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INVESTIGATING THE PARTICLE SIZE DISTRIBUTION OF SYNTHESIZED COPPER POWDER VIA ELECTRODEPOSITION

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Abstract

This paper describes an investigation into the effects of copper concentration, current density, and time of electrolysis on the particle size distribution and morphology of synthesized copper powder via electrodeposition. Characterization of copper powder was performed using Particle Size Analyzer to determine the size distribution, Scanning Electron Microscope to confirm particle size and shape, and X-Ray Diffraction to determine the phase and structure of copper powder. The result shows that copper powder has a single-phase, specifically Cu with purity of 98.42%, face-centred cubic (FCC) crystal lattice, and dendritic structure with cauliflower-like and corn-like shape particles. Electrolysis experiment at a condition of 0.2 A/cm^2 current density and 0.02 M Cu concentration results in the smallest particle size comprising 0.499 μm at 3 seconds, and the size distribution resembles a normal distribution at 15 minutes.

Keywords: Copper powder, Dendritic, Electrodeposition, Size distribution.

1. Introduction

Copper has high electrical and thermal conductivity, anti-bacterial, corrosion resistance and catalytic properties. For electrical applications, copper is a good alternative material after silver. Copper-based powder metallurgical products have been used as bearings, electrical parts, friction materials, structural materials, brushes, filters, alloying, catalysts, pigments, and paints [1]. Each product requires copper powder with a specific size and shape. The size and shape of particles influence flow and compaction properties.

Copper powder is mainly synthesized via methods of chemical reduction [2, 3], electrochemical [4], atomization [5], laser ablation [6], and the electric explosion of wire [7]. The advantages of copper powder that synthesized via the electrochemical method are environmentally more friendly and economically more competitive [4]. Moreover, this particular process can produce high-purity copper powder [8]. However, the copper powder prepared using an electrochemical method has a varying size and shape of particles, depending on the type and composition of electrolytes, current density, temperature, electrolysis time, presence of additives, and the type of cathode. [9].

To produce finer copper powders, parameters that should be organized are increasing current density, reducing the concentration of copper and limiting electrolysis time to the shortest possible time [9-11]. Parameter settings will affect the formation of the hydrogen gas evolution reaction simultaneously with the electrolysis of copper powder [9, 12, 13]. Anode reaction is copper dissolution:

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e$$

Cathode reactions are copper powder deposition:

$$Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}$$

and hydrogen gas evolution:

$$2H^{+}_{(aq)} + 2e \rightarrow H_{2(g)}$$

Properties of typical commercial grades of copper powders produced by the electrolytic process have been presented [1]. One of the properties listed is the particle size distribution. Particle size distribution was measured by sieve test and Particle Size Analyzer (PSA). The nominal aperture of sieves tests ranges from 20 μm to 200 mm. PSA can measure powder with the smallest size of 10 nm and the largest of 5 mm depending on the type of PSA used. The particle size distribution of copper powder obtained on PSA measurement results mentioned some information including the mean, median, mode, standard deviation or variance, coefficient of variation, distribution point (D10, D50, and D90), skewness, and kurtosis, automatically. Ideally, the particle size results are normally distributed, such as the mean, median, and mode are equal [14].

Skewness and kurtosis are measured to describe the distribution [14, 15]. Skewness is a measure of the lack of symmetry (Fig. 1). Skewness refers to the statistical metric that is used to measure the asymmetry of a probability distribution of random variables about its own mean and its value can be positive, negative, or undefined. Basically, the calculation of skewness equation is done based on the mean of the distribution, the number of variables, and the standard deviation of the distribution. The distribution is in the normal distribution category if the

skewness=0 and mean=median=mode. If the skewness is>0 (positively skewed), the distribution is in the right-skewed distribution category. The right-skewed distribution has an elongated right tail with mean > median > mode. If the skewness is < 0 (negatively skewed), the distribution is in the left-skewed distribution. The left-skewed distribution has an elongated left tail with mean<median<mode.

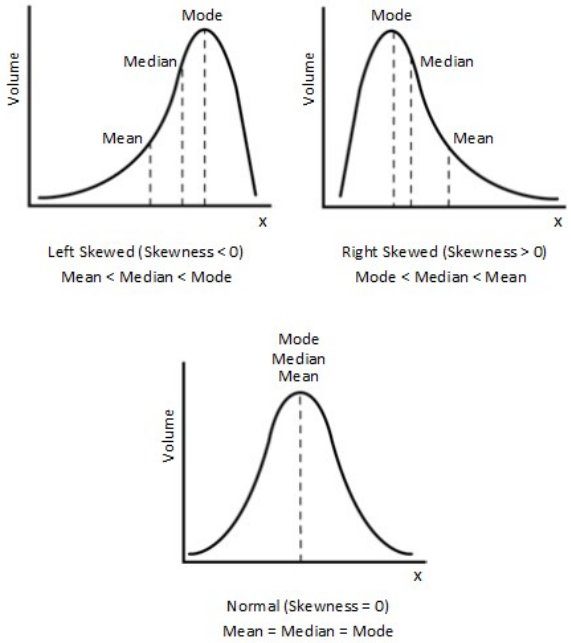

Fig. 1. Examples of Skewness [15].

The particle size distribution with left-skewed distribution would have a long tail at fine-size particles in the distribution. The right-skewed distribution would have a long tail at coarse size particles in the distribution. The skewness value is calculated from Eq. (1) [14]:

$$Skewness = \frac{\sum_{i=1}^{n}(X_i - \bar{X})^3}{(n-1)s^3} \quad (1)$$

where n is the sample size, s is the standard deviation, X_i is the i-th sample value, and $\bar{X}$ is the sample mean.

Kurtosis is a measure of how concentrated the distribution is relative to the mean (Fig. 2). The kurtosis formula [14] is as follow:

$$Kurtosis = \frac{\sum_{i=1}^{n}(X_i - \bar{X})^4}{(n-1)s^4} - 3 \quad (2)$$

There are three categories of kurtosis: mesokurtic, platykurtic, and leptokurtic. All measures of kurtosis are compared against a standard normal distribution. Mesokurtic distribution has kurtosis statistic similar to the normal distribution. A

negative kurtosis represents a platykurtic (or wide) distribution with a more extreme score than expected in the normal. Platykurtic distribution has a broad, flat, and shaped tops like a plateau peak. A positive kurtosis corresponds to a leptokurtic (or narrow) distribution with a fewer score in the tails than in the normal. The peak is very narrow and sharp with most particles having a size close to the mean.

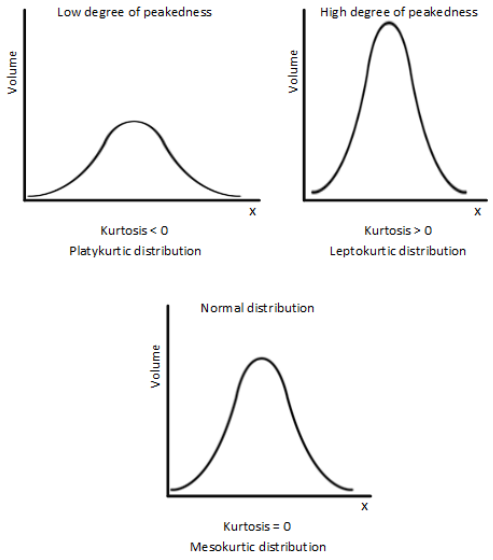

Fig. 2. Examples of Kurtosis [15].

The purpose of this work is to investigate the effects of copper concentration, current density, and electrolysis time on the particle size distribution of copper powder, and evaluate the statistical data on the particle size of copper powder as measured via PSA. The morphology of synthesized copper powder via electrochemical methods was studied, revealing a relationship with particle size. The expected impact of this research is the initiation of the application of electrodeposition techniques to produce the normal distribution of ultra-fine copper powder with the rounded shape.

2. Materials and Methods

Electrolyte solution was prepared by dissolving $CuSO_4.5H_2O$ industrial grade with copper concentration variations of 0.02, and 0.04 M and H_2SO_4 solution industrial grade with a concentration of 1 M and were placed into a single compartment of a two-electrode cell, as presented in Fig. 3. The total volume of the electrolytic bath solution was 1000 ml. The deposition was performed by employing a constant current density and using a stainless steel 316L sheet as the cathode and a copper plate as the anode.

Current densities of 0.1, 0.2, and 0.3 A/cm^2 were used in the investigation, and the electrolyte was maintained at room temperature (27 ± 1 °C). The duration of the deposition was set at 15 min. and 3 sec. Variations in the experimental conditions are presented in Table 1.

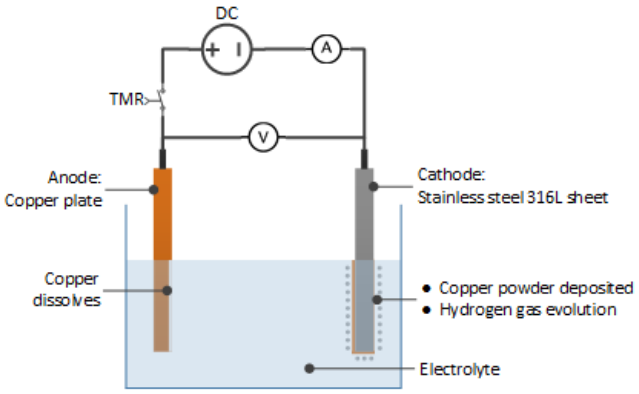

Fig. 3. Schematic of the experimental cell.

An automatic on / off switch timer was installed on the DC power supply output cable that connected to the anode; thus, the electrolysis time of 3 seconds can be reached precisely. The cathode which has been deposited with copper powder is rinsed carefully using distilled water. Then, the powder was removed by scrapping with an ultrasonic vibration in a glass with alcohol inside and then dried in an argon atmosphere at a temperature of up to 100°C. The dried powder then stored in vacuum-sealed plastic. The electrolytically produced powder was compared to the commercially supplied powder 99.99% Cu from Sanno Company. This powder is denoted as Cu-Product reference.

Table 1. Experimental conditions.

Exp. No.	Copper Concentration, M	CD, A/cm^2	Time
1	0.02	0.2	15 min.
2	0.04	0.2	15 min.
3	0.02	0.1	15 min.
4	0.02	0.3	15 min.
5	0.02	0.2	3 sec.

Phase characterization of copper powders was determined by X-Ray Diffraction (XRD) Rigaku SmartLab using CuKα radiation at the scan rate of 0.01 °/min. The particle size analysis was performed using a Beckman Coulter LS 13-320 Particle Size Analyzer (PSA). The morphology and composition of the copper powder were determined by using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) analyser JEOL Model JED 2300, respectively.

3. Results and Discussion

Copper powders can be produced by electrolysis at a higher current density than the limiting current density [9-11]. The determination of the applied current density in this study was based on the results of our previous investigation [16] where the potentiodynamic cathodic polarization at 0.075 M Cu^{2+} has 60 mA/cm^2 of limiting current density. The electrolysis times were set for 3 seconds and 15 minutes. The electrolysis time of 3 seconds and 15 minutes were set to determine the shape and growth of the dendrite precursor. The reaction that takes place on the surface of the cathode is the reaction of copper deposition and simultaneously occurs with the

reaction of hydrogen gas evolution. The higher current density and the lower Cu concentration enhanced the generated hydrogen gas evolution. These conditions affect the particle size distribution and morphology of copper powders.

3.1. Particle size distribution

Figure 4 and Table 2 show the result of PSA measurement of synthesized copper powder with varied parameters, which include copper concentration, current density, and electrolysis time. The data presented are mean, median, mode, standard deviation, skewness and kurtosis of copper powder. The particle size distribution curve and SEM image of particles are presented in Fig. 5.

Figure 4 shows the decrease in average particle size as Cu concentration decreases, current density increases and electrolysis time decreases. Micron-scale particle size in the range of 62.42-86.62 µm was obtained at the time of electrolysis of 15 minutes (experiment no. 1-4). Finer particle size of 0.499 µm was achieved at the time of electrolysis of 3 seconds (experiment no. 5). Lower Cu concentrations can reduce limiting current density [9]. Increasing the current density value that exceeds the limiting current density will increase the hydrogen gas evolution [9, 11, 13]. Meanwhile, the shorter electrolysis time will limit the growth of the nucleus.

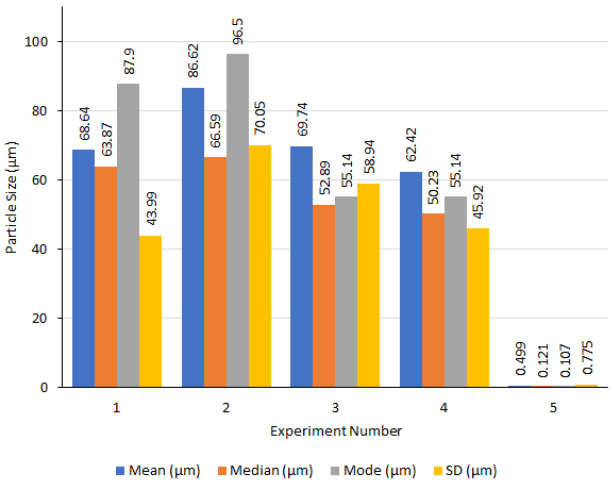

Fig. 4. Resume of PSA of copper powder for each experiment.

Table 2. Skewness and kurtosis of copper powder for each experiment.

Exp. No.	Skewness	Category	Kurtosis	Category
1	0.531	Right	-0.358	Platykurtic
2	1.055	Right	0.465	Leptokurtic
3	2.023	Right	7.365	Leptokurtic
4	1.096	Right	0.781	Leptokurtic
5	1.573	Right	0.661	Leptokurtic

Skewness and kurtosis are measured to describe the distribution [14, 15, 17]. All skewness shows a value greater than 0 and is included in the right-skewed category. Experiment no. 2-5 has skewness>1, which means that the particle size distribution of copper powder is in the highly skewed category [17]. In increasing

the skewness value, the particle size distribution of copper powder will have a longer tail on coarse particles. Meanwhile, skewness in experiment no. 1 is 0.531 and has the moderately skewed category. The particle size distribution of copper powder in experiment no. 1 is closer to the normal distribution.

Table 2 shows that experiments no. 2-5 have kurtosis>0 and are categorized as leptokurtic, while experiment no. 1 has kurtosis<0 and it categorized as platykurtic. Moreover, when compared, the particle size distribution of copper powder from the experiment no. 1 has kurtosis which is closer to the normal distribution as shown in Fig. 5(a), while that from in experiment no. 3 has the largest kurtosis which has the longest tail in size distribution as shown in Fig. 5(c). Under these conditions, the particle size distribution of copper powder will have higher skewness and kurtosis values at low current densities.

Figure 5 (e) shows the bimodal mode distribution resulted from the electrolysis process for 3 seconds. The two modes of particle size are 0.102 μm and 1.831 μm. In contrast to the 15 minute experiment, the 3 second electrolysis experiment produced particles with a bimodal distribution; therefore, sieving techniques (screening) is needed to obtain a more uniform particle size [18].

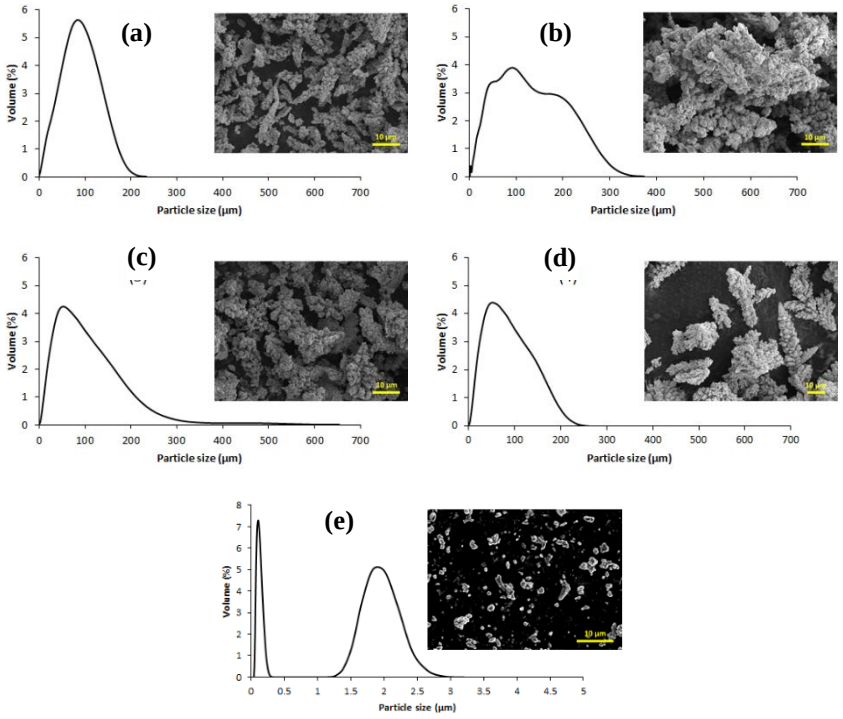

Fig. 5. Particle size distribution curve and SEM image of copper powder for experiment no. (a) 1; (b) 2; (c) 3; (d) 4; and (e) 5.

3.2. Morphology of copper powder

Figure 6 shows the morphology of the copper powders produced from the experimental conditions in Table 1. Figures 6(a), 6(c), 6(d), and 6(e) present the

particles of copper powder from experiment no. 1, 3, 4 and 5. The synthesized copper powder from experiment no. 1, 3, 4, and 5 show the globular dendritic. While in Fig. 6(b) that represent of experiment no. 2, the particle shape is polycrystalline face. Polycrystalline face-shaped particles are the hallmark of a controlled activation-diffusion [11] process in which crystal growth occurs by time. Dendritic structures with globular particles are typical characteristic of electrodeposit obtained from electrolytic deposition controlled by diffusion [11].

Decreasing Cu concentration tends to reduce the limiting current density. Thus, at the same current density, which is 0.2 A/cm^2, the hydrogen gas evolution at a concentration of Cu 0.02 M is stronger than that occurs at the concentration Cu of 0.04 M. The increase of hydrogen gas evolution causes the diffusion-controlled part to increase that leads to the formation of dendritic structure.

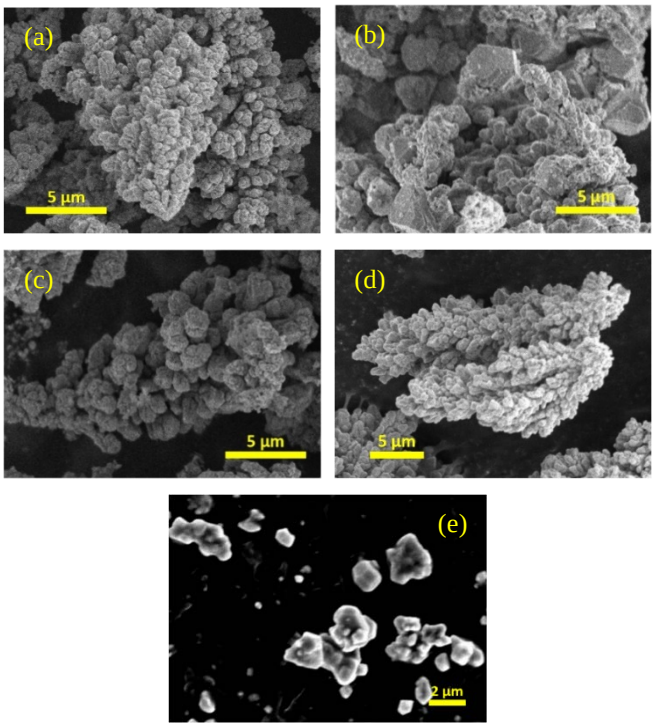

Fig. 6. Morphology of copper powder obtained from the experiment no. (a) 1; (b) 2; (c) 3; (d) 4; and (e) 5.

Figures 6(a), 6(c) and 6(d) show copper powders from the experiments with current density variations of 0.2 A/cm^2, 0.1 A/cm^2, and 0.3 A/cm^2. The particle morphology at a current density of 0.3 A/cm^2 shows more dendrites with cauliflower-like shape, whereas at the current density 0.1 A/cm^2, it shows larger particles. The increase of current density will increase the hydrogen gas evolution and cause the diffusion-controlled portion to increase; therefore, the deposit obtained tends to be more dendritic and the particle size will be smaller [11].

Figure 6(e) shows the copper powder produced at 0.04 M of Cu concentration, 0.2 A/cm^2 of current density and 3 seconds of electrolysis time. The particle

morphology at the electrolysis time for 3 seconds has produced dendrite precursors like cauliflower and very fine grain. The results obtained indicate that there is a growth of the existing deposit and the formation of new nuclei [13]. Compared to the morphology of copper powder obtained from 15 minutes of electrolysis time, the granules shape has similarities to the granules in the dendrite precursor. The globular of these cauliflower-like and corn-like shape was attributed to the spherical shape of the diffusion layer [19].

3.3. Characterization of copper powder

The composition of copper powder that dried in inert argon atmosphere was measured by EDX analysis. The EDX analysis results are shown in Fig. 7. Based on the EDX test results it is comprehended that the copper purity level is reaching up to 98.42%. The presence of oxygen is due to copper powder have been oxidized during storage while waiting for the analysis.

Figures 8(a) and 8(b) present the XRD pattern for copper powders obtained from the experiment no. 1 which was that dried in the argon atmosphere (Cu-Argon) and product reference copper powders (Cu-Product reference). Regarding the copper standard data (Cu-04-0836), it is shown that the Cu-Argon and the Cu-Product reference shows a similarity of diffraction pattern that has the peak at the same 2θ angle of 43.3° and 50.4° respectively. The crystal plane at these angles are (111) and (200). Under these conditions, the copper powder have the similar orientation of crystalline structure. The crystal has a structure of face-centred cubic (FCC).

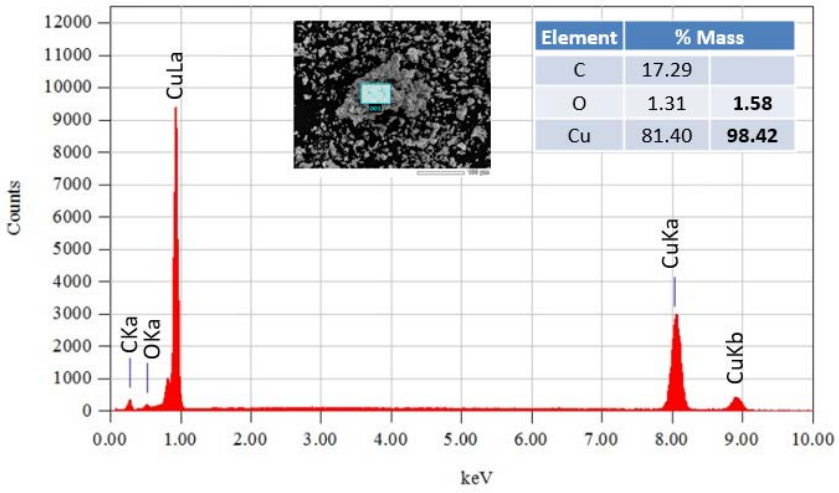

Fig. 7. Copper powder composition.

The comparison of particle size of copper powder in Cu-Argon and Cu-Product references can be analysed based on the peak intensity ratio (111)/(200) [9]. Table 3 shows the intensity ratio of Cu-Argon powder and Cu-Product reference which is almost the same. These conditions indicate that the particle size of the Cu-Argon is almost the same as Cu-Product reference. However, compared with the intensity ratio of Cu-04-0836, it appears that the particle size of Cu-Argon powder and Cu-Product reference are coarser than Cu-04-0836.

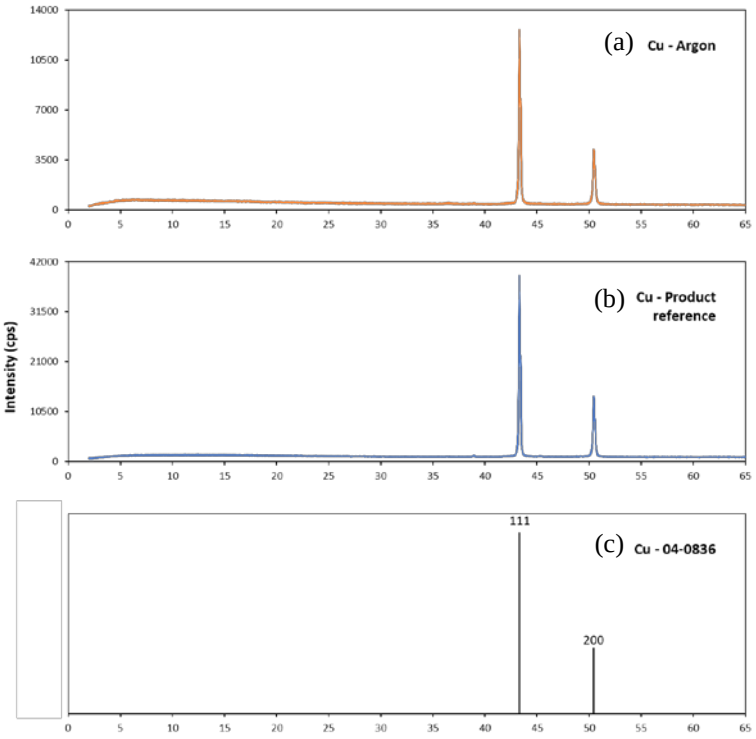

Fig. 8. XRD patterns of Cu particles obtained at (a) Cu-Argon; (b) Cu-Product reference; and (c) standard Cu-04-0836.

Table 3. The intensity ratio of diffraction peaks.

Type of Cu powder	Intensity ratio (111)/(200)
Cu-Argon	2.9
Cu-Product reference	2.8
Cu-04-0836	2.2

4. Conclusions

It can be concluded that Cu concentration, current density and electrolysis time affect the particle size distribution and morphology of electrolytically synthesized copper powder. The particle size distribution of copper powder most resembled a normal distribution curve under the conditions of a 0.2 A/cm^2 current density, 0.02 M Cu concentration and 15 minutes of electrolysis time. Additionally, the smallest particle size was measured as 0.499 μm for 3 seconds of electrolysis time. The particle morphology of copper powder has a dendritic structure with globular and polycrystalline-face shape. Synthesized copper powder has 98.42% Cu, a single-phase Cu and a face-centred cubic (FCC) crystal structure.

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References

1. Naboychenko, S.S.; Murashova, I.B.; and Neikov, O.D. (2009). *Handbook of non-ferrous metal powders: technologies and applications* (1st ed.). United Kingdom: Elsevier Ltd.
2. Khan, A.; Rashid, A.; Younas, A.; and Chong, R. (2016). A chemical reduction approach to the synthesis of copper nanoparticles. *International Nano Letters*, 6, 21-26.
3. Xiong, J.; Wang, Y.; Xue, Q.; and Wu, X. (2011). Synthesis of highly stable dispersions of nanosized copper particles using l-ascorbic acid. *Green Chemistry*, 13(4), 900-904.
4. Kadam, S.L. (2016). Synthesis and characterization of copper nanoparticles by using electrochemical method. *International Journal of Scientific & Engineering Research (IJSER)*, 7(11), 1067-1069.
5. Karibyan, A.N.; Medvedovskii, A.B.; Belyakov, V.A.; Sarkisyan, N.S.; Dyuzhakova, N.G.; Nichiporenko, O.S.; Aivazyan, V.T.; Poteshkina, V.P.; and Naida, Y.I. (1981). Atomized copper powders. *Soviet Powder Metallurgy and Metal Ceramics*, 20, 316-319.
6. Moniri, S.; Ghoranneviss, M.; Hantehzadeh, M.R.; and Asadabad, M.A. (2017). Synthesis and optical characterization of copper nanoparticles prepared by laser ablation. *Bulletin of Materials Science*, 40, 37-43.
7. Dash, P.K.; and Balto, Y. (2011). Generation of nano-copper particles through wire explosion method and its characterization. *Research Journal of Nanoscience and Nanotechnology*, 1(1), 25-33.
8. Boz, M.; and Hasheminiasari, M. (2013). The effect of process parameters on copper powder particle size and shape produced by electrolysis method. *Steel and Composite Structures*, 15(2), 151-162.
9. Avramovic, L.; Maksimovic, V.M.; Bascarevic, Z.; Ignjatovic, N.; Bugarin, M.; Arkovic, R.; and Nikoli, N.D. (2019). Influence of the shape of copper powder particles on the crystal structure and some decisive characteristics of the metal powders. *Metals*, 9(1), 1-15.
10. Nekouei, R.K.; Rashchi, F.; and Amadeh, A.A. (2013). Using design of experiments in synthesis of ultra-fine copper particles by electrolysis. *Powder Technology*, 237, 554-561.
11. Pavlovic, M.G.; Pavlovic, L.J.; Maksimovic, V.M.; Nikolic, N.D.; and Popov, K.I. (2010). Characterization and morphology of copper powder particles as a function of different electrolytic regimes. *International Journal of Electrochemical Science*, 5(12), 1862-1878.
12. Popov, K.I.; and Pavlovic, M.G. (1993). *Modern aspects of electrochemistry*. United State of America: Plenum Press.
13. Nikolic, N.D.; and Popov, K.I. (2012). *Electrochemical production of metal powders*. New York: Springer.
14. Rindskopf, D.M.; and Shiyko, M.P. (2010). *International encyclopaedia of education*, (3rd ed.). Oxford: Elsevier Ltd.
15. Wolfrom, R.L. (2011). The language of particle size. *Journal of GXP Compliance*, 15(2), 10-20.

16. Mubarok, M.Z.; Aji, N.L.; and Wahyudi, S. (2017). Sintesis serbuk tembaga dengan metode elektrolisis: Studi perilaku elektrokimia dan karakterisasi serbuk. *Conference: Seminar Nasional Metalurgi dan Material (SENAMM) X-2017*. Semarang, Indonesia, 623-632.
17. Bulmer, M.G. (1979). *Principles of statistics*. United State of America: Dover Publications.
18. Zhang, K.; Chanpura, R.A.; Mondal, S.; Wu, C.H.; Sharma, M.M.; Ayoub, J.A.; and Parlar, M. (2015). *SPE Drilling & Completion*, 30(02), 164-174.
19. Popov, K.I.; Zivkovic, P.M.; and Nikolic, N.D. (2016). Electrochemical aspects of formation of dendrites. *Zastita Materijala*, 5(1), 55-62.