Effect of Organic Acids on the Electrochemical Migration of Tin in Thin Electrolyte Layer

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Abstract: Background and Objective: The effects of representative solder flux residue weak organic acids on electrochemical migration (ECM) of tin in thin electrolyte layer were studied using a technique based on the coupling of in situ electrochemical measurements and optical observations, as well as ex situ characterizations.

Methods and Results: The results showed that the increasing amount of weak organic acid decreased the probability of ECM and dendrites formed were mainly composed of metallic tin. Tin ions reacted with organic compound ions from hydrolysis of weak organic acids to form complexes with electronegativity, which retarded the transfer of tin ions. Some complexes can be oxidized to the insoluble tin oxides on the anode surface and blocked the dissolution of anode during tin ECM.

Conclusion: The growth rate of tin dendrite was found to be limited by the dissociation of complexes. Mechanisms involved were proposed to explain the role of weak organic acid in the tin ECM.

Keywords: Tin, SEM, XPS, acid corrosion, organic acids, thin electrolyte layer.

1. INTRODUCTION

Innovations in electronic technology have resulted in the miniaturization and integration of high-density electronic circuits and components [1]. The reliability of electronic materials has become more sensitive to harsh environmental conditions and presence of ionic contamination. Failure of electrochemical migration (ECM), which is a form of corrosion influenced by bias voltage [2], occurs when two oppositely biased and closely spaced electrodes are connected by an aqueous electrolyte. This characteristic may result in the growth of metallic dendrites between the conducting parts to form short circuits [3]. ECM has been one of the major failure mechanisms in electronic packaging [4-6]. It is a fundamentally ionic process and requires electrical potential, continuous moisture layer and time [7, 8].

Using no-clean flux systems for soldering during printed circuit board assembling is a major source of ionic contamination on the printed circuit board assembly surface. The flux is used to act as a wetting agent and surface activator during the soldering process [9]. The commonly used no-clean flux systems typically contain the following constituents: solvent, a medium for mixing all the components of the flux, often a mix of organic alcohols; activators, mainly organic acids, or halogenides; and vehicle, a non-volatile compound, such as a resin or ester [10]. Conseil et al. [9] determined the absence of significant decomposition of fluxes and acids within the temperature regime of soldering using differential scanning calorimetry and thermogravimetric analysis. The potential acceleration of corrosion caused by flux residues creates reliability issues in electronic assemblies, especially under humid condition [11, 12]. The most aggressive corrosive component in the flux is the ionic activator, namely, the organic acids. The organic acids typically used in soldering fluxes are known to be hygroscopic. Thus, the residues can absorb moisture from the surroundings at lower humidity levels typical for moisture condensation on clean printed circuit boards [13].

The effect of organic acid on the ECM of pure tin and tin-based alloys has been widely investigated because of the significance of tin in electronic devices as conducting or electronic packaging material. Verdingovas et al. [14] illustrated that the probability of tin migration abruptly decreased with increasing concentration of adipic acid, and this reduction resulted from a pH change in the condensed electrolyte phase. Minzari et al. [2] found that increasing the amount of oxalic acid decreased the probability of tin migration because of the buffering effect of acid and the passivation effect of the organic compound. Organic poly-acids, with two
or more carboxylic groups, such as citrate and oxalate, have been used as a complexing agent in practical plating bath [15, 16]. We previously showed that the complexing ability of citrate ions significantly affects the ECM [17]. A similar observation has been reported, in which copper carbonate was reacted with a heated aqueous solution of oxalic acid, and the resultant compound was a chelated copper oxalate [18]. However, systematic investigations correlating the effect with the complexing ability of organic acid on the ECM behavior of tin have not been carefully conducted.

Thus, this work focuses on the elucidation of the effect of organic acid used in flux systems on the ECM of pure tin under thin electrolyte layer (TEL) condition. Two types of pure typical organic acids were chosen [19], namely, oxalic acid and glutaric acid, and the effect of varying concentrations of these organic acids on the probability of ECM was also evaluated.

2. EXPERIMENTAL

2.1. Materials and Setup for the TEL Test

Twin pure tin electrodes (>99.999 wt%, dimensions of 2 mm × 5 mm × 15 mm) were used. One electrode functioned as a working electrode as an anode, while the counter electrode served as a cathode. The electrodes were embedded in an epoxy resin cylinder with a gap size of 0.5 mm in parallel direction, and the exposed working area is 0.1 cm² (Figs. 1a and 1b). A copper wire was welded to the back of each electrode to ensure electric connection. All test surfaces were ground with 1200 grit silicon carbide papers. The surfaces were then rinsed with deionized water, degreased with acetone, and dried in cool air.

The oxalic acid and glutaric acid solutions were prepared with deionized water (18.2 MΩ cm in resistivity) and analytical grade reagents. The conductivity of each solution was tested by a JENCO Model 3173 conductivity tester. The pH of the solution was monitored by a ST2100/3Cpro pH meter (OHaus Corporation, America). Current flowing through the two electrodes was recorded simultaneously as a function of time after a constant bias voltage was applied between the two tin electrodes. After the ECM tests, typical morphologies of the electrode surface were recorded in situ by employing a VHX-1000E digital 3D microscope (Keyence, Japan). The experimental setup was based on our previous work with slight modification (Fig. 1a) [20]. Before ECM test, the conductivity and pH of electrolyte were measured the electrolyte was then added to the surface of the electrode to form a thin electrolyte layer. The thickness of the thin electrolyte layer was measured using a set-up consisting of a sharp Pt needle with a z-stage equipped with a micrometer. The TEL test was performed using the method described in our previous work [21-23]. All ECM measurements were repeated at least thrice to check the reproducibility.

2.2. Ex Situ Characterizations of Products after ECM Tests

After the ECM tests, the samples were dried under nitrogen gas at room temperature. Surface morphologies of dendrites generated after ECM tests were examined ex-situ with a Phillips Quanta 200 scanning electron microscope (SEM) coupled with an energy dispersive spectrometer (EDS). The precipitates on the unspattered surface of anode were analyzed using X-ray photoelectron spectroscopy (XPS) of the VG Multilab 2000 system. The base pressure in the experimental chamber was in the range of 10⁻⁷ Pa. The spectra were recorded using Al Kα (1486.6 eV) radiation and the overall energy resolution was approximately 0.45 eV. The surface charging effect during measurements was compensated by referencing the binding energy (BE) to the C1s curve of residual carbon at 284.6 eV. The spectra were decomposed by background subtraction using a least-square fitting program.

Fig. (1). (a) Schematic of electrochemical migration (ECM) under thin electrolyte layer (TEL): (1) 3D microscope, (2) TEL, (3) electrode, (4) horizontal stage, (5) thermal humidity chamber, and (6) electrochemical workstation; (b) Planform of the electrode.

3. RESULTS


Current density transients were measured between the two electrodes when a bias voltage was applied between the electrodes. The results showed that an abrupt increase in current density, which was due to the short circuit when dendrites joined the two electrodes [24]. Time to failure is the
time required for the dendrite to connect the cathode and the anode. The ECM susceptibility of tin unexpectedly decreased with an increase in organic acid concentration (Figs. 2 and 3). For example, the sudden current spike did not occur during the 10 h test under TEL containing 11.12 mmol.L\(^{-1}\) (about 1000 mg.L\(^{-1}\)) oxalic acid (Fig. 2e), but it appeared at 143 s under deionized water TEL (Fig. 2a). As shown in Fig. (3b), a similar phenomenon was observed when the concentration of glutaric acid increased to 1.89 mmol.L\(^{-1}\) (about 250 mg.L\(^{-1}\)). Meanwhile, the i-t curve without current spike clearly displayed two distinct stages during ECM. Fig. (2e) shows that, under TEL containing 11.12 mmol.L\(^{-1}\) oxalic acid, the current density decreased rapidly by 88 \%, from 2.3x10\(^{-4}\) A/cm\(^2\) to 2.8x10\(^{-5}\) A/cm\(^2\) within 500 s in the first stage. In the second stage, the current density remained at a low and steady level for the rest of the ECM.

3.2. Optical Observations After ECM Tests at Varying Organic Acid Concentrations

Figs. (4 and 5) show the optical images of the surface morphologies after ECM tests under 200-μm TELs containing varying concentrations of different organic acids. Tree-like or needle-like dendrites accompanied by white precipitates could be observed under deionized water TEL (Fig. 4a). At low organic acid concentrations, dendrites maintained the tree-like structure, and white precipitates were also observed. At high organic acid concentrations, the length of dendrite decreased sharply, while the number of dendrites increased (Figs. 4d, 4e, and 5b-5d). Moreover, the surface of the anode presented a dark brown color after ECM.

3.3. Real-time pH Distribution on the Electrode Surface During the ECM Tests

A universal pH indicator (pH 1-14) was added to the TEL to visualize the local pH development to understand the pH distribution on both electrodes during the ECM tests. Fig. 6 shows in situ images of the pH distribution as a function of time under deionized water TEL and organic acid TELs containing 11.12 mmol.L\(^{-1}\) oxalic acid and 7.56 mmol.L\(^{-1}\) (about 1000 mg.L\(^{-1}\)) glutaric acid at 3 V. Initially, the pH under TEL without organic acid ranged between pH 6 and pH 7 (yellow in color), while that of organic acid TELs were apparently near pH 3 (orange in color). Upon application of the bias voltage, the electrolyte under deionized water TEL on the cathode became alkaline (blue or purple in color), while the anode part became acidic (red or orange in color) after 10 s (Fig. 6a). The alkaline region then spread out to the anode edge after 30 s because of the increasing OH\(^-\) concentration with time and the convection effect by the evacuation of bubbles on the cathode surface. Under organic acid TELs, the pH of electrolyte on the cathode part changed to neutral (yellow in color) after 30 s (Figs. 6b and 6c). The localized acidification occurred with time on the anode in all cases.

3.4. Characterization of Dendrites and Precipitates after ECM Process

The microstructure and composition of the dendrites generated in the presence of various organic acids after ECM processes were obtained and characterized using SEM/EDS.
**Fig. (3).** Current density versus time curves for tin under 200-μm thick layers containing various concentrations of glutaric acid at 3 V: (a) 0.38 mmol.L⁻¹, (b) 1.89 mmol.L⁻¹, (c) 3.78 mmol.L⁻¹, (d) 7.56 mmol.L⁻¹.

**Fig. (4).** Optical graphs after ECM of Sn in 200-μm thick electrolyte layers containing various concentrations of oxalic acid at 3 V at different time intervals: (a) 0 mmol.L⁻¹, 145 s; (b) 0.56 mmol.L⁻¹, 232 s; (c) 2.77 mmol.L⁻¹, 116 s; (d) 5.55 mmol.L⁻¹, 10 h; (e) 11.12 mmol.L⁻¹, 10 h (anode is on the right and cathode is on the left).
Fig. (5). Optical graphs after ECM of Sn in 200-μm thick electrolyte layers containing various concentrations of glutaric acid at 3 V at different time intervals: (a) 0.38 mmol.L⁻¹, 191 s; (b) 1.89 mmol.L⁻¹, 10 h; (c) 3.78 mmol.L⁻¹, 10 h; (d) 7.56 mmol.L⁻¹ (anode is on the right and cathode is on the left).

Fig. (6). Visualization of localized pH distribution on both electrodes with a pH indicator in 200-μm thick electrolyte layers containing various concentrations of the different organic acids at 3 V within the same time intervals: (a) 0 mmol.L⁻¹ (Deionized water); (b) 11.12 mmol.L⁻¹ oxalic acid; (c) 7.56 mmol.L⁻¹ glutaric acid (anode is on the right and cathode is on the left).
Fig. (7). SEM images and EDS maps of dendrites formed at 3 V. Under deionized water TEL: (a) SEM image, (b) Sn map, and (c) C map; Under 0.56 mmol.L⁻¹ oxalic acid TEL: (d) SEM image, (e) Sn map, and (f) C map; and under 0.38 mmol.L⁻¹ glutaric acid: TEL (g) SEM image, (h) Sn map, and (i) C map.

Fig. (8). SEM images and EDS results of for dendrites formed at 3 V under the (a) 11.12 mmol.L⁻¹ oxalic acid TEL and (b) 7.56 mmol.L⁻¹ glutaric acid TEL.

Figs. (7 and 8) display the SEM images and the corresponding EDS results of dendrites formed after ECM tests under TELs containing various concentrations of the different organic acids at 3 V. At low organic acid concentrations, the dendrite maintained tree-like or needle-like structures (Figs. 7d and 7g). The branches of dendrite became rounded and coarser at high concentrations of organic acid (Fig. 8). According to the EDS analysis, dendrites formed in the presence of various concentrations of different organic acids mainly consisted of tin.
The evolution of the compositions of anodic products in relation to the distinct i-t stages was investigated (Fig. 2e). XPS measurement was performed on the unsputtered anode surface after ECM tests at 200 s and 3600 s in a 200-μm thick electrolyte layer containing 11.12 mmol.L\(^{-1}\) oxalic acid at 3 V. Fig. (9a) shows the full-range XPS survey spectra. Figures 9b, c, and d show the narrow X-ray photoelectron spectra of Sn\(3d_{5/2}\), O\(1s\), and C\(1s\), respectively. The corresponding elemental compositions calculated from the XPS results in Fig. (9a) are shown in Table 1. Previous studies [25-28] have shown that, at 200 s, the Sn\(3d_{5/2}\) region can be deconvoluted into three peaks located at 487.37, 486.45, and 484.35 eV, while the survey spectrum of Sn \(3d_{5/2}\) for 3600 s can be fitted with two contributions at BEs of 487.46 eV and 486.57 eV (Fig. 9). The 487.4±0.2 eV peak can be assigned to Sn(IV), 486.5±0.2 eV peak to Sn(II), and 484.35 eV may arise from Sn\(^0\). The high-resolution spectra of O\(1s\) in Fig. (9c) exhibit a wide and asymmetrical peak. After decompositions, O\(1s\) contained the states corresponding to –COO–Sn(II/IV) at 532.0±0.3 eV, HO–Sn(II/IV) at 531.2±0.2 eV, and O–Sn(II/IV) at 530.5±0.2 eV. The BE values of the resolved components of C\(1s\) in Fig. 9d were 283.6, 284.6, 285.4, and 288.34 eV for 200 s, while the C\(1s\) spectra were composed of four peaks centered at 283.77, 284.60, 285.38, and 288.51 eV for 3600 s. The peak near 288.4 eV can be assigned to the carboxylic or carboxylate group (–COO–), because the carbon atom in the –COO– group is located at 288.6±0.4 eV. The C\(1s\) curve at 284.60 eV could be attributed to the –C–, the C\(1s\) curve at 283.7±0.2 eV corresponds to the –C–H, and the peak centered at 285.4±0.2 eV can be assigned to –C–COO–.

For the tin and oxalic acid system, Sn\(^{2+}\), Sn\(^{4+}\), Sn(C\(_2\)O\(_4\))\(^{2-}\), SnO\(_2\), and SnC\(_2\)O\(_4\) were stable at low pH values, while HSnO\(_2\), SnO\(_3\)^{2-}, and SnO\(_2\) were thermodynamically stable species in the basic region [29]. Among these compounds, the insoluble stannic oxide and SnC\(_2\)O\(_4\) had whitish color [30]. However, in our case, the surface of the anode was covered with a dark film after ECM at high concentration levels for 10 h (Figs. 4 and 5), which was contrary to the white one expected for the stoichiometric SnO\(_2\) and/or SnC\(_2\)O\(_4\). This observation is consistent with the results obtained by Palacios-Padros [31], who found that as-formed anodic tin-oxide film presented a dark-brown color, because
its porous structures were amorphous or poorly crystalline. However, the exact nature of as-anodized porous tin-oxide layers remains uncertain. Long et al. [32] recently illustrated that the enhancement in the visible absorption for co-precipitated SnO2 nanoparticles may have resulted from Sn3+ doping. In this case, the dark products are supposed to be mainly composed of SnO2. Moreover, Table 1 shows that the atomic ratio of O and Sn decreased from 3.74 to 2.98 when the ECM time was increased from 200 s to 3600 s. This result indicates that the insoluble species states changed from SnC2O4 to SnO2 with time during ECM. Therefore, products generated on the surface of anode during ECM in the presence of oxalic acid mainly consisted of stannic oxide and stannic/stannous oxalate complexes. Moreover, according to the results reported by Mingliang Wang et al. [33], the morphology of the anodization product of tin in oxalic acid electrolyte at low applied voltages changed from micron-sized crystalline particles to the pyramidal microstructure during the anodization process.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>200</th>
<th>3600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Sn</td>
<td>O</td>
</tr>
<tr>
<td>At.%</td>
<td>7.37</td>
<td>27.55</td>
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### 4. DISCUSSION

#### 4.1. Possible Reactions Involved During the ECM of Tin Under Deionized Water TEL

Based on previous studies [34, 35], the possible anodic and cathodic reactions for tin under deionized water TEL with initial pH close to 7 under a bias of 3 V are as follows:

**Anode:**

\[
\begin{align*}
    Sn & \rightarrow Sn^{2+} + 2e^- \quad (1) \\
    Sn^{2+} & \rightarrow Sn^{4+} + 2e^- \quad (2) \\
    2H_2O & \rightarrow 4H^+ + O_2 + 4e^- \quad (3)
\end{align*}
\]

**Cathode:**

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (4)
\]

The dissolution of tin [Reaction (1)] and oxidation of water [Reaction (3)] should be the dominant anodic reactions, while the cathodic reaction is mainly the reduction of \( H_2O \) [Reaction (4)], in which large amount of \( OH^- \) will be produced during ECM. Most of \( Sn^{2+} \) will be further oxidized to \( Sn^{4+} \) [Reaction (2)]. Moreover, the pH distribution in Fig. (6) illustrates that the localized pH value at the anodic area was close to pH 3 during ECM process in all test conditions. This characteristic can be attributed to the hydrolysis of \( Sn^{4+} \) [Reaction (5)] and direct oxidation of tin to \( Sn(OH)_4^- \) as Reaction (6) [36], as follows:

\[
\begin{align*}
    Sn^{4+} + 4H_2O & = Sn(OH)_4^- + 4H^+ \quad (5) \\
    Sn + 4H_2O & = Sn(OH)_4^- + 4H^+ + 4e^- \quad (6)
\end{align*}
\]

\( Sn(OH)_4^- \) would be dissolved to form \( [Sn(OH)_3]^- \) under high \( OH^- \) concentration [Reaction (7)]. The following reactions are generally accepted in relation to tin dendrite growth:

\[
\begin{align*}
    Sn(OH)_4^- + 2OH^- & = Sn(OH)_6^{2-} \quad (7) \\
    Sn^{2+} + 2e^- & = Sn \quad (8) \\
    Sn^{4+} + 4e^- & = Sn \quad (9) \\
    [Sn(OH)_3]^2- + 4e^- & = Sn + 6OH^- \quad (10)
\end{align*}
\]

#### 4.2. Effect of Organic Acid on the Probability of ECM Migration

Figs. (4 and 5) show that the surface of anode became darker after ECM test under organic acid TELs. Similar variations during ECM under oxalic acid TEL and glutaric acid TEL could be observed, indicating that the two selected organic acids had similar effects on the ECM of tin. Organic acid would dissociate into hydronium ion and organic compound ions in water solution. Values for the primary and secondary dissociation constants \( (pK_a) \) of the two dicarboxylic acids used in this work are as follows (\( pK_a1 \) for \( H_2A = H^+ + HA \), and \( pK_a2 \) for \( H_2A = 2H^+ + A^{2-} \)): for oxalic acid, \( pK_a1 = 1.23 \), \( pK_a2 = 4.19 \); for glutaric acid, \( pK_a1 = 4.31 \), \( pK_a2 = 5.41 \) [37]. It is worth noting that the speciation of organic acid is dependent on the pH of the solution. For oxalic acid, oxalic acid exists mainly as \( H_2C_2O_4 \) below pH 1.2, whereas \( HC_2O_4^- \) is the most predominant species at pH 2.5-3.0. Above pH 4, \( C_2O_4^{2-} \) is the predominant species [38]. Under glutaric acid TEL, glutaric acid exists mainly as \( H_2C_4O_4 \) at pH below 4, with \( H_2C_4O_4^- \) dominating at pH 4-5 and \( H_4C_4O_4^{2-} \) is the predominant species at pH above 5.5 [37].

Under organic acid TEL, the main initial anodic reactions included the dissolution of tin [Reaction (1)] and oxidation of water [Reaction (3)]. Moreover, the XPS results show that stannic oxide and stannic/stannous oxalate complexes formed on the surface of the anode during ECM under oxalic acid TEL. Gouda et al. [39] showed that each \( Sn^{2+} \) ion could be chelated with two \( C_2O_4^{2-} \) ions to form a \( [Sn(C_2O_4)_2]^{2-} \) ion [Reaction (11)]. The formation of the \( [Sn(C_2O_4)_2]^{2-} \) and precipitation of \( SnC_2O_4 \) can ensure the establishment of an equilibrium concentration of \( [Sn(C_2O_4)_2]^{2-} \) ions [Reaction (12)]. \( Sn^{2+} \) ion may also be combined with \( C_2O_4^{2-} \) ion to directly form the insoluble \( SnC_2O_4 \) [Reaction (13)] [40]. Reaction (11) is a thermodynamically favored process than Reaction (13), because the chemical equilibrium constant for the formation of \( [Sn(C_2O_4)_2]^{2-} \) ion \( (K_{SnC_2O_4^{2-}}) = 8.91 \times 10^{11} \) [39] is approximately three orders higher than that of \( SnC_2O_4 \) \( (K_{SnC_2O_4} = 1 \times 10^8) \) [40]. Considering the above-mentioned pH-dependent species distribution for organic acid, reactions of tin with \( HC_2O_4^- \) or \( H_2C_2O_4 \) co-existed during ECM process as Reactions [14] and [15].
Under glutaric acid TEL [37], tin could form SnH$_6$C$_2$O$_4$ complex by reacting with H$_2$C$_2$O$_4$ at pH below 4 as the following reaction: $2\text{Sn} + 2\text{H}_2\text{C}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{SnH}_6\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$; for pH above 5.5, $\text{Sn}^{2+} + 2\text{H}_6\text{C}_5\text{O}_4^{2-} \leftrightarrow [\text{Sn(H}_6\text{C}_2\text{O}_4)]^{2-}$; whereas for pH 4-5.5, $2\text{Sn} + 2\text{H}_7\text{C}_5\text{O}_4^{-} + 2\text{H}^{+} + \text{O}_2 \rightarrow 2\text{SnH}_6\text{C}_2\text{O}_4 \downarrow + 2\text{H}_2\text{O}$.

Sn$^{2+} + 2\text{C}_2\text{O}_4^{2-} \leftrightarrow [\text{Sn(C}_2\text{O}_4)_2]^{2-}$ $K_{[\text{Sn(C}_2\text{O}_4)_2]} = 8.91 \times 10^{11}$ (11)

$[\text{Sn(C}_2\text{O}_4)_2]^{2-} \leftrightarrow \text{SnC}_2\text{O}_4 \downarrow + \text{C}_2\text{O}_4^{2-}$ $K_{\text{SnC}_2\text{O}_4} = 1.12 \times 10^{-4}$ (12)

$\text{Sn}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{SnC}_2\text{O}_4 \downarrow$ $K_{\text{SnC}_2\text{O}_4} = 1 \times 10^{8}$ (13)

$2\text{Sn} + 2\text{HC}_2\text{O}_4^{-} + 2\text{H}^{+} + \text{O}_2 \rightarrow 2\text{SnC}_2\text{O}_4 \downarrow + 2\text{H}_2\text{O}$ (14)

$2\text{Sn} + 2\text{H}_2\text{C}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{SnC}_2\text{O}_4 \downarrow + 2\text{H}_2\text{O}$ (15)

During ECM, the time before the short circuit was mainly an incubation time related to the time needed by the ions to be transported from the anode to the cathode and growth of a dendrite [2]. The formation of complex anion [Reaction (11)] remarkably restricted the mobility of Sn$^{2+}$ from the anode to the cathode in the electric field. The decrease in Sn$^{2+}$ mobility indicates that the ions had a lower probability to reach the cathode. Bradley et al. [41] indicated that, by assuming migration control during incubation, the incubation time is proportional to the inverse of cation mobility in spatially coupled bipolar electrodes. Thus, the formation of complex anion did not favor the tin dendrite growth. However, the XPS results show that the stable species changed from tin oxalates to the insoluble SnO$_2$ on the surface of the anode during ECM. This result corresponds well with the results obtained by Tsai et al. [29]. The insoluble SnO$_2$ and SnC$_2$O$_4$ could precipitate on the surface of the anode as a barrier layer and thus block dissolution of the anode during ECM, which reduces the probability of ECM.

Under organic acid TEL, the dominant cathodic reaction is the reduction of H$_2$O [Reaction (4)] before the dendrite growth, which is evidenced by the change of pH on the cathode (Fig. 6). The dendrite grew in the presence of varying concentrations of the different organic acids (Figs. 7 and 8). The dendrites maintained tree-like structure at low organic acid concentrations. With high organic acid concentration, the dendrite length decreased while the tip and branches of the dendrite became thicker and shorter simultaneously. This result indicated that the presence of organic acid affected the electrodeposition behavior of tin ion during ECM. Kazmierczak et al. [42] investigated the deposition of manganese with tin electrodeposition from aqueous citrate electrolytes. The rate of tin (II) reduction process [Reaction (8)] was limited by the dissociation of dominant tin (II) citrate complex. Organic polyacids have been used as complexing agents in the practical plating bath, and the main purpose of formation of the complex is to slow down the kinetics of the electrodeposition reaction [43]. XPS results show the existence of tin oxalate complexes under oxalic acid TEL during ECM test. The rate of dendrite growth is supposed to be limited by the dissociation of tin oxalate complexes [Reaction (11)]. Hence, by controlling the kinetic factors including tin ion mobility and redox rates, the presence of organic acid largely affected dendrite growth and reduced the probability of tin ECM.

### 4.3. Effect of Alteration of the System pH Caused by Organic Acid Hydrolysis on the Probability of ECM of Tin

The presence of varying concentrations of organic acids could simultaneously act as acidic buffer and drastically influence the conductivity of electrolyte (Fig. 10). The electrolyte conductivity increased dramatically, while the pH shifted toward acidic values with increase in organic acid concentration. For example, compared with that of deionized water, the conductivity of the electrolyte containing 5 mmol.L$^{-1}$ oxalic acid increased from 0.05 μS/cm to 177.1 μS/cm, and pH value decreased from 6.2 to 2.5.

![Fig. (10). pH and conductivity of electrolyte under TELs containing varied concentrations of the different organic acids.](image)

![Fig. (11). Mean time to failure for tin under 200-μm thick deionized water TELs with different initial pH values at 3V.](image)
Experiments were conducted under deionized water TELs with different initial pH values (adjusted by HNO₃) to elucidate the effect of initial pH on ECM behavior. Fig. (11) displays the mean time to failure as a function of the initial pH value. The mean failure time decreased with the initial pH value, indicating that a lowered pH condition was apparently favorable for dendrite formation. Warren et al. [44] found a similar phenomenon in the ECM of copper in bulk solution. This phenomenon was attributed to an increase in the concentration of dissolved copper resulting from corrosion with decreasing pH. However, the ECM is a complex process in which the formation of dendrite requires a balance of various factors [2]. The increased dissolution of tin does not necessarily result in increased migration probability, despite the presence of more tin ions. Under organic acid TEL, the increased tin dissolution was also correlated with the formation of precipitates and tin oxalate complexes without dendrites, which is in good agreement with our observation (Figs. 4 and 5).

4.4. Effect of Organic Acid Concentration on the ECM of Tin

Figs. (2 and 3) show that the initial current density increased with the concentration of organic acid. This result could be attributed to the increment of ionic conductivity (Fig. 10). Moreover, at low organic acid concentration, tree-like structure dendrites accompanied the white precipitates (Fig. 7). The growth of dendrites is mainly attributed to the direct reduction of Sn⁴⁺ or Sn²⁺. The increased organic acid concentration accelerated the dissolution of tin anode, which consequently formed thicker dendrites containing more metal (Fig. 8). Additionally, the high ionic conductivity of the electrolyte layer made the electric field distribution more uniform at the cathode-promoting uniform deposition [14]. This result was shown by the increase in the number of tin dendrite at high organic acid concentration levels (Figs. 4 and 5). Meanwhile, the surface of anode became darker with the increase in organic acid concentration. This phenomenon can be ascribed to the fact that the excess organic ions from the hydrolysis of organic acid reacted with more free tin ions to form tin oxalate complexes and then oxidized to the dark tin oxide.

CONCLUSION

The flux residues of organic acid, in a certain concentration range, decreased the probability of tin ECM in a TEL. Formation of chelate complexes significantly affected the ECM.

(1) The XPS results show that tin oxalate complexes were formed during the tin ECM under oxalic acid TEL. Formation of [Sn(C₂O₄)₂]⁻⁻ ions affected the dendrite growth by controlling the kinetic factors including the mobility of tin ions and redox rate of tin ions. The insoluble Sn₂C₂O₄ and SnO₂ could precipitate on the anode and block anode dissolution.

(2) Increasing organic acid concentration evidently affected the ECM of tin. Tree-like dendrites co-existed with white precipitates at low organic acid concentration levels. Dendrite growth was attributed to the direct reduction of Sn⁺⁺ or Sn³⁺. With the increase in organic acid concentration, the rate of tin dendrite growth was limited by the dissociation of chelate complexes. The number of tin dendrite increased, while the branches and tips of dendrite became coarser.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

FUNDING

The authors thank the National Natural Science Foundation of China (Nos. 51571098) for their financial support.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS

Declared none.

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