Electrodeposition behaviour of copper from ore leachate and copper ammonium sulphate

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Abstract

The deposition behaviour of copper ammonia complexes from ore leachate and synthetic copper ammonium sulphate solutions was investigated using cyclic voltammetry with platinum as counter electrode. The work is carried out to understand the deposition behaviour of the ore for hydrometallurgical and electro winning application. The chemical reduction and deposition of copper from both solutions consisted of two reversible electrochemical processes, each involving the transfer of a single electron. The $\text{Cu(NH}_3)_4^{2-}$ complex in the copper leachate is first reduced to $\text{Cu(NH}_3)_2^+$ before being reduced to metallic copper. With synthetic copper ammonium sulphate ($\text{Cu(NH}_3)_2\text{SO}_4$), the reduction to metallic copper is a ligand-coupled electron transfer reaction which proceeds as two sequential, single-electron transfer processes. The $\text{Cu/Cu(NH}_3)_2^{2-}$ redox reaction during deposition of copper from the leachate is fast compared to that of the $\text{Cu/Cu}^{2+}$ redox reaction in the $\text{Cu(NH}_3)_2\text{SO}_4$ synthetic solution. Investigation of the electrochemical kinetics shows that the linear relationship between the peak current and the square root of the scan rate is an indication that the $\text{Cu(NH}_3)_2^+$ and $\text{Cu(NH}_3)_2\text{SO}_4$ reduction to Cu proceeds through a diffusion-controlled process.

Keywords: Copper ore; Leaching; Cyclic voltammetry; Electrodeposition; Electro winning

Introduction

The importance of copper for applications in electronic devices such as electronic circuit board, transmission of electricity and electroplating purposes has continued to rise due to industrial expansion to meet with the increasing demand. The metal is usually obtained by electro deposition from aqueous solutions after leaching (Popescu et al., 2013). Copper electro deposition from alkaline solutions has been widely applied for industrial coating of materials and electro winning of the metal (Alam et al., 2007; Oishi et al., 2007; Popescu et al., 2013). One of the notable ways of understanding the behaviour of copper and deposition processes in solution is by investigating its electrochemical reactions. The approach has been shown to be of great advantage over other methods with regards to electrolytic reduction and kinetics of the metal deposition from solutions (Majidi et al., 2009; Ballesteros et al., 2011). Cyclic Voltammetry (CV) analytical technique is often used for the elucidation of the reactions occurring during the electrodeposition processes due to its relative ease of operation and high information content (Nila and González, 1996a; Laze and Neghmouche, 2013). In addition, the technique is mostly preferred because of its simplicity, compatibility, and good control over vacuum-based deposition processes (Grujicic and Pesis, 2005; Majidi et al., 2009; Sophia and Muralidharan, 2015).

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Electrodeposition of copper can be carried out typically in a complexing agent such as Ethylenediamine tetra acetic acid (EDTA) and ammonia (NH₃) (Koyama et al., 2006; Viswanatha and George, 2011). Factors influencing the rate of copper deposition such as pH, stability of complexes and concentration of ions from ammonium chloride complexes have been investigated (Nila and González, 1996a). Ammonium salts and other complex forming reagents are widely used for leaching copper from high gangue complex ores (Ekmekeyapar et al., 2012; Ochromowicz et al., 2014). The recovery process of the metal from the solution containing the metal complex can be carried out by adsorption, electro winning or solvent extraction (Nila and González, 1996a and 1996b; Awe and Sandström, 2010; Liu et al., 2012). The electrodeposition of copper from leachate obtained from the leaching of the ore in ammonium chloride lixiviant has scarcely been investigated.

In this present study, a Near Infrared (NIR) pre-concentrated copper ore was leached with ammonium chloride solution according to the method described by Baba and Adekola (2010), Baba et al. (2013) and Amos et al. (2019). The leachate obtained from the leaching of the ores containing copper ammonia complexes was subjected to cyclic voltammetry analysis to understand the electrochemical behaviour of copper from the complexes. The electrodeposition process and mechanism controlling the process was also investigated in order to generate data for developing an efficient copper recovery process. The influence of scan rates on the reduction of copper was also observed. A synthetic electrolyte containing copper ammonium sulphate was also examined and results of the electrodeposition behaviour of copper in the synthetic electrolyte compared with that of the ore leachate.

It should be noted that before the leaching and electrochemical studies was carried out on the leachate, the influence of interfering metals (Mn, Zn, Co and Ni) was minimised by first pre-concentrating the ore after the method described by Iyakwari et al. (2013). Subsequently, the high grade copper ores was selectively leached (Amos et al., 2019).

Materials and methods

Chemicals were purchased from VWR international Ltd, UK. All solutions used were freshly prepared from analytical-reagent grade chemicals without further purification. Leachate was obtained after leaching of copper oxide ore in 1 M NH₄Cl for 2 h. Solution pH of leachate was 8.5, the synthetic solution of copper ammonium sulphate (Cu(NH₃)₂SO₄) was prepared using CuSO₄·2H₂O and ammonia and pH adjusted to 9 unless otherwise stated. The flow diagram for the strategy of ore pre-concentration, leaching and electrochemical analysis is presented in Fig. 1.

Leaching operation

Prior to leaching the ore was crushed, ground and sieved to the desired particle size fraction of -63/+45 μm amenable particle size for effective chemical leaching. The leaching experiment was performed using 250 ml of freshly prepared aqueous solution of NH₄Cl of known molarity in a 500 ml reactor with a four-neck split flask in a thermostatically heating mantle with a temperature control unit. The reactor is designed with an overhead mechanical stirrer for agitation set at 300 rpm for 2 h and a rubber stopper for sampling of leachate. The desired temperature for leaching is obtained by adjusting the thermostatically-controlled electric heating mantle. 5 ml of leachate solution for electrochemical analysis was withdrawn and filtered using filter paper (Whatman No.540). The filtrate was then advanced for analyses as described in Fig.1.

Cyclic voltammetry

The cyclic voltammetry measurements were conducted using external bi-potentiotiostat from CHI Electrochemical Analyser Model 660D. It contains a 100 ml polarographic cell fitted with a three-electrode configuration. The working electrode (WE) consisted of 0.08 cm² and 0.5 cm²coiled platinum wire, the counter electrode (CE) was made of platinum sheet, and the reference electrode (RE) for cyclic voltammatic studies was leak-free Ag/AgCl in a 3 M KCl solution. All potentials are quoted with reference to the standard hydrogen electrode (= 0.222V). Potentiodynamic experiments were conducted across a range of cathodic potentials from 0.8 V to -1.0 V for selected scan rates (20, 50, 100, and 200 mV/s). All the experiments were carried out at room temperature (T = 25 °C).

Results and discussion

Electrochemical studies

Fig.2 show the cyclic voltammogram obtained from solution of copper ore leachate. The potential scan rates of
20, 50, 100, and 200 mV/s in the cathodic and anodic directions were carried out. The starting potential was from a positive potential of 0.8 V to a negative potential of -1.0 V. The excursion from the positive to negative potential reveals two reduction peaks (A and B) at cathodic potentials between -0.10 and -0.23 V. Similarly, in the reverse scan (anodic) direction, two peaks (C and D) were also observed at anodic potentials of around -0.10 and 0.39 V. The two cathodic peaks A and B are a result of the divalent copper ammonia complex undergoing reduction to the monovalent copper complex (peak A) and subsequently to copper metal (peak B). The peak depth increase with increasing scan rate in B suggests the electrodeposition of copper on the platinum electrode takes place at a negative potential between -0.10 and -0.23 V. The two-step reduction process occurring in peaks A and B is expressed in Equations 1 and 2, respectively.

\[ \text{Cu(NH}_3\text{)}_4^{2+} + e^- \rightarrow \text{Cu(NH}_3\text{)}_2^{+} + 2\text{NH}_3 \]  
\[ \text{Cu(NH}_3\text{)}_2^{+} + e^- + 2\text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}_2\text{Cu}^{+} + 2\text{NH}_3 \]  

Fig. 1. Flow diagram of the strategy for pre-concentration, leaching and electrochemical analysis
During the reverse scan, electrochemical regeneration of Cu(NH$_3$)$_4^{2+}$ complex takes place by the dissolution of copper and the formation of monovalent copper ammonia complex in the presence of the complexing agent. Two peaks (C and D) were observed which have different width to the forward scan peaks (A and B). The width of peak C suggests that the electro active species deposited (shown by peak B) undergoes a stepwise dissolution in the anodic or reverse scan direction. Equation 3 shows the oxidative dissolution of copper in the presence of ammonia (peak C):

$$\text{Cu} + 2\text{NH}_3\text{Cu(NH}_3)_2^{+} + e^{-} \quad (3)$$

The monovalent copper (I) ammonia complex is unstable and undergoes oxidation into the stable copper (II) ammonia complex. This oxidation, which is facilitated by oxygen in the solution, is indicated by the sharp anodic stripping peak D and by the high value of peak current. The equations for this reaction are presented in Equations 4 and 5 (peak D):

$$\text{Cu} + \text{Cu(NH}_3)_4^{2+} \rightarrow 2\text{Cu(NH}_3)_2^{+} \quad (4)$$

$$\text{Cu(NH}_3)_2^{+} + 2\text{NH}_3 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + e^{-} \rightarrow \text{Cu(NH}_3)_4^{2+} + 2\text{OH}^{-} \quad (5)$$

The increase in the peak C height as a function of scan rate reflects that the reduction of the copper (I) ammonia complex occurred as a reversible process while the peak D corresponds to a single electron transfer process. The clear difference in the peak areas of anodic peak C and cathodic peak A suggest that the reaction is partially reversible. Thus the closeness in the current of peaks (A and D) attributed to the reversible reactions suggest that the redox couple Cu(II)/Cu(I) is a reversible system. The electrochemical reaction in peaks C and D is an indication of the reversibility of electrodeposition and dissolution of copper on platinum electrode. This is in line with the observation by Popescu et al. (2013).

The difference in the number of ammonium ligands in the two peaks A and B (Equations 1 and 2) corresponding to [Cu(II)/Cu(I)] redox couple indicates that the overall reaction involves the decoupling of ligands. Shumilov et al. (1983) and Brown and Wilmott (1985) showed that the reduction occurs on the trimetallic complex (Cu(NH$_3$)$_3^{+}$). This observation is in line with the one reported by Darchen et al. (1997). Aravinda et al. (2000) reported that the electronation of divalent copper (II) solutions containing complexing agents occur by a stepwise process with ammonia and a number of amine and nitrogen-containing heterocyclic compounds given rise to electronation of the copper complexes. The two-step reductions of copper complexes were observed

**Fig. 2. Cyclic voltammograms of ore leachate at different scan rates. Inset: Cathodic peak current versus square root of scan rate**
Fig. 3. Cyclic voltammograms of synthetic Cu(NH₃)₄SO₄ electrolyte at different scan rates. Inset: Cathodic peak current versus square root of scan rate

by potentiometry (Darchen et al., 1997; Giannopoulou et al., 2009).

Fig. 3 shows the cyclic voltammogram of synthetic copper ammonium sulphate solution. A single pair of redox peak is observed for the complex, corresponding to Cu/Cu²⁺ redox couple as indicated by the cathodic and anodic peaks (E and F). The appearance of the two peaks instead of the four in Fig. 3 is an indication that the electrodeposition behaviour is different. Anodic Peak F signifies the dissolution of copper electrodeposited during the forward potential scan. Peak E suggests that the electroactive copper (II) is reduced, undergoing electron transfer predominantly from the copper ammonia complex. The unique electrochemical reactions observed for the Cu(NH₃)₄SO₄ solution is an indication of a quasi-reversible deposition/dissolution behaviour of Cu⁺ ion occurring in unison. The electrochemical behaviour observed is similar to that by Popescu et al. (2013). Thus the reduction of Cu²⁺ to Cu metal during the cathodic scan and its oxidation in the anodic scan is an indication of the reversibility of the reaction, as shown in Equations 6 (peak E) and 7 (peak F):

\[
\text{Cu(NH}_3\text{)}_4^{2+} + e^- \rightarrow \text{Cu(NH}_3\text{)}_2^{+} + 2\text{NH}_3 \quad (6)
\]

\[
\text{Cu(NH}_3\text{)}_2^{+} + e^- \rightarrow \text{Cu} + 4\text{NH}_3 \quad (7)
\]

Equations 6 and 7 suggest that Cu(NH₃)₂⁺ is an intermediate species during the reduction of Cu(NH₃)₂²⁺, which proceeds through a ligand-coupled electron transfer reaction and involves the conversion of the ammonium ion. Pecquilo and Panossian (2010) also used cyclic voltammetry technique to understand the electrodeposition mechanism of copper from strike alkaline bath and showed that Cu²⁺ reduction to Cu occurs via a direct reduction without formation of Cu⁺ intermediate. Majidi et al. (2009) and Meng and Bard (2015) indicated that the reduction of copper can occur by either ion transfer controlled regime or via ligand-coupled electron transfer reaction. This is consistent with the observations in Fig. 3.

**Electrochemical kinetics**

Figs. 2 and 3 can be used to infer the electrodeposition kinetics. The cyclic voltammograms obtained from the various scans show that the behaviour of ore leachate and synthetic solutions are distinct. The cathodic peak potential (B), for the reaction given by Equation 2, is -0.20, -0.21, -0.22 and -0.23 V at the scan rate of 20, 50, 100 and 200 mV/s, respectively (Fig. 2). The differences between the cathodic and anodic potentials are 0.19, 0.20, 0.21 and 0.23 V, only increased slightly with the scan rate. The gradual shift of oxidation/reduction peaks with scan rate is evidence of reversibility of electrochemical process taken
place. As shown in the inset of Fig. 2, the cathodic peak current exhibits a linear relationship with the square root of the scan rate, suggesting that reduction of Cu$^{2+}$ to Cu is mainly under diffusion control. The observed electrochemical behaviour is similar with that by Grujecic and Pesic (20015) and Popescu et al. (2013). The higher peak currents and smaller peak width provides further evidence of a highly reversible reaction. The cathodic peak (E ) for the synthetic solution of Cu(NH$_3$)$_4$SO$_4$ which correspond to Cu$^{2+}$/Cu redox couple, appear at -0.22, -0.30 and -0.38 V at the scan rate of 20, 50 and 100 mV/s respectively, (Fig.3). The difference between the cathodic and anodic peak potentials increased with the scan rate, which is characteristic of slow electron transfer kinetic. Therefore, comparison between the two experiments shows that the Cu$^{2+}$/Cu redox couple in the synthetic solution is a sluggish electron transfer process due to the large separation between the cathodic and anodic peak while the Cu/[Cu(NH$_3$)$_3$]$^+$ redox reaction in the ore leachate is more reversible, with fast electron transfer. While only one pair of redox peaks are observed for Cu(NH$_3$)$_4$SO$_4$ solution, this suggests two separate one electron transfer reactions attributed to simultaneous cathodic deposition of ionic Cu$^{2+}$ to copper and anodic dissolution of copper to Cu$^{2+}$. The inset of Fig.2 shows that the relationship between the peak current and the square root of the scan rate is linear; indicating that reduction of Cu$^{2+}$ to Cu (0) is also a diffusion-controlled process. With two pairs of redox peaks observed for the ore leachate, this indicates that the reduction of [Cu(NH$_3$)$_3$]$^+$ to Cuhas a higher rate constant compared to the reduction of Cu$^{2+}$to Cu As a result, when the peak current C increases peak A, which corresponds to the reduction of Cu$^{2+}$ to Cu(I), also increases consistently.

The cyclic voltammograms curves provide insight into the electrochemical behaviour and electrodeposition of copper from ore leachate solution and Cu(NH$_3$)$_4$SO$_4$ synthetic solution. The increase in copper deposition Cu (I) Cu (0) increases as a response to increase in scan rate. It was also observed that the increase in scan rates led to remarkable increase of both cathodic and anodic peaks in response to increase in current density. The observed behaviour depends on potential sweep rates, as presented in the Figs. 2 and 3. From the voltammetric scans, it is clear that the copper reduction is a stepwise process involving two steps, with the electronation of the Cu$^{2+}$ in the solution containing the complexing agent. The electrodeposition is an equilibrium process whereby the free Cu$^{2+}$ concentration is in equilibrium with Cu$^+$ concentration. Under transient polarisation conditions, the deposition of copper involves the formation of monovalent copper and the ammonia ligand. The reversibility of the Cu(II)/Cu(I) reactions established with the triammonia copper complex (Equation 8) as the intermediate specie in the redox reaction (Brown and Wilmott, 1985).

$$\text{Cu(NH}_3\text{)}_4^{2+} + e^- \rightarrow \text{Cu(NH}_3\text{)}_3^{+} \quad (8)$$

It is observed that the electrodeposition of copper is similar to the conventional electrowinning process of the metal which is known to proceed according to a two-step process. The kinetics of the electrochemical reactions indicated that copper deposition in both the solutions were under diffusion-controlled mass transfer process.

Conclusion

Electrochemical studies of two solutions of copper complexes were successfully investigated. The deposition behaviour of copper from solution of ore leachate was studied with cyclic voltammetry and compared with a synthetic electrolyte solution of Cu(NH$_3$)$_4$SO$_4$. The influence of scan rate and potential on the two solutions was investigated. It was found that the deposition of copper metal from the leachate solution is a two-step process while that of the copper ammonium sulphate consist of two separate one-electron transfer processes. The electrodeposition increases with increasing scan rates. The transition from the divalent state to the monovalent state is a reversible process, with electron transfer being a fast process. This suggests that the reactions are diffusion controlled.

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References

Alam MS, Tanaka M, Koyama K, Oishi T and Lee JC (2007), Electrolyte purification in energy-saving monovalent copper electro winning processes, Hydrometallurgy, 87(1): 36-44. DOI: org/10.1016/j. hydromet. 2006. 12.001
Amos IA, Shekwonyadu I and Glass HJ (2019), Selective leaching of copper from near infrared sensor-based pre-concentrated copper ores, *Physicochem. Probl. Miner. Process.* 56(1): 204-218

Aravinda CL, Mayanna SM and Muralidharan VS (2000), Electrochemical behaviour of alkaline copper complexes, *Journal of Chemical Sciences,* 112(5): 543-550.

Awe SA and Sandström Å (2010), Selective leaching of arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkali sulphide solution, *Minerals Engineering* 23(15): 1227-1236. DOI: org/10.1016/j.mineng.2010.08.018

Baba AA and Adekola FA (2010), Hydrometallurgical processing of a Nigerian sphalerite in hydrochloric acid: Characterization and dissolution kinetics, *Hydrometallurgy,* 101(1): 69-75.

Baba AA, Ayinla KI, Adekola FA, Bale RB, Ghosh MK, Alabi AG and Folorunso IO (2013), Hydrometallurgical application for treating a Nigerian chalcopyrite ore in chloride medium: Part I. Dissolution kinetics assessment, *International Journal of Minerals, Metallurgy and Materials* 20(11): 1021-1028.

Ballesteros JC, Chainet E, Ozil P, Meas Y and Trejo G (2011), Electrodeposition of Copper from Non-Cyanide Alkaline Solution Containing Tartrate, *Int. J. Electrochem. Sci.* 6: 2632-2651.

Brown OR and Wilmott MJ (1985), A kinetic study of the Cu (NH₄)₂/Cu(NH₃)₂ redox couple at carbon electrodes, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry,* 191(1): 191-199.

Darchen A, Drissi-Daoudi R and Irzho A (1997), Electrochemical investigations of copper etching by Cu(NH₄)₂Cl₂ in ammonia solutions, *Journal of applied electrochemistry,* 27(4): 448-454.

Ekmekeyapar A, Tanaydin M and Demirkiran N (2012), Investigation of copper cementation kinetics by rotating aluminium disc from the leach solutions containing copper ions, *Physicochem. Probl. Miner. Process* 48 (2): 355-367.

Giannopoulou I, Panias D and Paspaliaris I (2009), Electrochemical modeling and study of copper deposition from concentrated ammoniacal sulfate solutions, *Hydrometallurgy* 99(1): 58-66.

Grujicic Dand Pesic B (2005), Reaction and nucleation mechanisms of copper electrodeposition from ammoniacal solutions on vitreous carbon, *Electrochimica Acta* 50 (22): 4426-4443. DOI: org/10.1016/j.electacta.2005.02.012

Iyakwari S, Glass HJ and Kowalczyk PB (2013), Potential for near infrared sensor-based sorting of hydrothermally-formed minerals, *Journal of Near Infrared Spectroscopy* 21(3): 223-229.

Koyama K, Tanaka M, Miyasaka Y and Lee JC (2006), Electrolytic copper deposition from ammoniacal alkaline solution containing Cu (I), *Materials transactions* 47(8): 2076-2080.

Lanaz T and Nezhmouche NS (2013), Calculation of Diffusion Coefficients and Layer Thickness for Oxidation the Ferrocene using Voltammetry Technique, *Int. J Chem Studies* 1: 28-32.

Liu ZX, Yin ZL, Hu HP and Chen QY (2012), Leaching kinetics of low-grade copper ore containing calcium-magnesium carbonate in ammonia-ammonium sulfate solution with persulfate, *Transactions of Nonferrous Metals Society of China,* 22(11): 2822-2830.

Majidi MR, Asadpour-Zeynali K and Hafezi B (2009), Reaction and nucleation mechanisms of copper electrodeposition on disposable pencil graphite electrode, *Electrochimica Acta,* 54(3): 1119-1126. DOI: org/10.1016/j.electacta.2008.08.035

Meng Y and Bard AJ (2015), Measurement of Temperature-Dependent Stability Constants of Cu(I) and Cu(II) Chloride Complexes by Voltammetry at a PtUltramicroelectrode, *Analytical chemistry* 87(6): 3498-3504. DOI: org/10.1021/acs.analchem.5b0052

Nila C and González I (1996a), The role of pH and Cu(II) concentration in the electrodeposition of Cu(II) in NH₄Cl solutions, *Journal of Electroanalytical Chemistry* 401(1): 171-182.

Nila C and González I (1996b). Thermodynamics of Cu- H₂SO₄- Cl- H₂O and Cu- NH₄Cl H₂O based on predominance-existence diagrams and Pourbaix-type diagrams, *Hydrometallurgy* 42(1): 63-82.
Ochromowicz K, Jeziorek M and Wejman K (2014), Copper (II) extraction from ammonia leach solution, *Physicochem. Probl. Miner* **50**(1): 327-335.

Oishi T, Koyama K, Konishi H Tanaka M and Lee JC (2007), Influence of ammonium salt on electrowinning of copper from ammouniacal alkaline solutions, *Electrochimica Acta* **53**(1): 127-132. DOI: [10.1016/j.electacta.2007.06.024](https://doi.org/10.1016/j.electacta.2007.06.024)

Pecequilo CV and Panossian Z (2010), Study of copper electrodeposition mechanism from a strike alkaline bath prepared with 1-hydroxyethane-1, 1-diphosphonic acid through cyclic voltammetry technique, *Electrochim Acta* **55**(12): 3870-3875. DOI: [10.1016/j.electacta.2010.01.113](https://doi.org/10.1016/j.electacta.2010.01.113)

Popescu AM, Cojocaru A, Donath C and Constantin V (2013), Electrochemical study and electrodeposition of copper (I) in ionic liquid-reline, *Chemical Research in Chinese Universities* **29**(5): 991-997.

Shumilov VI, Kucherenko VI and Flerov VN (1983), Cathodic reduction of copper (II) ions in concentrated chloride solutions of copper ammonia complexes, *Soviet Electrochemistry* **19**(12): 1477-1479

Sophia J and Muralidharan G(2015), Gold nanoparticles for sensitive detection of hydrogen peroxide: a simple non-enzymatic approach, *Journal of Applied Electrochemistry*, **45**(9): 963-971.

Viswanatha SG and George S (2011), Electrowinning of copper powder from copper sulphate solution in presence of glycerol and sulphuric acid, *Indian journal of chemical technology* **18**(1): 37-44.