**Effect of Pulse Parameters on The Particle Size of Copper Powder Electrodeposition**

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**Abstract.** In this paper, copper powder fabrication has been made via electrolysis method using CuSO$_4$ and H$_2$SO$_4$ in aqueous media. Electrodeposition process of copper powder on a metallic surface is done by applying to continue current and pulse current with rectangular pulse waveform. Characterization of copper powder was carried out by SEM to confirm particle size and shape and EDX to determine the copper powder composition. In electrodeposition by applying to continue current to produce the copper powder with particle shape was dendritic, and the elemental composition of the powder was Cu and O. Regarding average particle size, pulse electrodeposition process produces the copper powder with average particle size up to 0.85μm, 72.6% smaller than if apply to continue current.

**Keywords:** Copper powder, Electrodeposition, Pulse current, Particle size

**1. Introduction**

Copper is a metal that has excellent optical, electrical and thermal conductivity, magnetic and catalytic properties which in the form of nano-scale powder is widely applied to microdevices, electrical and thermal conductivity, paint, catalyst and lubrication [1,2,3]. Electrolysis is a method that has been commercially applied to produce copper powders. The advantages of copper powder produced by electrolysis method compared with copper oxide reduction method, precipitation, and atomization are high purity, low oxygen content and a wide range of apparent density [4].
The mechanism of the formation of copper powders by electrolysis method occurs on the surface of the cathode under conditions of low copper ion concentrations and high current density than the limiting diffusion current density. Under these conditions, the electrodeposition process of copper powder occurs simultaneously with the evolution of hydrogen gas [4]. The copper powder produced by direct current electrolysis method still produces the powder with dendrite structure and high of particle size. The dendrite structure resembles a tree, which has stems and branches [5]. The dendritic structure formed can result in a non-uniform shape of powder and has a high specific surface area. To control the formation of dendritic structures and reduce the particle size of the powder can be done by shortening the growth time of the nuclei that have been formed. The technique can be applied with a pulse electrolysis [6-10].

In this study, the type of pulse wave applied is a rectangular pulse wave shape, as shown in Figure 1. The regulated pulse parameters are peak cell voltage ($E_p$), frequency ($f$), and duty cycle ($\gamma$) in order to know the pulse on time or pulse time ($T_{on}$), the pulse off time or pause time ($T_{off}$), the period of one cycle of pulse ($\theta$), and average cell voltage ($E_m$).

\begin{align}
  f &= \frac{1}{T_{on} + T_{off}} \quad (1) \\
  \gamma &= \frac{T_{on}}{T_{on} + T_{off}} \quad (2) \\
  \theta &= T_{on} + T_{off} \quad (3) \\
  E_m &= E_p \cdot \frac{T_{on}}{T_{on} + T_{off}} \quad (4)
\end{align}

![Figure 1. Pulse electrolysis with rectangular waveform at 100 Hz of frequency and 50% of duty cycle.](image-url)
By adjusting the pulse parameters, conditions of the morphology and the size of the copper powder particles can be controlled. The reasons are since on the $T_{off}$ condition where there is the relaxation on the interface occurred will allow the replenishment of concentration in the diffusion layer; and electroless adsorption, desorption, and recrystallization reactions on the surface. While on the $T_{on}$ condition will occur nucleation [11].

In this study, the comparison of copper powder produced by direct current electrolysis and pulse electrolysis in order to examine as well as the effect of frequency and duty cycle of the pulse on morphology and the particle size of the resulting powder.

2. Materials and Methods

Electrolyte solution containing CuSO$_4$.5H$_2$O with copper concentration of 0.01 M and an H$_2$SO$_4$ solution with a concentration of 1 M were placed into a single compartment of a two-electrode cell, as is shown in Figure 2. The total volume of the electrolytic bath solution was 100 ml. The anode electrode was a titanium grade 1 metal sheet (25 x 20 mm) and the cathode electrode was a copper 99.99% Cu plate. The deposition was carried out by employing (a) DC power supply and (b) DC-pulse power supply at room temperature (27 ± 1 °C) without stirring.

![Figure 2](image)

**Figure 2.** Schematic of (a) the experimental cell, (b) potentiostatic curve for pulse electrolysis, and (c) potentiostatic curve for DC electrolysis used in the experiment.

The cell voltage for DC electrolysis was 4 Volt. The peak cell voltage for pulse current electrolysis was 4 Volt. The pulsed waveform was rectangular with duty cycle variations of 30%, 50%, and 70% and frequency variations of 100, 1000, and 5000 Hz were used in the investigation. The duration of the deposition was set as 30 s to obtain an amount of powder that was sufficient for use in various analytical examinations. The duty cycle and frequency values as pulse electrolysis parameters with rectangular waveforms will produce different ton and toff values. Summaries of the pulse on time ($T_{on}$), the pulse off time ($T_{off}$), the period of
one cycle of pulse ($\theta$) in pulse electrolysis based on duty cycle and frequency values can be seen in Table 1.

The deposited powder on the cathode was washed slowly and several times using distilled water and then immersed in alcohol immediately. The morphology and composition of the copper powder were determined by using a scanning electron microscope (SEM) and energy-dispersive X-ray analyzer (JEOL Model JED 2300), respectively.

**Table 1.** Summaries of the pulse on time ($T_{on}$), the pulse off time ($T_{off}$), the period of one cycle of pulse ($\theta$) in pulse electrolysis based on duty cycle and frequency values.

| $\gamma$ (%) | $f$ (Hz) | $\theta$ (ms) | $T_{on}$ (ms) | $T_{off}$ (ms) |
|-------------|---------|--------------|--------------|--------------|
| 30          | 100     | 10           | 3            | 7            |
| 30          | 1000    | 1            | 0.3          | 0.7          |
| 30          | 5000    | 0.2          | 0.06         | 0.14         |
| 50          | 100     | 10           | 5            | 5            |
| 70          | 100     | 10           | 7            | 3            |

The particle size analysis of the SEM captured was performed by using ImageJ 1.52a, image-processing program [12]. Each image was converted to binary 8-bit type of image then using threshold adjustment, the contrast was modified under the B&W setting. Next, converted unit of length of image from pixel to micrometer with the ‘scale set’. Check the dialog box of ‘area’ at set measurement to measure the area of selection in square pixels or in calibrated square units ($\mu$m$^2$) if Analyze $\Rightarrow$ Set Scale… was used to spatially calibrate the image. The final step was to utilize the ‘analyze particles’ function then set the show function to ‘mask’ to display the 8–bit binary image containing filled outlines of the measured particles (Fig. 3) and check the dialog box of ‘display result’ to produce the measurements of area ($A$ in $\mu$m$^2$) for each particle.

**Figure 3.** (a) The ImageJ toolbar; (b) Original SEM image and (c) the 8–bit binary image of copper powder.
The result then saves in files with csv format. With the assumption that the shape of particle is circular, the value of particle size \((D \text{ in } \mu\text{m})\) of copper powder can be calculated with the equation below:

\[
D = 2 \cdot \sqrt{A/\pi}
\]  

By using MS Excel, the csv format file of the result can be calculated the average particle size and size distribution of particle size of copper powder.

3. Results and Discussion

During the electrodeposition process of the copper powder, the applied cell voltage was kept constant, and hydrogen gas was formed on the surface of the cathode in addition to copper powder. The effect of duty cycle and frequency variation on pulse electrolysis on the morphology, particle size and size distribution of copper powder will be shown. Then, compared with the copper powder that produced by DC electrolysis.

Figure 4. SEM image of copper powder with different duty cycle (a) 30%; (b) 50%; (c) 70%, in pulse electrolysis comparison with (d) SEM image of copper powder in DC electrolysis. The insert show the higher magnification SEM images of the copper powder structures formed.
3.1. Effects of duty cycle on particle size

Pulse electrodeposition of copper powder with duty cycle variation has been done. Figure 4 shows the results of SEM micrograph of copper powder in each duty cycle variation and Figure 5 shows the average particle size of copper powder in each duty cycle variation. As shown in Figure 4, the structure of copper powder particles decreases with decreasing duty cycle. Details of the shrinking of the copper powder structure are shown in the insert image. The decrease in the average particle size of the copper powder was confirmed by the 'analyze particle' results from ImageJ (Fig.5).

Based on Table 1, at fixed frequency, the pulse off time ($T_{off}$) will be longer if the duty cycle is smaller. $T_{off}$ condition where there is the relaxation on the interface will occur the replenishment of concentration in the diffusion layer; and electroless adsorption, desorption, and recrystallization reactions on the surface [11].

![Figure 5](image_url)

**Figure 5.** Effect of duty cycle on the average particle size of copper powder compared with the average particle size of copper powder produced from DC electrodeposition.

Compared with the results of pulse electrodeposition, it appears that the copper powder structure resulting from DC electrodeposition (Fig. 4.d) is greater. The copper powder produced by direct current electrolysis method still produces the powder with dendrite structure and high of particle size. The dendrite structure resembles a tree, which has stems and branches [5]. The dendritic structure formed can result in a non-uniform shape of the powder and has a high specific surface area. The average particle size of copper powder at 70% duty cycle was successfully decreased by 37.9% from that obtained by DC electrodeposition and decreased by 68.4% in a 30% duty cycle.

Based on Figure 6, the size distribution of copper powder in DC electrodeposition and pulse (at 70% duty cycle) is more fluctuating and has a longer tail than in pulse electrodeposition with duty cycle were 30% and 50%. By lowering the duty cycle it can decrease the particle size and the size distribution becomes more evenly distributed.
Figure 6. Effect of duty cycle on the particle size distribution of copper powder compared with the particle size distribution of copper powder produced from DC electrodeposition.

3.2. Effects of frequency on particle size

Figure 7 shows the SEM micrograph of the copper powder deposits produced from the pulse electrodeposition on the frequency variation. While in Figure 8 shows the average particle size of copper powder. The average particle size of copper powder will decrease as the pulse frequency increases [10].

In this experiment, the average particle size of copper powder decreased from 981 μm at a frequency of 100 Hz to 852 μm at a frequency of 1000 Hz. When pulse on time \( T_{on} \), the higher of frequency will be more often formed new nuclei on the surface of the cathode and the time required for growth becomes smaller. Under the same conditions, when pulse off time \( T_{off} \), is call relaxation time, will also be more frequent so adsorption of copper ion will be more frequent and particle growth more often inhibited. High frequencies can produce high instant overpotential during one pulse cycle so that the nucleation rate can be increased [10,11,13]. Therefore, the growth of the particles is inhibited and the morphology of the dendrite structure diminishes.

However, the average particle size of copper powder at a frequency of 5000 Hz indicates an increase. In the pulse electrodeposition known the transition time. The transition time \( \tau \) is the time needed to switch from the end of the pulse time \( T_{on} \) to the pause time \( T_{off} \) where if the pulse time \( T_{on} \) is shorter than the transition time so the chances of producing an increasing powder subtle still exists because the growth of the deposit starts after the transition time. A dimensionless criterion, \( k = T_{on}/\tau \) has been introduced for the time deposits of the pulse to the transition time in which no new dendrites appear [6].
Figure 7. SEM image of copper powder with different frequency (a) 100 Hz; (b) 1000 Hz; (c) 5000 Hz. The insert show the higher magnification SEM images of the copper powder structures formed.

Figure 8. Effect of pulse frequency on the average particle size of copper powder.
The Sand’s equation [6], the transition time equation in the case of direct current is:

$$I\sqrt{\tau}/S = zFC_0\sqrt{\pi D_0}/2 = \text{constant}$$  \hspace{1cm} (6)

where $I$ is current, $\tau$ is transition time, $S$ is the electrochemically active surface area, $C_0$ is the ion concentration in the solution bulk, $D_0$ is the diffusion coefficient of ions.

As the thickness of the deposit grows, electrochemically the active surface area ($S$) will increase; for $I$ = constant, transition time ($\tau$) will increase for each subsequent pulse [6]. Increasing the size of the copper powder particles occurring at a frequency of 5000 Hz is possible because the transition time is shorter than the pulse time ($T_{off}$).

Based on Figure 9, the size distribution of copper powder at a frequency of 5000 Hz is more fluctuating and has a longer tail, similar to DC electrodoposition. Compared with frequencies 100 Hz and 1000 Hz, by lowering the pulse frequency below 1000 Hz can decrease the particle size and the size distribution becomes more evenly distributed. Current distribution in pulse electrolysis tends to be smoother than in DC. In pulse electrolysis, the $T_{off}$ is the time of interruption where the nucleus growth stops and the concentration of metal ions lead to equilibrium so that it reduces the thickness of the diffusion layer. In addition, there are also the $T_{on}$ that take place very short. This condition limits the growth time of the nucleus. The mechanism of alternating $T_{off}$ and $T_{on}$ in pulses encourages nucleation and limits growth [14, 15].

3.3. Structure and morphology of copper powder

The SEM micrograph of morphological evolution of copper powder produced under the conditions of 0.01 M copper concentration, 1 M of H$_2$SO$_4$, 4 Volt of peak cell voltage at pulse
electrolysis, room temperature, and a 30-sec. in pulse electrodeposition then compared with DC electrodeposition were shown in Figure 10. The morphology of particles exhibited dendritic growth. This could be attributed to the hydrodynamic conditions surrounding the cathode [7]. The dendrite structure of copper powder in DC electrodeposition is the greatest compared to the dendrite structure of copper powder in the pulse.

![Figure 10. SEM of the morphological evolution of copper dendrites in (a-e) pulse electrolysis and (f) DC electrolysis.](image)

To control the formation of dendritic structures and reduce the particle size of the powder can be done by shortening the growth time of the nuclei that have been formed. The technique can be applied with pulse electrodeposition [6-10]. This is in line with the results obtained in this study in which DC electrolysis yields average particle size of 3.11 μm (Fig. 5) whereas in the pulse can effectively decrease average particle size and decrease the size of the copper powder dendrite structure. The average particle size of copper powder from the pulse resulted between 0.85-1.93 μm (Fig. 5 & Fig. 7).

3.4 Chemical composition of copper powder

Figure 11 shows the EDX analysis of the copper powder produced under the same conditions as those described above. EDX analysis shows that the powder comprised copper and a small amount of oxygen. The oxygen may have been produced as a result of environmental moisture oxidation during drying and storage, as oxidation of particles is difficult to control in
these stages [7]. The presence of carbon is attributed to the double-coated conductive carbon tape used to mount the sample.

![EDX analysis of copper powder.](image)

**Figure 11.** EDX analysis of copper powder.

4. Conclusions

Copper powder was prepared by DC electrodeposition in copper sulfate solution without any additives then compared by pulse electrodeposition with different duty cycle and frequency. Duty cycle and frequency on pulse electrodeposition affect the average particle size, size distribution and morphology of copper powder. The average particle size of the copper powder was decreased with decreasing duty cycle and increasing pulse frequency. However, the average particle size of copper powder will reach a minimum point on a certain larger pulse frequency.

The copper powder produced in both methods has a dendritic structure. However, dendritic structure and particle size of copper powder can be controlled by pulse electrodeposition. Regarding average particle size, pulse electrodeposition produces the copper powder with average particle size up to 0.85μm, 72.6% smaller than if apply to continue current.

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