



Influence of electrolyte on a composition and size of copper compound particles

M. Starowicz*, A. Sojka, B. Stypuła

Department of Chemistry and Metal Corrosion, AGH – University of Science and Technology, ul. Reymonta 23, 30-059 Kraków, Poland

* Corresponding author: E-mail address: mariast@agh.edu.pl

Received 12.07.2007; published in revised form 01.10.2007

ABSTRACT

Purpose: The aim of this paper was to investigate an effect of the applied electrolyte on a composition and morphology of synthesised particles, which consist of copper compounds.

Design/methodology/approach: We present electrochemical investigations of copper in organic solutions of LiClO_4 and LiCl , which are anhydrous or contained 3 % of water. The SEM with EDX investigations determined morphology and composition as well as estimated a size of the obtained copper-salts or copper oxide particles.

Findings: A type of anion and an addition of a very small quantity of water have a substantial influence on a composition and morphology of the anodic dissolution products. In anhydrous solution and in solution containing LiClO_4 copper-salts were obtained. In alcohol solution of LiCl containing 3 % of water copper oxide particles were obtained.

Research limitations/implications: In some cases the chemical composition of the produced nanoparticles could not have been determined because of fast decomposition of the product. In the future, it is planned to analyse an effect of the potential on a synthesis.

Practical implications: Synthesis of various nanoparticles is presented in the paper, what may have practical applications.

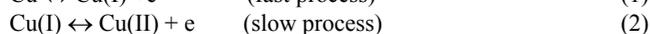
Originality/value: The paper proposes a new electrochemical method, which leads to a synthesis of copper oxide particles.

Keywords: Nanomaterials; Copper; Anodic polarisation

MATERIALS

1. Introduction

Anodic processes of copper dissolution in hydrous and organic solvents received much attention [1-7]. These investigations were carried out with respect to corrosion resistance of copper [1-5], ethanol oxidation on copper electrode [7] and copper dissolution in organic solvents [6]. In neutral solutions this metal is dissolved via an intermediate product, Cu(I) [1-3]:



Intensive etching is related to a creation of solvable compounds of divalent copper. In chloride solutions Cl^- ions stabilise Cu(I) compounds.

Until now not enough investigations were devoted to products of anodic copper dissolution. The paper of Stypuła et al. [8] reports that a production of copper oxide nanoparticles via electrochemical processes involving copper anode is possible. Nanoparticles of copper oxides have wide application in nanomaterials and composite materials [9-13].

The aim of the current work was to study an influence of the electrolyte composition on a formation copper compounds nanoparticles.

2. Experimental

The chemicals used in the experiment were: lithium chloride (LiCl) and lithium perchlorate (LiClO₄) produced by Merc company, anhydrous methanol, anhydrous ethanol (99.8 %), propanol from EUROCHEM BGD. These reagents were used as-received, without further purification.

Electrochemical measurement were performed in non-aqueous 0.1 M LiClO₄ - CH₃OH; 0.1 M LiClO₄ - C₂H₅OH; 0.1 M LiClO₄ - C₃H₇OH; 0.1 M LiClO₄ - CH₃COOC₂H₅; 0.1 M LiCl - CH₃OH; 0.1 M LiCl - C₂H₅OH and in the same solution containing 3 % of water.

For cyclic voltammetry measurements samples of copper were prepared from copper rod (99.99 %) with 0.5 cm diameter. The disc shape copper electrode was embedded in teflon. Samples were polished progressively from a 600 grit finish to a 1200 grit paper. Before electrochemical treatment electrodes were cleaned in anhydrous ethanol. Copper plate with 2 cm² was used for chronoamperometric measurement.

Electrochemical measurements were performed in one-compartment glass electrochemical cell. Applied three electrode system consisted of copper as a working electrode, a platinum plate as a counter-electrode and Ag/AgCl as a reference electrode. The values of the potential are given with respect to the Ag/AgCl electrode in this publication. Anodic properties of copper were investigated using AUTOLAB PGSTAT 30 potentiostat by means of the potentiostatic and potentiodynamic technique. Potentiodynamic polarisation sweeps of the working electrode were realised at a rate of 1.0 V / min. Potentiostatic studies were performed at 1.0 V for 4 hours. The process was performed in argon atmosphere at 25 °C. The curves presented in this work are the third potential cycles.

The precipitated products of anodic dissolution were analysed by means of scanning electron microscope with energy dispersive X-ray analyser (SEM/EDX) by a JEOL 5500 LV instrument.

3. Result and discussion

The polarisation curves obtained for copper in unhydrous solutions of alcohols (Fig. 1) show two oxidation peaks revealing two-stage process of copper oxidation. In a case of propanol the peaks are broadened. For ethyl acetate the curve is flat with no visible peaks what indicates a large resistance of the system.

From the Fig.1 it can be concluded that for the shorter carbon chains of the solvent, the dissolution process proceeds faster and more efficiently. The polarisation curves for the solutions containing water (Fig. 2) are characterised by the similar shape but with considerably higher peak currents. In a course of chronoamperometric polarisation at the potential of 1.0 V (Table 1 and 2) the electrolyte was losing transparency and was becoming blue or sea-green in a case of unhydrous solutions, or blue-sea-green turbidity appeared in a case of 3% of water present in the solution. Only in a case of ethyl acetate the solution remained unchanged. The colour of the solution as well as the literature data indicate formation of copper (II) salts in both unhydrous and hydrous alcoholic solutions [8].

Difficulties in the SEM/EDX analysis for the precipitates suggest that these compounds are unstable and are decomposed under irradiation.

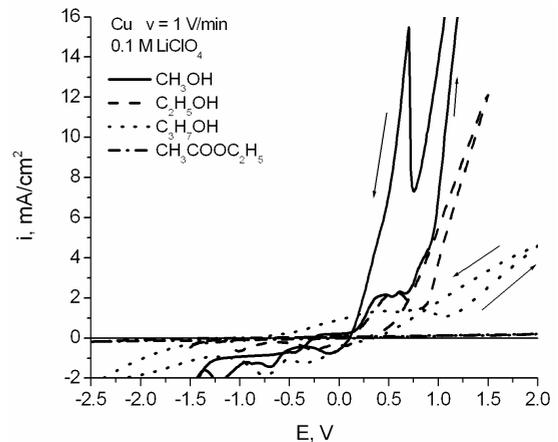


Fig. 1. Cyclic voltammetry polarisation curves for Cu in unhydrous solutions of 0.1 M LiClO₄

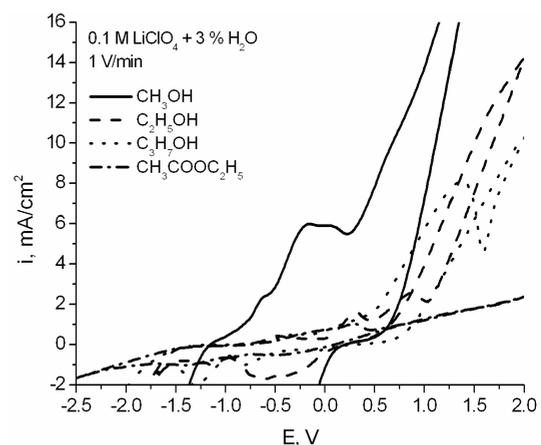


Fig. 2. Cyclic voltammetry polarisation curves for Cu in solutions of 0.1 M LiClO₄ containing 3 % of water

Table 1.

solution	effect
0.1 M LiClO ₄ - CH ₃ OH	blue suspension
0.1 M LiClO ₄ - C ₂ H ₅ OH	blue suspension
0.1 M LiClO ₄ - C ₃ H ₇ OH	light blue suspension
0.1 M LiClO ₄ - CH ₃ COOC ₂ H ₅	transparent solution

Table 2.

solution	effect
0.1 M LiClO ₄ - CH ₃ OH + 3 % H ₂ O	blue suspension
0.1 M LiClO ₄ - C ₂ H ₅ OH + 3 % H ₂ O	blue suspension
0.1 M LiClO ₄ - C ₃ H ₇ OH + 3 % H ₂ O	light blue suspension
0.1 M LiClO ₄ -CH ₃ COOC ₂ H ₅ + 3 % H ₂ O	transparent solution

The electrochemical studies of copper in unhydrous alcoholic solutions of 0.1 M LiCl are presented in Fig. 3. The anodic polarisation curves have similar course both in methanol and ethanol. They exhibit a plateau in a range of -1.25 to -0.25 V, what reveals high corrosion resistance of copper in this potential range. Above -0.25 V dissolution of copper takes place. An addition of 3 % of water (Fig. 4) do not alter considerably a shape of the curve but elongates its plateau to 0.5 V. In a case of both alcohols copper is dissolved above 0.5 V.

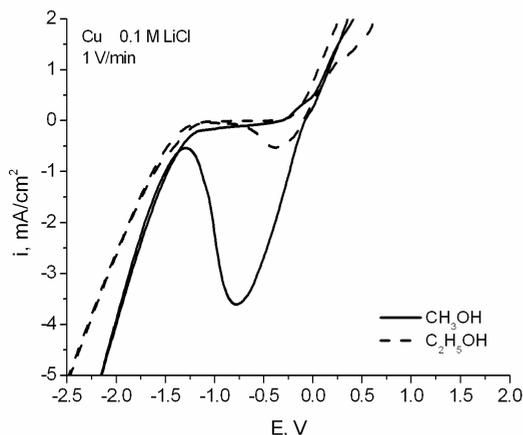


Fig. 3. Cyclic voltammety polarisation curves for Cu in unhydrous solutions of 0.1 M LiCl

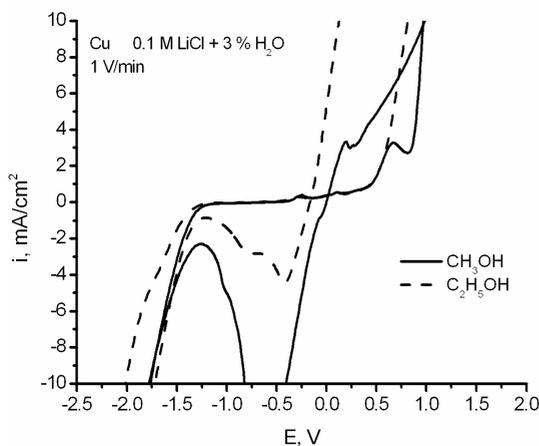


Fig. 4. Cyclic voltammety polarisation curves for Cu in solutions of 0.1 M LiCl + 3 % H₂O

The results of chronoamperometric polarisation shown in the Table 3 reveal an important influence of water on a composition of products resulted from anodic copper oxidation in the solutions of 0.1 M LiCl.

An addition of 3 % of water results in precipitation of an orange sediment. The molar ratio Cu/O would indicate a formation of CuO but the orange colour points to Cu₂O as a product [14-15]. The photographs of the copper oxide particles are presented in the Fig. 7 and 8. The particles have regular spherical shape and in the ethylic alcohol are characterised by the similar size; approximately 700 nm.

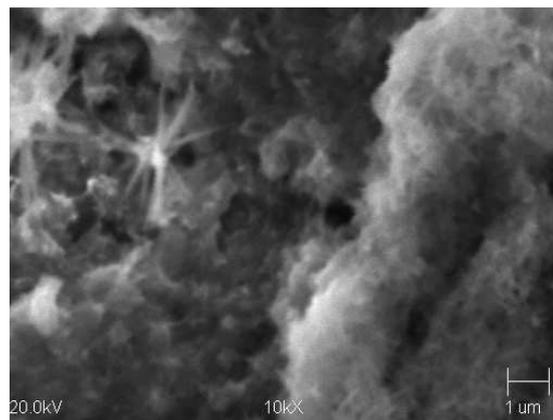


Fig. 5. SEM image of blue powder obtained during chronoamperometric polarisation of Cu in unhydrous 0.1 M LiCl – CH₃OH at 1 V for 4 h

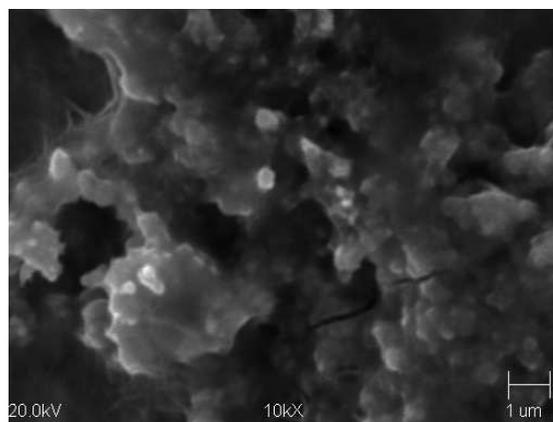


Fig. 6. SEM image of blue powder obtained during chronoamperometric polarisation of Cu in unhydrous 0.1 M LiCl – C₂H₅OH at 1 V for 4 h

Table 3. Chronoamperometric polarisation effect for Cu samples at 1 V for 4 hours

solution	Cu [%]	C [%]	O [%]	Cl [%]	suspension colour	size of particles [nm]
0.1 M LiCl – CH ₃ OH	11,5	0	60	28,5	blue	-
0.1 M LiCl – CH ₃ OH + 3% H ₂ O	34,21	22,43	38,55	4,81	orange	500 – 1200
0.1 M LiCl – C ₂ H ₅ OH	13,18	4,97	58,2	23,65	green – brown	400 - 1000
0.1 M LiCl – C ₂ H ₅ OH + 3% H ₂ O	33,65	13,15	51,06	2,13	orange	700

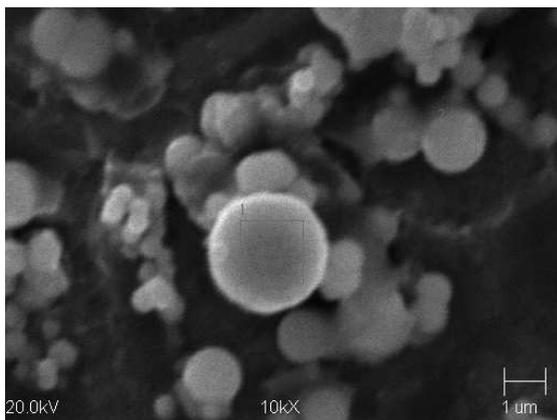


Fig. 7. SEM image of blue powder obtained during chronoamperometric polarisation of Cu in 0.1 M LiCl – CH₃OH + 3 % H₂O at 1 V for 4 h

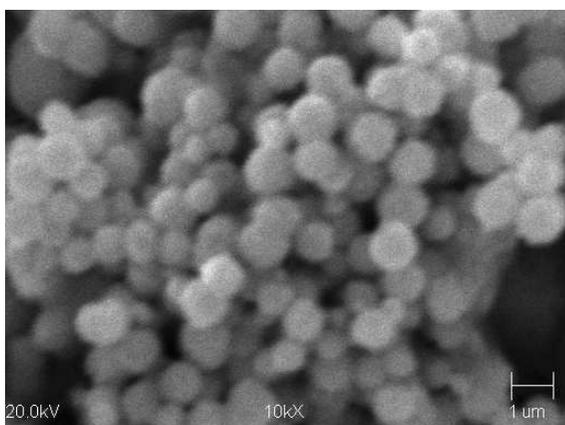


Fig. 8. SEM image of blue powder obtained during chronoamperometric polarisation of Cu in 0.1 M LiCl – C₂H₅OH + 3 % H₂O at 1 V for 4 h

4. Conclusions

Process of anodic copper dissolution depends considerably on a composition of electrolyte. The performed investigations indicate that copper is particularly susceptible to dissolution in methanol. In unhydrous and hydrous solutions of 0.1 M LiClO₄ the products of anodic dissolution are copper salts, what is a similar result to unhydrous solutions of 0.1 M LiCl. On the other hand, orange Cu(I) oxide nanoparticles are formed in the hydrous solution of 0.1 M LiCl in methylic or ethylic alcohol.

Acknowledgements

This work was financed by the Ministry of Science and Higher Education of Poland under project number 3 T08C 011 30.

References

- [1] S. Magaino, Corrosion rate of copper rotating-disc-electrode in simulated acid rain, *Electrochimica Acta* 42 (1997) 377-382.
- [2] Y. Feng, W.K. Teo, K.S. Siow, K.L.Tan, A.K. Hsieh, The corrosion behaviour of copper in neutral tap water. Part I: Corrosion mechanisms, *Corrosion Science* 38 (1996) 369-385.
- [3] Y. Feng, W.K. Teo, K.S. Siow, A.K. Hsieh, The corrosion behaviour of copper in neutral tap water. Part II: Determination of corrosion rates, *Corrosion Science* 38 (1996) 387-395.
- [4] A.G. Brolo, M.L.A. Temperini, S.M.L. Agostinho, Copper dissolution in bromide medium in the absence and presence of hexamethylenetetramine (HMTA), *Electrochimica Acta* 44 (1998) 559-571.
- [5] J. Klunker, W. Schäfer, Anodic behavior of copper in acetonitrile: the influence of carbon dioxide and dimethylamine, *Journal of Electroanalytical Chemistry* 466 (1999) 107-116.
- [6] A.P. Purdy, D. Godbey, L. Buckley, The dissolution of copper in common solvents used for low dielectric polymers, *Thin Solid Films* 308-309 (1997) 486-489.
- [7] T.R.L.C.Paixao, D. Corbo, M. Bertotti, Amperometric determination of ethanol in beverages at copper electrodes in alkaline medium, *Analytica Chimica Acta* 472 (2002) 123-131.
- [8] B. Stypuła, J. Banaś, M. Starowicz, H. Krawiec, A. Bernasik, A. Janas, Production of nanoparticles of copper compounds by anodic dissolution of copper in organic solvents, *Journal of Applied Electrochemistry* 36 (2006) 1407-1414.
- [9] J.P. Stobrawa, Z.M. Rdzawski, Dispersion – strengthened nanocrystalline copper, *Journal of Achievements in Materials and Manufacturing Engineering* 24/2 (2007) 35-42.
- [10] J.P. Stobrawa, Z.M. Rdzawski, W.J. Głuchowski, Microstructure and properties of nanocrystalline copper – yttria microcomposites, *Journal of Achievements in Materials and Manufacturing Engineering* 24/2 (2007) 83-86.
- [11] B. Ziębowicz, D. Szewiczek, L.A. Dobrzański, Manufacturing technology of the composite materials: nanocrystalline material – polymer type, *Journal of Achievements in Materials and Manufacturing Engineering*, 14 (2006) 37-42.
- [12] M.Greger, R. Kocich, L. Čížek, L.A. Dobrzański, M. Widomska, B. Kuřetová, A. Silbernagel, The structure and properties of chosen metals after ECAP, *Journal of Achievements in Materials and Manufacturing Engineering*, 18 (2006) 103-106.
- [13] B. Ziębowicz, L.A. Dobrzański, Application of nanostructural materials in manufacturing of soft magnetic composite materials Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉- PEHD type, *Journal of Achievements in Materials and Manufacturing Engineering* 24 (2007) 91-94.
- [14] S.A. Vorobyova, A.I. Lesnikovich, V.V. Muchinskii, Interphase synthesis and some characteristics of stable colloidal solution of CuO in octane, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 150 (1999) 297-300.
- [15] M. Aslam, G. Gopakumar, T.L. Shoba, I.S. Mulla, K. Vijayamohanan, S.K. Kulkarni, J. Urban, W. Vogel, Formation of Cu and Cu₂O Nanoparticles by Variation of the Surface Ligand: Preparation, Structure, and Insulating-to-Metallic Transition, *Journal of Colloid and Interface Science* 255 (2002) 79-90.