Asian Journal of Chemistry; Vol. 25, No. 10 (2013), 5707-5709

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.OH68

Electrochemical Behaviour of Arsenic on Copper Deposition Reaction in the Low Copper Concentration Electrolyte†

SHAOHUA CHEN[1,*], YI DING[1], DONGLIN ZHAO[1], DAORONG LU[2] and JIAQUAN WANG[3,*]

[1]College of Material and Chemical Engineering, Anhui University of Architecture, Hefei 230022, Anhui Province, P.R. China
[2]School of Chemical Engineering, Hefei University of Technology, Hefei 230009, Anhui Province, P.R. China
[3]School of Resource and Environmental Engineering, Hefei University of Technology, Hefei 230009, Anhui Province, P.R. China

*Corresponding authors: E-mail: chshaohua@yeah.net; jiaquan.wang@163.com

AJC-13311

During the electrolytic refining process of copper, arsenic as a common impurity ions, would affect the deposition reaction of the copper cathodes and thereby affected the quality of the cathode copper. In this paper, linear sweep voltammetry and cyclic voltammetry were used to analyze the electrochemical behaviour of arsenic ion in the low-copper electrolyte system. The effect of arsenic ion impacting the limiting current density in copper deposition, as well as co-deposition reaction mechanism on the cathode copper were also studied, which would provide a theoretical basis on the actual improvements of copper electrolysis process.

Key Words: Copper electrolyte, Arsenic ion, Linear scanning voltammetry, Cylic voltammetry.

INTRODUCTION

Copper, as an important metal, plays an important role in national economic life. The purity directly affects its conductive property, especially in the electrical industry the demand for high purity electrolytic refining copper is great. In the electrolytic refining of copper, however, the impurity ions contained in the blister copper and the electrolyte, such as As^{3+}, Sb^{5+} and Bi^{3+}, *etc*. would be also along with the deposition on the cathode refined copper, especially the arsenic ions[1-6]. This would reduce the quality of electrolytic copper. During the electrolytic refining process, copper ion concentration in the electrolyte would gradually reduce with the accumulation of arsenic ions. And arsenic ions in the low-copper system may be more easily deposited on the cathode with copper. In this paper, linear sweep voltammetry and cyclic voltammetry were used to study the electrochemical behaviour of arsenic ion in the low-copper system, which explore the impact of copper deposition reaction mechanism and provide a theoretical analysis of copper electrolytic refining effect.

EXPERIMENTAL

Confection of electrolyte: Electrolyte was confected with secondary distilled water in the electrolyte containing the following subastances: copper 10 g/L and 15 g/L, H_2SO_4 200 g/L, As^{3+}: 1 g/L, 3 g/L, 5 g/L,7 g/L,10 g/L,14 g/L respectively. All the regants used were AR grade.

Preparation of electrodes: Three electrodes system was used in the experiment. In the electrodylitical hall, work electrode was used by a thin copper thread which intercept area was 0.2 mm^2 as cathode and the counter electrode was used by pure lead foil as anode. Surface of study electrode was furnished by different kinds of sand paper before experiment,and dip in acetone and vitriol respectively and then washed with secondary distilled water to remove smear and oxide on the surface of the electrode. Mercurous sulfate electrode (MSE)was used as reference electrode.

Electrechemistry ananytic method: Linear scanning voltammetry and cylic voltammetry were choosed in the experimental. Linear scanning voltammetry was measured by potentiometer (8511B), scanning speed: 0.002 v/s. Cylic voltammetry was measured by the computer electrochemistry analytical system (LK98B II).

RESULTS AND DISCUSSION

Steady-state polarization curves of pure copper system without As^{3+}: Two curves in Fig. 1 were polarization curves (copper concentration 10 g/L and 15 g/L) with support electrolyte vitrol solution was 200 g/L. The value of the flat roof was called limited diffusion current. The value was 24.42 mA (copper concentration:10 g/L) and 68.47 mA (copper concentration:15 g/L) respectively.

---

†Presented to the 6th China-Korea International Conference on Multi-functional Materials and Application, 22-24 November 2012, Daejeon, Korea

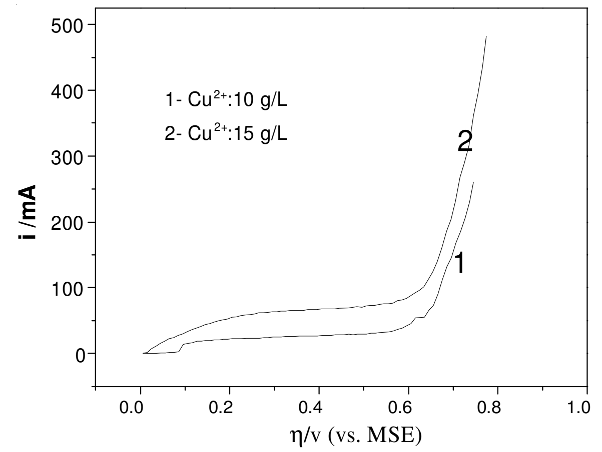

Fig. 1. Cathodic steady-state polarization curves of pure copper system

There were two processes in copper cathode deposition reaction which was called hopping control step and the diffusion control step respectively. When the cathode current density was slow, the process was controlled by hopping control step,with the increasing of cathode current density, the supply of metal ion was not enough, thus the reaction gradually transferred to the the diffusion step control. When η was further increased, the particle concentration of the vicinity of the electrode surface discharge reduced to zero (in the limit case), then the diffusion rate reached the maximum value. The cathode current density reached a maximum value and the diffusion limiting current density appeared as following relationships:

$$i_L = \frac{nFDC^0}{\delta} \tag{1}$$

As seen from the formula (1), the diffusion limiting current density and the discharge of the overall particulate concentration C^0 was inversely proportional to the effective thickness of the diffusion layer of δ, the smaller was δ, the larger was the limiting current density. Untill η increased enough to make the other cathode process take place, the cathode current i_L would again increase and then there would be two reactions at the same time on the cathode, becoming a double electrode. The existence of limiting current was disadvantageous for improving the productivity. In the actual production, methods such as elevated temperatures, intense agitation, *etc*. were frequently used to increase the current limit to increase the reaction rate.

Effect of As^{3+} on the steady-state polarization curves of cathode copper deposition reaction: The cathodic steady-state polarization curves of the low-copper system copper-arsenic codeposition reaction were shown in Fig. 2.

In Fig. 2, each polarization curve represented of different As^{3+} content in the electrolyte with the copper content of the above electrolyte, respectively 10 g/L (A) and 15 g/L (B) and the sulfuric acid content was both 200 g/L. We could deduce from the figures: in the low copper system, value of the limiting current density for copper deposition reaction increased with As^{3+} content increase and As^{3+} played depolarization on the reaction of copper deposition. During the process of line scan, this may be caused by the increase of electric potential and the deposition potential of the arsenic was reached, thus was deposited on the cathode to generate As and Cu alloy, so that the diffusion limiting current density of the system was increased.

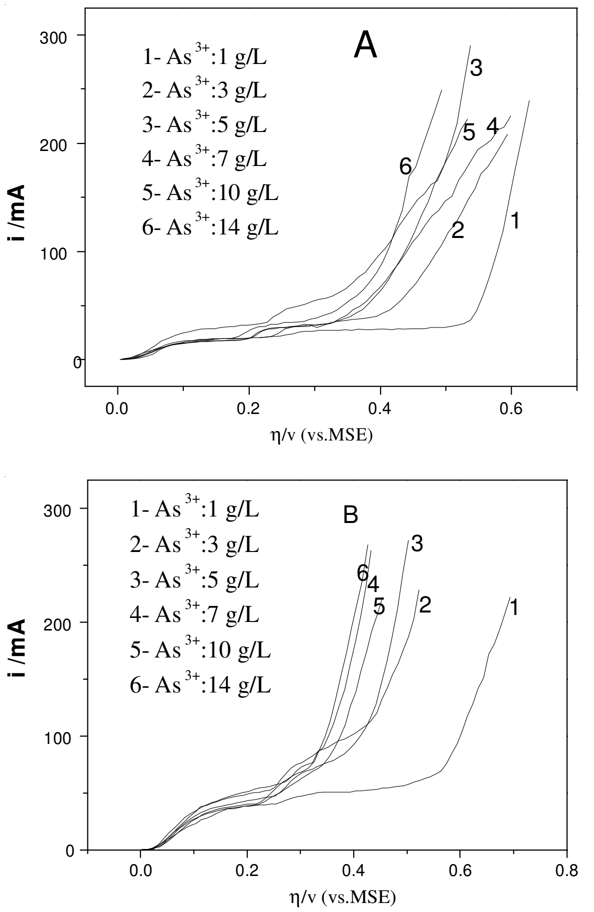

Fig. 2. Cathodic polarization curves of copper - arsenic system (A- Cu^{2+}: 10 g/L; B- Cu^{2+}: 15 g/L)

Effect of Cu^{2+} in the solution on cyclovoltammetric curves of copper deposition reaction without As^{3+}: Different Cu^{2+} in the solution on peak current and peak potential of copper deposition reaction was studied first. Scanning start potential: -0.380 v, scanning end potential: -1.00 v, scanning speed: 3.0 v/min, cycle times: 8. The eighth cycle curve was chosen to compare its behaviour (Fig. 3).

In Fig. 3, line 1 represented the solution containing Cu^{2+} (10 g/L), line 2 represented the solution containing Cu^{2+} (15 g/L). The results indicated that peak current and peak potential of copper deposition reaction in the solution containing Cu^{2+} 10 g/L was $i_p = 3530$ A/m² and $\phi_p = -0.464$ v respectively; while peak current and peak potential of copper deposition reaction in the solution (Cu^{2+}: 15 g/L)was $i_p = 4661$ A/m² and $\phi_p = -0.465$ v respectively. We could deduce from this: (1) on cyclovoltammetric curves, there was only cathode current peak, but no anode current peak, this domenstrated that copper deposition reaction was irreversible[7]. (2) peak current density of line 2 was higher than that of line 1, dedicated that i_p increased with copper concentration. This ccould be explained by the formula:

$$i_p = 269 n^{3/2} A D^{1/2} v^{1/2} C^0 \tag{2}$$

(3) peak potential of both two lines were nearly the same and this mean different copper concentration in the solution didn't infect the peak potential of cathode copper deposition reaction.

TABLE-1
PEAK CURRENT AND POTENTIAL OF COPPER ELECTROLYTE CONTAINING ARSENIC ION

Arsenic concentration (g/L)	0	1	3	5	7	10	14
Peak current (A/m^2)	4661	2732	1141	2214	1765	2152	5993
Peak potential (v)	-0.465	-0.500	-0.477	-0.475	-0.448	-0.457	-0.468

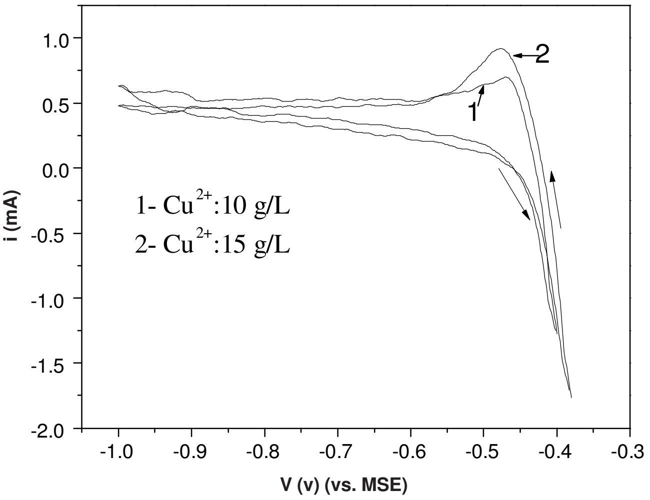

Fig. 3. Cyclovoltammetric curves of pure copper electrolyte without As^{3+}

Effect of As^{3+} in the solution on cyclovoltammetric curves of cathode copper deposition reaction: Effect of As^{3+} in the solution on cyclovoltammetric curve of cathode copper deposition reaction was also studied. The parameters were set as follows: beginning potential:-0.3800 v; on and off potential 1: -0.3800 v; on and off potential 2: -1.0000v; scanning speed: 0.0500 v/s; cylic times: 8 times; waiting time : 0 sec. We chose the solution containing cu^{2+} 15 g/L with different concentration arsenic ion concentration (1 g/L, 3 g/L, 5 g/L, 7 g/L,10 g/L, 14 g/L) and the results were shown in Fig. 4. The value of system peak current and peak potential were shown in Table-1.

From these figures and Table-1, we could deduce that when we put different arsenic ion concentration in the solution, cyclovoltammetric curves of cathode copper deposition reaction changed apparently. Peak current density were all decreased than the solution without arsenic ion except As^{3+} (14 g/L) and peak potential all moved to the left except As^{3+} (7 g/L and 10 g/L). The peak potential of As^{3+} (1 g/L) was a bit minus, others' were nearly the same as solution without arsenic ion. Some conclusions could be abained from CV curves of copper-arsenic co-deposition reaction on the cathode as follows:

(1) To low-copper containing electrolyte system, peak current of cathode of copper deposition reaction would increase with increasing of copper content in the solution, while peak potential would keep unchangeable nearly.

(2) To low-copper contaning electrolyte system, arsenic ion containing was below 10 g/L, would make peak current of cathode of copper deposition reaction decrease. This may caused by arsenic ion in the solution, which coulod decrease copper ion's diffusion coefficient.

(3) The peak current of cathode of copper deposition reaction would increase when arsenic ion concentration was 14 g/L. This may be caused by arsenic ion and copper ion react to be some kind alloy on the cathode, which increased the speed of copper ion deposition rate.

(4) Two current peak could be found on the cv curves when arsenic ion concentration was 3 g/L, 5 g/L, 7 g/L respectively. From the peak potential, we deduced that the first current peak may be caused by cuprous ion and arsenic ion react compound,and the second current peak may be caused by copper ion and arsenic ion react compound.

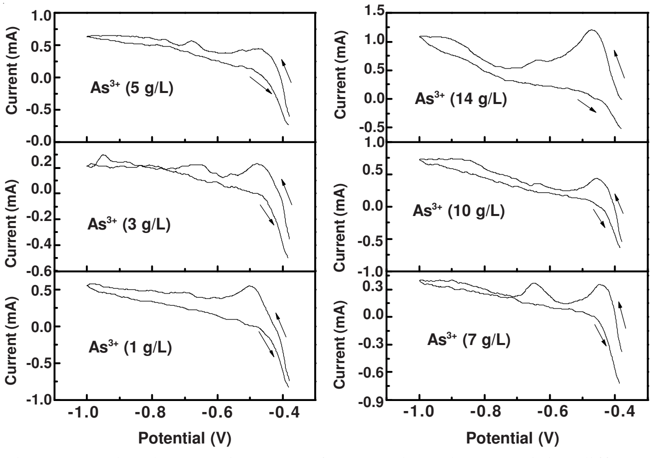

Fig. 4. Cyclovoltammetric curves of copper electrolyte containing different concentration of As^{3+}

Conclusion

The steady polarization curves results showed that in pure copper system, increasing the copper ions concentration would increase the limiting current density for copper deposition reaction and its value also increased with increase of As^{3+} in the electrolyte, which indicated that the As^{3+} played a role of depolarization on copper deposition reaction. The cyclic voltammograms results indicated that in certain range of concentration of arsenic ion would affect the mechanism of copper deposition reaction. In this article, we found two current peaks on the cv curves when the arsenic ion concentration was among 3-7 g/L.

ACKNOWLEDGEMENTS

The authors thank the financial support from the Ph.D. Start-up Fund of Anhui University of Architecture (K02644) and Innovation and Technology Plan of College Sudents of Anhui University of Architecture (C11044).

REFERENCES

1. Q.B. Zhang, Y.X. Hua, Y.T. Wang, H.J. Lu and X.Y. Zhang, *Hydrometallurgy*, **98**, 291 (2009).
2. E. Szocs, Gy. Vastag, A. Shaban and E. Kalman, *Corros. Sci.*, **47**, 893 (2005).
3. A.I. Danilov, E.B. Molodkina, A.V. Rudnev, Y.M. Polukarov and J.M. Feliu, *Electrochim. Acta*, **50**, 5032 (2005).
4. F.X. Xiao, Y.-J. Zheng, Y. Wang, H.-S. Jian, X.-Y. Huang and M.A. Yu-tian, *Trans. Nonferrous Met. Soc. China*, **18**, 1275 (2008).
5. S. Kologo, M. Eyraud, L. Bonou, F. Vacandio and Y. Massiani, *Electrochim. Acta*, **52**, 3105 (2007).
6. M.R. Majidi, K. Asadpour-Zeynali and B. Hafezi, *Electrochim. Acta*, **54**, 1119 (2009).
7. W.Z. Huang, Electrochemistry and Eleanalitical Chemistry, Peking University Press, Beijing, Vol. 2, p. 16 (1983).