Article

Analysis of the Particle Size and Morphology of Tin Powder Synthesized by the Electrolytic Method

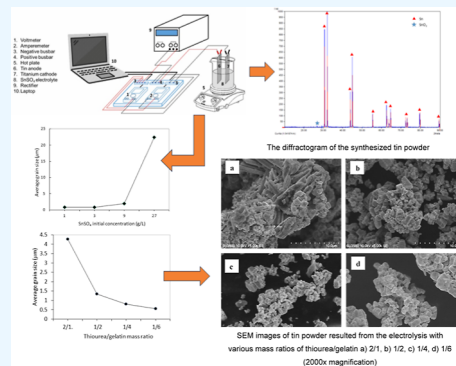Deviana Perdana, Soleh Wahyudi, and Mohammad Zaki Mubarok*

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ABSTRACT: This article discusses the effect of electrolysis parameters on the particle size and morphology of the tin powder synthesized by the electrolytic method. The electrolytic method is simple and can eliminate the risk of lead and arsenic gas emissions owing to the low temperature of the process. The effects of tin concentration in a sulfate-based electrolyte, a mass ratio of thiourea/gelatin as additives, current density, and electrolysis time on the particle size and morphology of the synthesized tin powder were examined. Pure tin and titanium plates were used as the anode and the cathode, respectively. After the electrolysis experiments were completed, the synthesized tin powders were analyzed by a particle size analyzer, a scanning electron microscope, and X-ray diffraction. The optimum condition of the experiment that resulted in the highest D90 was achieved at an initial concentration of $SnSO_4 = 3$ g/L, a mass ratio of thiourea/gelatin = 1/4, a current density of 1 A/dm^2, and a 10 min electrolysis time. Under this condition, 90% of the tin powder size obtained was smaller than 2.279 μm, showing a rounded morphology with a length-to-width ratio of 1.15. The current efficiency increased with increasing tin concentration, decreasing current density, and a shorter electrolysis time.

The diffractogram of the synthesized tin powder

SEM images of tin powder resulted from the electrolysis with various mass ratios of thiourea/gelatin a) 2/1, b) 1/2, c) 1/4, d) 1/6 (2000x magnification)

1. INTRODUCTION

The advanced development of electronic components goes to the miniaturization of electronic circuits and printed circuit boards.[1] Therefore, solder powder with a finer particle size is required. Nowadays, various types of solder powder are classified by their particle size range. Moreover, in accordance with Joint Industry Standard J-STD-005: Requirement for Soldering Pastes,[2] the solder powder should have a spherical morphology with a maximum length-to-width ratio of 1.25. According to Joint Industry Standard J-STD-006B, there are various alloy designations for solder powder, with tin powder remaining the main constituent having a tin mass percentage of up to 99.9%.[3]

Atomization is the most common method used for producing tin powder. In the gas atomization process, a high-pressure gas (i.e., air, argon, nitrogen, or helium) is utilized to convert the molten metal stream into tiny droplets. The molten metal droplets further cool and solidify into metal powder particles whose size ranges from 1 to 150 μm due to the cooling effect of the gas.[4] However, this method requires relatively complex equipment and has difficulty in producing powder particles finer than 1 μm.[5] In addition, there is a risk of lead evaporation from the lead-containing tin molten feed during the process, which can be harmful to the operator's health and the surrounding environment.

An alternative route for producing tin powder is the electrolysis method.[6] This method has several advantages: it can produce nanopowder particles, requires relatively simple equipment, and produces high-purity powder.[7,8] In contrast to the atomization method, there is no risk of lead fume emissions since this technique does not use a lead-bearing molten tin ingot for producing tin powder. One of the electrolysis method's drawbacks is the difficulty of generating a powder with spherical morphology. The electrolysis process can be carried out using either a constant current source or a pulse current.[6] The principle difference between these methods is the current output from the power source utilized for the electrodeposition. At a constant current method, the voltage and current output from the power source are constant during the electrolysis process. Meanwhile, in pulse current electrolysis, the current output from the power source is intentionally modulated between "on" and "off" periods. The "off" period is the period when the current supply is stopped.[9] During the "off-time" period, metal ions diffused from the bulk of the electrolyte solution to the electrode−electrolyte interface. Meanwhile, during the "on-time" period, the ions are ready to be deposited on the electrode.[9]

Natanson (1959)[10] proposed a method to synthesize tin powder by electrolysis using stannate electrolyte. It was reported that the tin deposits obtained are in the form of coarse powder. This is caused by the emulsification of the organic layer of the additives due to the presence of excess alkali in the electrolyte solution. In order to prevent this phenomenon, Khimchenko et al., 1975,[11] employed suitable surface-active agents. It was suggested that when an acid electrolyte is used and the upper part of the electrolyte contains oleic acid, no emulsification of toluene occurs, and tin particles become effectively dispersed in the upper part of the electrolyte. Nevertheless, this method needs an excessive amount of acid in the solution to prevent hydrolysis and to ensure that no tetravalent tin compounds are formed. The powder obtained was needle-like and rod-shaped and had branches forming in a short time after the electrolysis started. Zhelibo and Grechanyuk (1978)[12] synthesized tin powder with particle sizes ranging from 0.3 to 0.8 mm by electrochemical precipitation from a bath consisting of an aqueous phase of chloride/fluoride electrolyte and an organic solution of oleic acid diluted in toluene. At current density and temperature ranges of 50 to 500 A/m^2 and 293 to 333 K, tin is reduced from complex anions $[SnClF_2]^-$ and synthesized in the form of black powder, with particles being distributed uniformly in the organic layer of the bath. The morphology of the particles is dendritic, with short branches. The problem faced by this method is the formation of sodium oleate when sodium is present in the electrolyte.

Popov, Pavlović, and Jovićević (1989)[13] proposed an electrolysis method to produce tin powder from an electrolyte prepared by dissolving 20 g/L $SnCl_2 \cdot H_2O$ in 250 g/L NaOH solution. The electrodeposition was performed on a copper cathode with a constant and square-wave pulsating over-potential at room temperature. It was reported that the tin powder deposits obtained under the entire specified over-potential variations were dendritic in morphologies. Nikolic et al. (2022),[6] reported that the morphology and structure of Sn dendrites produced by applying both potentiostatic and galvanostatic regimes of the electrolysis in the alkaline hydroxide electrolyte depended on the applied cathodic potential, the current density, and the polarization character-istic during the electrolysis. Three types of Sn dendrites were obtained depending on the applied cathodic overpotential, namely needle-like, fern-like, and stem-like dendrites.[6]

Saito et al. (2012)[14] demonstrated the synthesis of tin nanoparticles (Sn-NPs) via electrolysis using potassium carbonate (K_2CO_3) solution. The Sn-NPs obtained in this study were reported to contain colloidal SnO_2 particles. In alkaline solutions, dissolved tin tends to react with hydroxyl (OH^-) ions in the solution to form $Sn(OH)_3^-$ ions, which are further transformed to $Sn_6O_4(OH)_4$ and SnO_2 crystals. This process requires surfactants such as cetyltrimethylammonium bromide (CTAB) to prevent the ionization of Sn.[15] The morphology of SnO_2 and Sn deposits was plate-like and rod-like, respectively. However, it is highly challenging to remove CTAB from the final product. Mulyani, Tanjung, and Prajitno (2019)[16] conducted a simpler tin powder synthesis by the electrolysis method using stannous sulfate ($SnSO_4$) dissolved in hydrochloric acid (HCl). A series of experiments were carried out under variations of applied currents (5, 6, and 7 A) and electrolysis time (20, 25, and 30 min), respectively, at a temperature of 50 °C. The electrolysis experiments resulted in

tin powder deposits, which are highly irregular with an average particle size of approximately 83 μm.[16]

Various kinds of additives are commonly used in the electrolytic deposition of metal to control the grain size and morphology of the deposit. The additives can serve as leveling agents as well as grain refiners, which promote the formation of new nuclei during electrolysis and result in a smooth surface of the deposit. The additives can form an inhibition layer or complex ions adsorbed on the substrate and modify the electrocrystallization behavior of the metal deposit.[17] Thiourea and gelatin are the most common additives that have been widely used in metal electrodeposition. To produce finer and more spherical metal powders, the nucleation mechanism of the electrolysis process must be instantaneous nucleation rather than progressive nucleation. Instantaneous nucleation is the type of nucleation that occurs at low site density, causing a high nucleation rate and resulting in a small particle size. Meanwhile, progressive nucleation is nucleation that occurs at high site density with a low nucleation rate and tends to generate larger particle size.[18] According to research conducted by Meudre et al. (2014),[19] the addition of gelatin in Cu−Sn electrodeposition causes a more homogeneous deposit and smaller crystallites size. The deposit grains have a smaller size (a few μm to 10−15 μm), and the growth of the deposit indicated that nucleation is instantaneous. On the other hand, dendritic growth was observed in the absence of additive, and the nucleation tends to be progressive.[19]

According to Nikolić, Branković, and Pavlović (2012),[20] Orhan and Hapçi (2010),[21] Pavlović et al. (2010),[22] and Wahyudi et al. (2021),[23] the size and morphology of metal powder particles synthesized by the electrolytic method are dependent on the electrolysis parameters such as current density, metal concentration in the electrolyte, and electrolysis time. Wahyudi et al. (2021)[23] reported that in the absence of additives, the morphology of copper powder particles synthesized by the constant-current electrolysis method in sulfate electrolyte is dendritic with a globular and polycrystal-line-face shape.

In this study, a series of electrolysis experiments to produce tin powder from the pure tin ingot were carried out to determine the optimum condition that results in tin powder with the largest D90 grain size and its grain morphology that tends to be rounded or nearly spherical with a length-to-width ratio of close to 1. Powders with a higher sphericity have better flowability, and this property is required for the solder powder.[24] The electrolysis experiments were conducted using stannous sulfate ($SnSO_4$) dissolved in sulfuric acid as the electrolyte solution. The experimental design using the Taguchi Method was performed by varying four (4) experimental variables, namely dissolved tin concentration, the mass ratio of thiourea and gelatin as additives, current density, and electrolysis time at three (3) levels of variation following the orthogonal matrix of L$_9$ 3^4. The optimum condition of the electrolysis experiment was determined by the signal-to-noise (S/N) ratio value, which is the largest. According to the Joint Industry Standard J-STD 005,[2] the current smallest size of solder powder is 2 μm. Too small a particle size is undesirable because the finer powder is more sensitive to oxidation than the coarser powder, which impairs the solder powder's reflow characteristic.[24] Therefore, this study aims to synthesize tin powder with a D90 larger than 2 μm, which is determined by a statistical approach using the parameter of S/N of the larger the better from the Taguchi

Method. After the optimum condition was obtained, the individual effects of the initial concentration of Sn, the mass ratio of thiourea and gelatin as additives, current density, and electrolysis time on the size and morphology of the tin powder were examined.

2. MATERIALS AND METHODS

2.1. Experimental Procedure and Variables. The experiments on tin powder synthesis by the electrolysis method were carried out in two stages. The first stage of the experiment was designed by the Taguchi Method to determine the optimum conditions which produce tin powder with the largest D90 grain size and a nearly spherical morphology with a maximum length-to-width ratio of 1.25. According to Joint Industry Standard J-STD 005, the current smallest size of solder powder is 2 μm.[2] Too small a particle size is undesirable because the finer powder is more sensitive to oxidation than the coarser powder, which impairs the solder powder's reflow characteristic.[24] Therefore, a parameter of a S/N ratio of the "larger the better" was used in the analysis of the D90 data obtained from the experiments to allow the particle size of tin powder to be larger than 2 μm. The first stage of the tin powder synthesis experiment was carried out based on the experimental design with the Taguchi orthogonal arrays L_9 method, in which four (4) factors (variables) were varied at three (3) levels of variation. The experiment design template using Taguchi orthogonal arrays L_9 is illustrated in Table 1.

Table 1. Experiment Design Template Using Taguchi Orthogonal Arrays L_9

experiment number	factors and levels			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

For the tin powder synthesis experiments, A = dissolved $SnSO_4$, B = thiourea/gelatin mass ratio, C = current density, and D = duration of electrolysis. The dissolved $SnSO_4$ (A) was varied at 3, 5, and 7 g/L, and the thiourea/gelatin mass ratio was varied at 1:3, 1:4, and 1:5. Meanwhile, the current density was varied at 1, 1.5, and 2 A/dm², and the duration of electrolysis was varied at 10, 20, and 30 min. Under these specified variation ranges of variables and the design template of Taguchi orthogonal arrays L_9, the tin powder synthesis experimental variation is shown in Table 2.

The resulting powder from each experiment was collected and dried in a reducing atmosphere. The analysis using a scanning electron microscope (SEM) and a particle size analyzer (PSA) was performed on the synthesized powder. The SEM images of the synthesized tin powder were used to determine the length-to-width ratio of the grains, and the measurement was performed using ImageJ software. The experiments were performed in duplicate, and the D90 of the synthesized tin powder was measured by PSA for each

Table 2. Experimental Variations Designed by Taguchi Orthogonal Arrays L_9

no.	experimental variables			
	dissolved $SnSO_4$ (g/L)	thiourea/gelatin mass ratio	current density (A/dm²)	duration of electrolysis (min)
1	3	1/3	1	10
2	3	1/4	1.5	20
3	3	1/5	2	30
4	5	1/3	1.5	30
5	5	1/4	2	10
6	5	1/5	1	20
7	7	1/3	2	20
8	7	1/4	1	30
9	7	1/5	1.5	10

experimental condition. The parameter of the S/N ratio of the "larger the better" was calculated for each factor-level combination using the following formula[25]

$$\text{S/N larger the better} = -10 \times \log\left(\sum (1/Y^2)/n \right) \quad (1)$$

where Y = responses (i.e., experimental data) for the given factor and level combination and n = number of responses (i.e., number of experimental data).

After the optimum condition of the first-stage experiment was obtained, the electrolysis experiments were carried out using the cathode with an active surface area of 1 cm × 1 cm to measure the cathode interface potential during the electrolysis. The cathode sample was isolated in a polymeric resin with an exposed area of 1 cm × 1 cm. The silver–silver chloride (Ag/AgCl) reference electrode was placed in a Luggin capillary whose tip was about 1 mm in front of the cathode surface. This measurement aimed to ascertain that Sn powder deposition co-occurs with H_2 gas evolution by evaluating the value of the cathode potential. The cathode interface potential was measured every 1 s, and the data was recorded by a data logger connected to a laptop.

The second experimental stage of the tin powder synthesis was designed by varying only 1 (one) experimental variable, with the other variables kept constant at the optimum condition obtained from the first stage of the experiments. The experiments with the variation of the dissolved $SnSO_4$ were initially performed, followed by those with the variations of the mass ratio of thiourea/gelatin, current density, and duration of the electrolysis. The second-stage experiment aims to determine the individual effects of the variables on the average particle size, the morphology of the deposit, and the current efficiency of the electrolysis. The detailed stage-2 experimental conditions are shown in Table 3. The average grain size of the tin powder from the second stage of the experiment was determined by ImageJ software using the SEM pictures of the synthesized tin powder. The ImageJ measured the diameters of representative grains, and the average grain size was determined.

2.2. Electrolyte and Electrode Preparation. The electrolyte solution was prepared by diluting 48.4 mL of 17.8 M H_2SO_4 (96% purity) in distilled water to prepare a sulfuric acid solution with a concentration of 1.02 M. Afterward, the analytical grade of $SnSO_4$ powder with various masses was dissolved in the 1.02 M sulfuric acid according to the experimental variations. Thiourea and gelatin as additives were then added to the solution according to the variation of the additive mass ratio used. The solution is then homogenized

Table 3. Experimental Conditions of Stage-2 of Sn Powder Synthesis[a]

variation	experimental variables			
	dissolved SnSO$_4$ (g/L)	thiourea/gelatin mass ratio	current density (A/dm^2)	duration of electrolysis (min)
dissolved SnSO$_4$ (g/L)	1	1/4	1	10
	9	1/4	1	10
	27	1/4	1	10
thiourea/gelatin mass ratio	3	2/1	1	10
	3	1/2	1	10
	3	16	1	10
current density	3	1/4	0.5	10
	3	1/4	2	10
	3	1/4	3	10
duration of electrolysis	3	1/4	1	30
	3	1/4	1	60
	3	1/4	1	120

[a]The optimum conditions obtained from the first-stage experiment are a SnSO$_4$ concentration of 3 g/L, a thiourea/gelatin ratio of 1/4, a current density of 1 A/dm^2, and an electrolysis duration of 10 min.

by stirring using a magnetic stirrer with a rotation speed of 900 rpm for 30 min.

The anode used in the electrolysis experiment was a tin plate of 99.99% purity, having a dimension of 10 cm × 4 cm × 1 cm. Meanwhile, the cathode is a titanium plate with a dimension of 10 cm × 4 cm × 0.2 cm. Before the electrolysis experiments were started, the electrodes' surfaces were polished with 240, 400, 600, and 800 grit silicon carbide paper to remove oxides and impurities on the electrode surfaces. After polishing, the electrode surface was rinsed with distilled water and dried with an electric dryer. After the surface preparation of the electrode was finished, the active surface area of the electrodes exposed to the solution was adjusted by isolating the inactive area using duct tape to obtain an anode and cathode with an active surface area of 4 cm × 4 cm, respectively. A similar procedure was implemented for the surface preparation of 1 cm × 1 cm of electrodes used in measuring the interface potentials using Ag/AgCl as a reference electrode during the electrolysis at the optimum condition. As previously mentioned, the anode and cathodes used in this experiment were isolated in a polymeric resin to expose an active surface area of 1 cm^2.

2.3. Electrolysis Experiment. The schematic of the electrolysis experiment to synthesize tin powder is shown in Figure 1. The prepared anode and cathode were immersed in

the electrolyte solution, and the distance of the anode−cathode surface was kept at 3 cm. The electrolysis cell was a 1000 mL beaker glass with an electrolyte solution volume of 850 mL. According to the current density required, a constant current was introduced to the cell from a DC power supply. The current and cell voltage were measured by an ammeter and a voltmeter, respectively, and the data were recorded by a data logger connected to a laptop. After the electrolysis experiment was finished, the cathode surface was rinsed with alcohol to remove the remaining electrolyte, and the tin powder was stripped. The stripping of tin powder was done by spraying the distilled water onto the cathode surface. The stripped powder was collected in a closed plastic bottle filled with alcohol to prevent the oxidation of the tin powder due to direct contact with the air. The tin powder in the bottle is then dispersed using an ultrasonic device for 6 min. The tin powder that had been dispersed was then dried in a heating tube at a temperature of 100 °C. During the powder drying, the heating tube was filled with argon gas to provide a reducing condition and avoid the oxidation of the tin powder. The drying process was carried out for 30 min. The tin powder that had been dried was then collected in vacuum plastic before being further analyzed by PSA and SEM.

3. RESULTS AND DISCUSSIONS

3.1. Optimum Condition of Tin Powder Synthesis Determined by the Taguchi Method. By the Taguchi method, the optimum condition of the experiment at the specified range of variables was determined based on the value of the S/N ratio parameter. Based on the data obtained from the first stage of the experiment, the S/N "larger the better" was used. Therefore, the largest particle size of tin powder will be obtained at each variable level, which results in the highest value of the S/N ratio. According to Joint Industry Standard J-STD 005 (2012), the minimum grain size of the tin powder is 2 μm for various types of tin powder used in solder.[2] As previously mentioned, too small a particle size is undesirable because the finer powder is more sensitive to oxidation than the coarser powder, which impairs the solder powder's reflow characteristic.[24] The average particle size, the value of the S/N larger the better, and the length-to-width ratio of the powder obtained from the stage-1 experiment are shown in Table 4. Meanwhile, the data on the S/N ratio of larger the better for each variable's variation are listed in Table 5. The S/N ratio profile for each variable and its level of variation are shown in Figure 2.
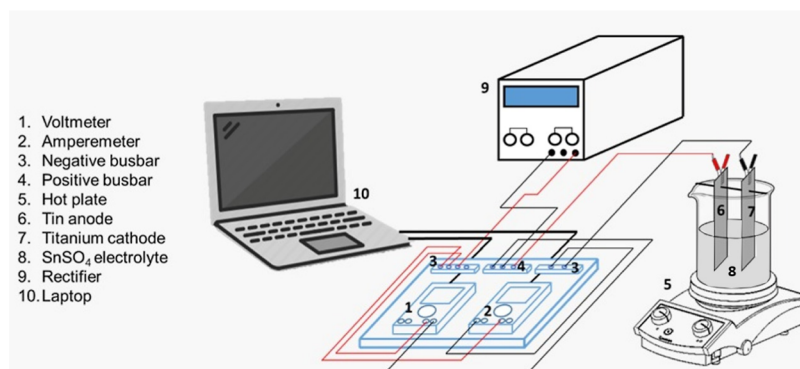

1. Voltmeter
2. Amperemeter
3. Negative busbar
4. Positive busbar
5. Hot plate
6. Tin anode
7. Titanium cathode
8. SnSO$_4$ electrolyte
9. Rectifier
10. Laptop

Figure 1. Schematic of the electrolysis experiment to synthesize tin powder.

Table 4. Particle Size of the Tin Powder Obtained at the Stage-1 Experiment and the Respective S/N "larger the better" Data

	D90 (μm)		calculation			
exp. no.	replicate I	replicate II	average	variance	S/N larger the better	length-to-width ratio
1	2.267	2.271	2.269	0.00001	7.117	1.12
2	2.134	2.188	2.161	0.001	6.691	1.11
3	2.06	1.72	1.890	0.058	5.424	1.21
4	1.968	1.926	1.947	0.001	5.786	1.13
5	2.177	2.127	2.152	0.001	6.655	1.09
6	2.001	2.121	2.061	0.007	6.271	1.14
7	2.133	1.913	2.023	0.024	6.081	1.18
8	2.006	2.073	2.040	0.002	6.187	1.13
9	2.247	1.92	2.084	0.053	6.296	1.15

Table 5. S/N Value Obtained for Each Level Variation of the Experimental Variable

experimental variable	level of variable	S/N larger the better
SnSO$_4$ concentration	1 gpl	6.410
	3 gpl	6.237
	9 gpl	6.188
thiourea/gelatin mass ratio	1:3	6.328
	1:4	6.511
	1:5	5.997
current density	1 A/dm^2	6.525
	1.5 A/dm^2	6.257
	2 A/dm^2	6.053
duration of electrolysis	10 min	6.689
	20 min	6.348
	30 min	5.799

The S/N peak point for each variable indicates the larger grain size obtained under the respective experimental conditions. The line gradient of the S/N graph versus variable variation indicates the influence of the variable change (i.e., at the specified range of variations) on the experimental output (i.e., the D90 particle size of the tin powder). The influence of a variable will be more significant if the gradient of the line is steeper, either positive or negative. On the other hand, the line that tends to be flat indicates that the variable does not significantly affect the powder's particle size.[21]

The optimum experimental condition, based on the value of S/N larger the better, was achieved at an initial SnSO$_4$ concentration of 3 g/L, a mass ratio of thiourea and gelatin 1/4, a current density 1 of A/dm^2, and an electrolysis duration of 10 min. The experiment was carried out at this optimum condition and resulted in tin powder with a D90 particle size of 2.279 μm (i.e., 90% powder particle size was smaller than 2.279 μm) and a morphology that tends to be rounded or nearly spherical with a length-to-width ratio of 1.15. Using the Faraday equation, the rate of tin mass production (r) can be determined by the following equation

$$r = \frac{m}{t} = \frac{aIt\epsilon}{nFA} = \frac{ai\varepsilon}{nF} \tag{2}$$

where m = mass of tin deposited (g), t = electrolysis time (s), A = active surface area of the cathode (m^2), a = atomic weight of Sn (118.71 g/mol), I = applied current, i = I/A = applied
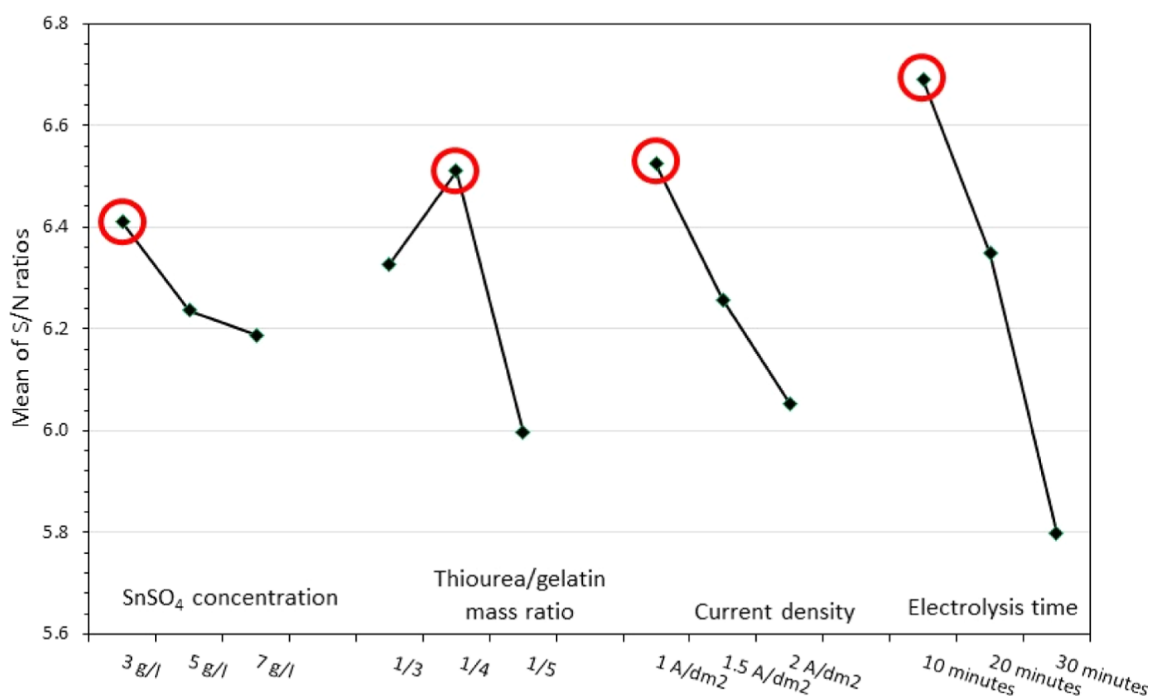
Figure 2. Profiles of S/N "larger the better" for Sn powder particle size resulted from the experiments with various conditions.

current density (A/m^2), ε = current efficiency for Sn deposition (%), n = number of electrons involved in the tin electrodeposition (2), and F = Faraday constant (C/mol). By substituting the parameters of the optimum conditions (i.e., current density 1 A/dm^2 = 100 A/m^2, and current efficiency at the optimum condition of 20.78%), the rate of tin powder production in $kg/m^2/day$ ≈1.1 $kg/m^2/day$. By introducing an operating factor of 90% to accommodate tin powder scrapping from the cathode surface and discharging from the cell, the tin yield is about 0.99 kg per m^2 of cathode surface per day.

Figure 3 shows the particle size distribution of the tin powder obtained from the experiment at the optimum conditions.
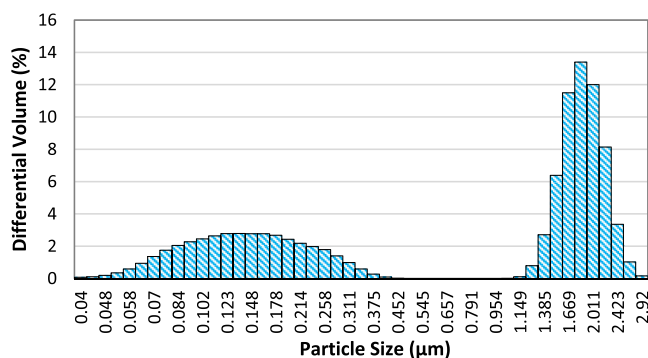
Figure 3. Particle size distribution of the synthesized tin powder at the optimum condition.

3.2. Profile of the Cathode Interface Potential and XRD Analysis of Sn Powder.
The cathode-electrolyte interface potentials during electrolysis at optimum conditions were measured by a voltmeter and a silver−silver chloride (Ag/AgCl) reference electrode. A Luggin capillary was used to place the reference electrode with a tip distance to the cathode surface of about 0.5 mm. The data of the measured cathode potentials were converted to the values versus a standard hydrogen electrode (SHE). A profile of the cathode interface potentials during 10 min of electrolysis with an initial $SnSO_4$ concentration of 3 g/L, a mass ratio of thiourea/gelatin of 1/4, and a current density of 1 A/dm^2 is shown in Figure 4. The cathode interface potentials range from about −0.6 to −0.5 V versus SHE at a solution pH of about −0.3.

Based on the Pourbaix Diagram of the Sn−H_2O system at room temperature (i.e., 27 °C) presented in Figure 5, it can be seen that the cathode interface potential (red dot) is in the region of tin metal (Sn) stability (i.e., within the brown shaded area) and is below the $2H^+/H_2$ equilibrium line (red dashed line). Therefore, thermodynamically, the tin deposition (Sn^{2+} + 2e = Sn) under the experimental condition would co-occur with hydrogen gas evolution resulting from dissolved hydrogen cation reduction (i.e., $2H^+ + 2e = H_2$). The gas bubble evolution from the cathode surface was visually observable, along with the deposition of Sn on the cathode surface. Hydrogen gas evolution is needed to facilitate powder formation and avoid the aggregation of particles that leads to the formation of a compact plate structure.

The XRD analysis of tin powder produced from the experiment at optimum conditions (initial $SnSO_4$ concentration of 3 g/L, a mass ratio of thiourea/gelatin of 1/4, a current density of 1 A/dm^2, and an electrolysis time of 10 min) is presented in Figure 6. The XRD data analysis with the
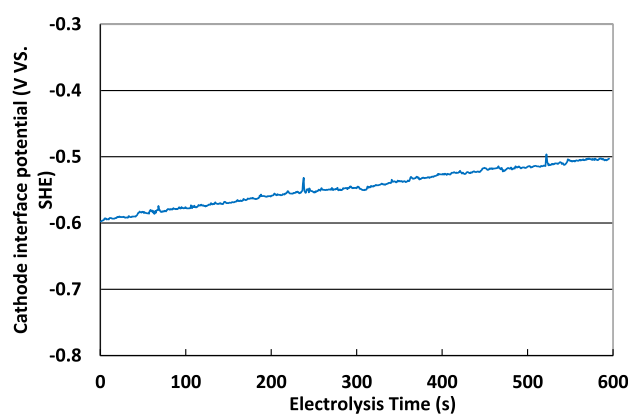

Figure 4. Profile of cathode interface potentials during 10 min electrolysis with an initial $SnSO_4$ concentration of 3 g/L, a mass ratio of thiourea/gelatin 1/4, and a current density of 1 A/dm^2 at room temperature.

Match! 3 software identified that the most dominant diffraction peaks are tin metal, with a minor peak of SnO_2 at 2θ of around 30. Semiquantitative analysis performed using the peak intensity of each crystalline phase with the reference intensity ratio methods resulted in a Sn content of 98.9%, and the rest is SnO_2 (1.1%). The results of this analysis indicate that the resulting powder product has high purity with a low oxygen content. As previously mentioned, the powder was dried in a heating tube that flowed with argon during heating. The tin powder that had been dried was then collected in vacuum plastic before being further analyzed by PSA and SEM. The synthesized tin powder deposits have a tetragonal crystal structure.

3.3. Effect of Tin Concentration on the Tin Powder Size and Morphology and Current Efficiency of the Electrolysis.
After the optimum condition based on Taguchi analysis was determined, series of electrolysis experiments were carried out under variations of single variable, namely initial $SnSO_4$ concentration, thiourea/gelatin ratio, current density, and electrolysis duration. The following is the result and discussion on the effects of these variable variations on the morphology of the synthesized tin powder. The effects of the initial $SnSO_4$ concentration and current density on the current efficiency of the electrolysis were also discussed.

3.3.1. Effect of Tin Concentration on the Particle Size and Morphology of Tin Powder. The particle size of the synthesized tin powder as a function of the initial $SnSO_4$ concentration is shown in Figure 7. SEM images of the synthesized tin powder at a magnification of 2000× for the initial $SnSO_4$ concentrations of 1, 3, 9, and 27 g/L are presented in Figure 8. It can be seen that the higher the dissolved tin concentration, the larger the particle size tends to be. As previously mentioned, the lower the dissolved tin concentration, the more hydrogen gas is formed, which aligns with the decrease in the size of the tin powder obtained. This result is in line with the experiment conducted by Wojtaszek et al. (2023),[26] which showed that elevating the copper concentration in copper powder synthesis on a rotating electrode by the electrochemical method leads to an enlargement in the size of the copper powder.

Based on the previous study conducted by Nikolić et al. (2021),[27] it was found that the hydrogen evolution reaction in the synthesis of metal powder by electrolytic method contributes to a significant effect on the shape of the powder
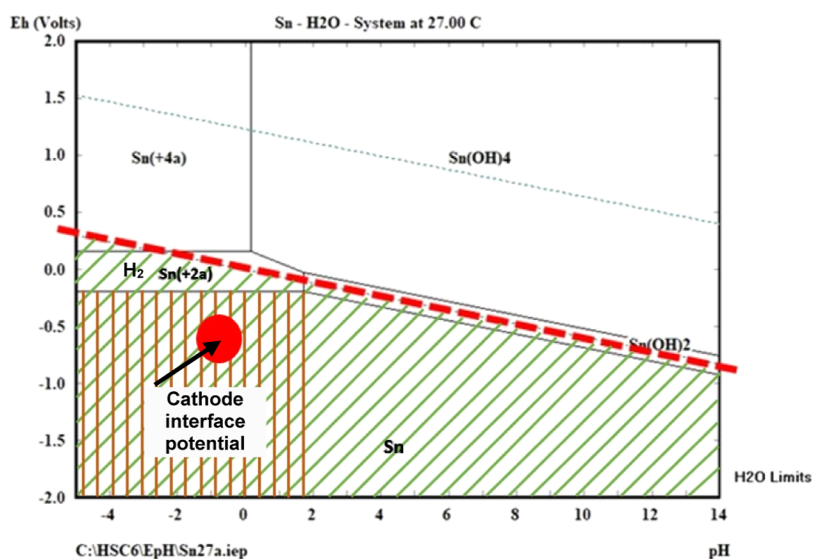
Figure 5. Pourbaix diagram of the Sn−H_2O system at T = 27 °C and ionic activity of 0.017 molal (constructed by HSC Chemistry version 7 software).
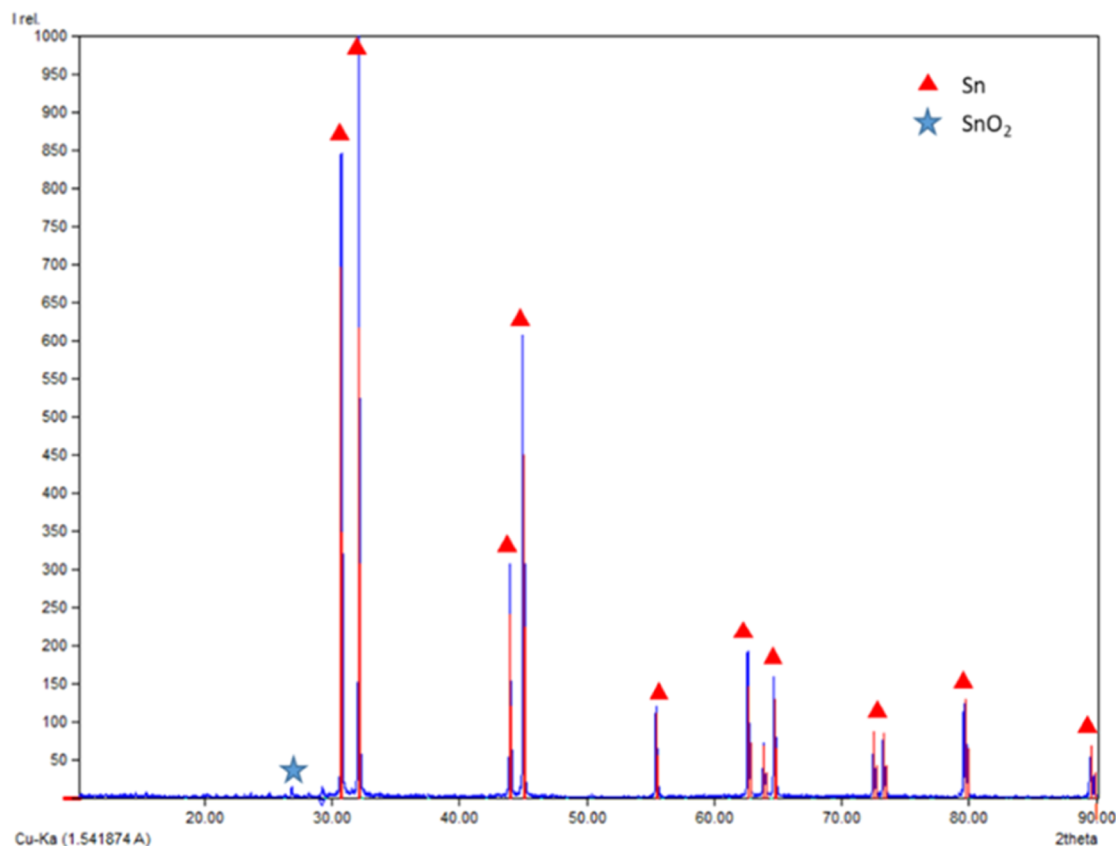

Figure 6. Diffractogram of the synthesized tin powder deposit from the experiment at optimum conditions with initial $[SnSO_4]$ = 3 g/L, mass ratio of thiourea/gelatin = 1/4, current density = 1 A/dm^2, and t = 10 min.

particles. Under intense hydrogen gas generation conditions during the electrolysis, the spongy cauliflower particles will likely be formed. This intense hydrogen gas generation also results in increased electrolyte mixing and alterations in fluid dynamics in the area adjacent to the electrode.[27]

Referring to ASTM F1877-05 regarding Standard Practice for Characterization of Particles, the morphology of tin powder obtained at concentrations of $SnSO_4$ 1 and 3 g/L tends to be spherical or spheroidal-agglomerated red blood cell-like and tends to be more dispersed with a length-to-width ratio of 1.21 and 1.15, respectively. Meanwhile, when the initial concentration of tin sulfate was increased to 27 g/L, the morphology of the tin powder deposit was granular and irregular-rough, with a length-to-width ratio of 1.44. At a lower concentration of tin, the limiting current density of Sn electrodeposition will be lower. With a constant current supply, the lower the limiting
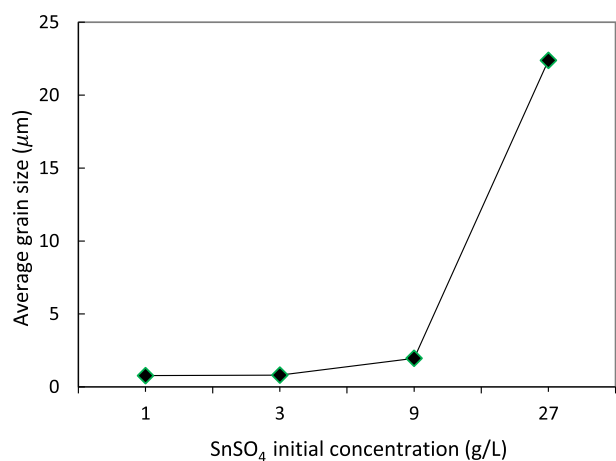
Figure 7. Average particle size of the synthesized tin powder from the electrolysis with various tin concentrations (current density = 1 A/dm^2, electrolysis duration = 10 min, and thiourea/gelatin ratio = 1/4).
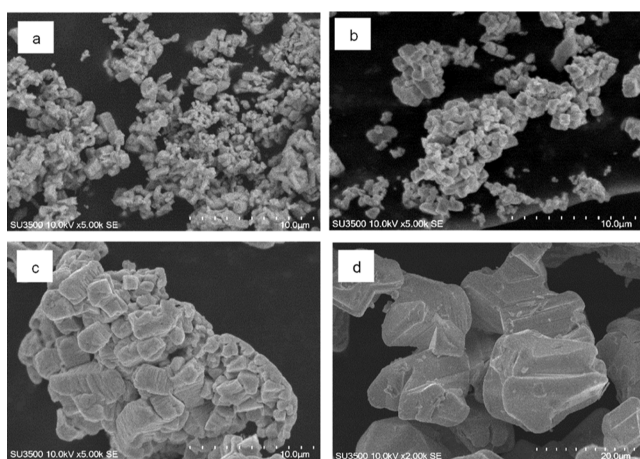

Figure 8. SEM images of tin powder from the electrolysis with the initial SnSO$_4$ concentration (a) 1, (b) 3, (c) 9, and (d) 27 g/L (2000× magnification).

Figure 9. Profile of current efficiency as a function of the initial SnSO$_4$ concentration (current density = 1 A/dm^2, electrolysis duration = 10 min, and thiourea/gelatin ratio = 1/4).

current density value, the more electrodeposition occurs in the region above the limiting diffusion zone.[21] In the area above the limiting diffusion zone, powders with a more dispersed morphology will be produced.[28]

3.3.2. Effect of Tin Concentration on Current Efficiency. The profile of the current efficiency of the electrolysis with variations of the initial SnSO$_4$ concentration is shown in Figure 9. The experiments with variations of the initial SnSO$_4$ concentration were carried out at a current density of 1 A/dm^2, a mass ratio of thiourea/gelatin of 1/4, and an electrolysis time of 10 min. The increase of the initial SnSO$_4$ concentration from 1 to 3 g/L enhanced the current efficiency from 17.99 to 20.78%. Furthermore, when the initial SnSO$_4$ concentration was increased further to 9 and 27 g/L, the current efficiencies were enhanced to 58.95 and 75.71%, respectively. The experimental results demonstrated that the increase in tin concentration in the electrolyte leads to an increase in the current efficiency of the electrolysis. The increase in the initial concentration of SnSO$_4$ ensures the availability of Sn^{2+} ions on the interface of the cathode and electrolyte, thereby reducing the fraction of the electrical current used for hydrogen gas formation from the H$^+$ ions.[29] The current efficiency is lower at t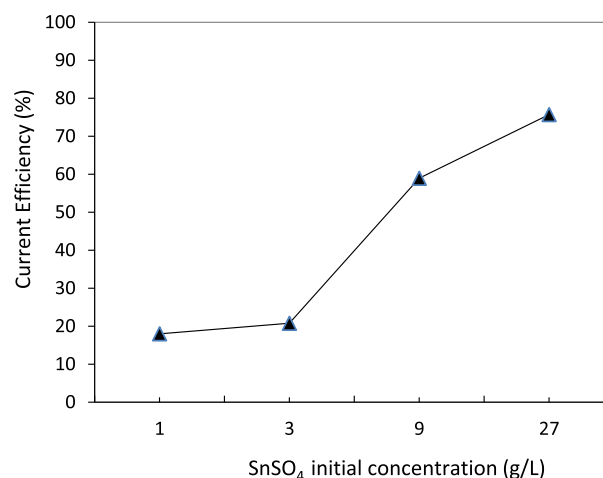he lower tin concentration because more electric current is consumed for the hydrogen gas evolution (i.e., 2H$^+$ + 2e = H$_2$).

The tin deposition takes place at a deposition potential lower than the following equilibrium potential of Sn^{2+}/Sn

$$E_{Sn^{2+}/Sn} = E^{\circ}_{Sn2+/Sn} + 2.303RT/nF\{\log(^a Sn^{2+})\} \qquad (3)$$

Meanwhile, hydrogen gas evolution occurs at a cathode potential lower than the following equilibrium potential of 2H$^+$/H$_2$

$$E_{2H^+/H_2} = E^{\circ}_{2H+/H_2} + 2.303RT/nF\{\log(^a H^+)^2\} \qquad (4)$$

where $^a Sn^{2+}$ and $^a H^+$ are the ionic activity of Sn^{2+} and H$^+$, respectively, E° is the standard reduction potential, R is the ideal gas constant (8.314 J/K/mol), T is the absolute temperature (K), n is the mole number of electrons involved in the electrochemical reaction, and F is the Faraday constant (96,500 C/mol).

Refers to eq 3, at a higher Sn^{2+} concentration, the equilibrium potential of Sn^{2+}/Sn is shifted to a more positive level, thus reducing the overpotential of Sn^{2+} deposition that promotes tin deposition and leads to an increase of current efficiency.

3.4. Effect of the Additives Mass Ratio on the Particle Size and Morphology of the Synthesized Tin Powder. During the electrodeposition process to produce tin powder, thiourea will be adsorbed on the Sn nuclei and form a soluble complex species with Sn^{2+} ions; thus, it will hinder the growth process and reduce the diffusion rate of an adatom on the cathode surface.[17] The low diffusion rate of the adatom on the cathode surface leads to the formation of new nuclei, and the nucleation process is more dominant than the grain growth process.[29] The limitation of the existing grain growth resulted in the tin powder having a smaller grain size.

On the other hand, the gelatin will be adsorbed on the cathode surface, forming an isolation layer, thereby reducing the number of active surfaces for nucleation. The gelatin adsorption on the electrode surface will also change the nucleation mechanism from progressive nucleation to instantaneous nucleation.[19] Instantaneous nucleation occurs at low site density, causing a high nucleation rate and small particle size. Meanwhile, progressive nucleation is the type of nucleation that occurs at high site density, low nucleation rate, and large

particle size will be formed.[18] In addition, when the gelatin concentration is increased, the limiting current density is decreased.[30] Therefore, the higher the gelatin concentration, the smaller the particle size of the synthesized tin powder. A profile of the average tin powder particle size as a function of the mass ratio of thiourea/gelatin is shown in Figure 10.
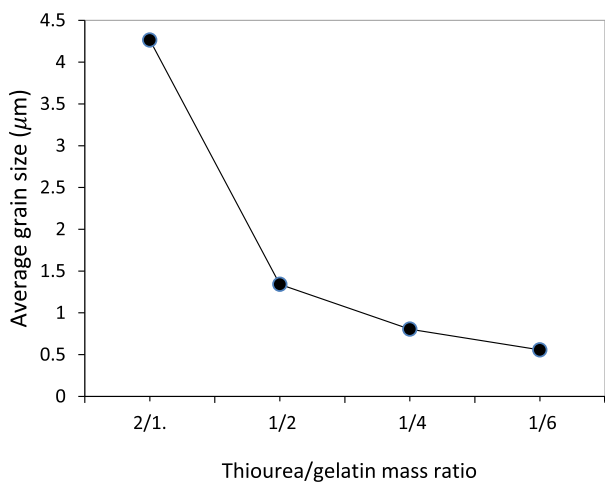
Figure 10. Profile of the average size of the tin particle as a function of the thiourea/gelatin mass ratio (current density = 1 A/dm^2, SnSO$_4$ initial concentration = 3 g/L, and electrolysis duration = 10 min).

The experiments with variations in the additive mass ratio were carried out at the initial SnSO$_4$ concentration of 3 g/L, current density of 1 A/dm^2, and electrolysis time of 10 min. At the lowest mass ratio of thiourea/gelatin of 1/6, the smallest average powder particle size of 0.557 μm was obtained. At the highest mass ratio of thiourea/gelatin of 2/1, the morphology of the powders was lathe-like or needle-like due to insufficient gelatin activity to promote instantaneous nucleation. At this condition, progressive nucleation more predominantly occurs. At higher gelatin dosages, instantaneous nucleation becomes predominant. Under the instantaneous nucleation mechanism, all nucleation sites are activated simultaneously, resulting in a more rounded powder morphology.[17] Therefore, the powders' morphology tends to be spherical or spheroidal-agglomerated red blood cell-like when the mass ratio of thiourea/gelatin is decreased from 2/1 to 1/2, 1/4, and 1/6. The results of this study are in agreement with the results of previous studies conducted by Meudre et al. (2014),[19] which showed that the morphology of tin deposits from the electroplating process tended to have a needle-like morphology when no additive was used, while a rounded and smoother morphology was obtained with the addition of gelatin. The morphologies of tin powder with various additive ratios are shown in Figure 11. It can be concluded that the gelatin acts as a grain refiner in the synthesis of tin powder by the electrolysis method, which modifies the tin powder's nucleation mechanism.

3.5. Effect of Current Density on the Morphology of Tin Powder. SEM images of tin powder deposits from the electrolysis with variations of current density are presented in Figure 12. The SEM image shows that the tin powder morphology obtained at the lowest current density of 0.5 A/dm^2 was in the form of a porous plate. In this condition, the current density has not reached its limiting level. When the current densities were increased to 1 and 2 A/dm^2, a smaller, dispersed deposit was obtained with length-to-width ratios of
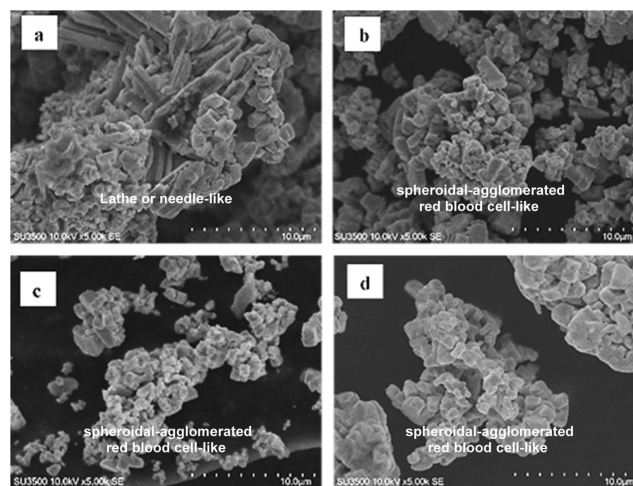

Figure 11. SEM images of tin powder resulted from the electrolysis with various mass ratios of thiourea/gelatin (a) 2/1, (b) 1/2, (c) 1/4, and (d) 1/6 (2000× magnification).
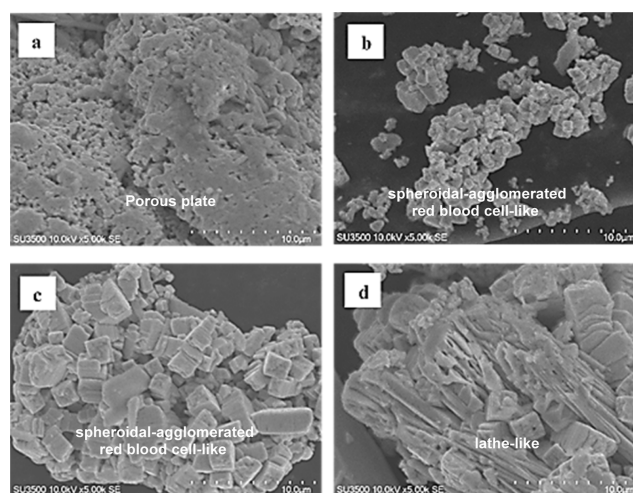

Figure 12. Morphology of tin powder resulting from electrolysis with various current densities of (a) 0.5, (b) 1, (c) 2, and (d) 3 A/dm^2.

1.15 and 1.43, respectively. This indicates that the current density has exceeded its limiting current density in these conditions. The morphology of the synthesized tin powder at the current density of 1 and 2 A/dm^2 tends to be nearly spherical, spherical, or spheroidal-agglomerated red blood cell-like when referring to the type of particle morphology listed in ASTM F1877-05. When the current density was further increased to 3 A/dm^2, the powder morphology tended to be lathe-like with a length-to-width ratio of 3.40. This study's results agree with the results of an experiment conducted by Pavlović et al. (2010).[22] This morphological change is correlated with large numbers of new crystallization centers that will be formed at a high current density, which triggers the growth of deposits to become dendritic. At this condition, there is an increase in the number of growth sites, resulting in a progressive nucleation and the formation of branched deposits.[21] A similar phenomenon was reported by Guo et al. (2022)[31] in the synthesis of Mg(OH)$_2$ powder by electrolytic method, which showed that increasing current density led to agglomeration of the crystal grains, resulting in an increase of the powder's particle size.

3.6. Effect of Electrolysis Time on the Morphology of Tin Powder. SEM images that show the morphologies of the synthesized tin powder obtained by the electrolysis at the variation of electrolysis time are presented in Figure 13.
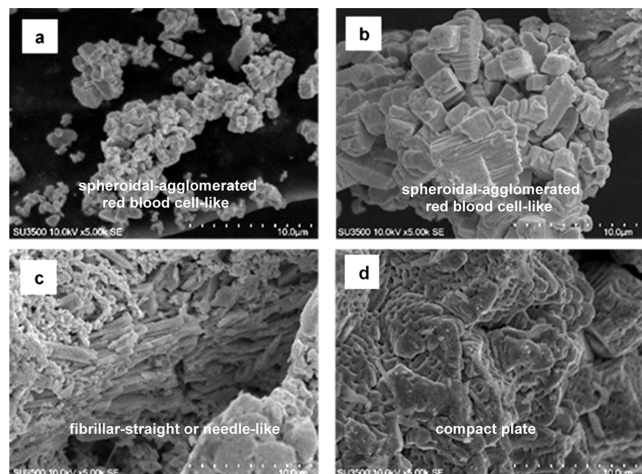

Figure 13. Morphology of tin powder obtained from the electrolysis with various times of (a) 10, (b) 30, (c) 60, and (d) 120 min (2000× magnification).

Shorter electrolysis durations (i.e., 10 and 30 min) resulted in a spherical or spheroidal-agglomerated red blood cell-like structure with length-to-width ratios of 1.15 and 1.42, respectively. As the electrolysis time was further increased to 60 min, the powder morphology changed to fibrillar-straight or needle-like, with a length-to-width ratio of up to 5.55. The change in the tin powder morphology at this condition is due to the formation of new nuclei on the other active surfaces of the deposit, which leads to the formation of dendritic deposits. Furthermore, with the depletion of Sn^{2+} ions at the interface of the cathode−electrolyte, a new crystallization center will form, which triggers the growth disorientation of the deposit and induces the formation of a branch/dendritic deposit. The phenomena of the formation of dendritic deposits due to the formation of new nuclei on the other active surfaces of the metal deposit and the depletion of metal cations in the interface of cathode−electrolyte were also reported by previous researchers.[32,33]

Increasing the duration of electrolysis to 120 min causes the formation of Sn deposits in the form of compact plates. The formation of a compact plate deposit at the electrolysis time of 120 min is due to a decrease in the concentration of adatoms on the cathode surface that leads to the growth of the existing grains rather than the process of forming new nuclei. In addition, the electrolysis time is inversely proportional to the rate of electrocrystallization.[29] As a result, when the electrolysis time reached 120 min, a deposit was in the form of a compact plate with a larger grain size than the shorter electrolysis duration.

It can also be seen from the SEM images in Figure 13 that the increase in electrolysis time causes an increase in the size of a tin powder particle. Based on grain size analysis using ImageJ software, the average grain size of tin powder at 60 min of electrolysis time was 5.014 μm. When the electrolysis time was increased to 120 min, compact plate deposits were obtained with an average grain size of 8.99 μm. The profile of the average particle size as a function of electrolysis duration is shown in Figure 14.
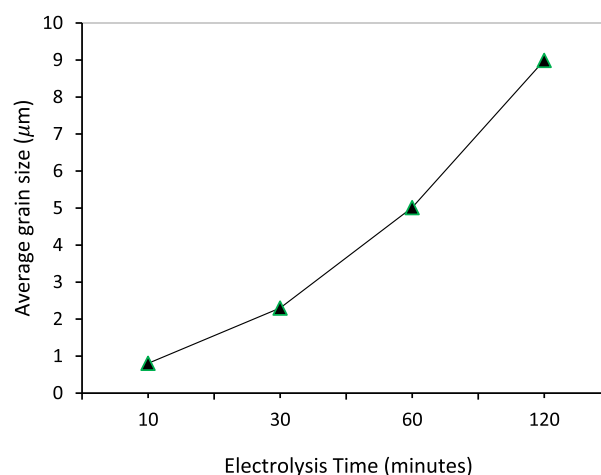

Figure 14. Profile of the average particle size as a function of electrolysis duration (current density = 1 A/dm^2, SnSO$_4$ initial concentration = 3 g/L, and thiourea/gelatin ratio = 1/4).

4. CONCLUSIONS

The present study demonstrated that tin powder could be synthesized by a constant-current electrolysis method from a stannous sulfate electrolyte. The optimum condition of the experiment that resulted in the highest D90 was achieved at an initial concentration of SnSO$_4$ of 3 g/L, a mass ratio of thiourea/gelatin of 1/4, a current density of 1 A/dm^2, and a 10 min electrolysis time. Under this condition, 90% of the tin powder size obtained was smaller than 2.279 μm, showing a rounded or nearly spherical morphology with a length-to-width ratio of 1.15. The synthesized powder has high purity and a low oxygen content of 1.1%. The electrolysis at a lower initial SnSO$_4$ concentration in the range of 1 to 27 g/L resulted in a smaller tin particle with a more spherical and dispersed morphology. Meanwhile, the higher the gelatin concentration in the range of thiourea/gelatin mass ratio 1/6 to 2/1, the size of the obtained powder was getting smaller, and the morphology tended to be more rounded. The increased current density to 3 A/dm^2 resulted in a powder deposit with a length-to-width ratio of 3.40 and a powder with a more branched morphology. The longer the electrolysis time, the smaller the current efficiency due to the increase of hydrogen gas evolution, and the particle size of the synthesized powder was larger. At a current density of 1 A/dm^2 and an initial SnSO$_4$ concentration of 3 g/L, the morphology of the tin powder tends to change from rounded to needle-like when the electrolysis time is longer than 30 min and becomes a compact plate when the electrolysis time is increased from 60 to 120 min.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Lukacs, P.; Rovensky, T.; Otahal, A. A Contribution to Printed Circuit Boards' Miniaturization by the Vertical Embedding of Passive Components. *J. Electron. Packag.* **2024**, *146* (1), 011004.

(2) IPC. *IPC J-STD-005A Joint Industry Standard—Requirements for Soldering Pastes Paperback*; IPC, January 1, 2012.

(3) IPC. *IPC J-STD-006B with Amendments 1 & 2—Requirements for Electronic Grade Solder Alloys and Fluxed and Non-Fluxed Solid Solders for Electronic Soldering Applications*; IPC, January 2006.

(4) Anwar, M. Y.; Khaliq, A.; Ali, A.; Ajmal, M. R.; Butt, T. Z. Production of Tin Powder Using Gas Atomization Process. *J. Facul. Eng. Technol.* **2014**, *21* (1), 159−165.

(5) Lagutkin, S.; Achelis, L.; Sheikhaliev, S.; Uhlenwinkel, V.; Srivastava, V. C. Atomization Process for Metal Powder. *Mater. Sci. Eng., A* **2004**, *383* (1), 1−6.

(6) Nikolic, N. D.; Lovic, J. D.; Maksimovic, V. M.; Živković, P. M. Morphology and Structure of Electrolytically Synthesized Tin Dendritic Nanostructures. *Metals* **2022**, *12*, 1201.

(7) Wahyudi, S.; Soepriyanto, S.; Mubarok, M. Z.; Sutarno. Synthesis and Applications of Copper Nanopowder − A Review. *IOP Conf. Ser.: Mater. Sci. Eng.* **2018**, *395*, 012014.

(8) Chang, I.; Zhao, Y. *Advances in Powder Metallurgy: Properties, Processing, and Applications*; Elsevier, 2013.

(9) Rosyad, S. S.; Mubarok, M. Z. Effect of Pulse Current on Morphology and Crystal Structure of Electrolytic Manganese Dioxide. *AIP Conf. Proc.* **2023**, *2517*, 020017.

(10) Natanson, S. *Colloidal Metals*. Kiev: Akad. Nauk SSSR,1959; pp 302−327.

(11) Khimchenko, Y.; Zhelibo, E.; Kushnir, V. Electrodeposition of Fine Tin Powders. *Poroshk. Metall.* **1975**, *14* (3), 193−195.

(12) Zhelibo, E. P.; Grechanyuk, V. Electrodeposition of Fine Tin Powders From Chloride-Fluoride Electrolytes. *Poroshk. Metall.* **1978**, *17* (7), 497−500.

(13) Popov, K. I.; Pavlović, M. G.; Jovićević, J. N. Morphology of Tin Powder Particles Obtained in Electrodeposition on Copper Cathode by Constant and Square-Wave Pulsating Overpotential from Sn(II) Alkaline Solution. *Hydrometallurgy* **1989**, *23*, 127−137.

(14) Saito, G.; Hosokai, S.; Tsubota, M.; Akiyama, T. Influence of Solution Temperature and Surfactants on Morphologies of Tin Oxide Produced Using a Solution Plasma Technique. *Cryst. Growth Des.* **2012**, *12* (5), 2455−2459.

(15) Saito, G.; Zhu, C.; Akiyama, T. Surfactant-Assisted Synthesis of Sn Nanoparticles via Solution Plasma Technique. *Adv. Powder Technol.* **2014**, *25* (2), 728−732.

(16) Mulyani, R.; Tanjung, Y.; Prajitno, D. Pengaruh Variasi Arus dan Waktu terhadap Pembuatan Serbuk Timah Putih (Sn) melalui Proses Elektrodeposisi. *Jurnal Kartika Kimia* **2019**, *2*, 7−16.

(17) Azpeitia, L. A.; Gervasi, C. A.; Bolzán, A. E. Effects of Temperature and Thiourea Addition on the Electrodeposition of Tin on Glassy Carbon Electrodes in Acid Solutions. *Electrochim. Acta* **2017**, *257*, 388−402.

(18) Scharifker, B.; Mostany, J. Electrochemical Nucleation and Growth. *Encyclopedia of Electrochemistry*; Wiley, 2003; pp 512−539.

(19) Meudre, C.; Ricq, L.; Hihn, J. Y.; Moutarlier, V.; Monnin, A.; Heintz, O. Adsorption of Gelatin during Electrodeposition of Copper and Tin-Copper Alloys from Acid Sulfate Electrolyte. *Surf. Coat. Technol.* **2014**, *252*, 93−101.

(20) Nikolić, N. D.; Branković, G.; Pavlović, M. G. Correlate between Morphology of Powder Particles Obtained by the Different Regimes of Electrolysis and the Quantity of Evolved Hydrogen. *Powder Technol.* **2012**, *221*, 271−277.

(21) Orhan, G.; Hapçı, G. Effect of Electrolysis Parameters on the Morphologies of Copper Powder Obtained in a Rotating Cylinder Electrode Cell. *Powder Technol.* **2010**, *201* (1), 57−63.

(22) Pavlović, M. G.; Pavlović, L. J.; Maksimovic, V. M.; Nikolic, N. D.; Popov, K. I. Characterization and Morphology of Copper Powder Particles as a Function of Different Electrolytic Regimes. *Int. J. Electrochem. Sci.* **2010**, *5* (12), 1862−1878.

(23) Wahyudi, S.; Soperiyanto, S.; Mubarok, M. Z.; Sutarno; Iqbal, M.; Qodratillah, A. T. Investigating The Particle Size Distribution Of Synthesized Copper Powder via Electrodeposition. *J. Eng. Sci. Technol.* **2021**, *16*, 3072−3083.

(24) Nobari, A. H.; Laurent, S. St. Effect of Fine and Ultra-Fine Lead-Free Solder Powder Characteristics on the Reflow Property of Pastes. *Proceedings of SMTA International, Sep. 25−29, 2016, Rosemont, IL, USA*, 2016; pp 327−333.

(25) Yang, K.; El-Haik, B. *Design for Six Sigma: Roadmap to Product Development*, 2nd ed.; McGraw-Hill, 2008.

(26) Wojtaszek, K.; et al. Electrochemical Method of Copper Powder Synthesis on Rotating Electrode in the Presence of Surfactants. *Arch. Metall. Mater.* **2023**, *68*, 375−386.

(27) Nikolić, N. D.; Maksimović, V. M.; Avramović, L. Correlation of Morphology and Crystal Structure of Metal Powders Produced by Electrolysis Processes. *Metals* **2021**, *11* (6), 859.

(28) Walsh, F.; Herron, M. E. Electrocrystallization and Electrochemical Control of Crystal Growth: Fundamental Considerations and Electrodeposition of Metals. *J. Phys. D: Appl. Phys.* **1991**, *24*, 217−225.

(29) Garich, H.; McCrabb, H.; Taylor, E. J.; Inman, M. Controlling Whisker Formation in Tin-Based Solders Using Electrically Mediated Electrodeposition. *ECS Trans.* **2007**, *6* (8), 153.

(30) Wen, S.; Szpunar, J. A. Nucleation and Growth of Tin on Low Carbon Steel. *Electrochim. Acta* **2005**, *50*, 2393−2399.

(31) Guo, L.; Li, Z.; Deng, X.; Chen, N.; Yang, L.; Su, Y.; Wang, X. Effect of Processing Parameters on the Properties of Electrolytically Prepared $Mg(OH)_2$ Powders. *Mater. Res. Express* **2022**, *9* (8), 085504.

(32) Boz, M.; Hasheminiasari, M. The Effect of Process Parameters on Copper Powder Particle Size and Shape Produced by Electrolysis Method. *Steel Compos. Struct.* **2013**, *15*, 151−162.

(33) Pomosov, A. V.; Krymakova, E. E. Effect of Certain Electrolysis Factors on the Current Efficiency and Dispersity of Copper Powder. *Powder Metall. Met. Ceram.* **1962**, *1*, 109−114.