearly the same overpotential, within experimental error, whether the working electrode was Pt-RDE or Cu-RDE and whether or not the solution contained additives. These results show that under such plating conditions, adsorption of 4-methyl 2-pentanone on the electrode surface was too small to alter the electrode potential. In the case of large adsorption, as with benzaldehyde and acetophenone, the high overpotential is maintained in the steady state (Fig. 1, curves 4 and 5).

In the steady state, on comparison of the electrode potential of curve 3 (4-methyl 2-pentanone additive) with curve 4 (benzaldehyde additive) or 5 (acetophenone additive), we find that a solution containing a carbonyl compound as additive which, having a phenyl group, had a more negative electrode potential than one having only an alkyl group; accordingly, an additive with a phenyl group was easily adsorbed on an electrode surface, resulting in greater electrode potential needed to deposit tin on Cu-RDE. Therefore, we can reasonably predict that a plating solution containing benzaldehyde or acetophenone additive enables more compact, smooth and fine-grained electrodeposits of tin.¹⁴ Com-



Fig. 4—Cyclic voltammograms of Cu-RDE in acidic solution of tin(II) sulfate at various scanning rates: (1) 50 mV/sec; (2) 100 mV/sec.



Fig. 5—Cyclic voltammograms of Sn-RDE in acidic solution of tin(II) sulfate at scanning rate of 100 mV/sec.



Fig. 6—Voltammograms at times after one drop H_2O_2 added to an acidic solution of tin(II) sulfate at a scanning rate of 50 mV/sec: (1) t = 0; (2) 5 min; (3) 30 min; (4) 60 min; (5) 75 min.



Fig. 7—Cyclic voltammograms of Pt-RDE in various solutions at a scanning rate of 2 mV/ sec: (1) scanning forward and backward in SnSO₄ (0.01 M) + H₂SO₄ (3%); (2) scanning forward in SnSO₄ (0.01 M) + H₂SO₄ (3%), but backscan in H₂SO₄ (3%) only.

parison of all curves in Fig. 1 indicates that at the initial stage (less than 100 sec) of deposition of tin on Pt-RDE, a somewhat larger electrode potential is exhibited than that on Cu-RDE, regardless of whether the plating solution contained an additive.

Tafel Plots

Tafel plots, electrode potential against log i, appear in Fig. 2. Addition of any of the three specified additives to the plating solution had little effect on the capilibrium potential (chaut 0.5 V up

equilibrium potential (about -0.5 V vs. SCE) of Eq. (1):

$$\operatorname{Sn}_{+2} + 2e \rightarrow \operatorname{Sn}$$
 (1)

Calculation of the Tafel slope (b) and transfer coefficient (α) of anodic or cathodic electrodes in various plating solutions led to the results listed in Table 1. These values of the Tafel slope and transfer coefficients of anodic and cathodic reactions are approximately constant, whether the plating solution contain an additive or not. According to Nageswar's investigation,¹⁵ the variation of Tafel slope indicates whether the reaction mechanism of the active species remains the same. Therefore, from the values of the Tafel slope (Table 1), the reaction mechanism of Eq.(1) remains the same regardless of whether the solution contains an additive or not.

The sum of values of $\alpha_a + \alpha_c$ is another important parameter in Table 1; the sum is about 1.7 (i.e., approaching 2), whether the plating solution has an additive or not. Therefore, for all plating solutions, the discharge of Sn(II) ions is a two-electron transfer per Sn(II) ion.¹

Cyclic Voltammetry

The reaction mechanism of Sn(II) in acidic solution, according to cyclic voltammetry, is not clearly elucidated in the literature; therefore, qualitative assignments of voltammograms were primary objectives in the cyclic voltammetry experiments. The effects of the working electrode on the cyclic voltammetry of the Sn(II) reaction are



Fig. 8—Voltammogram of Pt-RDE in acidic solution of tin(II) sulfate, scanning from -0.8 V to -0.3 V at 100 mV/sec.

Table 2 Diffusion Coefficient (10-6cm²/sec) Of Sn(II) for Solution With or without Additive

no additive 6.23 ±0.04

benzaldehyde 5.48 ±0.13

acetophenone 5.24 ±0.10

4-methyl 2-pentanone 3.98 ±0.11



Fig. 9—Cyclic voltammograms of Cu-RDE in acidic solution of tin(II) sulfate: (1) no additive; (2) benzaldehyde, 1 mL/L; (3) benzaldehyde, 2 mL/L.

shown in Figs. 3, 4 and 5. Whether the working electrode was Pt-RDE, Cu-RDE or Sn-RDE, these figures exhibit similar shapes (i.e., every curve has three maxima at about the same electrode potential); when the scan rate was 2 mV/sec, only two maxima appeared in Fig. 3, but the magnified curve also exhibited three maxima.

Sn(II) is easily oxidized by oxygen; accordingly, the tin(II) sulfate compound without purification may contain Sn(IV) species as a small fraction.

When the potential was scanned cathodically, each curve in Figs. 3, 4 and 5 consisted of two reduction peaks. Peak I, about -0.47 V, was smaller, corresponding to the Sn(IV)-Sn(II) reaction, whereas peak II, about -0.53 V, corresponded to the Sn(II)-Sn couple reaction. These two maxima resembled those observed by Glodowski et al.,¹⁶ for reduction of Sn(IV) at a dropping mercury electrode. The reason that peak II was the Sn(II)-Sn couple reaction at the electrode substrate requires further discussion.

When a drop of hydrogen peroxide solution was added to the acidic solution of tin(II) sulfate, the results were as shown in Fig. 6. The maximum current of peak II was gradually diminished to some extent after 5 min; thereafter there was almost no effect. The reason is that a small fraction of Sn(II) was oxidized by hydrogen peroxide to Sn(IV); consequently, the concentration of Sn(II) was decreased, resulting in decreased peak current at II. Evidently, peak II corresponds to the Sn(II)-Sn couple reaction, and belongs to a two-electron transfer reaction. This result is consistent with the Tafel plots (i.e., reduction of tin(II) ions was a two-electron transfer reaction. The maximum current of peak I did not increase explicitly, but resulted in a gradually decreased maximum current. An explanation is that Sn(IV) formed a white precipitate (SnO₂) in our test solution, and the reduction potential of SnO₂ was beyond our experimental range.

When the potential was scanned from -0.8 V to -0.3 V, there was only one oxidation maximum peak (III) in each curve in Figs. 3, 4 and 5. The area of peak III is larger than that





Fig. 12—Regression lines describing limiting

rig. 12—Regression lines describing infining current density vs. square root of rotational speed for solution with and without additives: ■ no additive; ▲ benzaldehyde; * acetophenone; • 4-methyl 2-pentanone.

Fig. 10—Cyclic voltammograms of Cu-RDE in acidic solution of tin(II) sulfate: (1) no additive; (2) acetophenone, 1 mL/L; (3) acetophenone, 2 mL/L.

acidic solution of tin(II) sulfate: (1) no additive; (2) 4-methyl 2-pentanone, 1 mL/L; (3) 4-methyl 2-pentanone, 2 mL/L.

of peaks I and II, showing that in the anodic reaction range (i.e., potential between -0.5 V and -0.4 V), there might be superimposed oxidation of Sn and Sn(II). This prompted investigation of the reaction of peak III.

Figure 7 shows cyclic voltammograms on Pt-RDE for various electrolytes. In the backscan process of curve 2, H_2SO_4 solution (3%) was used instead of an acidic solution of tin(II) sulfate. The area of peak II (curve 2) was smaller than that of peak II (curve 1), indicating that the Sn-Sn(II) couple oxidation reaction really appeared at a potential between -0.5 V and -0.4 V.

Voltammograms of Pt-RDE in acidic solution of tin (II) sulfate, scanned from -0.8 V to -0.3 V, appear in Fig. 8. There is an oxidation peak at a potential between about -0.5 V and -0.38 V, this peak indicates the Sn(II)-Sn(IV) couple oxidation reaction. The couple oxidations of Sn-Sn(II) and of Sn(II)-Sn(IV) were actually superimposed on each other at potentials between about -0.5 V and -0.4 V. Therefore, in Figs. 3, 4 and 5, the area of peak (III) is larger than that of peak (I) and (II). As electroplated tin was oxidized to Sn(II) and promptly to Sn(IV), so in curve 2 (Fig. 7) the area of peak II exceeded that of peak I.

The effects of organic additives on cyclic voltammograms on Cu-RDE in acidic solution of tin(II) sulfate are shown in Figs. 9-11. According to Fig. 1, in the initial step, the electrode potential of deposition of tin on Cu-RDE was nearly the same, regardless of whether an additive was used. As evident in Figs. 10 and 11, the cyclic voltammograms of a solution containing up to 2 mL/L of acetophenone or 4-methyl 2-pentanone additives are similar to those of a solution without additive. Because of adsorption of acetophenone or 4-methyl 2-pentanone (slight) on the electrode surface, resulting in decreased deposition or dissolution of tin, the total peak area of the anodic reaction was smaller than for an additive-free solution. Figure 9 shows that when 2 mL/L (curve 3) of benzaldehyde was added to the acidic solution of tin(II) sulfate, the shape of the voltammograms differed from that of the corresponding solution without additives (curve 1). An explanation is that benzaldehyde can be oxidized to benzoic acid or reduced to benzyl alcohol in approximately the same potential range,⁶ thereby affecting the shape of the voltammograms; at a smaller concentration of benzaldehyde (1 mL/L), only the anodic oxidation peak was affected (curve 2). The limiting current decreased gradually when the system reached the region of control by mass transfer.

Diffusion Coefficient

The diffusion coefficient of Sn(II) in solution, with or without additives, was determined with an RDE system. According to Fig. 12, the limiting current of four types of solution was proportional to the square root of the speed of rotation and obeyed a linear relationship; the diffusion coefficient was then calculated from the slope of these lines according to Levich's equation.¹² The results appear in Table 2. It is known that when the solution contains more electrolyte or molecules, the active ions coordinate with these foreign electrolytes or molecules, or form a chemical interaction with them, thereby resulting in decreased rate of diffusion of active ions; accordingly, the diffusion coefficient of active ions decreases. Figure 1 shows that the overpotential of a solution containing benzaldehyde or acetophenone additive is greater than that of 4-methyl 2-pentanone, so benzaldehyde or acetophenone additives are more easily adsorbed on the electrode surface. The former additives remain in solution for shorter times than the latter, and the diffusion coefficient of Sn(II) is more strongly affected by 4-methyl 2-pentanone additive than by the other two. The results in Table 2 show that the diffusion coefficient of Sn(II) was the largest in acidic solution of tin(II) sulfate without additive, smaller for benzaldehyde and acetophenone and smallest for 4-methyl 2-pentanone, consistent with our predictions.

Summary

The effects of two aromatic carbonyl compounds, benzaldehyde and acetophenone, and an aliphatic ketone, 4-methyl 2-pentanone, on the kinetics of tin electrodeposition from an acidic solution of tin(II) sulfate were investigated. In the steady state, benzaldehyde and acetophenone additives had a greater overpotential on electrodeposition of tin in acidic solution of tin(II) sulfate than for 4-methyl 2-pentanone additives. Therefore, a carbonyl compound containing a phenyl group may act as a good grain refiner. Under some plating conditions, an aldehyde compound, such as benzaldehyde, can be oxidized to carboxylic acid or reduced to alcohol, so may be able to affect the deposition properties of tin or the limiting current of deposition of tin, but a ketone compound cannot be oxidized or reduced during deposition of tin; therefore, a ketone compound containing a phenyl group may be a better additive than an aldehyde.

According to cyclic voltammetry and Tafel plots studies, electro-deposition of tin in an acidic solution of tin(II) sulfate was a two-electron transfer reaction. In voltammograms, the oxidation couples, Sn-Sn(II) and Sn(II)-Sn(IV), were superimposed on each other in the potential range of approximately -0.5 V to -0.4 V. When a plating solution contains a more hydrophobic additive, such as benzaldehyde or acetophenone, the diffusion coefficient or limiting current is less influential than that of a more hydrophilic additive, such as 4-methyl 2-pentanone.

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About the Author

Giing-Shing Tzeng is an associate professor in the Dept. of Mathematics & Science Education, Hualien Teachers College, Hualien, Taiwan, R.O.C. His research activities include pulse plating of metals, alloys and related fields. He holds MS and PhD degrees from the National Tsing Hua University.