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ORIGINAL PAPER

Effect of electrolyte characteristics on electrowinning of copper powder

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Abstract This paper is concerned with studying the effect of electrolyte characteristics on the production process of electrolytic copper powder from partially depleted Cu containing synthetic electrolytes by electrowinning technique. The main electrolyte characteristics are temperature, circulation rate, Cu and H_2SO_4 concentrations, residence time in the cell, and utilization of organic bath additives. The process is positively affected by increasing the values of all of the studied parameters except for the addition of organic bath additives, which causes a negative effect. However addition of organic bath additives remarkably increases the degree of refinement of the produced powders. In most cases pure and fine copper powders were obtained with a dendritic shape, as indicated by scanning electron microscope (SEM) analysis.

Keywords Electrolytic copper powder · Electrolyte characteristics · Electrowinning · Powder metallurgy · Electrometallurgy

1 Introduction

Electrolyte characteristics are considered some of the main important parameters affecting the production process of metals or metal powders by both electrowinning and electrorefining techniques [1–13]. To date, the literature does not include any publications that directly report the effect of these conditions on electrowinning process of copper powder production and also on the quality of the produced powders. The main important electrolyte characteristics can be summarized as: electrolyte temperature, electrolyte circulation rate, electrolyte Cu and H_2SO_4 concentrations, electrolyte residence time in the cell, and addition of organic materials. In this work, these electrolyte characteristics have been extensively studied using an electrolytic cell which consists of pure lead plates as inert anodes and aluminum sheets as permanent starting cathodes. In a previous study, I have shown that aluminum sheets are the best candidate cathode material [14]. Scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) analyses were utilized to identify the composition and microstructure of the electrodeposited copper powders.

2 Experimental details

2.1 Materials

Pure lead plates (90 × 90 × 10 mm^3) were used as inert anodes [15]. Pure aluminum sheets (100 × 100 × 3 mm^3) were used as permanent starting cathodes. An organic polyvinylpyrrolidone K90 was used as the bath additive [8]. All the chemicals used for electrolyte preparation (pure Cu sulfates and 96% conc. H_2SO_4), organic additives, and chemical analysis were analytical-grade reagents obtained from FLUKA Company, Austria.

2.2 Experimental apparatus and procedure

Figure 1 shows schematic illustration of the experimental setup used in different experiments. In this setup two cells were used. Each cell consisted of a 5 dm^3 glass beaker. The

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two cells were connected to a 20 dm^3 excess electrolyte Plexiglas container which was used to supply the electrolyte and maintain a constant Cu concentration in the electrolyte by gradual addition of copper sulfate. Two tube electrolyte pumps (Watson Marlow, USA) were positioned between each glass beaker and the 20 dm^3 container for recirculating the used electrolyte and to ensure the homogenization of Cu ions in the electrolyte solution. Two hot plates (RCT basic IKA WERKE, Germany) with magnetic stirrers were used to heat and agitate the electrolyte before and during the experiment. An electrorotator was used in the 20 dm^3 container to agitate the electrolyte and help in the dissolving of the added Cu sulfate powders.

All experiments were carried out at constant current density (1,000 A m^{-2}) using a constant direct-current supplier (power supply EA-PS 9018-100, Germany). The output cell voltage was recorded using a digital DAQ Rack with DASYLAB-V 8.00.00 computer software (measuring level up to 10 V, ±0.5% error range).

At the beginning of each experiment the concentration of Cu and H_2SO_4 in electrolyte must be adapted to a constant level by the addition of some copper sulfates and dilution of sulfuric acid concentration by the addition of distilled water. During the experiment, precalculated amount of copper sulfates is gradually added into 20 dm^3 electrolyte container to keep a constant concentration of Cu ions in the electrolyte solution.

At the end of the experiment the electrodeposited copper powder were extensively washed with water, dried, weighed, and analyzed. Scanning electron microscope (FEI QUANTA 200, USA) with energy-dispersive X-ray analysis was used to investigate the particle shape and produced powder.

3 Results and discussion

3.1 Effect of electrolyte temperature

Table 1 and Fig. 2 show that increasing electrolyte temperature from 35°C to 65°C increases the efficiency of the process from 76.39% to 102.24% and consequently

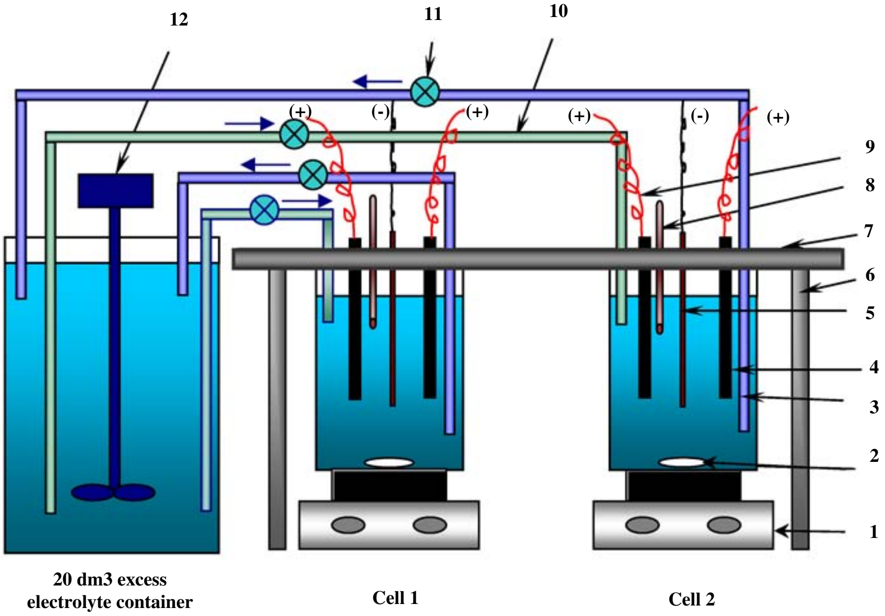


Fig. 1 Schematic representation of the used experimental setup. (1) Heater with a magnetic rotator; (2) Magnetic stirrer; (3) Electrolyte outlet; (4) Anode 1 (+); (5) Cathode (−); (6) Steel stand; (7) PVC cell cover; (8) Thermometer; (9) Anode 2 (+); (10) Electrolyte inlet; (11) Electrolyte pump; (12) Electro rotator

Table 1 Effect of electrolyte temperature on electrowinning of copper powder

Electrolyte temperature (°C)	Duration (h)	Average cell voltage (V)	Cathodic deposition (g)	Cathodic current efficiency (%)	Sp. energy demand (kWh kg^{-1})	Space/time yield (kg m^{-3} d^{-1})	Productivity (g A^{-1} h^{-1})
35	4.22	2.853	65	76.39	3.148	2.906	0.906
50	4.22	2.729	81	95.19	2.417	3.622	1.129
65	4.22	2.430	87	102.24	2.003	3.890	1.213

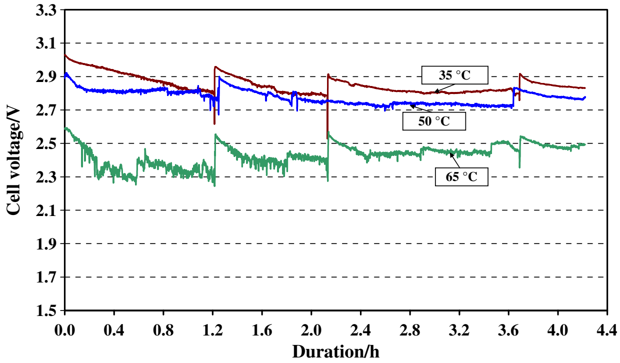


Fig. 2 Effect of electrolyte temperature on electrowinning of copper powder from a synthetic electrolyte with initial concentration of 15 g dm^{-3} Cu and 150 g dm^{-3} H_2SO_4 at 3.37 dm^3 h^{-1} electrolyte circulation rate

decreases the energy demand from 3.148 to 2.003 kWh kg^{-1} Cu powder. This can be attributed to the decrease of electrolyte viscosity and consequent increase of ions diffusion through the electrolyte bath, which reduces the concentration polarization and consequently decreases the cell voltage (lower energy demand). An increase of the cathodic current efficiency by more than 100% was obtained and can be attributed to the effect of cementation phenomenon of Cu on Al cathode sheets as shown in reaction 1 [16, 17].

$$Cu^{2+} + 2/3Al = Cu + 2/3Al^{3+}. \qquad (1)$$

The deposited copper powders at different temperatures are highly pure, as indicated by EDX analysis, with a dendritic structure as always obtained from electrowinning technique [11, 18, 19]. The particle size of the produced powders is finer with increase of the electrolyte temperature, as shown in Fig. 3.

3.2 Effect of electrolyte circulation rate

Electrolyte circulation rate has a moderate effect on the efficiency of the electrowinning process where the cathodic current efficiency is increased from 100.2% to 105.8% with the increase of the circulation rate from 3.37 to 6.92 dm^3 h^{-1}. At the same time, the required energy decreased from 2.078 to 1.976 kWh kg^{-1} (Table 2 and Fig. 4). This can be due to the enhancement of Cu ions transfer from the bulk solution to the cathode surface and also to the decrease of concentration polarization, which

Fig. 3 SEM micrographs of polished copper powder sample electrowon from a synthetic electrolyte with an initial concentration of 15 g dm^{-3} Cu and 150 g dm^{-3} H_2SO_4 and 3.37 dm^3 h^{-1} electrolyte circulation rate at different temperatures

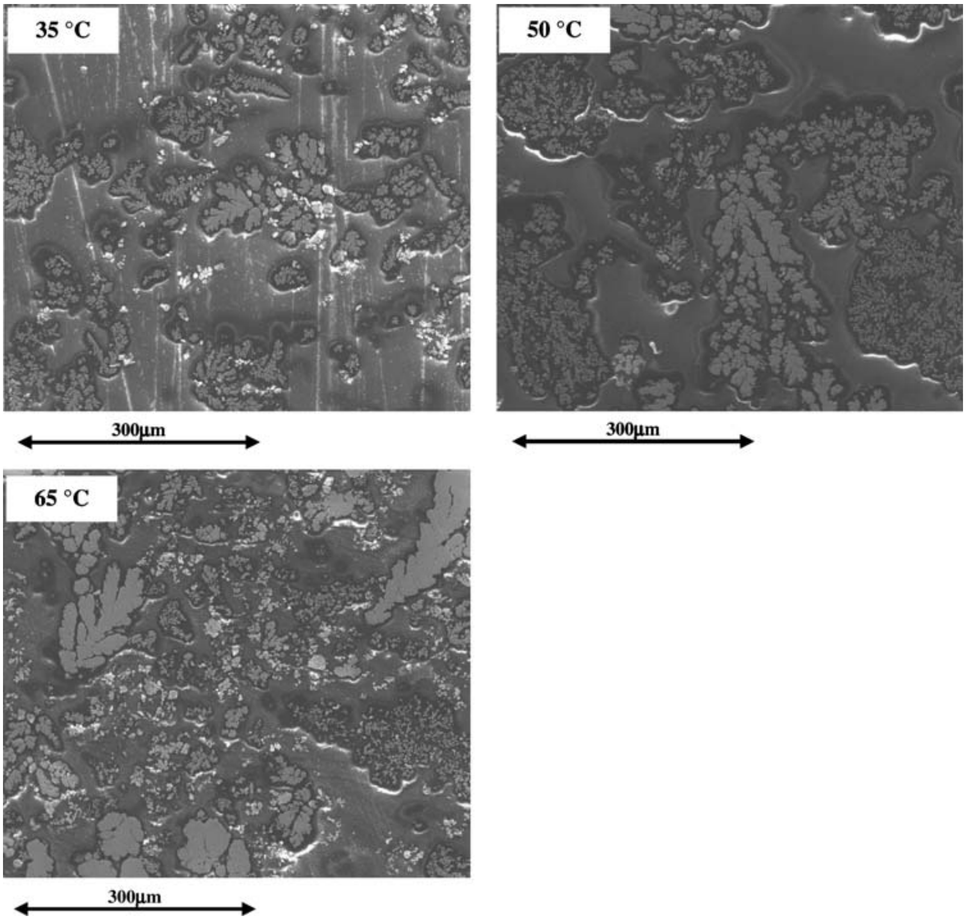


Table 2 Effect of electrolyte circulation rate on electrowinning of copper powder

Circulation rate ($dm^3\ h^{-1}$)	Duration (h)	Average cell voltage (V)	Cathodic deposition (g)	Cathodic current efficiency (%)	Sp. energy demand ($kWh\ kg^{-1}$)	Space/time yield ($kg\ m^{-3}\ d^{-1}$)	Productivity ($g\ A^{-1}\ h^{-1}$)
3.37	4.947	2.4710	100	100.23	2.078	3.813	1.189
6.92	4.874	2.4798	104	105.80	1.976	4.025	1.255

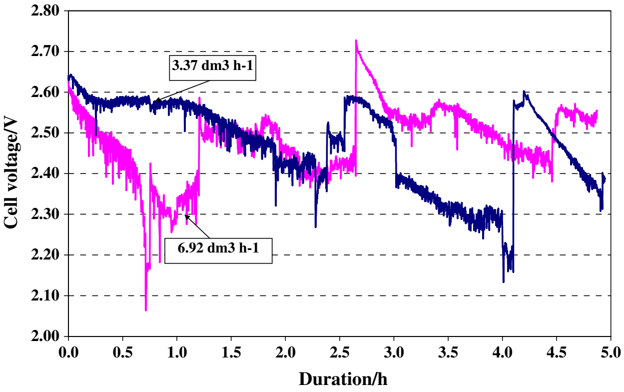


Fig. 4 Effect of electrolyte circulation rate on electrowinning of copper powder from a synthetic electrolyte with an initial concentration of 15 g dm^{-3} Cu and 150 g dm^{-3} H_2SO_4 at 50°C electrolyte temperature

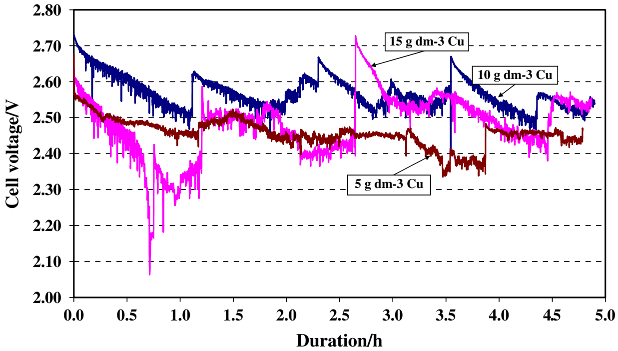


Fig. 6 Effect of electrolyte Cu concentration on electrowinning of copper powder from a synthetic electrolyte with an initial concentration of 150 g dm^{-3} H_2SO_4 at 50°C electrolyte temperature and 6.92 $dm^3\ h^{-1}$ electrolyte circulation rate

subsequently decreases the specific energy required. Circulation rate higher than 6.92 $dm^3\ h^{-1}$ may cause strong agitation of the deposited powders, which become separated to float in the electrolyte bath and cause a short circuit between anode and cathode, besides increasing electrolyte viscosity. In contrast, decreasing the circulation rate to levels lower than 3.37 $dm^3\ h^{-1}$ may cause a slowing of convection and diffusion of ions to the cathode surface and consequently decrease the rate of deposition.

SEM micrographs (Fig. 5) indicate that there is no obvious difference in the size of Cu particles deposited at the mentioned circulation rates.

3.3 Effect of electrolyte copper concentration

Figure 6 and Table 3 show that the best starting copper concentration in electrolyte is 15 g dm^{-3}, for which the resulting efficiency is better than those obtained when

Fig. 5 SEM micrographs of copper powder electrowon from a synthetic electrolyte with an initial concentration of 15 g dm^{-3} Cu and 150 g dm^{-3} H_2SO_4 and 50°C electrolyte temperature at different electrolyte circulation rates

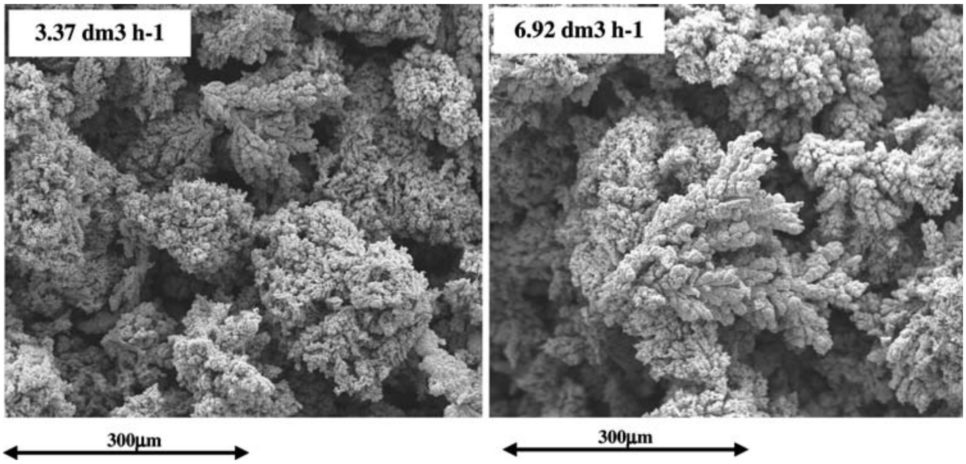


Table 3 Effect of electrolyte copper concentration on electrowinning of copper powder

Copper concentration ($g\ dm^{-3}$)	Duration (h)	Average cell voltage (V)	Cathodic deposition (g)	Cathodic current efficiency (%)	Sp. energy demand ($kWh\ kg^{-1}$)	Space/time yield ($kg\ m^{-3}\ d^{-1}$)	Productivity ($g\ A^{-1}\ h^{-1}$)
5	4.786	2.4566	69	71.48	2.897	2.719	0.848
10	4.900	2.5681	89	90.06	2.404	3.426	1.068
15	4.874	2.4798	104	105.80	1.976	4.025	1.255

using other concentrations (5 and 10 g dm^{-3}). Also the specific energy demand is lower at higher concentration of Cu, with better powder productivity and better space/time yield. The explanation for this can be that increasing the Cu ion concentration in the electrolyte will feed a sufficient and constant amount of Cu^{2+} to the cathode surface, which improves the deposition rate and consequently the efficiency as well as other parameters. Another effect of increasing the Cu^{2+} concentration is the decrease of concentration polarization and the accompanying decrease of H_2 overvoltage [20]. An increase of Cu concentration to more than 15 g dm^{-3} causes deposition of coarse copper particles, whereas a decrease of copper concentration below 5 g dm^{-3} causes an increase in H_2 evolution and consequently the cell voltage and the required electrical energy, besides the bad effect of sulfuric acid mist.

As indicated by EDX and SEM (Fig. 7), pure and fine copper powders were produced from all electrolytes containing different concentrations of Cu ions. The dendritic shape of powders deposited from electrolyte containing 15 g dm^{-3} Cu is distinguishable from the other powders deposited from electrolytes containing lower Cu concentrations.

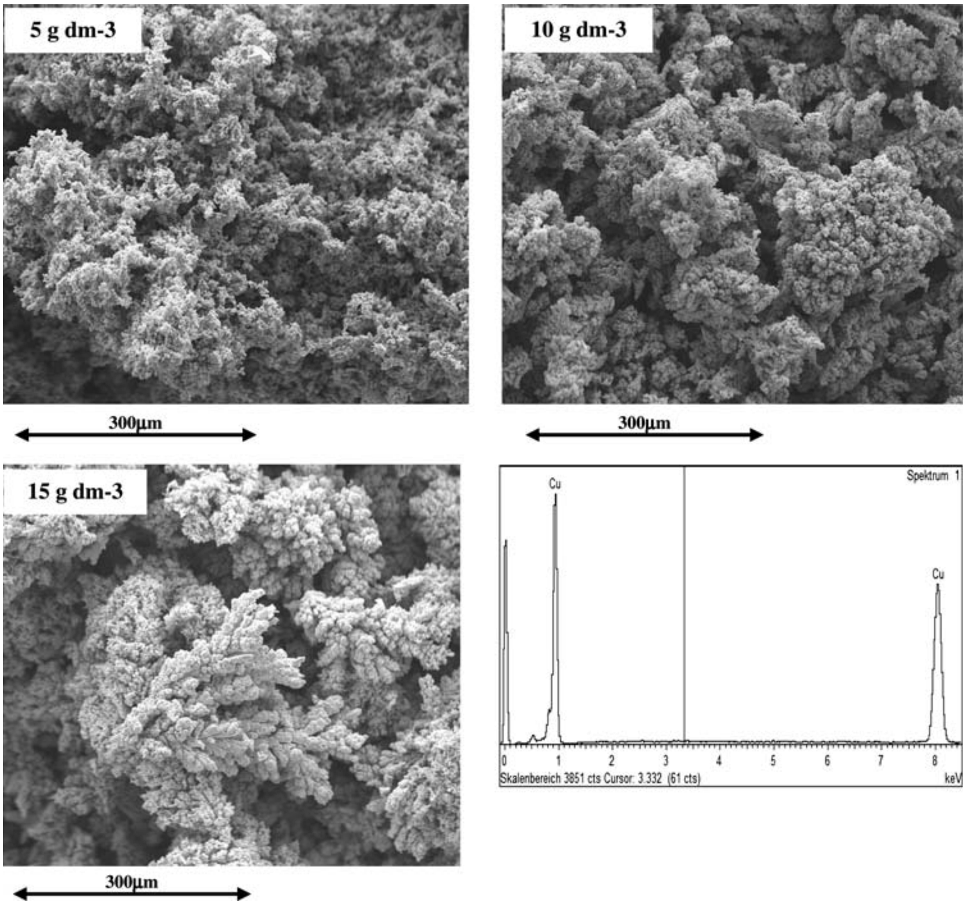


Fig. 7 SEM micrograph and EDX spectra of electrowon copper powder from a synthetic electrolyte with an initial concentration of 150 g dm^{-3} H_2SO_4 at 50°C electrolyte temperature and 6.92 $dm^3\ h^{-1}$ electrolyte circulation rate at different electrolyte Cu concentrations

Table 4 Effect of sulfuric acid concentration on electrowinning of copper powder

H_2SO_4 concentration (g dm^{-3})	Duration (h)	Average cell voltage (V)	Cathodic deposition (g)	Cathodic current efficiency (%)	Sp. energy demand (kWh kg^{-1})	Space/time yield (kg m^{-3} d^{-1})	Productivity (g A^{-1} h^{-1})
50	5.096	2.9218	101	98.27	2.506	3.739	1.166
150	4.874	2.6036	97	98.67	2.224	3.754	1.171
300	4.900	2.4946	116	117.38	1.791	4.465	1.393

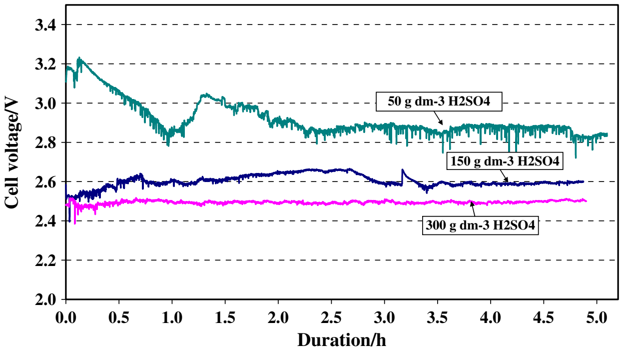


Fig. 8 Effect of H_2SO_4 concentration on electrowinning of copper powder from a synthetic electrolyte with an initial concentration of 15 g dm^{-3} Cu at 65°C, 6.92 dm^3h^{-1} using 5 g dm^{-3} polyvinylpyrrolidone as bath additives

3.4 Effect of H_2SO_4 concentration

The increase of H_2SO_4 concentration in electrolyte from 50 to 300 g dm^{-3} has a positive effect on all of the parameters of the electrolysis process (Table 4): cathodic current efficiency, productivity, and space/time yield are increased, whereas cell voltage and specific energy demand are decreased (Fig. 8). This can be due to improved electrolyte conductivity and hence polarization of electrolyte, together with improved dissolution of Cu ions in the electrolyte. The main drawback of increasing H_2SO_4 concentration in the electrolyte is the increase of viscosity and decrease of diffusion of ions to the cathode surface. This side-effect was not shown until this concentration level (300 g dm^{-3}).

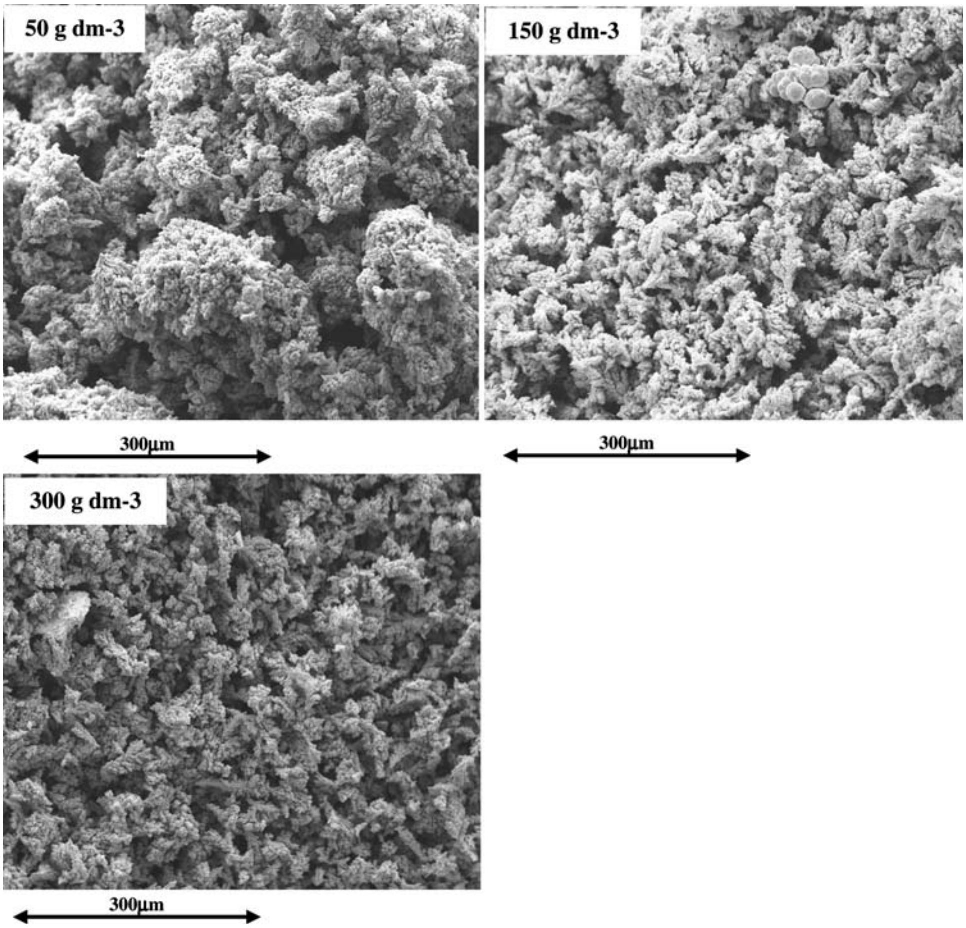


Fig. 9 SEM micrograph of copper powder electrowon from a synthetic electrolyte with an initial concentration of 15 g dm^{-3} Cu at 65°C, 6.92 dm^3 h^{-1} using 5 g dm^{-3} polyvinylpyrrolidone as bath additives at different electrolyte H_2SO_4 concentrations

Table 5 Effect of addition of organic materials on electrowinning of copper powder

Addition of organic bath additives	Duration (h)	Average cell voltage (V)	Cathodic deposition (g)	Cathodic current efficiency (%)	Sp. energy demand (kWh kg^{-1})	Space/time yield (kg m^{-3} d^{-1})	Productivity (g A^{-1} h^{-1})
Without	4.219	2.4302	87	102.24	2.003	3.890	1.213
With	4.874	2.6036	97	98.67	2.224	3.754	1.171

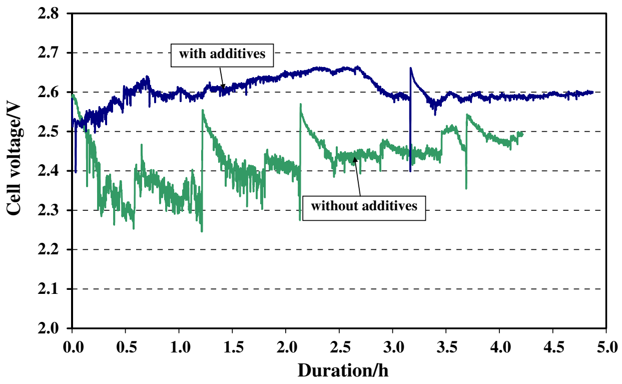


Fig. 10 Effect of addition of organic materials on electrowinning of copper powder from a synthetic electrolyte with an initial concentration of 15 g dm^{-3} Cu and 150 g dm^{-3} H_2SO_4 at 65°C electrolyte temperature and 6.92 dm^3 h^{-1} electrolyte circulation rate

SEM/EDX investigations of powders deposited at different H_2SO_4 concentrations indicate that pure copper powders are deposited with fine dendritic structure (Fig. 9). Increasing the electrolyte acid concentration to 300 g dm^{-3} has a positive effect on the refinement of the produced powders.

3.5 The effect of the addition of organic materials

The addition of polyvinylpyrrolidone K90 as an organic bath additive has a negative effect on the process parameters, as shown in Table 5 and Fig. 10. However, the addition of organic additives reduces the particle size of deposited powder (Fig. 11).

3.6 Effect of electrolyte residence time in the cell

As shown from Table 6 and Fig. 12, the continuous reuse of electrolytes in the electrolysis process has a positive effect on the electrowinning parameters. Only Cu and H_2SO_4 concentrations must be controlled at the beginning of the experiment. Cathodic current efficiency was increased from 84.07% to 100.23% while specific energy demand was decreased from 2.347 to 2.078 kWh kg^{-1} Cu when old

Fig. 11 SEM micrograph of copper powder electrowon from a synthetic electrolyte with an initial concentration of 15 g dm^{-3} Cu and 150 g dm^{-3} H_2SO_4 with and without the addition of polyvinylpyrrolidone K90 organic materials at 65°C electrolyte temperature and 6.92 dm^3 h^{-1} electrolyte circulation rate

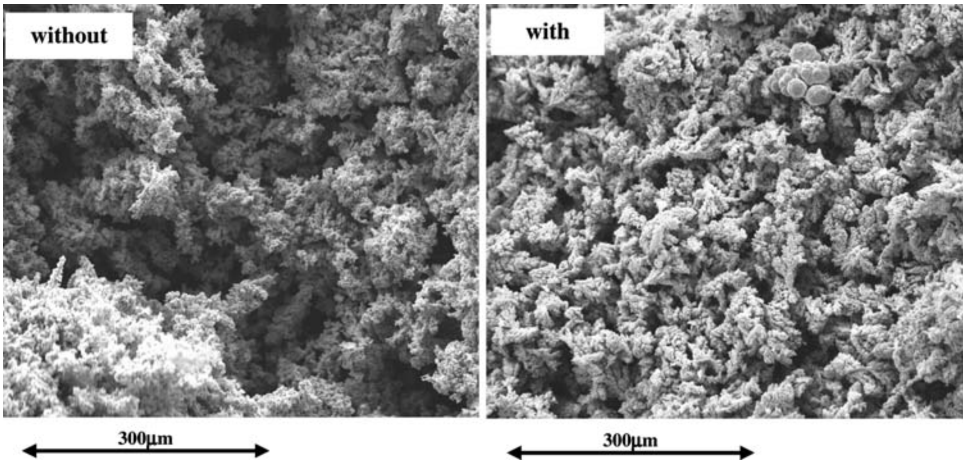


Table 6 Effect of electrolyte residence time in the cell on electrowinning of copper powder

Residence time of electrolyte before experiment (h)	Duration (h)	Average cell voltage (V)	Cathodic deposition (g)	Cathodic current efficiency (%)	Sp. energy demand (kWh kg^{-1})	Space/time yield (kg m^{-3} d^{-1})	Productivity (g A^{-1} h^{-1})
0	5.013	2.7565	99	84.07	2.347	3.725	0.997
35	4.947	2.4710	100	100.23	2.078	3.813	1.189

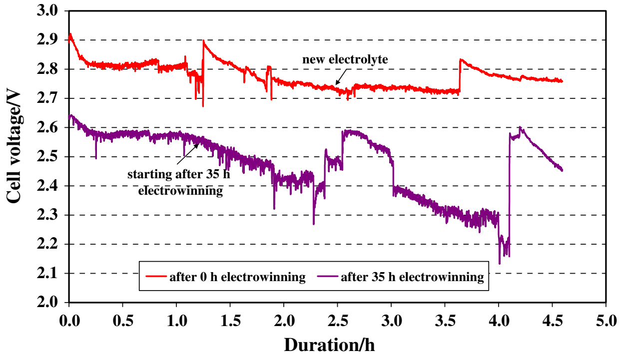


Fig. 12 Effect of residence time of electrolyte in the cell on electrowinning of copper powder from a synthetic electrolyte with an initial concentration of 15 g dm^{-3} Cu and 150 g dm^{-3} H_2SO_4 at 50°C electrolyte temperature and 3.37 dm^3 h^{-1} electrolyte circulation rate

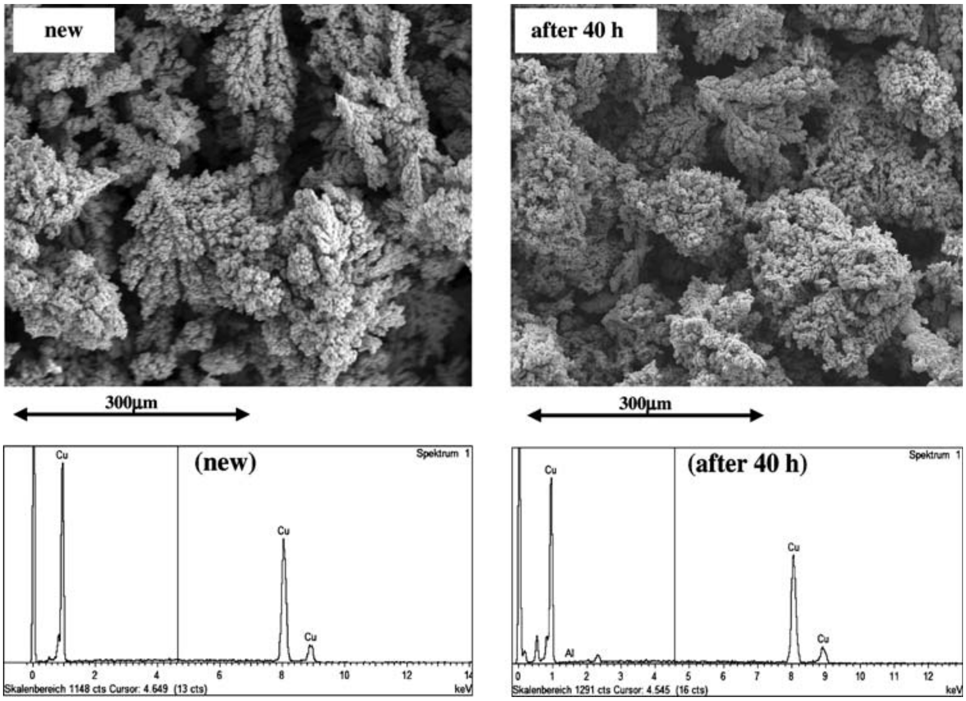
electrolytes were used. The reason for this improvement may be due to the presence of Al ions in electrolyte, which results from the dissolution of Al cathode sheets due to the effect of cementation phenomenon. This result must be extensively studied by using different Al concentrations in electrolyte and showing its effect on the process parameters and also on the quality of deposited powders.

The microstructure of the produced powders (Fig. 13) indicates that there is no sharp difference in particle size and shape between the two types of deposited powders. EDX analysis indicates that the produced powder from the new electrolyte is pure while that obtained from the old electrolyte is contaminated with about 0.4% Al. This can be due to the entrapment of aluminum sulfates, resulting from the cementation of Cu ions on Al cathode sheets, into the pores of the copper powders.

4 Conclusions

Electrowinning of electrolytic copper powders in a partially depleted synthetic Cu electrolytes (5–15 g dm^{-3} Cu) with a constant electrolyte temperature (35°C, 50°C or 65°C) using pure aluminum sheets as starting cathodes and pure lead plates as inert anodes at 1,000 A m^{-2} is affected positively by all studied parameters except for the addition of organic materials, which has only a positive effect on the grain refinement of the produced powders. The utilization of a spent electrolyte after electrorefining and electrowinning processes as a starting solution for the winning of Cu powder must be extensively studied by adding different elements separately and showing the effect of each on the electrowinning process. SEM and EDX analyses of the deposited powders indicated that pure copper powders can be produced with a fine dendritic microstructure. An amount of aluminum (0.4%) is precipitated with copper powders when electrolyte is reused for a long period (after about 40 h). This can be due to the entrapment of aluminum sulfates, resulting from the cementation of Cu ions on Al cathode sheets, into the pores of the copper powders. This may be eliminated by intensive washing of powders with distilled water to remove the sulfates from the surface of the powders.

Fig. 13 SEM micrograph and EDX spectra of copper powder electrowon from a synthetic electrolyte with an initial concentration of 15 g dm^{-3} Cu and 150 g dm^{-3} H_2SO_4 with two different electrolyte residence times in the cell at 50°C electrolyte temperature and 3.37 dm^3 h^{-1} electrolyte circulation rate



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