Report 2

Evaluating ionic migration in lead-free solder using the Quartz Crystal Microbalance Method

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The Quartz Crystal Microbalance Method (QCM) has been attracting widespread attention as a way to measure minute variations in mass. The QCM measurement method is able to detect trace amounts of weight changes in the magnitude of 10^{-9} *g/cm*^{2} *in both gas and liquid phases by utilizing the piezoelectric effect of a quartz crystal oscillator. QCM is also being applied to real time measurement of minute levels of corrosion.*

*Since ionic migration is one form of electrochemical corrosion, we have been applying QCM as a tool for analyzing the growth process of ionic migration in lead-free solder. Our results indicate that lead-free solder is superior to conventional lead solder in resisting migration. This migration resistance is a result of tin, the main element of lead-free solder, forming a stable passive film on the surface of the electrodes, and thus suppressing both metallic dissolution at the anode*1 (the elution electrode), as well as metallic deposition at the cathode*1.*

1. *Introduction*

The drive to miniaturize electronic devices has spawned the development of high-density mounting techniques for printed circuit boards (PCBs). The reduced tolerances of these systems have brought to the fore the problem of ionic migration (hereafter, “migration”), which affects insulation reliability.

Migration occurs when moisture adheres to the gap between electrodes and voltage is applied to the metallic electrodes. Metallic dissolution is generated at the anode, and these metallic ions migrate to the cathode and form metallic deposits. As this process is repeated, short circuits form. The corrosion mechanism of alloys such as solder in particular is quite complex, affected by a variety of factors such as the potential for forming surface film, the adhesive strength of that film, the anode dissolution characteristics, and the electrode potential.1) A method of measuring trace quantities of metallic dissolution and metallic deposition can be assumed to be an effective means of more clearly understanding this corrosion mechanism.

Conventional methods of evaluating migration have been confined to evaluating whether migration occurs. The evaluation is based on observing electrical characteristics such as changes in insulation resistance, which correspond to the precipitation distance attained by the deposits. However, this type of evaluation cannot provide quantitative measurements of changes in electrode weight, which strongly affects ionic migration.

The authors of this report used the Quartz Crystal Microbalance Method (QCM) to detect minute amounts of dissolution and deposition of electrode materials, and have developed new experimental equipment to measure the process of ionic migration in real time.2), 3)

Conventional lead solder also poses an environmental hazard. Items such as electronic equipment discarded from homes and factories are first demolished, and then only components such as the metals are collected for recycling. The major portion of the discarded electronic equipment is buried in landfills without further treatment. As a result, the lead used in the solder on the PCBs is dissolved by acid rain, contaminating the ground water. Because this process is thought to cause serious problems for human health, a drive to develop lead-free solder has ensued.4)

For these reasons, this research has focused on the QCM to study the process of ionic migration generation in various types of lead-free solder plating (Sn-3.5Ag, Sn-5Bi, Sn-9Zn, and Sn-0.8Cu).

In addition, we also investigated the anode dissolution characteristics of the elements in each type of solder alloy by measuring the current-potential curve in solution.

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2. *Experimental method*

2-1 QCM principles [5), 6)]

QCM utilizes the piezoelectric effect of a quartz crystal oscillator. This method is able to analyze trace amounts of mass by measuring minute changes in the resonance frequency occurring at the surface of the quartz crystal oscillator and correlating these frequency changes with changes in weight.

Fig. 1 shows the QCM electrode and measuring probe used in these experiments. When voltage is applied the quartz crystal oscillator produces resonance vibration, and this resonance frequency is measured. The resonance frequency fluctuates in response to matter dissolving from or adhering to the surface of the quartz crystal oscillator, and so these fluctuations can be calculated as fluctuations in mass. Sauerbrey's formula is applicable here to the minute fluctuations in mass (Δm) and the minute fluctuations in resonance frequency (Δf).

$$\Delta m/\Delta f = -(\mu\rho)^{1/2}/2f_s^2)$$

f_s: initial resonance frequency (Hz)
μ: Liquid crystal modulus of elasticity in torsion
2.95×10^{11} ($g \bullet cm^{-1} \bullet s^{-2}$)
ρ: Liquid crystal density 2.65 ($g \bullet cm^{-3}$)

A quartz crystal oscillator with a basic oscillation frequency of 5 MHz was used for these measurements, and so a 100 Hz change in oscillation frequency corresponds to an approximately 2.42 μg change in weight. As a result, this method is able to detect trace weight changes caused by the occurrence of migration.

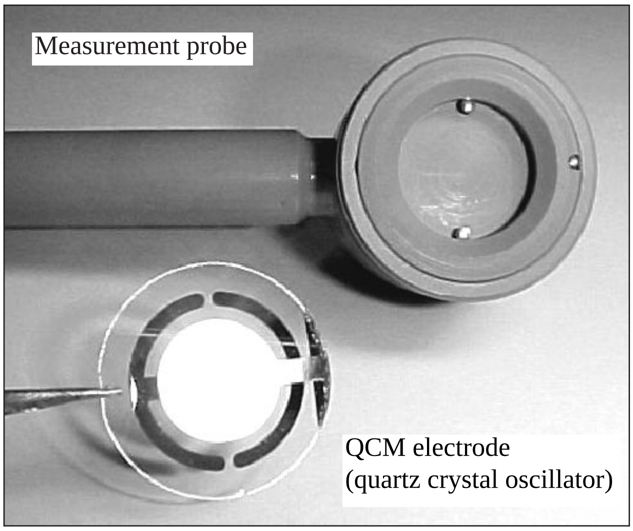


Fig. 1 QCM electrode system

2-2 The experimental method employing QCM

Table 1 shows the composition of the electrode materials and the lead-free solder used in these experiments. The working electrodes used were plated with each type of lead-free solder using an AT cut quartz crystal[*2] (MAXTEK, Inc.) with a resonance frequency of 5 MHz. Tin rods with a diameter of 3.0 mm were used to plate the counter electrodes with lead-free solder of the same composition as used on the QCM electrodes.

Table 1 Electrode materials and solder composition

Electrode	W.E.: AT cut quartz crystal C.E.: φ 3.0 mm Sn metallic rod
Solder composition (mass%)	Sn–3.5Ag Sn–9Zn Sn–5Bi Sn–0.8Cu Sn–37Pb (reference)
Solder plating thickness	W.E.: 2 μm C.E.: 14 μm

Fig. 2 shows the layout of the equipment used in the experiment, and Fig. 3 shows an expanded view of the measurement area of the electrode. The distance between electrodes was set by using a micrometer to separate the electrodes 0.3 mm from the point at which the QCM electrode was in contact with the counter electrode. One milliliter of de-ionized water was dripped onto the electrode gap, and a potentiostat (Hokuto Denko Corp., HA-301) was used to apply 1.5 volts of DC. At this time, changes were measured in the time variability of both the current and the QCM electrode resonance frequency, with either the cathode or the anode serving as the QCM electrode.

Measurements for the investigation into the effect of dissolved oxygen were made in a nitrogen atmosphere. To make the measurements, the entire electrode system was completely cut off from the atmosphere, and N_2 was flowed in from the upper section of an acrylic pipe and vented out from the lower section of the pipe. After the N_2 gas displacement was completed, the de-ionized water drip was begun, and the comparison experiments were carried out in the same way as in the normal atmosphere environment. After measurements were completed (1000 seconds after), the surface of the electrodes was observed with an SEM (Scanning Electron Microscope) and then analyzed with an EDX (Energy Dispersive X-ray micro analyzer).

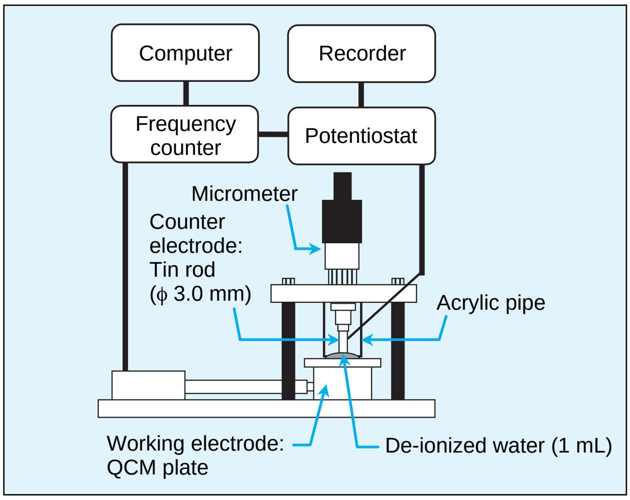


Fig. 2 Experiment equipment layout

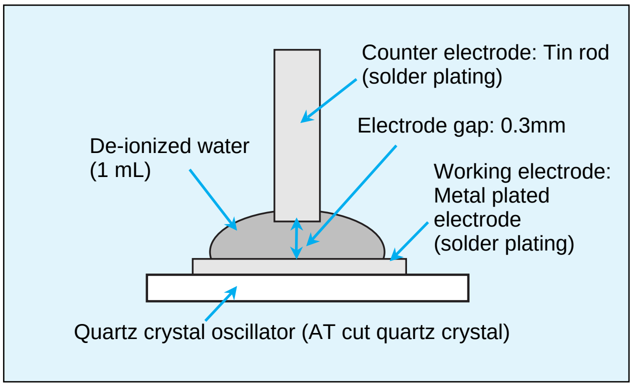


Fig. 3 Expanded view of the measurement area of the electrode

2-3 Anode dissolution measurements

The specimens for the experiment were made by cutting each type of molten lead-free solder material into 1 x 1 cm squares, and polishing the surface with water-resistant sandpaper. Next, masking was applied to the 0.6 cm round diameter (electrode surface area, 0.28 cm^2). Anode dissolution was measured using Pt-Ti net on the counter electrodes and saturated calomel electrodes as reference electrodes. After the dissolved oxygen was removed, KNO_3 solution (concentration, 0.1 M) was used as the electrolytic solution.

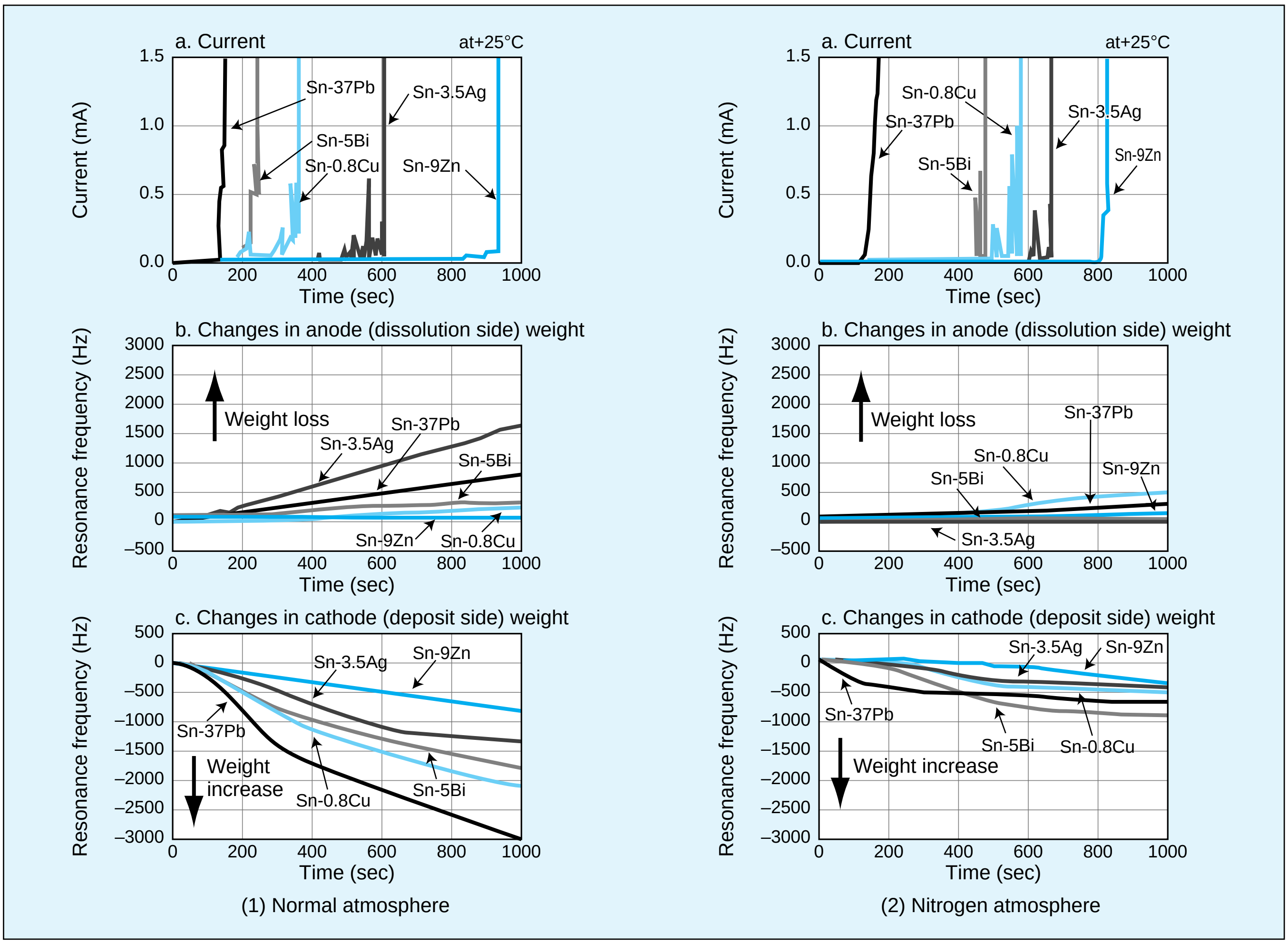
The measuring equipment used consisted of a function generator (Hokuto Denko Corp., HB-105) and a potentiostat (Hokuto Denko Corp., HA-503G). Measurement conditions included a scanning speed of potential at 10 mV/sec, and polarization up to –2000 mV vs. SCE from the natural potential in the direction of the base metal[*3], and a temperature of +25°C. Next, a sweep was made to +2000 mV vs. SCE in the direction of the noble metal[*3], and the current-potential curve was measured.

3. *Experiment results and discussion*

3-1 Experiment results using QCM

Fig. 4 shows the changes in current and in resonance frequency during the migration generation process of the lead-free solder in normal atmosphere and in nitrogen atmosphere. Sharp rises in current indicate short circuiting between the electrodes caused by growth of migration. Increases in resonance frequency indicate metal elution at the surface of the electrodes. Decreases in resonance frequency indicate metallic deposits or metallic oxide deposits on the surface of the electrodes.

By observing the changes in resonance frequency following the voltage application, we were able to grasp the conditions of the process of dissolution from the anode, and the deposition at the cathode. The growth of migration was subsequently accompanied by sharp rises in current leading to short circuiting.



(1) Normal atmosphere

(2) Nitrogen atmosphere

Fig. 4 Changes in current and in resonance frequency in the migration growth process

Considering the time to short circuiting after migration growth has begun provides the following order of tendency for migration growth. Sn-37Pb has the greatest tendency to form migration, followed by Sn-5Bi, then Sn-0.8Cu, with Sn-3.5Ag exhibiting the least tendency. However, Sn-9Zn did not experience short circuiting within the measurement time. All of the specimens (except Sn-9Zn) exhibited a tendency for the process to take longer in a nitrogen atmosphere.

The lead-free solder showed a tendency for migration growth to take comparatively longer than in Sn-37Pb, in which migration occurred more quickly.

Considered from changes in resonance frequency, both dissolution and deposition showed a tendency for increased quantity in a normal atmosphere (with dissolved oxygen) than in a nitrogen atmosphere. This is thought to be a result of migration occurrence being triggered by the reduction reaction of dissolved oxygen7), and the solder is thought to experience oxygen consumption corrosion.

Table 2 shows the standard electrode potential of each type of solder material.8) Fig. 5 shows Pourbaix potential-pH diagrams[*4] for lead and tin. The reason for lead-free solder having a smaller amount of anodic dissolution and cathodic deposition than Sn-37Pb in the presence of dissolved oxygen is that the formation of a passive film by these alloys suppresses the process of dissolution and deposition.

Table 2 Standard electrode potential of each type of solder material8)

	Material	Reaction	E° (V vs. SHE)
Base	Zinc	$Zn^{2+} + 2e^- = Zn$	–0.763
↑	Tin	$Sn^{2+} + 2e^- = Sn$	–0.138
	Lead	$Pb^{2+} + 2e^- = Pb$	–0.126
↕	Hydrogen	$2H^+ + 2e^- = H2$	0.000
	Bismuth	$Bi^{3+} + 3e^- = Bi$	+0.215
↓	Copper	$Cu^{2+} + 2e^- = Cu$	+0.337
Noble	Silver	$Ag^+ + e^- = Ag$	+0.799

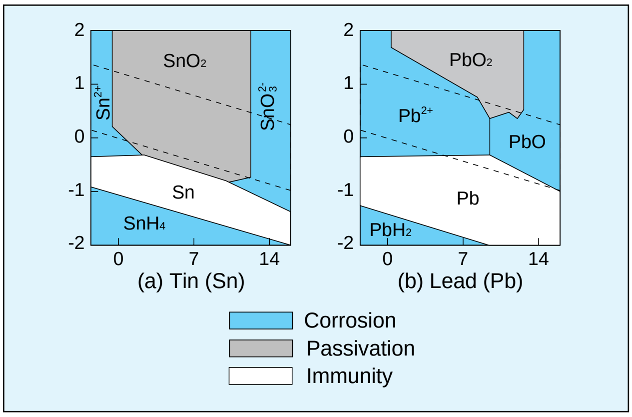


Fig. 5 Pourbaix potential-pH diagram for tin and lead 8)

3-2 Surface observation results

Fig. 6 shows SEM photos of cathode surfaces. In both normal and nitrogen atmospheres, the form of the Sn-37Pb deposits remained the same, with a number of dendrites occurring on the surface of the electrodes. Those deposits were composed of the element lead (Pb). The alloys Sn-3.5Ag, Sn-5Bi, and Sn-0.8Cu all exhibited linear migration growth. More so than in the normal atmosphere, migration growth in the nitrogen atmosphere was confirmed to occur perpendicular to the narrow rod-shaped electrode surface, and the element forming the deposits was tin (Sn).

While deposit growth was not seen on the surface of Sn-9Zn in the normal atmosphere, a number of small, fern-shaped deposits were observed in the nitrogen atmosphere. From those deposits, the element zinc (Zn) was detected in greater quantity than alloy elements directly behind the plating. With Sn-9Zn, the base metal element Zn forms an alloy with the element Sn, and the element Zn is thought to take priority in dissolving and forming oxides. In normal atmosphere, the element Zn combines with the element Sn to form oxides or a metallic salt film on the electrode surface. In the nitrogen atmosphere, however, Zn is thought to have less capacity to form this passive film, contributing to the process of Zn dissolving and forming deposits.

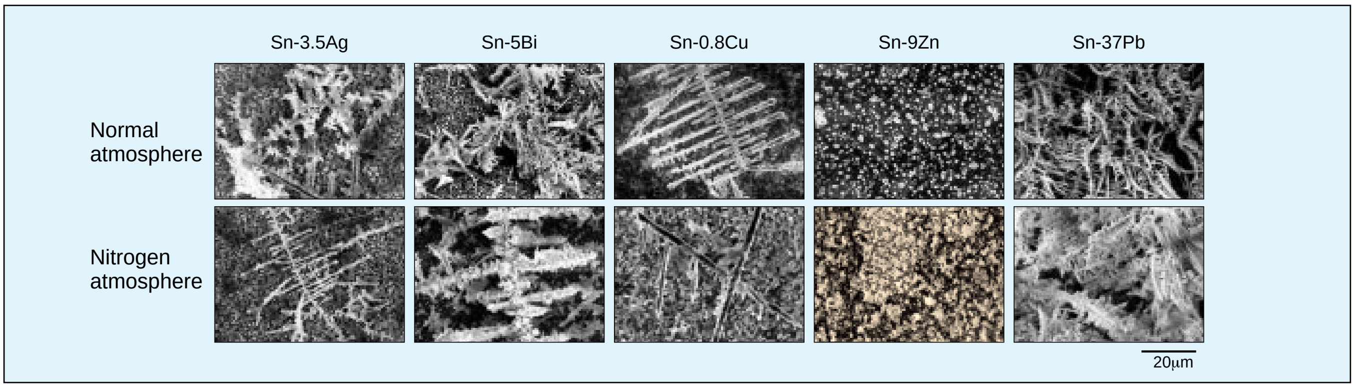


Fig. 6 SEM photos of migration growth (cathode electrode surface photographed at 1000 sec of experiment)

3-3 Anodic dissolution characteristics

Fig. 7 shows the current-potential curve of Sn-3.5Ag, Sn-0.8Cu, Sn-9Zn, Sn-37Pb, Sn (99.9% pure), and Zn (99.9% pure). Sharp rises in current density indicate metallic anodic dissolution.

The anodic dissolution potential for Sn-3.5Ag and Sn-0.8Cu was the same as for Sn, approximately -180 mV vs. SCE. This trend is due to the element Sn having priority in dissolving. Because of this, the secondary elements Ag and Cu in the lead-free solder specimens combined with Sn to form stable compounds, and so did not dissolve into solution. As a result, the selective dissolving of the element Sn is thought to affect the dissolution characteristics of this solder.11)

The Zn anodic dissolution potential was approximately –700 mV vs. SCE. However, the Sn-9Zn anodic dissolution potential was approximately –180 mV vs. SCE. Therefore, it is believed that the Zn in the Sn formed an alloy, which gave the condition of a noble metal to the dissolution potential, resulting in the Sn suppressing the dissolution reaction of the Zn.

The Sn-37Pb has an anodic dissolution potential of approximately –450 mV vs. SCE, which is more like a base metal than Sn. This is thought to result from the element Pb having priority in dissolving, giving Sn-37Pb a greater tendency to form a dissolution reaction than the other types of lead-free solder.

From the above observations related to migration growth, we can assume that binary compound solder alloys have the capacity to use dissolved oxygen to form an oxide film and stabilize. The dissolution characteristics of each element in the alloy in the anode can be assumed to affect short-circuit time as well as the form and composition of the deposits on the cathode.

4. Conclusion

In evaluating the resistance of migration of lead-free solder, we have employed QCM to analyze the migration process. Our main conclusions are as follows.

(1) The QCM method is clearly effective in analyzing the migration process. This is achieved in real time by analyzing the metallic dissolution quantity at the anode and the metallic deposition quantity at the cathode.

(2) The occurrence of solder migration is affected by dissolved oxygen in the moisture. Furthermore, in the presence of dissolved oxygen, lead-free solder tends not to exhibit migration growth leading to short circuiting as slowly as Sn-37Pb, and overall tends to exhibit less anodic dissolution as well as less cathodic deposition. These results are based on the stability achieved by lead-free solder forming a passive film.

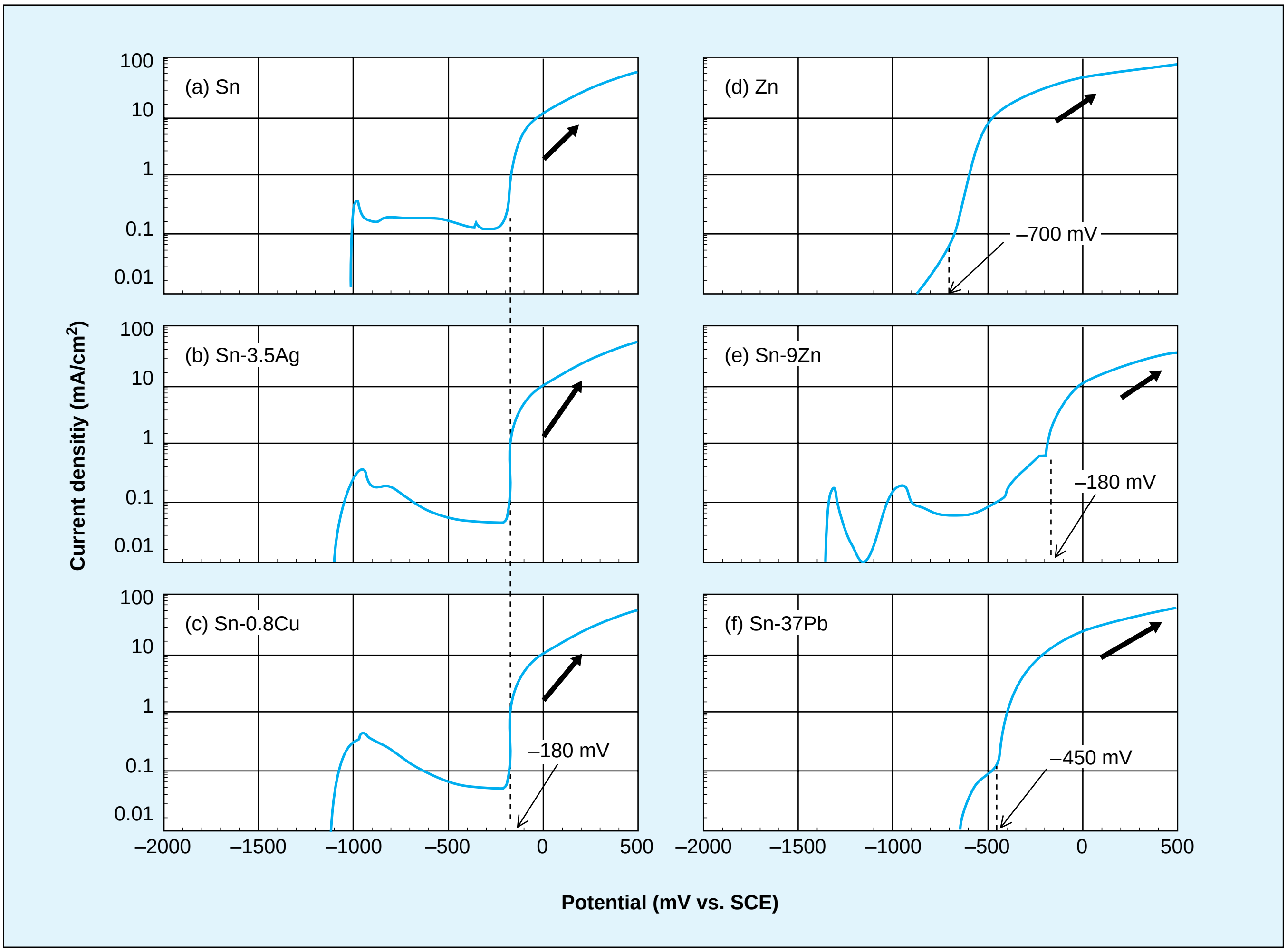


Fig. 7 Current-potential curves of solder in 0.1M KNO_3 solution

(3) The deposits formed on the cathode by Sn-37Pb consisted of the element Pb. The limited stability of the passive region of Pb is less than that of Sn, and so Pb is thought to have priority in dissolving and forming deposits. On the other hand, the deposits of lead-free solder on the cathode are mainly composed of Sn, since this alloy element selectively dissolves and forms oxides due to the difference in electrode potential. Therefore, lead-free solder, which has Sn as the main element, can be assumed to have formed a stable passive film of oxides of Sn on the surface of the electrodes, thus suppressing anodic dissolution.

(4) The above observations lead to the conclusion that factors in the occurrence of solder migration can be related to the stability of the passive region oxide film. Additionally, lead-free solder with Sn as the main element is believed to have a higher resistance to migration than lead solder due to the formation of a stable passive film.

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Terminology

***1. Anode and Cathode**: The anode and cathode were named by Michael Faraday, who selected them due to the Greek meaning of “the way up” for anode and “the way down” for cathode. In general, the anode is the electrode that has current flowing out toward the electrolytic solution, while the cathode is the electrode that has current flowing in from the electrolytic solution.

***2. AT cut quartz crystal**: This term expresses the cutting azimuth from the crystal axis of the quartz crystal oscillator. Other types of quartz cuts include BT cut, CT cut, DT cut, and so on. Among quartz crystal oscillators, the AT cut quartz crystal is the most widely used, and it has less frequency change in response to changes in temperature.

***3. Base metals and Noble metals**: These terms are used to describe standard electrode potential. Base metals are metals that tend to oxidize (i.e., have a tendency to ionization), and include metals such lithium, aluminum, and zinc, which are known as metals with low standard electrode potential. On the other hand, noble metals are metals that are strongly anti-corrosive (i.e., have less tendency to ionization) and have a high standard electrode potential. Gold and platinum are prime examples.

***4. Pourbaix potential-pH diagram**: Marcel Pourbaix of the Belgian Centre for Corrosion Study (CEBELCOR) originated this type of diagram showing the relationship between electrical potential and pH for elements that are at equilibrium with water. Metals and their environment are divided into a corrosion region, a passive region, and an immunity region, and the diagram serves as a guide to corrosiveness.

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