

On the catalytic behavior of copper toward oxygen reduction reaction in alkaline solution

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Article history:

Received: 26 November 2012

Received in revised form: 10 January 2013

Accepted: 27 January 2013

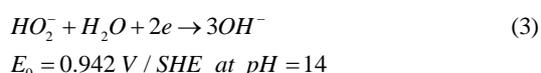
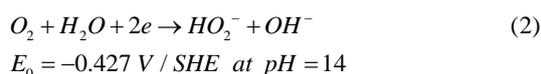
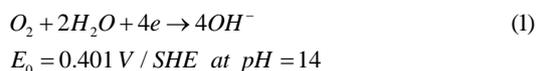
Abstract

The kinetic and mechanistic aspects of the oxygen reduction reaction as well as the electrocatalytic effect of copper surface in alkaline solution were studied by cyclic voltammetry and rotating disk electrode technique. In the potential range of -0.4 to -1.4 V/SCE time dependent cathodic peaks at -0.9 V/SCE, -1.2 V/SCE and plateau extending through this domain were observed. Direct reduction of oxygen along with the dominating reduction of copper oxides which formed during time delay at open circuit potential is discussed in the light of electrochemical techniques. The number of electrons transferred per O₂ molecule (n) obtained on different copper surface is close to 4 on oxide free surface and gradually decreases to 2 when the oxide layers cover the copper surface. Moreover calculation of rate constant of oxygen reduction on copper surface, demonstrated a faster kinetic of reaction on oxide free surface of copper. Tearing down and building up of the surface causing increased surface area is also observed.

Keywords: Oxygen reduction reaction, Copper, Alkaline solution, Cyclic Voltammetry

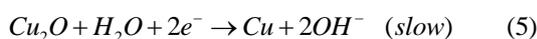
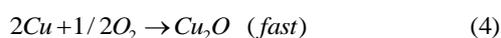
1. Introduction

Oxygen Reduction Reaction (ORR) has become one of the most extensively studied electrochemical reactions due to interest for the development of polymer electrolyte fuel cells [1]. In aqueous alkaline solutions, oxygen reduction is a multi electron reaction that may proceed according to two main pathways; a direct four-electron reduction (Eq. 1) and a peroxide pathway that involves a two-electron reduction step leading to peroxide as intermediate which can undergo further reduction or decomposition (Eqs. (2), (3)) [2, 3]. The oxygen reduction proceeding via reactions (2) and (3) is called the serial mechanism while the reduction through reactions (1) and (2-3) is the parallel mechanism.



The situation becomes more complicated if the electrocatalyst happens to be non-noble transition metals where the formation and involvement of the oxide layers even further complicate the mechanism [4, 5]. Also, these metals may chemically interact with the soluble oxygen to form species acting as intermediates in the ensued reduction process. Corrosion of copper in alkaline solutions has been found to be slow [6, 7] and copper lends itself to be used as a surface for electrochemical oxygen reduction.

Schiffirin and coworkers [4] have studied the ORR on copper in borax buffered solution using Rotating Disc Electrode (RDE) and reported a 4 electron process. It was also shown that the formation of a duplex layer comprising of Cu /Cu₂O /CuO inhibits the electro-reduction and a mechanism based on both the participation of metallic copper in electron-transfer and the parallel fast formation of surface oxides layers followed by its slow electrochemical reduction have been proposed, Eqs. (4), (5)



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The findings were amplified in the presence of anionic complexing agents (Cl^-) that tends to remove the oxide layer and accentuates the electrochemical reduction on the bare surface. King et al [8] studied the reduction of oxygen on copper in neutral unbuffered 1M NaCl solution where total reduction to hydroxyl entity on the less catalytic surface, Cu(0) sites, and both the formation of peroxide and hydroxyl entities on the more catalytic surface containing both Cu(0) and Cu(I) sites were reported.

In this work ORR was studied on copper in 1M NaOH solution in a wide range of potential with the aim of the determination of the mechanism of this reaction. For this purpose cyclic voltammetry and RDE technique were employed.

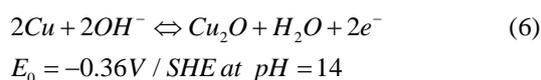
2. Experimental

Sodium hydroxide used in this work was analytical grade Merck product and oxygen was 99.9% pure provided by a local supplier. Water was deionized and distilled and subsequently deoxygenated by purging with nitrogen (99.99%). Cylindrical copper of 99.99% purity was placed in Teflon holder exposing circular areas of 0.283 cm^2 . Its surface was polished to mirror finish by emery paper No's 1000, 2000, 3000 followed by rinsing in distilled water. Experiments were conducted in a conventional thermostated three electrode cell with copper forming the working electrode. Its potential was monitored against a glass frit separated SCE and a large platinum plate forming the counter electrode. The electrolyte was bubbled by O_2 (N_2) while being stirred by a magnetic stirrer. In the course of electrochemical runs both bubbling and stirring were stopped. The cell was powered by a VoltaLab PGZ100 Potentiostat/Galvanostat run by a PC through its commercial software's.

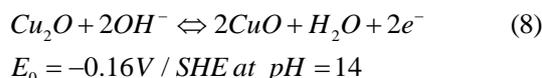
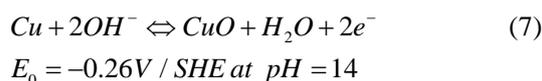
3. Results and discussion

3.1. Cyclic voltammetry studies

Figure 1 presents a cyclic voltammogram of Cu in 1M NaOH solution in the potential range of 0.5 to -1.6 V/SCE. Anodic peaks designated as A1, A2 and A3 and three cathodic peaks C1, C2 and C3 dominate the voltammogram. A1 is associated [9] with Cu-Cu (I) oxide (hydroxide) conversion with possibly the overall reaction of



While A2 is due [10, 11] to Cu-Cu(II) oxide and also probably Cu(I)-Cu(II) oxide conversions where E_0 's are only 100 mV apart. (Eqs. 7, 8)



The broad peak, A3, at 0.19 V/SCE is probably due to the formation of soluble, perhaps $HCuO_2^-$, species [12]. In the cathodic half cycle, C1 is due to the reduction of Cu(II) to Cu(I) while C2 represents the Cu(I) to Cu(0) conversion. C3 at the far cathodic end of the voltammogram may be due to the reduction of soluble Cu(II) [13] or adsorption of hydrogen atoms [14]. All the mentioned processes are quasi-reversible as presented in the voltammogram.

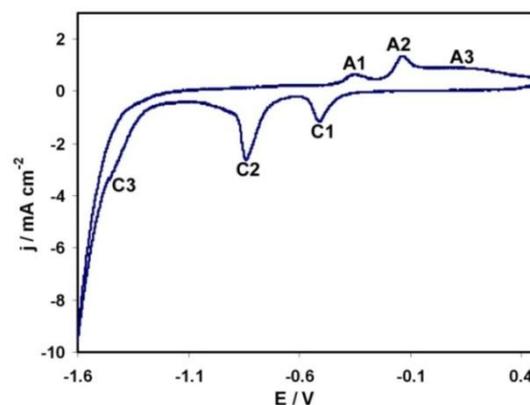


Figure 1. Cyclic voltammogram of Cu electrode in N_2 saturated 1M NaOH solution at $27\text{ }^\circ\text{C}$ with scan rate of 40 mV/s.

Figure 2 presents the cyclic voltammograms recorded in the absence (a) and presence (b) of oxygen. Due to the time dependence of the shapes of the voltammograms similar delays at open circuit potential (here 3 minutes) between subsequent voltammograms are obeyed. For comparison a cyclic voltammogram recorded with no time delay in O_2 saturated solution (c) is also overlaid on the graph. Distinct rise of the cathodic current throughout the entire potential domain with the distinct peaks at -0.9 and around -1.2 V/SCE have been observed. While the current in the region of -0.9 to -1.0 V/SCE stabilize after 30 minutes, the peak at -1.2 V/SCE keeps on rising and stabilize only after several hours, Figure 3. At the same time the anodic peak at around -0.45 V/SCE which part of it is due to copper oxidation slightly increases in size and seems to be influenced by both of the processes occurring at -0.9 and -1.2 V/SCE.

From Figure 2-a, it is obvious that in N_2 saturated NaOH solution a single cathodic peak at around -0.6 V/SCE and also a single anodic peak at around -0.4

V/SCE correspond to this cathodic peak exist in cyclic voltammogram which are related to copper redox process according to Eq. 6. Also when cyclic voltammogram recorded with no time delay (Figure 2-c) in O_2 saturated solution the above mentioned process is accompanied with the direct reduction of oxygen. On the other hand, when cyclic voltammogram recorded with specific time delay (Figure 2-b) in addition to the direct oxygen reduction, two distinct peaks at around -0.9 and -1.2 V/SCE observed which are probably related to bulk copper oxides (formed chemically from dissolved oxygen and copper during time delay at open circuit potential) reduction.

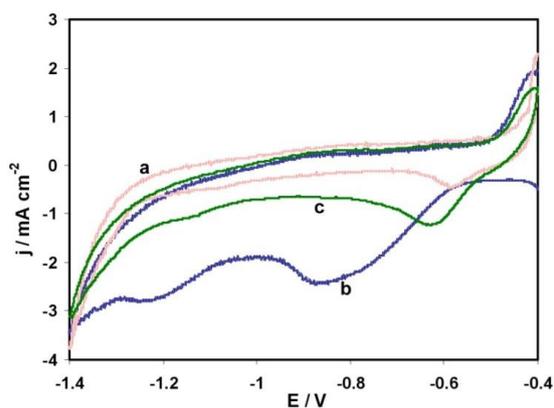


Figure 2. Cyclic voltammograms of Cu electrode in 1M NaOH solution at 27 °C recorded with 3 minutes time delay at open circuit potential between consecutive sweeps, N_2 saturated (a), O_2 saturated (b) and O_2 saturated and with no time delay (c). Potential sweep rate is 40 mV/s.

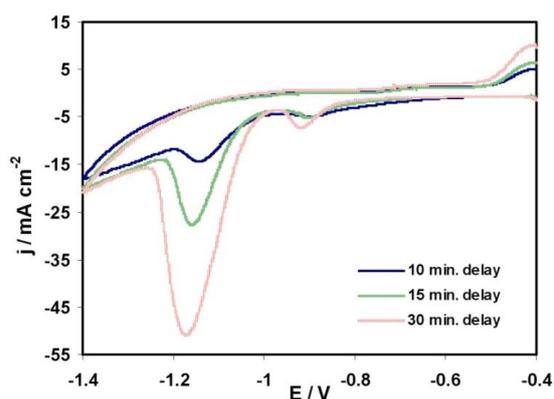


Figure 3. Cyclic voltammograms of Cu electrode in O_2 saturated 1M NaOH solution at 27 °C with different time delays at open circuit potential between voltammograms. Potential sweep rate is 40 mV/s.

Figure 4 presents the cyclic voltammograms in the range of -0.4 to -0.85 V/SCE with different time delays where the extensive reduction process has not been allowed to occur. The cathodic processes occurred in Figure 4-a,b are due to the direct

reduction of oxygen which be inhibited in Figure 4-c by Cu/Cu₂O/CuO layer formed on the copper surface with increasing time delay at open circuit potential. According to the reference [4] copper becomes less active for ORR as it's surface is more oxidized.

Figure 5 presents the cyclic voltammograms recorded with 15 minutes time delay at different potentials. As can be seen in this figure if time delay has been applied at open circuit potential or -0.4 V/SCE, the reduction processes at -0.9 and -1.2 V/SCE observe (according to Figure 1 the copper oxides are formed at potential more positive than -0.4 V/SCE) while if time delay has been exercised at -0.75, -0.9 and -1.2 V/SCE, the reduction processes at -0.9 and -1.2 V/SCE do not observe which indicate that the mentioned processes are due to the bulk copper oxide reduction (formed chemically at time delay). According to Jian-Bo He [15] when potential of delay set at this region (open circuit potential of our work) no solid Cu(II) specie(s) can present at this potential. On the other hand we observed the reduction peak of Cu(II) specie(s) at around -0.9 V/SCE. Also different Cu(I) species such as Cu₂O and Cu₂O.H₂O formed from reduction of Cu(II) species which these product reduced at different potentials[15] but we observed a single cathodic peak related to the reduction of Cu(I) specie at around -1.2 V/SCE. Recent studies [16] have shown that CuO is first reduced in a neutral solution (0.1M KCl) followed by the reduction of Cu₂O. However, it has also been shown that the reductions of both Cu₂O and CuO occur simultaneously in such a neutral solutions. On the other hand in a strongly alkaline solution (i.e., 6M KOH + 1M LiOH) a perfect separation between two cathodic peaks can be observed and CuO is reduced prior to the reduction of Cu₂O [17].

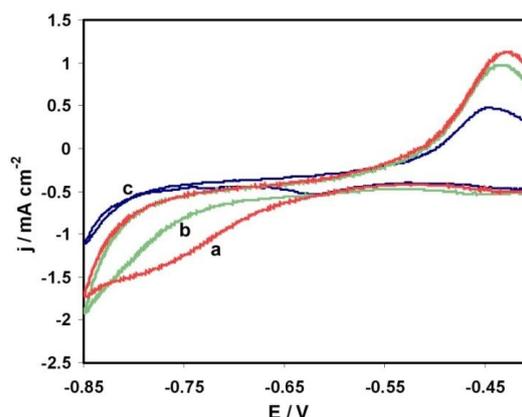


Figure 4. Cyclic voltammograms of Cu electrode in O_2 saturated 1M NaOH solution at 27 °C with different time delays at open circuit potential between voltammograms, 2 min. (a) 5 min. (b) and 30 min. (c) Potential sweep rate is 40 mV/s.

Figure 6 presents the second and the twelfth cyclic voltammograms recorded in the time span of

3 hours with the various time delays of 2 to 30 minutes between consecutive potential sweeps. Both the cathodic and anodic peak currents have increased by a factor of nearly 2.5 that we attribute to the increased surface area and roughening of the surface caused by tearing down and building up of the surface by redox processes of copper.

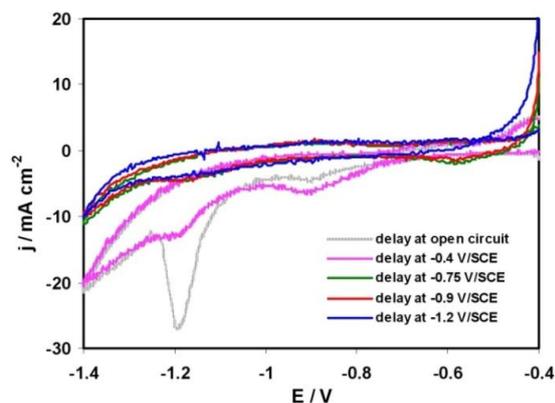


Figure 5. Cyclic voltammograms of Cu electrode in O_2 saturated 1M NaOH solution at 27 °C with 15 minutes time delay at different potential between voltammograms. Potential sweep rate is 40 mV/s.

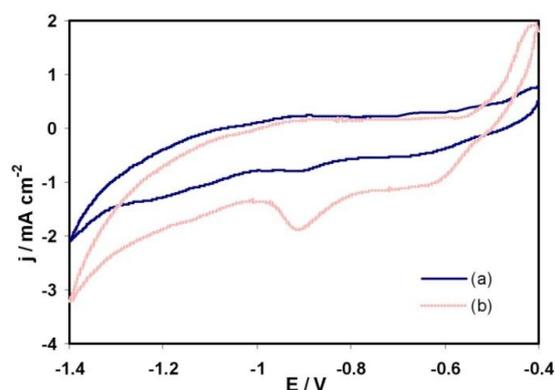


Figure 6. Cyclic voltammograms of Cu electrode in O_2 saturated 1M NaOH solution with 2 minutes time delay at open circuit potential at 27 °C (a) the second cycle, (b) the twelfth cycle. Potential sweep rate is 40 mV/s.

3.2. RDE analyses

For the investigation of direct oxygen reduction on copper surface RDE technique was employed. Figure 7 shows current-potential curves for oxygen reduction on copper in O_2 saturated 1M NaOH solution at 27 °C obtained over a range of rotation rates (200–1000 rpm) where 5 minutes time delay at open circuit potential employed between voltammograms. Similar curves (not shown here) were obtained for no time delay and 20 minutes time delay. Kinetic analyses of the current-potential curves are presented in the mixed kinetic-diffusion control region in the form of Koutecky-Levich plots (Figure 8) and in the diffusion controlled region in the form of Levich plots (Figure 9).

From the Koutecky-Levich analysis, kinetic currents were calculated by means of the equation

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \quad (9)$$

Where j is the measured current density, j_k is the kinetic current density and j_d is the diffusion limited current density given respectively by

$$j_k = nFkC_{O_2} \quad (10)$$

$$j_d = 0.62nFD_{O_2}^{2/3}v^{-1/6}C_{O_2}\omega^{1/2} \quad (11)$$

Where n is the number of electrons transferred per O_2 molecule, F is the Faraday constant (96485 C mol^{-1}), k is the rate constant for oxygen reduction, 0.62 is a constant used when ω (rotation rate of disk electrode) is expressed in radians per second, C_{O_2} is the concentration of oxygen in the bulk solution (0.84 mol m^{-3}), D_{O_2} is the diffusion coefficient of oxygen ($1.85 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), and v is the kinematic viscosity of the solution ($1.06 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$) [18].

Koutecky-Levich plots for various potentials yield straight lines (Figure 8) with intercepts corresponding to the kinetic currents density, j_k , which give the reaction rate constants, k . The results are presented in Table 1. As can be seen in this table with increasing time delay at open circuit potential, kinetic currents density and so rate constants decreased which indicate that the formation of copper oxides with increasing time delay on the surface of copper electrode reduce the rate of oxygen reduction. Also, the slope of the straight lines allows us to assess the number of electrons involved in the oxygen reduction reaction. The number of electrons involved is consistent with the Levich analysis presented in Figure 9 and Table 2. The number of electron transferred per O_2 reduction decreased from 4 to 2 with increasing time delay indicating the formation of per oxide species according to Eq. (2).

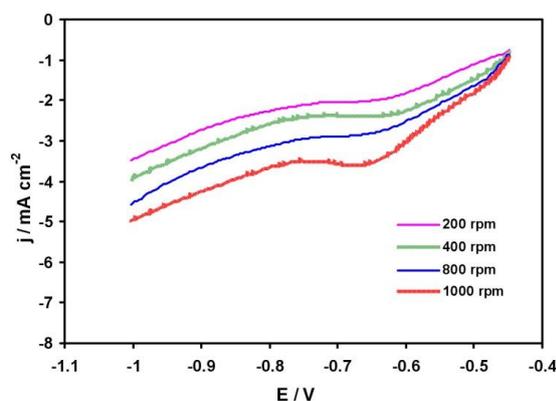


Figure 7. Current-potential curves for oxygen reduction on copper rotating-disc electrode in O_2 saturated 1M NaOH solution at 27 °C with 5 minutes time delay at open circuit potential

between consecutive cycles and at different rotation rates. Potential sweep rate is 40 mV/s.

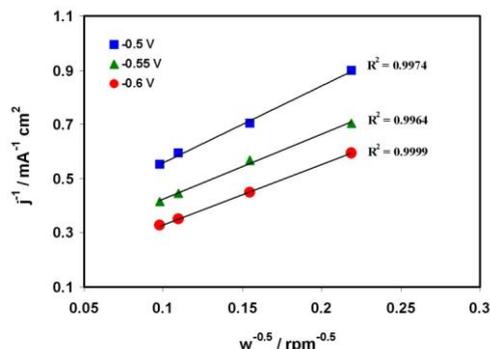


Figure 8. Koutecky-Levich plots for oxygen reduction on copper rotating-disc electrode in O_2 saturated 1M NaOH solution at 27 °C with 5 minutes time delay at open circuit potential between consecutive cycles and at different potentials.

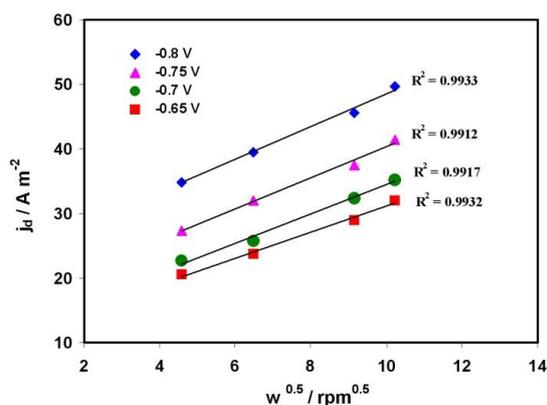


Figure 9. Levich plots for oxygen reduction on copper rotating-disc electrode in O_2 saturated 1M NaOH solution at 27 °C with 5 minutes time delay at open circuit potential between consecutive cycles and at different potentials.

Table 1. Kinetic parameters for oxygen reduction on copper electrode in O_2 saturated 1M NaOH solution calculated from Eqs. (9, 10) at 27 °C.

E(V)	no time delay		5 min. time delay		20 min. time delay	
	J_k	K	J_k	K	J_k	K
	mA/cm_2	cm/s	mA/cm_2	cm/s	mA/cm_2	cm/s
-0.50	3.88	0.042	3.58	0.039	1.92	0.021
-0.55	6.14	0.067	5.33	0.058	2.71	0.029
-0.60	10.15	0.111	9.17	0.099	3.48	0.038

Table 2. The number of electrons transferred per O_2 molecule calculated from Eq. (11) at 27 °C.

E(V)	n		
	no time delay	5 min. time delay	20 min. time delay
-0.65	3.61	2.85	1.88
-0.70	3.85	3.23	2.03
-0.75	3.97	3.43	2.23
-0.80	4.05	3.61	2.33

To account for the findings and the time dependencies of the shapes of the voltammograms we suggest a mechanism based on simultaneous direct oxygen reduction and copper oxide reduction. At -0.7 V/SCE it seems that oxygen reduces on oxide free copper surface to OH^- by 4 electron reduction and slowly adsorbs on the copper surface covered by oxide layers most likely in undissociated form with subsequent 2 electron reduction to form $HO_2(ads)$ species. Extending the reduction potential to -1.0 V/SCE starts a new course of reduction at -0.9 V/SCE. The reduction process at -0.9 V/SCE is probably the reduction of copper (II) oxides which formed during time delay at open circuit potential. The huge, time dependent peak at -1.2 V/SCE is due to the copper (I) oxide reduction. The charge under the voltammogram peak corresponds to over 5000 mono layers and the reduction process can not be a purely surface phenomenon, Figure 3. The repeated cycle causes increased area which is due to the increased porosity caused by penetration/removal of oxygen species as well as the redox processes of copper, Figure 6.

4. Conclusion

The electrochemical reduction of oxygen in alkaline solution was studied by cyclic voltammetry and RDE technique. On the basis of the experimental findings it is concluded that direct oxygen reduction is accompanied by the electrochemical reductions of copper oxides which formed during time delay at open circuit potential. The number of electrons transferred per O_2 molecule (n) obtained on different copper surface is close to 4 on oxide free copper surface and gradually decreases to 2 when the oxide layers cover the copper surface. Also, calculation of rate constant of oxygen reduction on copper surface, showed a faster kinetic of reaction on oxide free surface of copper. The copper oxidation/reduction process which accompanies oxygen reduction in the potential domain of study results in the tearing down and building up of the interface with the consequence of increased porosity and surface area.

5. Acknowledgements

The authors gratefully acknowledge the financial support of Sharif University of Technology and Semnan University Research Council.

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رفتار کاتالیتیکی مس برای واکنش کاهش اکسیژن در محلول قلیایی

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تاریخ پذیرش: ۹۱/۱۱/۸

تاریخ تصحیح: ۹۱/۱۰/۲۱

تاریخ دریافت: ۹۱/۰۹/۶

چکیده:

در این مقاله جنبه‌های سینتیکی و مکانیزمی واکنش کاهش اکسیژن و همینطور اثرات الکتروکاتالیتیکی سطح مس به کمک روشهای ولتامتری چرخه‌ای و الکتروود دیسک چرخان مورد مطالعه قرار گرفت. در محدوده پتانسیل -0.4 تا -1.4 V/SCE دو پیک وابسته به زمان و یک قسمت صاف در ولتاموگرامهای چرخه‌ای مشاهده گردید. کاهش مستقیم اکسیژن همراه با کاهش اکسیدهای مس که در فواصل زمانی مشخصی که الکتروود در پتانسیل مدار باز قرار می‌گیرد تشکیل می‌شوند به کمک روشهای الکتروشیمیایی مورد بررسی قرار گرفت. تعداد الکترونهای مبادله شده برای کاهش اکسیژن روی سطح مس در حالت‌های مختلف محاسبه و مشاهده گردید که روی سطح مس عاری از اکسید، تعداد الکترون ۴ و با رشد لایه اکسیدی روی سطح مس تعداد الکترونها به ۲ کاهش می‌یابد. همچنین، محاسبه ثابتهای سرعت نشان داد که کاهش اکسیژن روی سطح مس عاری از اکسید با سرعت بیشتری انجام می‌شود. افزایش سطح فعال مس که به خاطر نفوذ و خارج شدن اکسیژن و تخریب و بازسازی مجدد سطح اتفاق می‌افتد نیز مشاهده گردید.

کلمات کلیدی: واکنش کاهش اکسیژن، مس، محلول قلیایی، ولتامتری چرخه‌ای

