

COLLOID CHEMISTRY
AND ELECTROCHEMISTRY

Composition and Particle Size of Electrolytic Copper Powders Prepared in Water-containing Dimethyl Sulfoxide Electrolytes

Aigul' Mamyrbekova^{a,*}, B. S. Abzhalov^b, and Aizhan Mamyrbekova^b

^aAuezov South Kazakhstan State University, Shymkent, 160012 Kazakhstan

^bAkhmet Yassawi University, Turkestan, 161200 Kazakhstan

*e-mail: aizhan.mamyrbekova@ayu.edu.kz, aigul_akm@mail.ru

Received May 25, 2016

Abstract—The possibility of the electroprecipitation of copper powder via the cathodic reduction of an electrolyte solution containing copper(II) nitrate trihydrate and dimethyl sulfoxide (DMSO) is shown. The effect electrolysis conditions (current density, concentration and temperature of electrolyte) have on the dimensional characteristics of copper powder is studied. The size and shape of the particles of the powders were determined by means of electron microscopy; the qualitative composition of the powders, with X-ray diffraction.

Keywords: dimethyl sulfoxide, copper(II) nitrate trihydrate, electroconductivity, electrolysis, copper powder, X-ray diffraction

DOI: 10.1134/S0036024417070226

INTRODUCTION

Among the developing areas of modern research, fine powders whose microstructure gives them a number of valuable properties and the possibility of wide application in catalysis, medicine, ecology, and tribology, are of particular interest. In recent years, fine copper powders have been of great importance, since they have special properties (anti-friction, high electric conductivity) that allow their use in engineering and as composite materials [1, 2].

Developing new ways of the electrochemical synthesis of fine copper powders is thus a topic of great interest. Metal reduction on a cathode without the concomitant (parallel) hydrogen evolution reaction that is characteristic of electrolysis in aqueous solutions can be conducted using solvents with greater electrochemical stability than water. Aprotic organic solvents that do not contain labile hydrogen and are reduced at relatively high cathode potentials are the best in this respect [3, 4]. In this work, dimethyl sulfoxide (CH₃)₂SO, a cationotropic compound characterized by high dissolving and ionizing power ($\epsilon = 47$) was selected as a solvent. The high adsorption activity of DMSO on copper metal/electrolyte interface is also well known [5].

A review of the literature data showed that a considerable number of works have been devoted to studying the possible electrodeposition of copper from non-aqueous media. Acetic acid has been used as a protogenic solvent; acetone, acetonitrile, methanol, ethanol, propanol, isopropanol, *tert*-butanol, glyc-

erol, and ethylene glycol have been used as amphiprotic solvents [6, 7]; pyridine, formamide, dimethylformamide, dimethylethanolamine, and dimethyl sulfoxide (DMSO) have been used as protophilic solvents [8]; and acetonitrile, tartaric, citric, sulfosalicylic acid, and propylene carbonate have been used as additives [9]. Copper sulfate, acetate, monochloride, dichloride, and dibromide were used as electrolytes. Electrolytic method is easy to use, does not require expensive equipment, and allows obtaining chemically pure copper powders that have unique and stable properties (dendrite shape, dense texture of the particles). The main advantage of these method is the possibility of controlling a powder's structure and properties by varying the parameters of electrochemical synthesis. This enables us to adjust the structure, size, shape, and chemical composition of the powders [10, 11].

Despite such a long list of nonaqueous solvents in which the possibility of copper electroextraction has been demonstrated, there are few works on the electrodeposition of copper from electrolytes based on DMSO or mixtures of it and other compounds. Among the solvents mentioned above, such aprotic solvents as DMSO have attracted much attention of researchers [12–14]. Dipolar organic solvents are able to form complexes with some *ds* metals and exhibit high adsorptivity toward metals. Molecules of (CH₃)₂SO, like their cationotropic counterparts, form fairly stable complexes with ions of copper(II). Analysis of the electronic structure of the (CH₃)₂SO mol-

ecules and features of copper's metal lattice allows us to conclude that the orientation of the adsorbed DMSO molecules with oxygen atoms toward the metal is the one most probable. The electrolyte proposed in this work, which is obtained by dissolving copper nitrate trihydrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DMSO, has a simple composition and, due to the presence of a surfactant and the complexing properties of Cu^{2+} and NO_3^- ions with solvents, does not require other additives that affect the kinetics of the copper reduction.

The aim of this work was to obtain fine powders of copper from dimethyl sulfoxide aqueous solutions with particle sizes of up to 50 μm , and to study their physicochemical properties.

EXPERIMENTAL

The electrocrystallization of copper powder was conducted in solutions of copper(II) nitrate trihydrate in DMSO. Copper nitrate was synthesized according to the procedure described in [15] and purified by recrystallization from aqueous solution. DMSO of chemically pure grade was subjected to vacuum distillation ($n_D^{25} = 1.4816$). Prior to electrolysis, the prepared electrolyte solutions were held for at least a day to achieve ionic equilibrium.

The electrodeposition of the copper powder was conducted in the galvanostatic mode without forced stirring in a thermostatted glass cell equipped with a polyvinyl chloride cap with parallel fixed anodes. A cylindrical steel rod placed in the center of the cap was used as a cathode. Plates made of electrolytic copper were used as soluble anodes. One advantage of using soluble anodes is that electrolysis can be conducted for a fairly long time. After electrolysis, the resulting precipitate was repeatedly rinsed with bidistilled water to the constant value of conductivity of the rinsing water and dried to a constant mass.

The size and shape of the powder particles were determined via electron microscopy. We used a JSM 6490 LA scanning electron microscope at a magnification of $\times 2000$. An LS 13320 particle laser analyzer equipped with an aqueous liquid module equipped with an ultrasonic probe was used to examine the size distribution of the copper powder. The range of particle size measurement ranged from 0.020 to 200 μm . XRD analysis of electrolytic copper powders was performed using a DRON-2.0 unit with CuK_α monochromatic radiation. The rate of detector rotation was 2 deg/min.

Polarization was measured in the potentiodynamic mode using a PI-50-1 potentiostat. The sweep rate was 5 mV/s. The working electrode was a platinum wire, preliminarily coated with a copper layer 18–20 μm thick, electrodeposited under standard conditions. Ag/0.01 M AgNO_3 silver electrode in DMSO was used

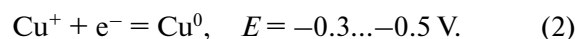
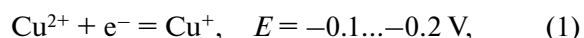
as the reference electrode [16], the potential of which was measured relative to a saturated mercury sulfate electrode ($\text{Hg}/\text{Hg}_2\text{SO}_4$, 1 N H_2SO_4). It was +0.3 V, relative to hydrogen.

RESULTS AND DISCUSSION

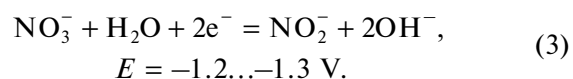
As was shown in studying the bulk and transport properties of copper(II) nitrate trihydrate solutions in DMSO, the maximum of electrical conductivity is observed in a 0.4 M copper(II) nitrate solution in DMSO at 15°C, which shifts to 0.6 M at higher temperatures [17]. An 0.1–0.6 M interval of copper salt concentrations was therefore chosen to study the possible electrodeposition of copper powder from DMSO. In solutions with 0.5 M (and higher) concentrations of copper salts in DMSO, viscosity grew considerably and the mobility of the metal ions was reduced.

Copper(II) ions, nitrate ions, $[\text{Cu}(\text{DMSO})_4(\text{H}_2\text{O})_2]^{2+}$ solvate complexes, and $[(\text{CH}_3)_2\text{SO} \cdot \text{NO}_3]^-$ ion adducts that provide the conductivity of the solution probably form in the electrolyte used to obtain copper powder as a result of interaction between its components [18]. The effect DMSO has on the electrocrystallization of copper powder is obviously associated with its surfactant and complexing properties.

The kinetics of cathodic processes of electrochemical copper deposition was studied in the potentiodynamic mode in a 0.4 M solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DMSO in the temperature range of 25–55°C. At 25°C, two distinct current maxima are observed on voltammograms (Fig. 1), indicating a two-step discharge of solvate complexes of copper(II) $[\text{Cu}(\text{DMSO})_4(\text{H}_2\text{O})_2]^{2+}$ on the electrode. This can be presented schematically as



The formation of dimethyl sulfoxide complexes of copper(II) leads to certain inhibition of reduction process, and shifts the reduction potential of copper(II) ion to a more negative region ($E = -0.5 \text{ V}$). At 35–55°C, there is a third wave in the polarization curves (Fig. 2) at more negative potential range. This maximum likely corresponds to the reduction of nitrate ions:



Raising the temperature to 35°C and higher obviously contributes to the partial desorption of the solvent and the breaking of hydrogen bonds between H_2O and $(\text{CH}_3)_2\text{SO}$ molecules, resulting in the decomposition of heteronuclear complexes, and structural fluctuations associated with nitrate complexes decompo-

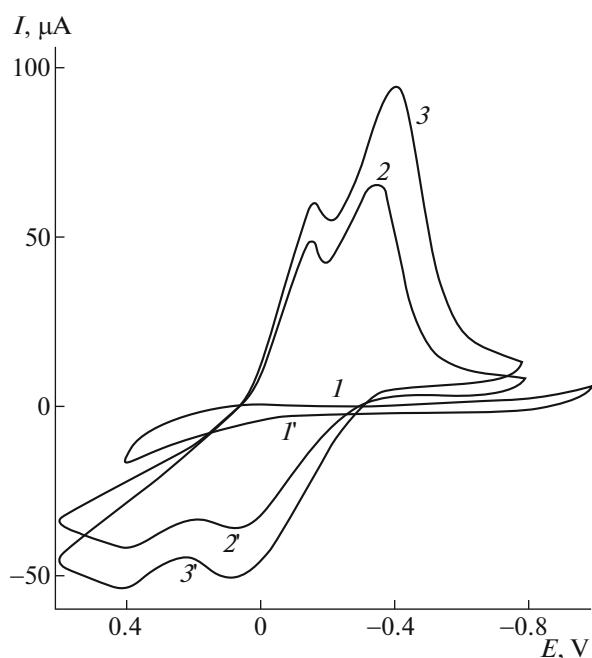


Fig. 1. Cyclic voltammograms of Cu^{2+} in 0.4 M solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DMSO at 25°C. The background electrolyte is 0.5 M LiClO_4 in DMSO: (1) 0.05, (2) 0.05, and (3) 0.1 V/s.

sition. These processes consequently favor the reduction of nitrate ions less solvated with the molecules of the organic solvent, improving their reactivity as the temperature rises.

Upon increasing the concentration of copper(II) salt, the cathodic potential in the organic solvent shifts to more electronegative values, resulting in lower values of the maxima and values of the cathodic currents. This is explained by the increased viscosity of the solution, which reduces the degree of copper(II) salt dissociation in DMSO and lowers the diffusion coefficient of copper ions. In solutions with higher concentrations (>0.6 M), ionic association is enhanced, resulting in increased viscosity, lower permittivity, and a drop in conductivity, all of which were established in [19].

The transfer coefficients of copper ions (α) were calculated voltammetry data (Table 1). As can be seen from the table, increasing the potential sweep rate gradually reduces the value of α_1 at temperatures of 25–35°C to 0.20–0.24, which is typical of irreversible processes. The values of α_2 for the second stage of the discharge of copper(I) ions at the same temperatures display greater irreversibility of the process at the higher sweep rates, as the difference between the ratios at low and high scan rates increases.

The low values of the transfer coefficients of copper(II) ions discharge allow us to conclude that the second stage of electron transfer is appreciably slower. However, the conclusion drawn in this work that the

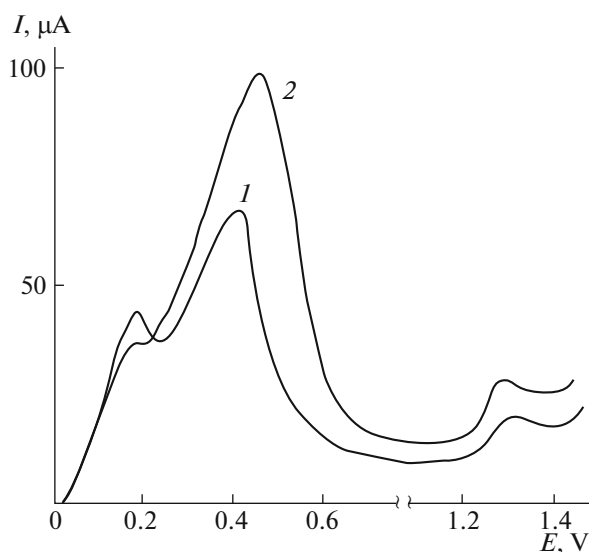


Fig. 2. Cathodic polarization curves of copper reduction from 0.4 M copper(II) nitrate trihydrate solution in DMSO at 35°C.

reduction of copper(II) ions in DMSO is a two-stage process requires detailed investigation and additional polarization studies.

The compositions of electrolytes and conditions of electrolysis used for the deposition of the dispersed copper are given in Table 2. The sizes and shapes of the powders' particles were determined from micrographs taken with a JSM 6490 LA scanning electron microscope. For each preparation of the copper powder, several micrographs were taken to determine the particle-size distribution of the dispersion powder (Table 3). The data suggest that DMSO plays a role in the formation of fine particles. The maximum amount of powder particles with sizes of 20–60 μm was obtained at 0.4 M copper nitrate trihydrate concentration.

Table 1. Transfer coefficients (α) of the discharge of copper(II) ions in dimethyl sulfoxide

$t, ^\circ\text{C}$	$v, \text{V/s}$			
	0.02	0.05	0.10	0.20
First stage (α_1)				
25	0.34	0.27	0.24	0.20
35	0.41	0.29	0.25	0.24
Second stage (α_2)				
25	0.37	0.13	0.15	0.08
35	0.45	0.13	0.23	0.15

Table 2. Composition of the electrolytes and conditions of electrolytic deposition of the copper powder (the volume of DMSO is <1 L)

No.	c , mol/L	i , A/m ²	T , °C	d , μm	I , %
1	0.1	400	25	30	96.8
2	0.15	500	30	30	95.7
3	0.2	600	35	40	94.5
4	0.25	700	40	40	93.6
5	0.3	800	25	40	96.6
6	0.35	900	30	30	96.2
7	0.4	1000	25	30	98.7
8	0.45	1100	25	30	98.7

c is the concentration of copper(II) nitrate trihydrate, i is the cathodic current density, d is the size of the powder particles, and I is the current yield.

Table 3. Particle size distribution at 0.4 M concentration of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DMSO

d , μm	N	c , %
20–39	459	67.30
40–59	121	17.74
60–79	33	4.84
80–99	50	7.33
100–120	19	2.79

N is the number of the particles and c is fraction.

The chemical composition of the copper powder was determined via powder X-ray diffraction. In the diffraction pattern of the copper powder obtained in 0.4 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DMSO at a current density of 800 A/m² and at 25°C, we observe distinct peaks with reflections characteristic of pure copper at 1.277, 1.81, and 2.08 Å; the reflexes at 1.81 Å are the most intense. The observed XRD pattern proves the high purity and crystalline structure of the obtained copper powder. Upon raising the current density to 1000 A/m², the diffraction patterns are similar to the previous ones, but there is a notable increase in the intensity of the reflections at 1.277 and 2.08 Å. When the temperature is raised to 35°C, along with the reflexes of pure copper at 1.089, 1.277, 1.81, and 2.08 Å, we observe reflexes of the other phases at 1.51, 2.12, and 2.45 Å. These peaks correspond to copper(I) oxide Cu_2O , which is probably formed via the oxidation of copper in air. The intensity of these peaks is negligible.

Our data show that during the electrolysis of a dilute solution of copper nitrate in DMSO, low temperatures (up to 25°C) favor the formation of high quality powders. Under these conditions, the main cathodic process proceeds according to Eqs. (1) and (2). Upon raising the temperature to 35°C and higher, hydrogen bonds break in the electrolyte, complicating the physicochemical phenomena and gain fluctuations in the solution. As a result of the decomposition of nitrate ions complexes with DMSO, the overvoltage is reduced, facilitating their reduction according to Eq. (3). As a consequence, the rate of nitrate ion reduction grows substantially, the pH of the near-cathode volume rises, the current yield of metal falls, and the quality of the powder deteriorates sharply. In the near-cathode electrolyte layer, the probability of the formation of poorly soluble compounds of copper(I) (CuOH and Cu_2O) captured by the growing precipitate grows, coloring the resulting powder somewhat.

CONCLUSIONS

Fine copper powders with particle sizes of 50 μm were obtained from dimethyl sulfoxide aqueous solutions via electrochemical synthesis, and their physicochemical properties were studied. It was found that the powders obtained from 0.1–0.4 M solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DMSO contained the maximum amount of particles with sizes of 30–40 μm. According to XRD measurements, the resulting powders contain Cu and Cu_2O phases.

REFERENCES

1. G. N. Sosnovskii and N. G. Sosnovskaya, *Electrolytic Production of Metallic Powders and Electrolysis of Molten Media* (AGTA, Angarsk, 2006) [in Russian].
2. M. V. Tesakova and V. I. Parfenyuk, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **53** (5), 106 (2010).
3. M. I. Nomberg, *Production of Copper Powder by Electrolytic Method* (Metallurgiya, Moscow, 1971) [in Russian].
4. B. B. Demeev, R. A. Nurmanova, and N. A. Kaltaev, *Vestn. Kazan. Univ., Ser. Khim.*, No. 3, 69 (2012).
5. R. S. Vakhidov, *Elektrokhimiya* **30**, 1165 (1994).
6. A. M. Ahmed, *Bull. Electrochem.* **7**, 167 (1991).
7. R. S. Vakhidov and A. M. Kazakov, *Gal'vanotekh. Obrab. Poverkhn.* **1** (3–4), 27 (1992).
8. T. Tatsuko, *Bull. Chem. Soc. Jpn.* **47**, 257 (1974).
9. L. Duda, T. Tlaczala, and E. Skonecki, *Chem. Stosowana* **33**, 687 (1989).

10. R. S. Akpanbayev, Mishra Brajendra, A. O. Baikonurova, et al., *Int. J. Electrochem. Sci.* **8**, 3150 (2013).
11. A. A. Vnukov and E. I. Demchenko, *Vestn. KhNADU*, No. **51**, 147 (2010).
12. Yu. A. Karapetyan and V. N. Eichis, *Physicochemical Properties of Nonaqueous Electrolyte Solutions* (Khimiya, Moscow, 1989) [in Russian].
13. H. L. Schlafer and W. Schaffernicht, *Angew. Chem.* **72**, 618 (1990).
14. J. B. Kinsinger, M. M. Tannahill, M. S. Greenberg, et al., *J. Phys. Chem.* **77**, 2444 (1973).
15. Yu. V. Karyakin and I. I. Angelov, *Pure Chemical Reagents* (Khimiya, Moscow, 1974) [in Russian].
16. V. N. Kudryavtseva and V. N. Varypaev, *Practical Course on Applied Electrochemistry* (Khimiya, Leningrad, 1990) [in Russian].
17. A. K. Mamyrbekova, *Russ. J. Phys. Chem. A* **87**, 414 (2013).
18. D. Martin and H. Haupthal, *Dimethylsulfoxid* (Academie, Berlin, 1981).
19. A. K. Mamyrbekova, *Russ. J. Gen. Chem.* **83**, 1799 (2013).

Translated by R. Safiullin