



XV International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov

AC electrochemical copper and aluminum oxidation in sodium acetate solutions

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Abstract

Electrochemical copper and aluminum oxidation using alternating current of industrial frequency was carried out in an aqueous sodium acetate solution. Simultaneous oxidation of metals accelerates copper oxidation, but does not significantly influence the aluminium oxidation rate. It results in the preparation of the copper-aluminum oxide system with a high content of copper oxide (up to 70 wt %). High energy consumption due to the voltage loss to overcome the resistance of the oxidation product layer on the electrode surface considerably limits the process and its product application. Furthermore, the chemical aluminum oxidation in alkaline medium of an aqueous sodium acetate solution instead of electrochemical one does not result in the power-saturated, nanosized metal oxide formation. The results obtained do not only underline the new technology of nanomaterial production, but also allow scientists to consider the mechanisms of the metal oxidation AC-process.

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Peer-review under responsibility of Tomsk Polytechnic University

Keywords: AC electrolysis, copper oxide, aluminum oxide, sodium acetate, electrode potential, phase composition

1. Introduction

Electrochemical processes are used in different ways. The most widespread ways are listed: the electrochemical methods of analysis; the coating of various parts with metals to obtain decorative, functional properties, to prevent them from corrosion; the production of different types of functional materials.

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It is known that the significant energy consumption is the main unfavorable feature of electrochemical synthesis of functional materials. It results in the high cost price of products. At the same time, the power-saturated nanomaterials may be electrochemically produced¹.

Electrochemical, simultaneous copper and aluminum oxidation in a sodium chloride solution using alternating current of industrial frequency results in the production of copper-aluminum oxide system [2] that is used in different catalytic and sorption processes³⁻⁷.

AC electrochemical oxidation of metals is characterized by a relatively low current output because of partial reduction of oxidized metal when the electrode potential is reversed. It was previously determined that simultaneous oxidation of metals in sodium chloride solution accelerates the copper oxidation in comparison with separate copper oxidation². Higher current output of copper is reached but it is distant from maximum possible value and the copper content in the oxide system is not high enough. Hence, it is required to find out the acceleration way of simultaneous copper and aluminum oxidation.

High dispersity and increased reactivity of the oxide system formed at non-equilibrium electrolysis cause interaction of electrolysis product with carbon-containing air compounds to layered double hydroxide (LDH) formation⁸. Heat treatment transforms LDH to oxide system possessing a number of features that support its use in catalytic and sorption processes⁹⁻¹².

The solubility of CO₂ in water and aqueous NaCl solutions depends on temperature, pressure and other air parameters. Therefore, air conditions influence the rate of the process of the electrolysis product carbonization by air carbon-containing compounds¹³. It results in the instability of the composition and properties of the electrolysis product. Thus, the investigation of LDH formation by the solution-owned carbon-containing compounds is required. According to the literature it is possible to produce copper carbonate hydroxide Cu₂(OH)₂CO₃ at the electrochemical process in the solutions containing NaHCO₃ and Na₂CO₃^{14, 15}.

Among carbon-containing compounds it is advisable to use sodium carbonate and sodium acetate as an electrolyte. The use of other organic compounds is impractical because of low conductivities of their solutions. The basic energy consumption of the electrochemical process is noticeable; therefore, high energy consumption to overcome the solution resistance markedly reduces the competitiveness of the product.

Thus, the work is aimed at investigating electrochemical copper oxidation together with aluminum to yield a double oxide system with high copper content that is steady transferred to carbon-containing layered double hydroxide.

2. Experimental

The procedure of electrochemical metal oxidation by industrial frequency alternating current was as follows: electrochemical metal oxidation was carried out in an aqueous sodium acetate solution with concentrations of 3 and 15 wt % at the temperature of 100 °C and current density of 1 A/cm². The plates of copper (mark M1) and aluminum (mark A0) were used as soluble electrodes.

Electrolysis products were washed with distilled water and air-dried at the temperature of 110 °C for 3 hours.

X-ray diffraction (XRD) measurements were performed using DRON-3M diffractometer with CuK_α radiation (λ=1.5418 Å) at 25 mA and 35 kV. The data were collected from 10 to 70° at a counting rate of 40/min. PDF 2 database was used to identify the phase composition.

3. Results and discussion

A distinctive feature of the metal oxidation process in sodium acetate solutions is the formation of dense layers of oxidation products on the electrode surfaces. The layers that possess the high diffusion resistance significantly prevent metals from oxidation. This is one of the reasons that the rate of separate metal oxidation in sodium acetate solutions is lower than in sodium chloride solutions (table 1).

Additional voltage required to overcome the resistance of the layers is believed to result in the high decomposition voltage which causes the copper polarization up to the electrode potential of hydrogen production. As a consequence, the high copper oxidation rate will occur. The comparison of separate copper oxidation in the aqueous solutions of sodium acetate and sodium chloride shows 15 % deceleration using CH₃COONa solution with

the concentration of 3 wt % and about 3 times deceleration when the process is carried out in CH₃COONa solution with the concentration of 15 wt %. Thus, the rate of separate copper oxidation seems to be determined by the electrode potential, but is limited by the diffusion resistance of layers on the metal surface.

Table 1. AC electrochemical, separate copper and aluminum oxidation in the solutions of sodium chloride and sodium acetate

Electrolyte solution concentration, wt %	Oxidized metal			
	Cu	Cu	Al	Al
	NaCl	CH ₃ COONa	NaCl	CH ₃ COONa
Metal oxidation rate, g/cm ² ·h				
3	0.05	0.035	0.32	0.15
15	0.017	0.006	0.32	0.21
Voltage, V				
3	4.7	16.7	20	73.4
15	2.5	5.2	18	53.2

Metals can be divided into two types. The standard electrode potential of one metal type (e.g., copper) is positive, but of other metal type (e.g., aluminum) is negative. At AC electrochemical oxidation, the metal is oxidized at an anodic half-cycle and partially reduced at a cathodic half-cycle. The formation of molecular hydrogen also occurs at the cathodic half-cycle. The main cathodic reaction of first metal type is metal reduction whereas molecular hydrogen preferably occurs in the cathodic half-cycle at oxidation of second metal type. Therefore, the total metal oxidation rate is defined not only by the metal oxidation rate, but also by the metal reduction rate. If the nature and rate of the main cathodic reaction is defined by the sign of electrode potential, the rate of anodic reaction depends on the metal nature. Among metals of second type undergoing AC electrochemical oxidation, aluminum is characterized by the highest oxidation rate that exceeds the oxidation rate of other metals several times. It is caused by low aluminum density ($\rho_{Al}=2.7$ g/cm³, $\rho_{Cu}=8.9$ g/cm³), which makes it easier to separate the atomized aluminum from the electrode surface. Also a rougher surface complicates the formation of a thick, continuous layer of oxidation products that significantly prevent metal from oxidation.

On the contrary, irrespective of the electrolyte nature the main cathode reaction of aluminum oxidation process is the hydrogen reduction, therefore the polarization does not contribute significantly to the aluminum oxidation rate. In this case, the aluminum oxidation rate is generally determined by the diffusion resistance of the oxidation product layer on the aluminum surface along with the rate of electrochemical aluminum oxidation, but not by the electrode potential reached. At the same time, alkaline medium of the sodium acetate solution results in the aluminum oxidation without external current source. With time the oxidation process is stopped due to the formation of a tight oxidation layer. AC-polarization of aluminum do not let overcome the passivation and do not cause the high rate of electrochemical aluminum oxidation in the sodium acetate solution. The electric energy is not significantly assumed on the electrochemical metal oxidation processes, but is mainly used to overcome the various resistances in the system. It results in the fact that the aluminum oxidation rate in the sodium acetate solution is 1.5–2 times lower than the oxidation rate in the sodium chloride solution (table 1). The high aluminum oxidation rate in the sodium chloride solution is caused not only by the electrochemical mechanism of this process, but also by the depassivating effect of chloride ions resulting in the formation of a loose oxidation product layer of low resistance. Furthermore, this layer is periodically removed from the metal surface by the gaseous products of electrolysis.

Significant acceleration of copper oxidation may be realized at simultaneous copper and aluminum oxidation in the sodium acetate solution. It can be explained as follows. In comparison with copper, the aluminum surface is covered with a dense layer that requires higher additional voltage to be overcome. It results in such copper polarization that the molecular hydrogen formation is preferably occurs in cathode life-cycle. Also, copper oxidation is contributed by AC rectification because of the formation of an oxide layer on the surface of aluminum.

Thus, at simultaneous copper and aluminum oxidation in the sodium acetate solution with the concentration of 3 wt % the copper oxidation rate is 14 times higher than the rate of separate copper oxidation. Carrying out the

process in a solution with the concentration of 15 wt % allows increasing the oxidation rate more than 80 times (table 2).

Table 2. AC electrochemical, simultaneous copper and aluminum oxidation in the solutions of sodium chloride and sodium acetate

Electrolyte solution concentration, wt %	Oxidized metal			
	Cu		Al	
	NaCl	CH ₃ COONa	NaCl	CH ₃ COONa
	Metal oxidation rate, g / cm ² · h			
3	0.055	0.491	0.323	0.122
15	0.007	0.482	0.32	0.128

Fig. 1 and 3 show that copper oxide Cu₂O (JCPDS card No. 5-0667) is formed in the sodium chloride solution whereas the product of copper oxidation in the sodium acetate solution is copper oxide CuO (JCPDS card No. 5-0661). This refers to the literature: in alkaline medium the stable copper-containing compound is copper (II) oxide. The reflexes of copper carbonate hydroxide in fig. 1 (malachite, Cu₂(OH)₂CO₃, JCPDS card No. 41-1390) confirm the spontaneous air-carbonation process. The reflexes are broad, fuzzy, and low intensive. However, this process is considerably less intensive than the carbonization of the product obtained in the sodium chloride solution⁸.

Aluminum oxidation product is slightly crystallized aluminium oxyhydroxide (boehmite, AlOOH, JCPDS card No. 17-0940). (fig. 2, 3).

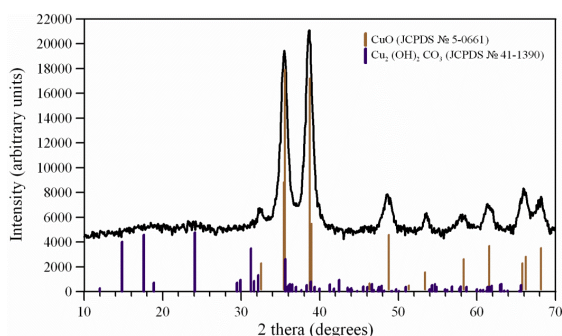


Fig. 1. XRD pattern of the product of AC electrochemical copper oxidation in sodium acetate solution

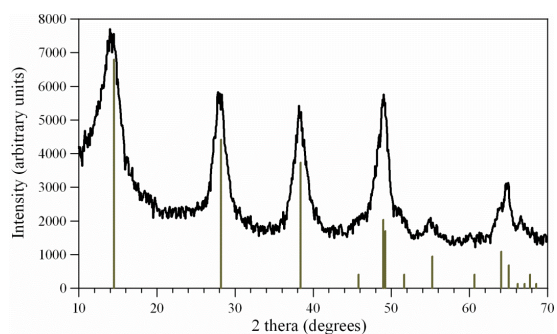


Fig. 2. XRD pattern of the product of AC electrochemical aluminum oxidation in sodium acetate solution

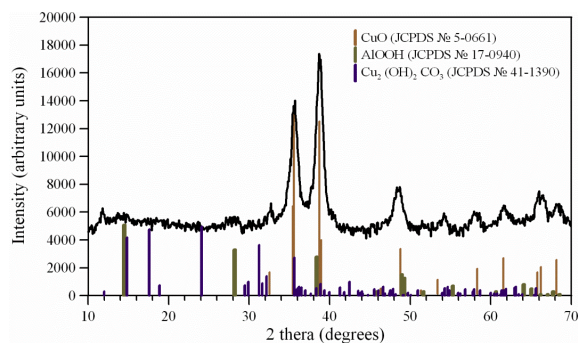


Fig. 3. XRD pattern of the product of AC electrochemical copper and aluminum oxidation in sodium acetate solution

The XRD measurement reveals that the carbon-containing compounds are not formed at AC electrochemical oxidation and air carbonization does not massively occur. The improved stability in air arises from the increased hydrophobicity of finely dispersed and highly dehydrated products of electrolysis in the sodium acetate solution at the high rate of electrode potential change.

4. Conclusion

It is shown that AC electrochemical, simultaneous oxidation of copper and aluminum in the sodium acetate solution is an effective way of intensifying the process of copper oxidation and produces a copper-aluminum oxide system with a high content of copper oxide (up to wt 70%). At the same time, high energy consumption of the process, due to a significant voltage loss to overcome the resistance of the layer of oxidation product on the electrode surface, significantly limit the process application. Furthermore, the product of the chemical aluminum oxidation in alkaline medium of the aqueous sodium acetate solution does not possess the properties that the metal takes at AC electrochemical oxidation. The disadvantages of the electrolysis process in the sodium acetate solution significantly limit the process application; however, the obtained results allow scientists to consider the ways of intensifying of the ac-process of metal oxidation.

Acknowledgments

The authors thank Viktor Ignatov (PhD, Institute of High Technology Physics, National Research Tomsk Polytechnic University) for help in X-ray diffraction measurements.

References

1. Korobochkin VV. Protsessy polucheniya nanodispersnykh oksidov s pomoschyu elektrokhimicheskogo okisleniya pod deystviem peremennogo toka [Processes of nanodispersed oxide obtaining using alternating current electrochemical oxidation of metals]: dissertation for the degree of doctor of engineering science, Tomsk Polytechnic University, Russia. 2004.
2. Korobochkin VV, Usoltseva NV, Balmashnov MA. Non-equilibrium electrochemical synthesis of copper-aluminium oxide system. *Fundamental research* 2012; **11**:143–147.
3. Kovanda F, Jiratova K. Supported layered double hydroxide-related mixed oxides and their application in the total oxidation of volatile organic compounds. *Applied Clay Science* 2011; **53**: 305–316.
4. Bradu C, Frunza L, Mihalche N, Avramescu S-M, Neatã M, Udrea I. Removal of Reactive Black 5 azo dye from aqueous solutions by catalytic oxidation using CuO/Al₂O₃ and NiO/Al₂O₃. *Applied Catalysis B: Environmental* 2010; **96**: 548–556.
5. Structure and Bonding. Vol. 119. Layered double hydroxides. Edited by X. Duan, D.G. Evans. Berlin, Heidelberg: Springer-Verlag Berlin Heidelberg. 2006.
6. Trujillano R, Holgado MJ, Pigazo F, Rives V. Preparation, physicochemical characterisation and magnetic properties of Cu–Al layered double hydroxides with CO₃²⁻ and anionic surfactants with different alkyl chains in the interlayer. *Physica B* 2006; **373**: 267–273.
7. Tanasoi, S., Tanchoux, N., Urdã, A., Tichit, D., Sãndulescu, I., Fajula, F., Marcu, I.-C. (2009) New Cu-based mixed oxides obtained from LDH precursors, catalysts for methane total oxidation. *Applied Catalysis A: General*, 363, 135–142.
8. Korobochkin V.V. Usoltseva N.V. Balmashnov M.A. Phase composition of nanosized products of non-equilibrium electrochemical oxidation of copper and aluminium. *Bulletin of Tomsk Polytechnic University. Chemistry*, 321, 59–63.
9. Handbook of Layered Materials. Edited by Scott M. Auerbach, Kathleen A. Carrado, Prabir K. Dutta. New York: Marcel Dekker, Inc., 2004. 646 p.
10. Rives V. Layered double hydroxides: present and future. New York: Nova Science Publishing, Inc., 2001. 499 p.
11. Britto S, Kamath PV. Thermal, solution and reductive decomposition of Cu–Al layered double hydroxides into oxide products. *Journal of Solid State Chemistry* 2009; **182**: 1193–1199.
12. Mattisson T. Materials for Chemical-Looping with Oxygen Uncoupling. *ISRN Chemical Engineering*, 2013, 1–19.
13. Duana Z, Sun R. An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chemical Geology* 2003; **193**: 257–271.
14. Zhang Weixin, Wen Xiaogang, Yang Shihe Controlled reactions on a copper surface: synthesis and characterization of nanostructured copper compound films. *Inorganic chemistry* 2003; **42**: 5005–5014.

15. Zhou A, He D, Xie N, Xie Q, Niex L, Yao Sh. Electrochemical quartz crystal microbalance probing the electro-formed and electro-reduced products on a copper electrode in aqueous solutions containing NaHCO_3 and Na_2CO_3 . *Electrochimica Acta* 2000; **45**: 3943–3950.