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In-situ study of electrochemical migration of tin in the presence of bromide ion

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Abstract

The miniaturization of electronic devices and the consequent decrease in the distance between conductive lines have increased the risk of short circuit failure due to electrochemical migration (ECM). The presence of ionic contaminants in the devices can accelerate the ECM process. This work systematically investigates the ECM of tin (Sn) in the presence of bromide ions (Br^-) in the range of 10^{-6} M to 1.0 M. Water drop test (WDT) was conducted in the two-probe semiconductor characterization system under an optical microscope for in-situ observations. Anodic polarization test (APT) was carried out to study the correlation between corrosion properties of Sn and its ECM behaviour. The products of ECM were characterized by scanning electron microscope coupled with an energy dispersive X-rays spectrometer (SEM/ EDX) and X-ray photoelectron spectrometer (XPS). The results confirm that the rate of anodic dissolution of Sn monotonously increases with Br^- concentration. However, the probability of ECM failure follows a normal distribution initially, but later increases with the Br^- concentration. The main products of the ECM reactions are identified as Sn dendrites and tin hydroxide precipitates. The mechanism of the ECM process of Sn in the presence of Br^- is also suggested.

Introduction

The increasing demand for miniaturized electronic devices has led to the development of higher density electronic packages with smaller components. Increased number of leads and closer spacing between them made electronic devices more vulnerable to corrosion related damage^{1,2}. During manufacturing and in service, the devices may be exposed to humid environment which can lead to the formation of a corrosion cell. The reduced distance between the conduction lines due to a smaller pitch can accelerate the corrosion process. Consequently, the life span of devices is reduced, sometimes experiencing failure catastrophically.

One of the corrosion related problems encountered in electronic devices is the electrochemical migration (ECM)³⁻⁷. ECM is an electrochemical reaction which occurs in the presence of an electrolyte and under an applied potential difference. The electrolyte results from the adsorption or condensation of moisture which connects the two conduction lines in the presence of contaminants. Under the influence of a bias voltage, the conduction lines turn into two oppositely charged electrodes. The conductive metal anode dissolves due to corrosion and forms metal ions as a result of corrosion. This is then followed by migration of metal ions from anode to cathode. Subsequently, the dissolved metal ions are electrodeposited at the cathode as dendrites. The dendrites propagate through the electrolyte and connect the two electrodes. This eventually leads to short-circuiting, which is a catastrophic failure in electronic devices^{7,8}.

ECM can be categorized into humid ECM and condensed ECM^{1,9}. Humid ECM occurs when a thin invisible moisture film is adsorbed on the surface. Condensed ECM occurs in a visible layer of condensed water. The risk of condensed ECM increases as an electronic device is often exposed to temperature fluctuation due to the difference between the device interior conditions and external climates¹⁰. The presence of contaminants, especially those with

hygroscopic nature, facilitates water condensation on surface and increases the electrolyte conductivity. These contaminants accelerate the corrosion process and is expected to promote ECM. Ionic contaminants can arise from service environment, human handling or from the manufacturing processes^{1,11} such as the assembling process¹². The most commonly found ionic contaminants in electronic devices are the halides and sulphates (SO_4^{2-})^{7,12}.

Studies in the past^{1,5} reported that higher chloride (Cl^-) concentration results in a higher anodic dissolution rate of tin (Sn) from 10 ppm – 1,000 ppm. However, the probability of dendrite formation due to ECM did not increase with Cl^- concentration^{1,5}. This is attributed to the generation of excessive tin hydroxides precipitate which hinders the migration of charged ions at higher concentrations¹³. However, a later study found that a further increase in Cl^- concentration beyond 0.07 M (~ 4,091 ppm) leads to the re-dissolution of the precipitate and the subsequent dendritic deposition at the Sn cathode¹⁴.

Medgyes et al.¹⁵ varied the concentration of SO_4^{2-} from zero to saturated concentration (~1.86 M) to study their effects on the ECM of pure Sn. The ECM lifetime was the shortest in low concentration of SO_4^{2-} (0.1 mM) instead of the highest concentration. Similar to the results reported in Cl^- ^{1,5,13}, only precipitate was formed instead of dendritic growth in the SO_4^{2-} intermediate concentration (10 mM)¹⁵. Based on the previous studies^{1,5,11,13-17}, it appears that the increase in ionic contaminants concentration does not necessarily lead to the increase in ECM failure, even though the corrosion of anode is more favourable at higher concentrations.

The relationship between the corrosion properties and the ECM lifetime of Sn-based solders is elucidated in the literature¹⁸⁻²². Yoo et al.^{18,19} found that the corrosion rate (I_{corr}), corrosion potential (E_{corr}) and pitting potential (E_{pitt}) of Sn-based solders are affected by the addition of alloying elements such as lead (Pb) and bismuth (Bi). They reported that the time-to-failure (TTF) of the Sn-based solders increases with E_{corr} and E_{pitt} in 0.001 wt.% sodium

chloride (NaCl) and 0.001 wt.% sodium sulphate (Na₂SO₄). However, the TTF is poorly related to the I_{corr} of the solders^{18,19}. Jung et al.^{20,21} compared the TTF of Sn-based solders in 0.001 wt.% NaCl and in 0.001 wt.% Na₂SO₄. It was reported that the TTF is higher in 0.001 wt.% NaCl than in 0.001 wt.% Na₂SO₄ due to the higher E_{pitt} of Sn-based solders in 0.001 wt.% NaCl. Liao et al.²² discovered that by adding 1 mM – 500 mM tri-sodium citrate dehydrate into 1 mM NaCl, the growth of Sn dendrite is effectively inhibited because the E_{pitt} of pure Sn is increased. In general, the ECM of Sn-based solders in the presence of ionic contaminant is suppressed when the E_{pitt} is higher, and is not directly affected by the I_{corr} ¹⁸⁻²².

Bromide (Br^-) is another common ionic contaminant found trapped in electronic components²³. The presence of Br^- is due to the utilization of halides such as hydrogen bromide (HBr) and carbon tetrabromide (CBr₄) in the etching process during chip fabrication^{24,25} or the use of brominated flame retardants (BFR) in printed circuit board (PCB) laminates and in moulding compounds²⁶. Recently, there is a necessity to phase out the use of BFR due to its harmful effects on human and environment²⁷. However, the Restriction of Hazardous Substances Directive (RoHS) still allows the presence of certain types of BFRs such as polybrominated biphenyls (PBB) and tetra-bromobisphenol A (TBBA) up to 1,000 ppm, as effective flame retardants in electronic devices^{27,28}. The degradation of BFR remnants in electronics components subsequently releases the Br^- ²⁹.

To date, most of the investigations on the ECM of electronic devices are focused mainly on the effects of Cl^- and SO_4^{2-} . The information on the effects of Br^- on ECM process is still scarce. The only report available⁵ investigated the effects of Br^- concentration ranging from 10 ppm – 250 ppm (equivalent to $8.4 \cdot 10^{-5} \text{ M}$ – $2.1 \cdot 10^{-3} \text{ M}$) on ECM behaviour of pure Sn. The probability of ECM failure was reported to first increase then decrease with Br^- concentration. It was suggested that further increase in Br^- concentration beyond 250 ppm does not favour

dendritic growth as higher concentration leads to just precipitate formation without dendrite⁵. However, other work^{14,17} found that the precipitate can re-dissolve in extremely alkaline environment created in high concentration of halide contaminant. This consequently leads to the dendritic deposition at the Sn cathode.

Literature reveals that the effects of ionic contaminants concentration on ECM is complex. Higher concentration of contaminants may or may not favour dendritic growth, depending on the contaminants and mechanisms involved^{1,5,14,17}. Correlation between the ECM behaviour and anodic corrosion behaviour is also not straight forward^{5,18,19}. This work attempts to obtain a comprehensive understanding of the mechanism of ECM in an extended range of Br^- concentration (10^{-6} M – 1.0 M, which equivalent to 0.1 ppm – 102,894 ppm). Based on both in-situ video microscopy and ex-situ characterizations by scanning electron microscopy (SEM) coupled with energy dispersive X-rays spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS), ECM reaction mechanisms are proposed, and the roles of precipitate and electrolyte flow during ECM in the presence of sodium bromide (NaBr) are discussed. It is demonstrated that the ECM probability is linked to the synergistic effects of anodic dissolution rate, presence of precipitate and effects of convective liquid flow inside the water droplet.

Methods

Materials and setup for in-situ WDT.

Two identical chemically pure (C.P.) Sn sheets with dimensions of 0.4 mm × 10 mm × 15 mm were aligned parallel and embedded in an epoxy resin mould. A 0.5 mm-thick polytetrafluoroethylene (PTFE) sheet was used as the spacer between the two identical Sn sheets as shown in Fig. 1. The total exposed area of two pure Sn sheets was 8 mm². Copper wire was soldered at the back side of each Sn sheet. The exposed surfaces of the Sn sheets were ground to 3,000 grit, polished using the MD-Nap disk (Struers A/S) and lubricated by DiaPro

Suspension Nap R1 (1 μm ; Struers) to minimize the effects of surface roughness on ECM. Prior to the water drop tests (WDT), the Sn surfaces were rinsed in distilled water, degreased with isopropyl alcohol and dried in air.

Figure 1. (a) Schematic of the WDT setup. (b) Top view of test sample.

WDT was carried out using two-probe Semiconductor Characterization System (SCS) (Tektronix Keithley Model 4200-SCS). Sodium bromide (NaBr) solutions with concentrations of $1 \cdot 10^{-6}$ M to 1.0 M were used as the electrolytes. During the WDT, 5 μL of electrolyte droplet was placed on the exposed surfaces, covering both Sn sheets. A direct current (DC) with a bias voltage of 3 V was applied between the two Sn sheets, each of them acts as the anode and the cathode respectively. The current flow through the electrodes and electrolytes was measured and recorded as a function of time for 450 s. Simultaneously, the video of whole WDT process was recorded in-situ under an optical microscope (MPI TS150). The TTF was determined based on the presence of first current surge and the observation of dendritic bridge from the optical microscope.

Ex-situ characterizations.

The morphology of dendrites and precipitate that formed during the tests were characterized using SEM coupled with EDX (Carl Zeiss, model no: Auriga) at an accelerating voltage of 15

kV. XPS was performed on the precipitate using ULVAC-PHI Quantera II system. The source of X-ray was Al Ka (1,486.6 eV) and the base pressure in the chamber was in the range of 10^{-9} mbar. The energy resolution for wide scan and narrow scan were 1 eV/step and 0.1 eV/step, respectively. The spectral deconvolution was performed by the MultiPak software. In order to eliminate the surface charging effects, calibration of the binding energy (BE) was done by referring to the carbon spectrum of C-C at 284.8 eV.

Polarization test.

The anodic polarization tests (APT) were conducted using a potentiostat (Autolab, PGSTAT30, Netherlands). The counter electrode and reference electrode were platinum (Pt) wire and silver-silver chloride (Ag-AgCl), respectively. The working electrode was a pure Sn sheet with an exposed area of 0.32 cm². The polarization curves were measured in NaBr solutions with varying concentrations ranging from 10^{-6} M to 1.0 M. The polarization test was performed using linear scan voltammetry from -1.3 V to +1.3 V and at a scan rate of 1 mV/s. The results were analysed using general purpose electrochemical software (GPES).

Statistical Analyses.

In order to obtain the statistical averages of current flow and TTF, WDT was repeated for ten times under each experimental condition. The means and standard errors of current flow were calculated from ten replications. The ECM failure probability was calculated by dividing the total number of samples failed during the test by the total number of WDT (10) done under the same condition. The means and standard errors of TTF were then calculated based on the total number of samples failed during the test.

Results

In-situ ECM investigation during WDT.

Figure 2 shows a typical current-time curve and the corresponding microscopic images recorded in-situ during WDT, using $8 \cdot 10^{-4}$ M NaBr solution, at an applied bias voltage of 3 V. Figure 2b–g presents the occurring events as a function of time during the WDT. The initial condition of the test sample surface upon the application of a 3 V bias potential (t_1) is shown in Fig. 2b. A clean hemispherical water droplet is observed on the test sample that consists of two oppositely charged Sn electrodes. The presence of bright dotted rings on the surface of the water droplet is due to the reflected light from the microscope. At the early stages ($t_1 - t_2$) of ECM, a white precipitate formed in the NaBr electrolyte and gas bubbles evolved at the cathode as shown in Fig. 2c. The amount of white precipitate increased gradually, while the bubbles grew continuously in size. The latter coalesced and eventually disintegrated with time. Simultaneously, Sn corrosion was observed from the change of the anode appearance from a shining metallic surface to greyish surface. Dendrites that appear dark in Fig. 2d started to nucleate on the cathode at 198s (t_3) and propagated for 6s before bridging at 204s (t_4). When the dendritic bridging occurred between the oppositely charged electrodes at t_4 (Fig. 2e), the current surged from 10^{-3} mA to ~ 3 mA ($\sim 1,000$ times increment), confirming the short-circuiting between the two electrodes. The current dropped to 10^{-3} mA after 12 s, indicating the collapse of the dendritic bridge between the anode and the cathode. During the WDT, the flow of liquid was observed in the static droplet (see Supplementary Vid. S1 online). The liquid flow direction is shown in Supplementary Fig. S1. The dendrites could collapse due to the convective liquid flow of electrolyte from the opposite direction or the burning off effects caused by the high current¹. At 271 s (t_5), the second peak was observed in the current-time curve (Fig. 2a) along with the second dendritic bridging (Fig. 2f).

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 2. (a) Current vs. time curve obtained from the ECM test of Sn in $8 \cdot 10^{-4}$ M NaBr and applied bias of 3 V and the corresponding in-situ microscopic images at: (b) 0 s; (c) 76 s; (d) 198 s; (e) 204 s; (f) 271 s ; (g) 450 s (C: cathode; A: anode).

The dendrites collapsed but were reconnected for a few times before the end of the WDT (t_6). The time-to-failure (TTF) in this test was determined to be 204 s (t_4) based on the occurrence of the first short circuit, which was confirmed from the observation of the dendritic bridging and the sudden current spike^{30,31}. It is important to note that the gas bubbles and precipitate acted as mechanical obstructions to the growth of dendrite during WDT.

Figure 3 shows a typical current-time response depicting the current surges in varying Br^- concentrations. In general, the time of the first current surge decreases with the Br^- concentrations. However, the time of the first current surge at the highest Br^- concentration (1.0 M) was longer than the time recorded in lower concentrations ($2 \cdot 10^{-4}$ M – 0.5 M). This could be due to the strong effervescence and strong electrolyte convection of electrolytes which obstruct the dendritic propagation at the highest Br^- concentration. The current surged and dropped for a few times in most cases, suggesting that the dendrites collapsed and reconnected many times after the first bridging, indicating that more vigorous reactions occurred at higher concentrations.

Figure 3. Current vs. time curves for the ECM of Sn at various bromide concentrations and applied bias of 3 V. Red arrows pinpoint the time of the first current surge or the TTF.

Figure 4a–d show the corresponding microscopic images acquired at the end of each WDT (450 s) at different Br^- concentrations. The amount of gas bubbles and precipitate formation increases with the Br^- concentration.

Figure 4. In-situ microscopic images of Sn electrodes at the end (450 s) of the ECM process at 3 V applied bias, in various bromide concentrations: (a) 10^{-4} M; (b) $2 \cdot 10^{-4}$ M; (c) 0.5 M and (d) 1.0 M (C: cathode; A: anode).

Mean time-to-failure (MTTF) and probability of failure due to ECM.

The in-situ study on ECM of Sn shows variations in the results, with some clear short-circuiting events whilst others not, although the test parameters such as Br^- concentration and applied voltage were kept constant. The variations in the results revealed that the dendritic growth of Sn in the presence of Br^- is probabilistic in nature.

Table 1 summarizes the quantitative data obtained from ten repetitions of WDT in varying Br^- concentrations. In extremely low Br^- concentrations ($10^{-6} \text{ M} - 10^{-5} \text{ M}$), the probability of failure was zero, as none of the 10 samples tested under the same condition showed any current surge or short-circuiting during the WDT. The test samples started to fail when the Br^- concentration was increased to 10^{-4} M , where 1 out of 10 samples had failed. The highest probability of failing was found at the intermediate Br^- concentration ($2 \cdot 10^{-4} \text{ M}$), where 6 out of 10 samples experienced short-circuiting. A further increase in the Br^- concentration reduces the probability of the ECM failure. The samples did not short-circuit at the concentration range of $10^{-3} \text{ M} - 0.1 \text{ M}$. However, a still further increase in the concentration to 0.5 M and 1.0 M resulted in the ECM failure. Supplementary Figure S2 illustrates the trend of ECM probability in graphical form. In short, the probability of Sn failure due to the ECM initially increases but later decreases with the Br^- concentration, while a still further increase in the Br^- concentration enhances the risk of failure due to the ECM in the WDT.

Concentration of NaBr (M)	Probability of ECM failure	MTTF (s)
10^{-6}	0/10	∞
10^{-5}	0/10	∞
10^{-4}	1/10	350.00
2×10^{-4}	6/10	192.50 ± 49.08
5×10^{-4}	3/10	137.29 ± 28.68
8×10^{-4}	4/10	173.25 ± 21.61
10^{-3}	0/10	∞
10^{-2}	0/10	∞
0.1	0/10	∞
0.5	1/10	39.00
1.0	5/10	287.04 ± 71.66

Table 1. Probability of ECM failure and mean time-to-fail (MTTF) of Sn at various Br^- concentrations. Standard errors were calculated from the total number of failures during WDT.

The average TTF or mean time-to-fail (MTTF) of the short-circuited samples were calculated and tabulated in Table 1. A higher MTTF implies a longer lifetime of the samples, while ∞ indicates that short-circuiting did not occur at those concentrations throughout the WDT. The shortest and the longest MTTF recorded were 39 s (0.5 M) and 350 s (10^{-4} M), respectively.

Ex-situ characterizations of dendrites and precipitate.

Figure 5a–d presents the microstructures of the ECM products formed from the WDT in the presence of different Br^- concentrations. Figure 5a shows a clean sample surface at an extremely low Br^- concentration where no reaction products such as dendrites or precipitates could be observed. When the concentration of Br^- was increased to 10^{-4} M, two types of reaction products are formed: long tree-like dendrites and precipitate (Fig. 5b). The dendrites are seen to be arranged such that they connect the anode and the cathode. The dendrites with long branches are typically arranged at about right angle with respect to the main stem. The individual dendrites could grow as long as about 175 μm in length. The precipitate appears to be dense in nature. A further increase in the Br^- concentration to a higher level (10^{-3} M) results in the formation of massive precipitates (Fig. 5c). A higher magnification shows that the precipitate actually consists of many tiny dendrites (inset of Fig. 5c). These tiny dendrites found in the precipitate phase grew to a length of about 7 μm . At a very high Br^- concentration (0.5 M), the amount of precipitate increases further.

Figure 5. SEM images of the products formed at the area between two oppositely charged Sn electrodes, at an applied bias voltage of 3 V, in electrolytes with various bromide concentrations: (a) 10^{-6} M; (b) 10^{-4} M; (c) 10^{-3} M; (d) 0.5 M (C: cathode; A: anode).

The EDX analysis of the long dendrites formed in $2 \cdot 10^{-4}$ M NaBr (see Supplementary Fig. S3a online) reveals them to be Sn. The presence of fluorine (F) and carbon (C) peaks in the spectrum is attributed to the PTFE underneath the dendrite. It should be noted that PTFE was used as the separator between the Sn electrodes. The presence of oxygen (O) peak could be due to the contamination caused by the precipitate. The EDX analysis of the precipitate

formed in 0.5 M NaBr (see Supplementary Fig. S3b online) shows the presence of Sn (24.0 wt.%), O (18.1 wt.%), Na (9.8 wt.%) and Br (48.2 wt.%) elements.

XPS analysis was performed to investigate further the chemical nature of the precipitate. Figure 6 shows the XPS spectra of the precipitate formed in 0.5 M NaBr. The XPS wide-scan spectrum of the precipitate in Fig. 6a shows the presence of peaks belonging to C, O, Na, Br and Sn elements. The corresponding elemental composition obtained from the XPS results is shown in Table 2. The presence of C could be due to the contaminants from the experimental procedures. The presence of Sn, O, Na and Br suggests that the precipitate is a mixture of tin oxides and residue of NaBr salt.

Figure 6. (a) XPS wide-scan spectrum; (b) XPS high resolution spectrum of Sn3d_{5/2}; (c) O1s and (d) Br3d of precipitate formed during the ECM test of tin in the presence of 0.5 M NaBr at a bias voltage of 3 V.

Element	C1s	O1s	Na1s	Br3d	Sn3d
At%	39.01	25.77	15.48	8.56	11.19

Table 2. Elemental composition obtained from XPS of precipitate formed in 0.5 M NaBr and bias voltage of 3 V.

The high-resolution spectra of Sn3d_{5/2}, O1s and Br3d are shown in Fig. 6b–d. The oxidation states of Sn in the precipitate are verified in Fig. 5b,c. The Sn3d_{5/2} peak shown in Fig. 6b is composed of two Gaussian functions centred at about 485.35 eV and 486.05 eV, which corresponds to Sn²⁺ and Sn⁴⁺ respectively. The deconvolution of O1s curve shown in Fig. 6c shows three Gaussian functions centred at around 529.55 eV, 530.25 eV and 531.55 eV, which corresponds to O-Sn²⁺, O-Sn⁴⁺ and water (H₂O), respectively. Based on these results, stannic compounds (Sn⁴⁺) and stannous compounds (Sn²⁺) co-exist in the precipitate. The amount of Sn⁴⁺ was slightly higher compared to Sn²⁺. The resolved components of Br3d (Fig. 6d), centred around 69.55 eV and 68.25 eV, may arise from the SnBr₂ and residual NaBr respectively.

Anodic polarization curves.

Figure 7a shows the anodic polarization curves of pure Sn in solutions containing various concentrations of Br[−] ions (10^{−6} M – 1.0 M) recorded at the ambient temperature. The values of E_{corr} and I_{corr} were calculated from the Tafel plots obtained from Fig.7a. E_{pitt} was also obtained from Fig. 7a from the onset of breakdown potential of the passivation. Figure 7b shows the relationship between the concentration of Br[−] and the electrochemical parameters such as E_{corr}, E_{pitt} and I_{corr}. Generally, E_{corr} and E_{pitt} decrease while I_{corr} increases with the Br[−] concentration.

Figure 7. (a) Polarization curves of Sn in various bromide concentrations. (b) Comparison of the electrochemical properties of pure tin in various bromide solutions.

Discussion

It was found that pure Sn is susceptible to ECM in Br⁻ environment. Based on the in-situ investigation of WDT, the main reactions involved in the ECM of Sn include anodic dissolution of Sn, formation of white precipitate, evolution of gas bubbles at the cathode and growth of Sn dendrites at the cathode.

Based on the data obtained in this work and reaction mechanisms suggested in the literature^{5,7,17,31,32}, the possible reaction steps that occur during the ECM of Sn are suggested. Figure 8 illustrates the suggested reactions involved during the ECM of Sn. In the presence of Br^- , ECM of Sn begins with the dissolution of Sn anode to form Sn^{2+} ions as shown in (i), followed by further oxidization of Sn^{2+} to form Sn^{4+} as shown in (ii)^{5,7,17,32,33}.

Reactions at the anode:

Figure 8. Schematic of plan view of electrochemical cell formed during WDT at applied bias of 3 V, in NaBr concentration of (not drawn to scale).

The anodic dissolution is followed by the transport of ions^{5,7}. Positively charged Sn^{2+} and Sn^{4+} produced at the anode migrate and are transported through the electrolyte towards the negatively charged Sn cathode due to electrical field, concentration gradient and electrolyte convection⁷. The Na^+ released from NaBr is also attracted to the negative terminal. As Sn^{2+} or

Sn^{4+} reaches the cathode, the discharge of Sn ions and deposition of metallic tin dendrites occur as described in (iii) and (iv)^{5,7,14,17,32}.

Reactions at the cathode:

The reduction of dissolved O_2 (v) in the electrolyte and reduction of H_2O (vi) also occur at the cathode to release hydroxide ions (OH^-)^{5,7,33,34}.

Reaction (vi) is suggested as the main reaction as the concentration of dissolved oxygen (O_2) is relatively low as compared to that of H_2O in the electrolyte^{7,17}. The evolution of gas bubbles at the cathode is due to the release of hydrogen gas (H_2) as shown in (vi).

Precipitation is observed during the in-situ investigation of WDT. The XPS results in Fig. 6 reveal the co-existence of stannous and stannic compounds. This is attributed to the formation of stannous hydroxide [$\text{Sn}(\text{OH})_2$] and stannic hydroxide [$\text{Sn}(\text{OH})_4$] from (vii) and (viii)^{7,17}.

Based on the standard Pourbaix diagram of Sn, both $\text{Sn}(\text{OH})_2$ and $\text{Sn}(\text{OH})_4$ are stable compounds in neutral environment³⁴. Owing to the low solubility product constant (K_{sp}) of $\text{Sn}(\text{OH})_4$ ($1.0 \cdot 10^{-57}$ at 25 °C)^{7,35} and $\text{Sn}(\text{OH})_2$ ($5.45 \cdot 10^{-27}$ at 25 °C)³⁵, the white precipitates of

Sn(OH)_4 and Sn(OH)_2 form rapidly upon the application of a bias voltage. Sn(OH)_4 can also be formed from the direct oxidation of Sn anode or hydrolysis of Sn^{4+} as shown in reactions (ix) and (x), respectively^{5,7}.

In addition to hydroxides, XPS data also reveal the presence of NaBr and SnBr_2 (Fig. 5d) in the precipitate. The presence of NaBr is attributed to salt crystallization from the evaporation of water, as the samples were left to dry in the air before the ex-situ characterizations. Based on the thermodynamics data, SnBr_2 ($\Delta_f G_m^0 = -237.9 \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K)³⁶ and SnBr_4 ($\Delta_f G_m^0 = -359.5 \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K)³⁶ can form from (xi) and (xii), as the Sn^+ and Br^- migrate and encounter each other under the influence of an electric field.

The formation of SnBr_2 and SnBr_4 are as follows:

SnBr_4 , however, was not detected in the XPS spectrum (Fig. 6d) due to the insufficient database.

It should be noted that tiny dendrites ($\sim 7 \text{ }\mu\text{m}$ in length) are observed in the precipitate (Fig. 5c). These are in addition to the longer Sn dendrites ($\sim 175 \text{ }\mu\text{m}$) which are conductive in nature and are responsible for the short-circuiting failure. Observation of tiny dendrites was also reported in the ECM of Sn-2Pb in 10 ppm NaCl³⁰. By using transmission electron microscopy (TEM) and the electron diffraction patterns, it was confirmed that these tiny dendrites are tin hydroxides. Thus, it is also suggested that the small dendrites observed in this work are also tin hydroxides.

It is suggested that the mechanism of Sn dendritic growth changes at a very high Br⁻ concentration (0.5 M – 1.0M). It was reported that in highly alkaline condition, further reaction of Sn(OH)₄ with OH⁻ forms the complex ion [Sn(OH)₆]²⁻ as shown in (xiii)^{17,37}.

At high Br⁻ concentrations (≥ 0.5 M NaBr), excessive OH⁻ is produced from the cathodic reactions and thus creates a highly alkaline environment in the vicinity of the cathode. The [Sn(OH)₆]²⁻ complex ion is then reduced to form the Sn dendrites as shown in (xiv)^{5,7,17,37}.

This reaction is a widely accepted mechanism for the alkaline plating process used in industry³⁷.

The effect of Br⁻ concentration in the ECM of Sn was investigated in a wide range of concentrations (10⁻⁶ M – 1.0 M). The results showed that the rate of reactions, corrosion properties and probability to ECM failure of Sn are influenced by the Br⁻ concentration.

The effects of different NaBr concentration was investigated using the in-situ observation of WDT and APT. It is obvious that the ECM reactions including corrosion of anode, formation of precipitates and evolution of gas bubbles at the cathode, are more vigorous with increasing Br⁻ concentration. The average current in the first 10 s passing through water droplet electrolyte during WDT increases significantly with Br⁻ concentration (Fig. 9). This is linked with the increased amount of electrically charged species³⁸. Since NaBr solution is a strong electrolyte that dissociates completely in water to form Na⁺ and Br⁻, the conductivity of NaBr electrolyte increases with the number of ions dissolved in the solution with the NaBr concentration^{11,39}. Therefore, the reaction rate increases with the solution concentration, due to the increase in conductivity of the electrolyte.

Figure 9. Mean current measured during the first 10 s of WDT. Error bars indicate the standard errors of the means calculated from 10 replications.

The increase in the rate of reaction with Br⁻ concentration is also revealed in the APT. Figure 7b shows that the increase in Br⁻ concentration obviously increases I_{corr} and therefore accelerates the anodic dissolution step. Concurrently, E_{corr} and E_{pitt} show an opposite trend. E_{pitt} represents the breakdown of the passivation film on the Sn metal^{40,41}. The increase in Br⁻ concentration leads to the decrease in E_{pitt} , therefore facilitates the dissolution of the passivation film on the Sn surface. This indicates that pure Sn is more prone to corrosion in the environment that contains heavier Br⁻ contaminant.

Despite of the accelerated reactions at higher Br⁻ concentrations, the probability of short-circuiting due to the ECM dendritic growth does not increase monotonously with the Br⁻ concentration. The dendritic growth and consequently the short-circuiting events do not seem to depend only on the corrosion properties such as E_{corr} , E_{pitt} and I_{corr} . This rather depends on the synergistic interplay among different factors involved. Figure S2 illustrates the experimentally determined probability as a function of Br⁻ concentration. Overall, the probability of short-circuiting initially increases (10⁻⁶ M – 2·10⁻⁴ M) but later decreases (2·10⁻⁴ M – 0.1 M) with the Br⁻ concentration. The probability to short-circuiting increases again upon further increase in the Br⁻ concentration (≥ 0.5 M).

When the Br^- concentration is extremely low ($\leq 1 \cdot 10^{-5} \text{ M}$), the Sn dendritic growth is not initiated as the rate of reaction is extremely slow. The increase in the Br^- concentration results in an accelerated dissolution of the Sn anode, which in turn promotes the feasibility of ECM. The probability is thus increased at intermediate Br^- concentrations ($2 \cdot 10^{-4} \text{ M} - 8 \cdot 10^{-4} \text{ M}$). The highest probability was found at $2 \cdot 10^{-4} \text{ M}$. The precipitate formation is likewise accelerated with more metal ions and hydroxyl ions being generated at increased Br^- concentration. The formation of massive precipitate at higher concentrations ($10^{-3} \text{ M} - 0.1 \text{ M}$) increases electrolyte resistance between the electrodes and acts as barrier to the migration of charged ions¹⁷. Therefore, only accelerated corrosion without the formation of Sn dendrites is observed at higher concentrations ($10^{-3} \text{ M} - 0.1 \text{ M}$) under the optical microscope. A further increase in the Br^- concentrations to 1.0 M leads to the formation of a highly alkaline environment. This results in the re-dissolution of the stannic hydroxide precipitates to form the $[\text{Sn}(\text{OH})_6]^{2-}$ complex ion as shown in (xii). The complex ions then further reaction to form the Sn dendrites at the cathode.

Minzari et al.⁵ reported the probability of ECM of Sn to anodic reaction rate in a Br^- concentration range of 10 ppm – 250 ppm ($8.4 \cdot 10^{-5} \text{ M} - 2 \cdot 10^{-4} \text{ M}$). The probability of Sn dendritic growth was found distributing normally around a bell curve as a function of the anodic dissolution rate. It was suggested that the highest probability of dendrite formation occurs at an optimum anodic dissolution rate. The result obtained in this work at Br^- concentrations lower than 0.5 M agrees with the trend observed in previous work⁵. However, at 0.5 M , it was observed that the ECM failure probability increased again from zero to 0.1. This could be attributed to the re-dissolution of precipitates which ceases to act as barrier against Sn dendritic growth.

Zhong et al.¹⁴ investigated the effects of varying Cl^- concentrations ($10^{-4} \text{ M} - 0.5 \text{ M}$) on the ECM of Sn. They found that Sn dendrites grew in low and high concentrations ($\leq 0.005 \text{ M}$ and $\geq 0.07 \text{ M}$), while the dendritic growth was hindered at intermediate Cl^- concentrations ($0.01 \text{ M} - 0.03 \text{ M}$) because the precipitate acts as a spatial barrier that hinders migration of ions. The mechanisms of dendritic growth reported is related to the direct reduction of Sn ions at less than 0.005 M NaCl and the reduction of $[\text{Sn}(\text{OH})]^{2-}$ at concentrations higher than 0.07 M Cl^- . The similarities between the findings which involved Cl^- and this work which involve Br^- show that the ECM of Sn in the presence of halide contaminants in general shares the common mechanisms.

Literature¹⁸⁻²² suggested that the probability of the Sn dendritic growth is related to E_{pitt} and I_{corr} which in turn determines the corrosion of Sn. However, no such relationship is observed in this work, the reason of which is explained above.

The convection inside the water droplet affects the ECM of Sn significantly in the condensed ECM. During the WDT, the liquid flow is from the cathode to the anode at the centre of droplet but bounces back from the anode to the cathode at the droplet boundary (see Supplementary Fig. S1 online). The liquid flow is attributed to the natural convection and forced convection⁴². Natural convection arises from the concentration gradients of ionic species^{42,43}. Forced convection is commonly related to the evolution of hydrogen gas bubbles and its consequent collapse after coalescence^{7,42}. The convection could be also due to the evaporation of the electrolyte⁴⁴. The loss of water was observed from the reduction of droplet thickness after performing the WDT for 450 s (see Supplementary Fig. S4 online).

The fluid motion inside a water droplet is one of the mechanisms that aids ion transportation from the anode to the cathode and vice versa apart from the electrical field and concentration gradient^{7,45}. The convection process accelerates or decelerates the process of dendritic growth

during the ECM, depending on the direction of the liquid flow. Since the growth location of dendrites on the cathode occurs randomly, there is a large deviation in the MTTF (Table 1). The time of dendritic propagation is shortened if the dendrites grow at the location where the liquid flow is from the cathode to the anode but is lengthen when the dendritic growth is against the direction of the liquid flow. The turbulent flow of electrolytes could dislodge the bridged dendrites, causing the current to drop dramatically in the current versus time graphs obtained during the WDT. The convection inside the electrolyte droplet plays an important role in the condensed ECM, and therefore should not be neglected.

Conclusions

The effects of Br^- concentration ($1 \cdot 10^{-6}$ M to 1.0 M) on the ECM behaviour of Sn were investigated. Overall, the reactions during ECM such as corrosion of anode, formation of precipitates and evolution of gas bubbles are more vigorous at higher Br^- concentrations. The anodic polarization curves showed that I_{corr} of Sn increases, while E_{corr} and E_{pitt} of Sn decrease with Br^- concentration from 10^{-6} M to 1.0 M. However, the probability to ECM failure is not related to the electrochemical properties. The probability of ECM failure initially follows the trend of bell-curve, where short-circuiting occurred at intermediate Br^- concentration range (10^{-4} M – $8 \cdot 10^{-4}$ M). Lower Br^- concentrations ($\leq 10^{-5}$ M) do not initiate dendritic nucleation, while higher Br^- concentrations (10^{-3} M – 0.1 M) lead to the formation of excessive precipitates which hinder dendritic growth. The further increase in Br^- concentration (≥ 0.5 M) leads to the re-dissolution of precipitate to form the $[\text{Sn}(\text{OH})_6]^{2-}$ complex ions, followed by the reduction of the complex ions to form the dendrites. The presence of physical factors such as excessive precipitates, gas bubbles and fluid motion in the electrolyte outweigh the influence of the electrochemical properties in the ECM of Sn in presence of Br^- contaminant.

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Author contributions

E.L.L., A.S.M.A.H., W.J.B., Y.H.W., M.F.M.S. and B.Y.L. conceptualized and designed the experiments. E.L.L. conducted the experiments, performed data analyses and prepared the manuscript. A.S.M.A.H. and W.J.B. supervised the experiments. All authors reviewed and revised the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Video

Supplementary Figures

Figure legends

Figure 1. (a) Schematic of the WDT setup. (b) Top view of test sample.

Figure 2. (a) Current vs. time curve obtained from the ECM test of Sn in $8 \cdot 10^{-4}$ M NaBr and applied bias of 3 V and the corresponding in-situ microscopic images at: (b) 0 s; (c) 76 s; (d) 198 s; (e) 204 s; (f) 271 s ; (g) 450 s (C: cathode; A: anode).

Figure 3. Current vs. time curves for the ECM of Sn at various bromide concentrations and applied bias of 3 V. Red arrows pinpoint the time of the first current surge or the TTF.

Figure 4. In-situ microscopic images of Sn electrodes at the end (450 s) of the ECM process at 3 V applied bias, in various bromide concentrations: (a) 10^{-4} M; (b) $2 \cdot 10^{-4}$ M; (c) 0.5 M and (d) 1.0 M (C: cathode; A: anode).

Figure 5. SEM images of the products formed at the area between two oppositely charged Sn electrodes, at an applied bias voltage of 3 V, in electrolytes with various bromide concentrations: (a) 10^{-6} M; (b) 10^{-4} M; (c) 10^{-3} M; (d) 0.5 M (C: cathode; A: anode).

Figure 6. (a) XPS wide-scan spectrum; (b) XPS high resolution spectrum of $\text{Sn}3d_{5/2}$; (c) O1s and (d) Br3d of precipitate formed during the ECM test of tin in the presence of 0.5 M NaBr at a bias voltage of 3 V.

Figure 7. (a) Polarization curves of Sn in various bromide concentrations. (b) Comparison of the electrochemical properties of pure tin in various bromide solutions.

Figure 8. Schematic of plan view of electrochemical cell formed during WDT at applied bias of 3 V, in NaBr concentration of (not drawn to scale).

Figure 9. Mean current measured during the first 10 s of WDT. Error bars indicate the standard errors of the means calculated from 10 replications.

Table legends

Table 1. Probability of ECM failure and mean time-to-fail (MTTF) of Sn at various Br^- concentrations. Standard errors were calculated from the total number of failures during WDT.

Table 2. Elemental composition obtained from XPS of precipitate formed in 0.5 M NaBr and bias voltage of 3 V.

Figures

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(a)

(b)

(c)

(d)

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(b)

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