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## STUDY ON THE ELECTRO-REFINING OF TIN IN ACID SOLUTION FROM ELECTRONIC WASTE

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The tin metal could be retracted from wasted tin scrap, sludge, and wasted electroplated solution hydrometallurgical treatment, and purification process. In order to be used as resource of electronic devices, the retracted crude metal should be purified to the extent of higher than 99.9%. In this study, tin electro-refining process was performed to purify the casted tin crude metal at various experimental conditions: at the current density of 3, 5A/dm<sup>2</sup>, and in various electrolytes such as hydrochloric acid, sulfuric acid and methansulfonic acid. Additional experiment was conducted using Rotating Disk Electrode (RDE) in order to investigate the rate determining step of tin electro-refining process. The current efficiency, 65.6%, was achievable at the condition of current density, 5A/dm<sup>2</sup>, and in the electrolyte of Hydrochloric acid. During tin electro-refining process, impurity dissolved from tin crude metal into the electrolyte was analyzed using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), and the result showed the concentration of impurity metal gradually increased. Quantitative analysis on casted tin crude metal showed that it consists of tin with 93.9 wt.% and several impurity metals of Ag, Bi, Pb, Cu, and etc. After tin electro-refining process, the purity of tin increased up to 99.985 wt.%.

*Keywords:* Electro-refining, Tin, Electronic waste, Recycling, High purity

## 1. Introduction

The amount of waste electronic products is increasing, because it is due to the rapid advancement and development of IT technology and faster life cycles of small electronic devices. There rises a much attention on retrieving metal resource from wasted electronic devices which contain valuable metal such as tin, silver, copper, and etc [1]. Recovery of tin metal has been studied using various recycling methods. Generally, two processes are usually used to retract tin metal from wasted tin solder, dross, and scrap: pyrometallurgical treatment which fabricates an ingot by melting all scraps, hydrometallurgical treatment that consists of several steps of selective leaching process, solvent extraction process and precipitation process [2-4]. Pyrometallurgical treatment, compared to latter process, needs higher energy to keep high temperature and additional purification process due to requirement for high purity, higher than 99.9%. During electro-refining process, the dissolved tin from casted anode in electrolyte was deposited on the cathode at the applied current, but the impurities of the anode do not dissolve into electrolyte because of higher oxidation-reduction potential (Cu, Ag, Bi, Au and etc). It is generally known that the alkaline electrolyte solution is not widely used for electro-refining process in industry owing to its high temperature, high solubility of impurity, but the homogeneous and

dense deposited film could be achievable on the surface [5]. Meanwhile, the acid electrolyte solution for tin electro-refining process is widely used in industry with the advantages of low temperature process and low solubility of impurities but the sludge and slime occurred on surface of anode, which could lead to gradual decrease of current efficiency [6]. Organic additives in acid electrolyte are necessary to obtain smooth and dense tin films because tin of cathode was electrodeposited in the shape of needles, whiskers and dendrites [7, 8].

In this study, tin electro-refining process was performed to purify the tin crude metal at various experimental conditions: at the current density of 3, 5A/dm<sup>2</sup>, and in various electrolytes such as hydrochloric acid, sulfuric acid and methansulfonic acid. Additional experiment was conducted using Rotating Disk Electrode (RDE) in order to investigate the rate determining step of tin electro-refining process.

## 2. Experimental

The electro-refining of tin was operated that agitation of the solution was possible at the temperature of 298K by mechanical puddle system. The anode was cast after melting the waste solder, dross and scrap. The Titanium plate for cathode was grounded with #180, #320, #600, #800 and #1200

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grit SiC abrasive paper. The immersed surface of anode and cathode plate was 8 cm×8 cm, direct current was used and the applied current density was ranged from 3 to 5 A/dm<sup>2</sup>. The chemical reagents consisted of tin metal sources, aqueous acid electrolytes and additives: tin (II) chloride and tin (II) sulfate as metal sources, hydrochloric acid, sulfuric acid and methansulfonic acid as acid electrolyte,  $\beta$ -naphthol and gelatin as additives. The detailed chemical compositions of electrolytes are listed in Table 1. Applied potential was controlled using a DC power supply (YPP15100A, Yamamoto) or potentiostat (EG&G 273A, Princeton Applied Research). The impurities of electro-refined cathode were analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Integra XL, GBC Scientific). Rotating Disk Electrode (RDE) system was used to investigate the rate determining step of tin electro-refining process. Electro-refining of tin was carried out using RDE of 2 cm in diameter which was wrapped with Teflon, dimensionally stable anode (DSA) was used as an anode and a saturated calomel electrode as a reference electrode.

TABLE 1  
Concentration of chemical reagents in electro-refining electrolyte of tin

	Hydrochloric Acid	Sulfuric Acid	Methansulfonic Acid
Tin(II) Chloride	0.2 mol / L	-	-
Tin(II) Sulfate	-	0.1 mol / L	0.1 mol / L
Acid	2 mol / L		
Organic Additives	100 ~ 1,000 ppm		

### 3. Results and discussion

The electrodeposited reaction is a heterogeneous reaction including both material transfer and electrochemical reaction and thus, it is important to investigate the reaction mechanism for optimized conditions of electrodeposited process. Kinetic energy of tin electro-refining was obtained under various RDE test conditions: temperature from 298 to 313 K, rotating disk speed of 400 rpm, and applied potential of 2.15 V. The applied potential was measured when electro-refining in the hydrochloric acid solution was performed at the current density of 3A/dm<sup>2</sup>. The constant potential was used in order to analyze the reaction rate, i.e., current, at each process parameter such as temperature and stirring rate. The results as a function of process temperature were presented in Fig. 1, illustrating effects of temperature on the electro-refining rate of tin using RDE. With the increase of temperature, the electro-refining rates of tin ascended. In order to clarify the rate determining step, Arrhenius plot that shows a relationship between the reciprocal of temperature and the apparent rate constant, was obtained as shown in Fig. 2. The calculated activation energy of tin was 5.38 Kcal/mol at the temperature range of 293 to 313 K. Thus, these results indicate that the reaction rate of tin was controlled by a mixed mechanism, partly by chemical reaction and partly by mass transfer.

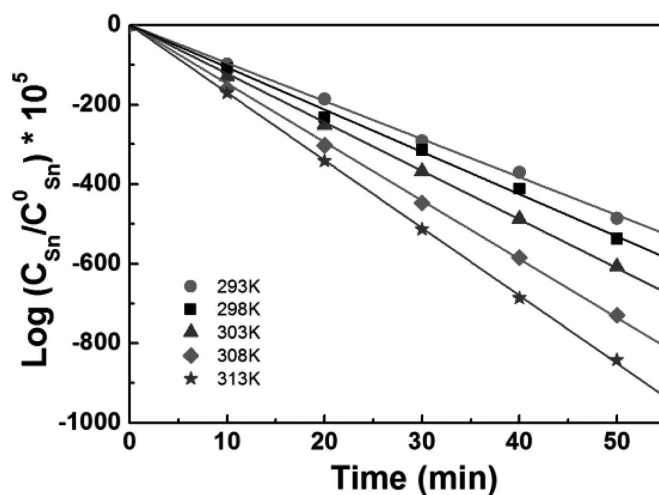


Fig. 1. Variations of electrodeposition rates of tin as function of temperature at 2.15 V and 400 rpm

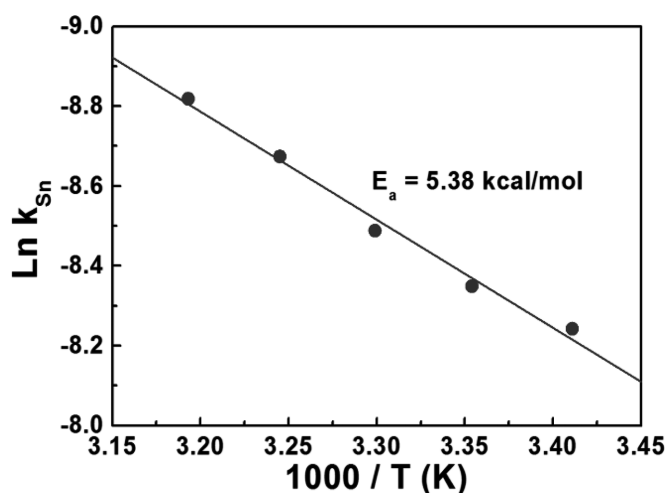


Fig. 2. Arrhenius plots for electrodeposition of tin at 3 V and 400 rpm

In order to investigate the variation in the purity of tin deposited on cathode during the experiment for 30 hours, electro-refining for tin was performed in various electrolytes such as hydrochloric acid, sulfuric acid and methansulfonic acid. The impurity concentrations of anode metal and deposited metal in cathode were analyzed using ICP-OES as shown in Table 2. The anode metal by casting consisted of tin with 93.9 wt.% and several impurity metals of Ag, Bi, Pb, Cu and etc. The current efficiency of the electro-refining is 65.6%, the purity of tin is significantly improved up to 99.985 wt.% at the condition of current density 5 A/dm<sup>2</sup> and in the electrolyte of Hydrochloric acid. The current efficiency was 84.7% and 84.3%, and the purity of the tin after electro-refining was 99.322 wt.% and 99.914 wt.% at the condition of current density 3 A/dm<sup>2</sup>, in the electrolyte of sulfuric acid and methansulfonic acid, respectively. Figure 3 shows impurity concentrations in acid electrolyte as electro-refining time varied. The higher concentration of all impurities was detected in the sequence of lead, copper, bismuth, and silver. The impurity concentrations of silver, bismuth, and copper decreased in the solution of Methansulfonic Acid but lead showed about 10 times higher concentration, compared with

TABLE 2

Quantitative analysis of impurity concentration in the anode metal and electro-refined cathode metal by ICP-OES

		(wt.%)									
Cathode		Ag	Bi	Pb	Cu	Zn	Ni	Al	Au	Fe	Sn
	Anode	2.492	1.659	1.239	0.574	0.038	0.035	0.025	0.017	0.019	93.902
	Hydrochloric Acid	0.00159	0.00181	0.00854	0.00337	N/A	N/A	N/A	N/A	N/A	99.985
	Sulfuric Acid	0.03085	0.08397	0.41323	0.15004	N/A	N/A	N/A	N/A	N/A	99.322
	Methansulfonic Acid	0.00008	0.00004	0.08527	0.00038	N/A	N/A	N/A	N/A	N/A	99.914

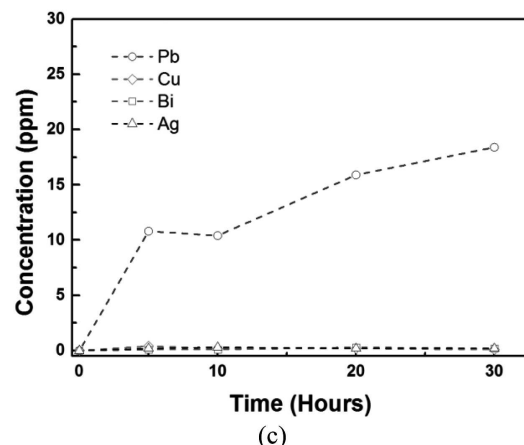
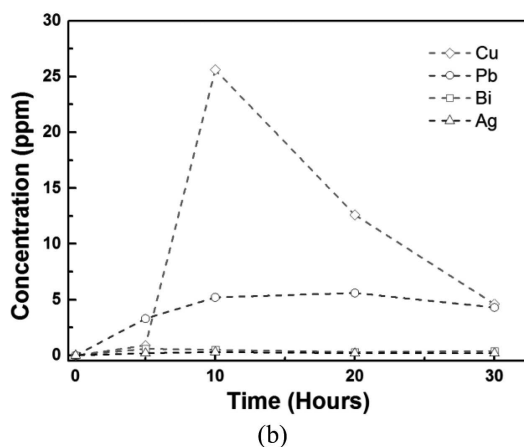
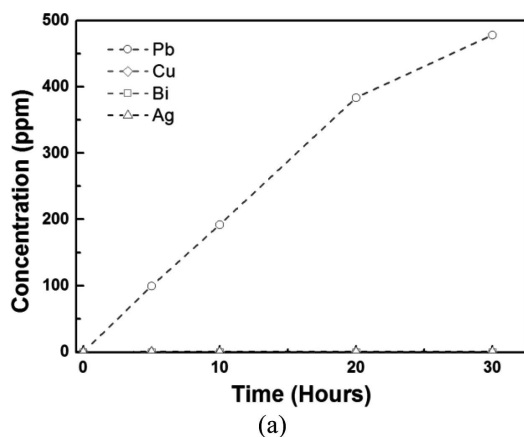


Fig. 3. Impurity concentrations in electrolyte as function of electro-refining time: (a) hydrochloric acid, (b) sulfuric acid, and (c) methansulfonic acid

the concentration of impurities in Hydrochloric Acid. Table 3 presents the standard reduction potential of impurities for cathode electro-refining reaction. The tin and lead has reduction potential of  $-0.136$  V and  $-0.127$  V, respectively, and those elements can be reduced at low current density conditions. However, bismuth, copper and silver have reduction potential of  $+0.286$  V,  $+0.339$  V and  $+0.799$  V, respectively, and the reduction reaction of impurities does not occur in the cathode, which could imply the purity of the tin is significantly improved. Hydrochloric acid and methanesulfonic acid is usually used for ionization and the dissolution of tin and lead, so it is widely used in industry. Therefore, it is deduced that the concentration of lead should be lower in casted metal in order to obtain high purity of tin by electro-refining process.

TABLE 3

The standard reduction potential of various impurities chemical reaction for electro-refining [9]

Half Chemical Reaction	Standard Reduction Potential
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	$-0.136$ V
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	$-0.127$ V
$\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}$	$+0.286$ V
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$+0.339$ V
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	$+0.799$ V

Sludge is generated in the anode due to ion reaction in electro-refining process. Since its thickness increases as process time increases, it could lead to increase of applied voltage and decrease of current efficiency of tin electro-refining. In this case of the hydrochloric acid, sludge was formed on the surface of anode, which is similar to the mud. The anode sludge was formed in shape of fractured grit in electrolyte of methansulfonic acid. However, the anode sludge was formed with very thin thickness in electrolyte of sulfuric acid. The impurity metal was deposited on the surface of cathode after it was dissolved in the electrolyte sulfuric acid solution. Therefore, the amount of impurities on the surface of cathode remarkably increased. The metal concentrations of anode sludge were analyzed using ICP-OES as shown in Table 4. The metals of anode sludge were identified as silver, bismuth, lead, copper and tin. The concentration of tin and lead on the surface of anode sludge decreased in hydrochloric acid, which could be due to dissolution of the metal into electrolyte by electro-chemical reaction. However,

the concentration of the other impurity such as silver, bismuth and copper increased, because the ionization does not occur at anode surface. These reactions could also occur even in methanesulfonic acid. The lead concentration of anode sludge in electrolyte of methansulfonic acid was higher than that in the electrolyte of hydrochloric acid. It seems to be related the sludge in shape of grit at the anode surface which contains higher concentration of lead.

TABLE 4

Quantitative analysis of concentration in the sludge of anode metal surface by ICP-OES.

(wt.%)

	Ag	Bi	Pb	Cu	Sn
Hydrochloric Acid	18.12	9.15	0.85	6.41	31.06
Methansulfonic Acid	23.30	3.46	5.45	2.43	19.90

#### 4. Conclusions

The rate determining step was clarified with the activation energy of the electro-refining reactions for the each process conditions estimated from Arrhenius Plot. The calculated activation energy was 5.38 kcal/mole at the temperature from 293K to 313K, implying that it was controlled by a mixed mechanism, partly by chemical reaction and partly by mass transport.

The current efficiency, 65.6%, was achievable at the condition of current density, 5A/dm<sup>2</sup>, and in the electrolyte of Hydrochloric acid. During tin electro-refining process, impurity

dissolved from tin crude metal into the electrolyte was analyzed using ICP-OES, and the result showed the concentration of impurity metal gradually increased. Quantitative analysis on tin crude metal showed that it consists of tin with 93.9 wt.% and several impurity metals of Ag, Bi, Pb, Cu, and etc. After tin electro-refining process, the purity of tin increased up to 99.985 wt.%.

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