Cyclic Voltammetric Behavior of Copper Powder Immobilized on Paraffin Impregnated Graphite Electrode in Dilute Alkali Solution

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Cyclic voltammetric behavior of electrolytic grade copper powder immobilized on paraffin impregnated graphite electrode is studied in 0.1 M KOH solution. Few micrograms of copper powder is mechanically immobilized on the surface of paraffin impregnated graphite electrode and subjected to electrochemical characterization. Well separated, stable and sharp redox peaks for both Cu (I) and Cu (II) oxides are observed. Lowering the upper positive potential limit by increments of 5 mV is found to be directly proportional to the changes in the reduction peaks of both oxides which in turn is decided by the hydrous oxide film. In the absence of hydrous oxide film, the solid state redox transformations were stoichiometrically controlled and quasi reversible. This study helps to understand the 95-99 % efficiency of copper recovery process in our pilot plant.

1. INTRODUCTION

Copper electrochemistry has been studied at various levels in view of its numerous applications in electrocatalysis, sensors, batteries, microelectronics, electroplating and electroless plating. The electrochemical characteristics of Cu^{II}/Cu^{I} system is reported to be parallel to Fe^{III}/Fe^{II} couple in aqueous electrolytes [1]; on the other hand, the behavior of hydrous oxide on copper is found to be quite similar to that of noble metals like platinum, palladium and gold [2-4]. Copper acts as a bridge between the noble and non-noble metals resembling some of the both characteristics which justify the diverse applications, the metal being used. Most of the literature on copper electrochemistry reports that the oxide films on copper consist of both cuprous oxide (Cu_2O) and/or cupric oxide (CuO). There

are conflicting views regarding the order of reduction of oxides. Some authors have claimed that the reduction of Cu_2O occurs first, followed by the reduction of CuO [5-8]. Other authors have shown that CuO is reduced initially followed by the reduction of Cu_2O to Cu [9-11]. Deutscher and Woods insisted the same but they could not get separate reduction peaks for Cu_2O and CuO [12]. XRD and XPS analysis combined with the chronopotentiometric measurements led to the conclusion that CuO was first reduced to Cu in one step, followed by the reduction of Cu_2O. Here the electrolyte used was 0.1 M KCl [13]. S. Nakayama et al have developed a new LSV (linear sweep voltammetry) for qualitative and quantitative characterization of copper oxide films that employs a strong alkaline electrolyte (6 M KOH + 1 M LiOH) to clear the conflicting views that exists on the order of reduction of oxides [14]. They proved that the CuO was reduced first followed by the reduction of Cu_2O. L. D. Burke and M. A. Murphy in their elaborate studies on hydrous oxide growth on cooper in base have shown that the upper and lower potential limits are important for the oxide growth when the film was grown using cyclic voltammograms and the primary product in the hydrous oxide reduction reaction is an active state of the metal (Cu^*) which is not usually reversible and is responsible for the over potentials of oxide reduction in base [15].

The main aim of the present investigation is to study the redox behavior of metallic copper powder in alkali solution; this work is undertaken in order to understand the copper refining process that is been carried out in our pilot plant. Scrap of industrial copper alloy was made into anodes and pure copper sheets as cathodes for the recovery of copper from the scrap. During the process, we observed that the copper recovered was in the range of 95 to 99 wt. %, irrespective of the current applied for the electrolysis. During the electrolysis, the cupric ions dissolved from the anode reaches the cathode, get reduced and deposit as metallic copper. This part of reaction is purely electrochemical. The copper anode may also react with the electrolyte to under go the following chemical dispropotionation reaction:

$$2Cu_{(sol)}^+ \longrightarrow Cu_{(sol)}^{2+} + Cu^0 \qquad (1)$$
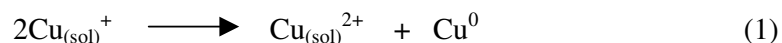
In such a situation, copper formed in the solution would settle down as slime and the efficiency of the recovering process would decrease; in reality, this was found to be so. In our copper recovery process, we found 10 wt. % of copper in the slime [16, 17]. Herein, we immobilized the copper powder on the surface of a paraffin impregnated graphite electrode and studied the redox behavior by cyclic voltammetry in dilute alkali solution. Incremental changes in applied anodic potential limits of the cyclic voltammgrams were done to trap the changes occurring on the electrode surface.
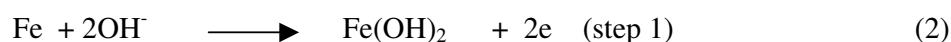
2. EXPERIMENTAL PART

All electrochemical experiments were conducted with a PGSTAT 302 Autolab system (Ecochemie, Utrecht, The Netherlands). It was connected to a PC running with Eco-Chemie GPES software. GPES software was used for all electrochemical data analysis. The reference electrode was

Ag/AgCl (3M KCl) and the counter electrode was a platinum foil supplied along with the instrument. The electrolyte solution was 0.1 M KOH.
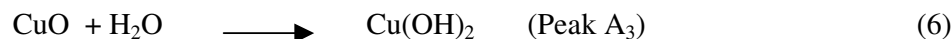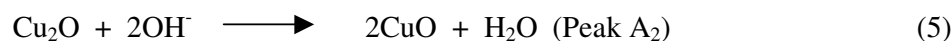
Paraffin-impregnated graphite electrodes (PIGE) were used as working electrodes with the surface immobilized with the active electrode material. A few micrograms of copper powder (particle size 40-50 µm) were placed on a clean glass plate, and the surface of PIGE electrode was pressed over the copper microparticles which would mechanically transfer the particles to the tip of the electrode [18, 19]. After immobilizing the copper powder, the electrode was cycled between the -1.1 to 0.6 V for 10 times to get a stabilized response; such repetitive potential cycling was shown to be a convenient technique for producing hydrous oxide film in aqueous solution [15].

3. RESULTS AND DISCUSSION

Fig. 1 shows the cyclic voltamamogram (CV) recorded for copper powder immobilized on the surface of paraffin impregnated graphite electrode (PIGE) in 0.1 M KOH solution. The limit on the positive end of potential window was 0.5 V and on the negative end, it was -1.1 V vs. Ag/AgCl. In all the CV measurements, the negative lower potential limit was kept constant while the potential at the positive upper end was changed in increments of 5 mV to note the changes in the reduction behavior. An analogy between aqueous electrochemistry of Fe and Cu was mentioned by M. D. Benari and G. T. Hefter [1]. Some aspects of the oxidation and reduction processes occurring on an iron electrode in alkaline solution are presented here so that copper electrochemistry can be easily followed. Based on the cyclic voltammetric responses, the oxidation of iron in alkali solution proceeds via two steps [20-22]:

$$Fe + 2OH^- \longrightarrow Fe(OH)_2 + 2e \quad (step\ 1) \tag{2}$$
$$Fe(OH)_2 + OH^- \longrightarrow FeOOH + H_2O + e \quad (step\ 2) \tag{3}$$

The CV in Fig. 1 shows three anodic peaks A_1, A_2 and A_3 and two cathodic peaks C_1 and C_2. Peak A_3 was broad in shape whereas all the other peaks were sharper in appearance. In accordance with the earlier reports [23-25], the appearance of anodic peaks may be written as follows:

$$2Cu + 2OH^- \longrightarrow Cu_2O + H_2O \quad (Peak\ A_1) \tag{4}$$
$$Cu_2O + 2OH^- \longrightarrow 2CuO + H_2O \quad (Peak\ A_2) \tag{5}$$
$$CuO + H_2O \longrightarrow Cu(OH)_2 \quad (Peak\ A_3) \tag{6}$$

The anodic and cathodic peak potentials (E in volts) and charges under the peaks (Q in coulombs) are presented in Table 1. Cathodic peaks C_1 and C_2 are due to the reversal of reactions occurring at the anodic peaks A_1 and A_2 so that A_1/C_1 and A_2/C_2 form respective redox couples. With regard to peak A_3, there is some discrepancy in literature claiming the formation of mixed oxide/hydroxide, top layer being $Cu(OH)_2$ [26, 27] . It is well known that the oxide film on copper are

composed of both cuprous oxide (Cu_2O) and/or cupric oxide (CuO) [28]. Very recently, S. Nakayama et al showed that the cross sections of the oxide film observed via scanning ion microscopic (FIB/SIM) image have the two oxide films in the order of construction as $Cu/Cu_2O/CuO$, CuO being the topmost layer [14]. Formation of Cu (III) species was reported to occur at ca. 0.6 V in strong alkaline solutions. Therefore, the upper potential limits employed in the present study do not allow the formation of Cu (III) species.
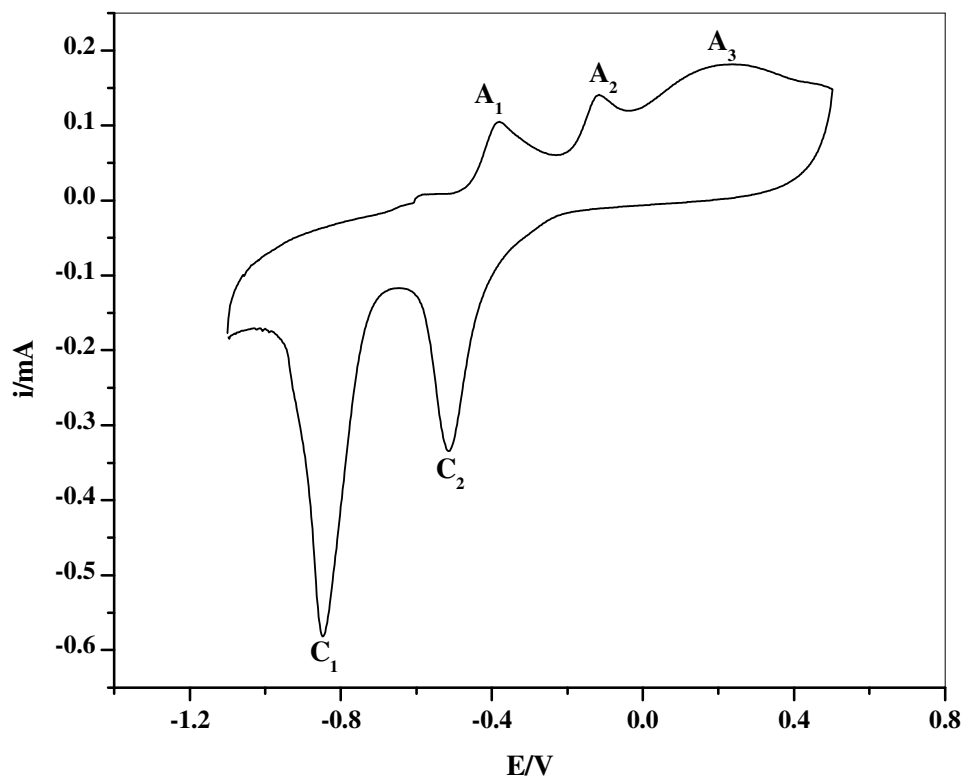

Figure 1. Cyclic voltammogram (recorded after stabilization ~10 scans) of Cu powder immobilized on PIGE electrode in 0.1 M KOH solution at the scan rate of 50 mVs^{-1}; $E_u = 0.5$ V.

The formation of broad anodic peak A_3 could be attributed to the formation of hydrous oxide of copper which originates from the hydrated cupric hydroxide. Appearance of broad peak on oxide surface confirms the formation to hydrous oxide. Similar behavior has been reported for transition metals in alkali solutions [29]. In the case of iron, the hydrous oxide redox peak was assumed to be due to Fe^{II}/Fe^{III} transition in a polymeric hydrous oxide layer formed initially by hydration of the outer regions of the $Fe(OH)_2$. The process involved may be written as:

$$\{Fe_2(OH)_6\ 3H_2O\}^2\ +\ OH^- \longrightarrow \{Fe_2(OH)_9\}^{3-}\ +\ 3H_2O\ +\ 2e \qquad (7)$$
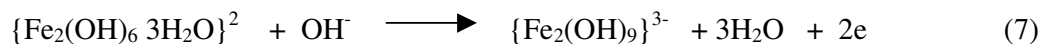
The composition of the oxidized state resembles that of gold. In accordance with N. Sato, the formation of aqueous complex can be explained as follows [30]: Water acts as a base to Fe^{2+} ions and

also as an oxidizing agent iron metal. This is due not only to the relative energies of the filled and empty orbitals, but also to their large energy separation which prevents their orbitals from interacting with each other. Anodic polarization leads to the hydration of iron ions die to the lowering of the Fermi level of Fe. The hydration of iron ions results from the frontier orbital interaction due to the configurational co-ordination of water molecules which act as Lewis bases around iron ions which act on a Lewis acid leading to the formation of bonding and anti-bonding molecular orbitals. The valence electrons of water occupy the bonding orbitals and a stable aquo-complex of metal ion was formed. The same explanation holds good for copper also.

Table 1. Parameters determined from the CVs of copper powder immobilized on PIGE electrode at varying upper potential limits and cycled in 0.1 M KOH solution; $\upsilon = 50$ mVs^{-1}.

Upper positive potential limits	Peak A_1		Peak A_2		Peak C_2		Peak C_1	
	E(V)	Q(C) x 10^{-4}	E(V)	Q(C) x 10^{-5}	E(V)	Q(C) x 10^{-4}	E(V)	Q(C) x 10^{-4}
0.50 V (curve 1)	-0.38	1.66	-0.12	8.24	-0.51	5.84	-0.85	9.93
0.45 V	-0.38	1.75	-0.12	7.43	-0.50	4.72	-0.84	10.3
0.40 V (curve 2)	-0.38	1.71	-0.12	7.67	-0.47	3.83	-0.84	9.66
0.35 V	-0.38	1.68	-0.12	8.01	-0.45	2.56	-0.83	8.57
0.30 V (curve 3)	-0.38	1.62	-0.12	8.44	-0.43	1.28	-0.82	7.48
0.25 V (curve 4)	-0.38	1.61	-0.12	8.50	-0.42 (C_2) -0.28 (C_{2a})	0.33 0.59	-0.80	6.59
0.20 V (curve 5)	-0.38	1.60	-0.12	8.56	-0.45 (C_2) -0.27 (C_{2a})	0.27 0.97	-0.76	5.75
0.15 V (curve 6)	-0.38	1.59	-0.12	8.49	-0.48 (C_2) -0.27 (C_{2a})	0.02 1.03	-0.73	5.01
0.10 V (curve 7)	-0.38	1.59	-0.12	8.46	-0.49 (C_2) -0.26 (C_{2a})	0.04 0.98	-0.71	4.46
0.0 V (curve 8)	-0.38	1.59	-0.12	7.99	-0.25 (C_{2a})	0.94	-0.68	3.86
-0.10 V (curve 9)	-0.38	1.61	-	-	-0.23	0.61	-0.67	3.69
-0.20 V (curve 10)	-0.37	1.63	-	-	-	-	-0.66	3.53

Fig. 2 shows the curves recorded at three upper potential limits; curve 1 ($E_u = 0.5$ V); curve 2 ($E_u = 0.4$ V); curve 3 ($E_u = 0.3$ V) and in Table 1, the respective changes in terms of peak potentials

and charges were summarized. In curve 2, where the E_u was limited to 0.4 V, the reduction in Q_p values was in the order of $C_2 > C_1$; also peak potential of C_2 shifts towards positive potentials by 40 mV. This reduction of charges under both the peaks implies that peaks C_1 and C_2 appear not only due to the reduction of Cu (I) (peak A_1) and Cu (II) (peak A_2) but also due to the reduction of copper species in hydrous oxide formed at peak A_3. This inference was further confirmed by observing the curve 3 where the upper potential limit was reduced to 0.3 V i.e. hydrous oxide formation on the copper electrode was till further inhibited. The response at the peaks C_1 and C_2 is quite interesting. While the Q_p decreased for both C_1 and C_2 considerably, peak C_2 split into two (designated as C_2 and C_{2a}) with a shift of 80 mV (C_2) toward the positive direction. Such a shift usually denotes favorable reaction kinetics. However, the positive shift was predominant only at C_2 but not at C_1 suggesting the reduction of copper species at C_1 was not yet affected. The appearance of new hump (which developed into a peak subsequently) at -0.28 V (C_{2a}) was also interesting; this result confirms the presence two kinds of Cu (II) oxide getting reduced i.e. the Cu (II) oxide that was formed during the solid state oxidation at peak A_2 and the Cu (II) oxide/hydroxide that was formed at peak A_3. It is already reported that an over potential is needed to reduce the hydrated CuO in base which is a pointer to the appearance of twin peaks (denoting two states of Cu (II) species) for the same reduction process.
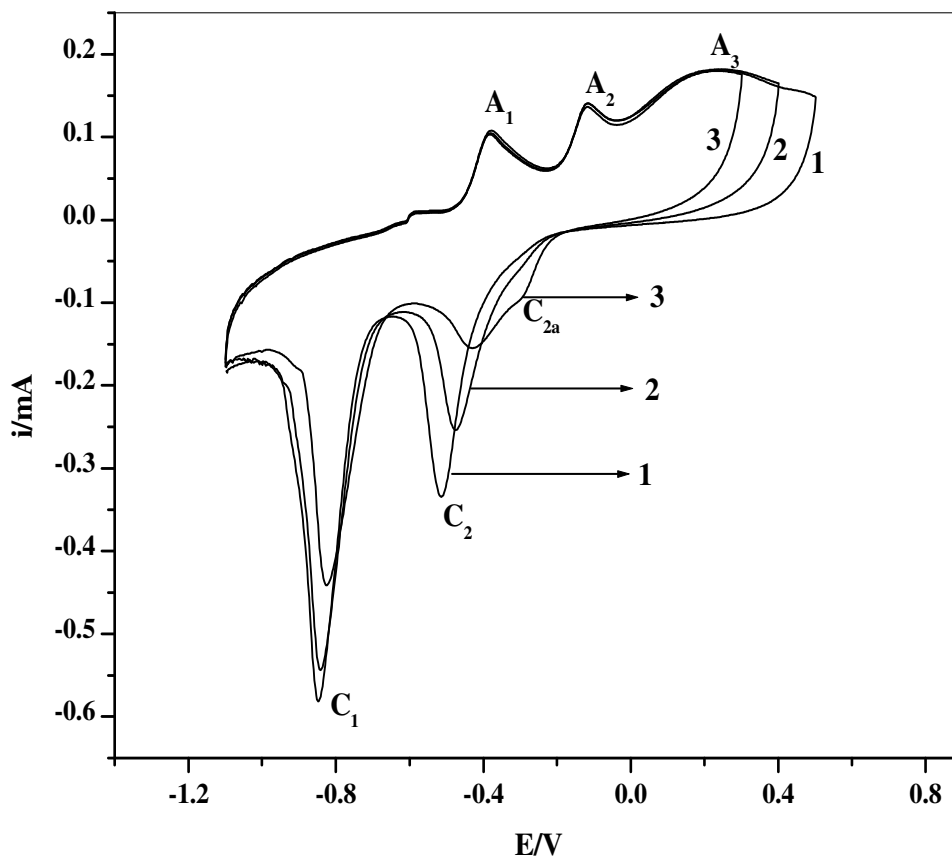

Figure 2. Cyclic voltammograms of Cu powder immobilized on PIGE electrode in 0.1 M KOH solution at the scan rate of 50 mVs^{-1}; curve 1, E_u = 0.5 V; curve 2, E_u = 0.4 V; curve 3, E_u = 0.3 V.

Fig. 3 shows the following CVs: curve 3 ($E_u = 0.3$ V), curve 4 ($E_u = 0.25$ V), curve 5 ($E_u = 0.2$ V) and curve 6 ($E_u = 0.15$ V). One could see the changes occurring in the reduction peaks very clearly on changing the upper potential limits which dictates the hydrous layer presence on the copper electrode surface. There were two noticeable differences between Figs. 2 and 3; initially, the cathodic peak C_2 eventually started disappearing with the concurrent appearance of sharp peak C_{2a} at still more positive potentials and secondly, C_1 peak charge decreased in increments in par with the upper potential limit along with the shift of (ca. 90 mV) peak potentials towards positive direction. These results confirm the following facts: (1) not only CuO but Cu_2O reduction also is influenced by the hydrous oxide film (peak A_3); (2) shift of C_1 peak potentials toward positive direction indicates that the Cu_2O reduction occurs more feasibly in the absence of hydrated species that also get reduced at C_1; (3) the predominace of peak C_{2a} could be due to the reduction of CuO, a solid state reaction that occurs is reversible to the oxidation of species at peak A_2; (4) the disappearance of peak C_2 is a direct proof that this peak represents the reduction of hydrated CuO species.
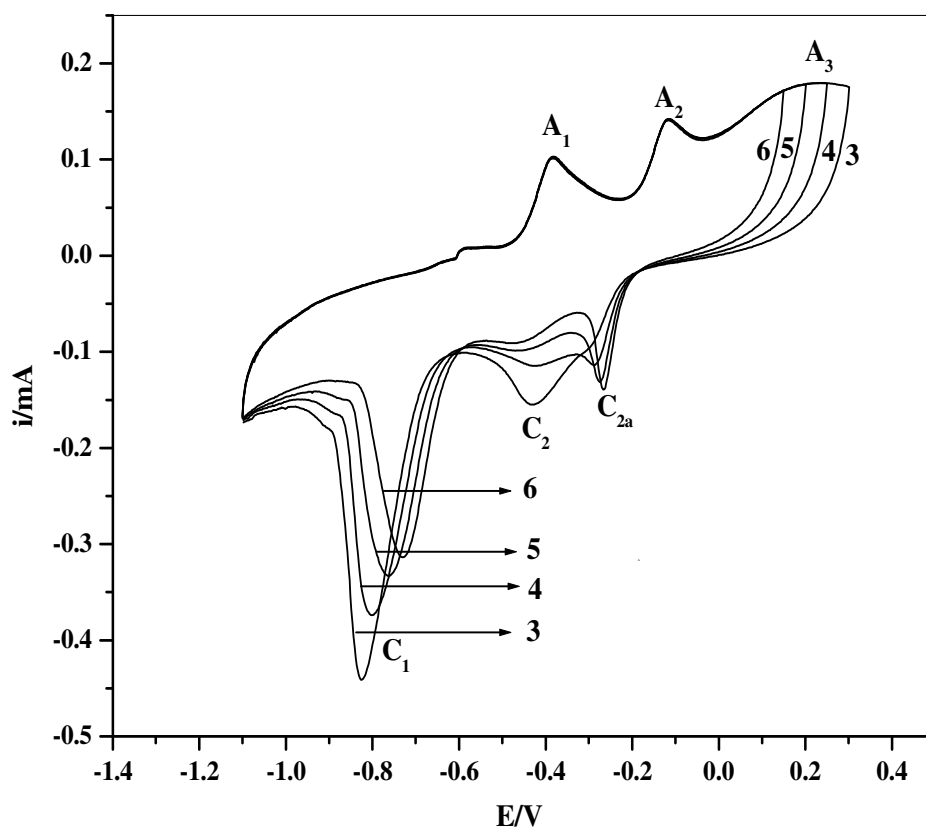

Figure 3. Cyclic voltammograms of Cu powder immobilized on PIGE electrode in 0.1 M KOH solution at the scan rate of 50 mVs^{-1}; curve 3, $E_u = 0.3$ V; curve 4, $E_u = 0.25$ V; curve 5, $E_u = 0.2$ V; curve 6, $E_u = 0.15$ V.

Hydrous oxide growth on copper and its reduction in base is reported to resemble that of gold and platinum [15]. L. D. Burke and M. A. Murphy have published a series of papers on this subject.

They surmised that the most surprising feature in the reduction of hydrous oxide is its over potential or the reluctance to get reduced [4, 31]. Our CV results concur with their observations. Both oxides either Cu_2O or CuO present in the hydrous oxide film gets reduced at a potential more negative than their solid state counterparts as shown by peaks C_1 and C_2 in Fig. 3. This shows that the regular bulk metal was not merely a support system for the hydrous oxide film to under go redox transformations. In consistent with the earlier work [15], the CVs confirm the inference that the redox behavior of the two states, the regular surface (usually the predominance one) and the surface active hydroxide film are quite different and are only indirectly related.
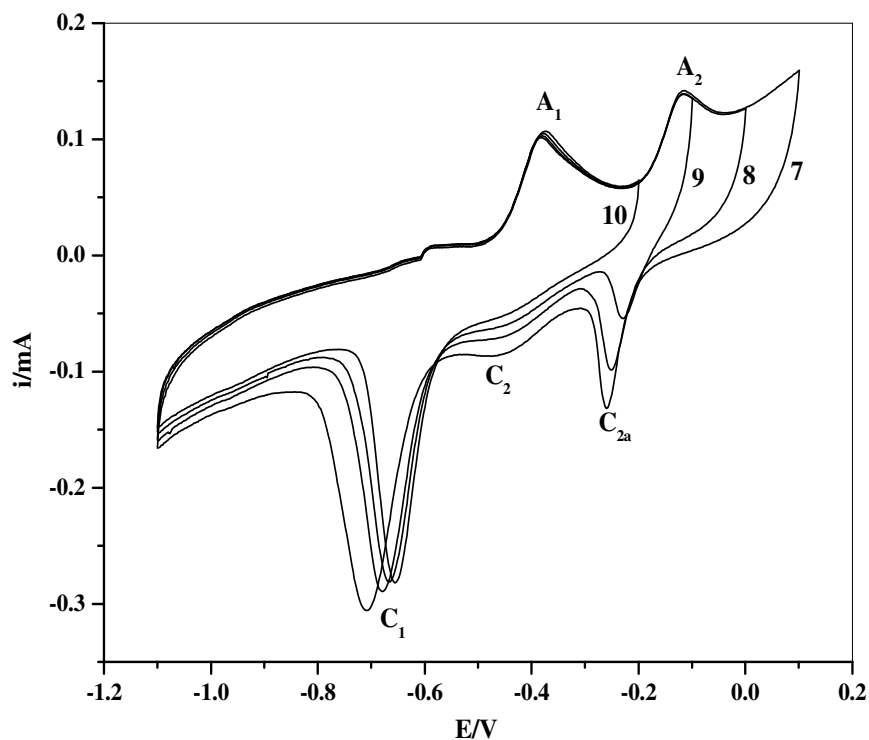

Figure 4. Cyclic voltammograms of Cu powder immobilized on PIGE electrode in 0.1 M KOH solution at the scan rate of 50 mVs^{-1}; curve 7, $E_u = 0.1$ V; curve 8, $E_u = 0.0$ V; curve 9, $E_u = -0.1$ V; curve 10, $E_u = -0.2$ V.

In all the CVs recorded, irrespective of the upper potential limit, an uniform behavior of Q_a/Q_c < 1 (i. e. the cathodic peak charges were much higher than the anodic peak charges) was observed. From the peak potentials and charges of anodic peaks shown in Table 1, it was obvious that the anodic peaks remain unperturbed due to the change in upper potential limit except for the minor variations. This observation itself is a direct proof about the two states behaving differently, one being the copper species in solid state undergoing regular redox transformations; the anodic peaks A_1 and A_2 appear due to the solid state oxidation of Cu to Cu_2O and Cu_2O to CuO respectively. The other state, surface active state present in the hydroxide film formed at peak A_3 undergoes reduction by a different mechanism and the product of these reductions, say Cu present in the double layer moves away from

the electrode surface with time; this explains why the reduction charges are always higher than the oxidative charges and why the oxidative charges remain consistent.

Further changes in upper potential limit could be monitored by the curves 7, 8, 9 and 10 shown in Fig. 4. Once the hydrous oxide formation potential was intentionally prohibited, its role in the reduction of copper oxides remains to be eliminated so that $Q_a/Q_c = 1$ for a perfect reversible charge transfer reaction. It does happen so within the marginal error. The $Q_a/Q_c = 0.41$ for A_2/C_2 redox couple and $Q_a/Q_c = 0.45$ for A_1/C_1 redox couple (curve 8) i. e. the reduction charges were slightly higher than the oxidation charges for both copper oxides. Such a result is expected for copper which undergoes facile reduction process due to its inherent electronic structure.
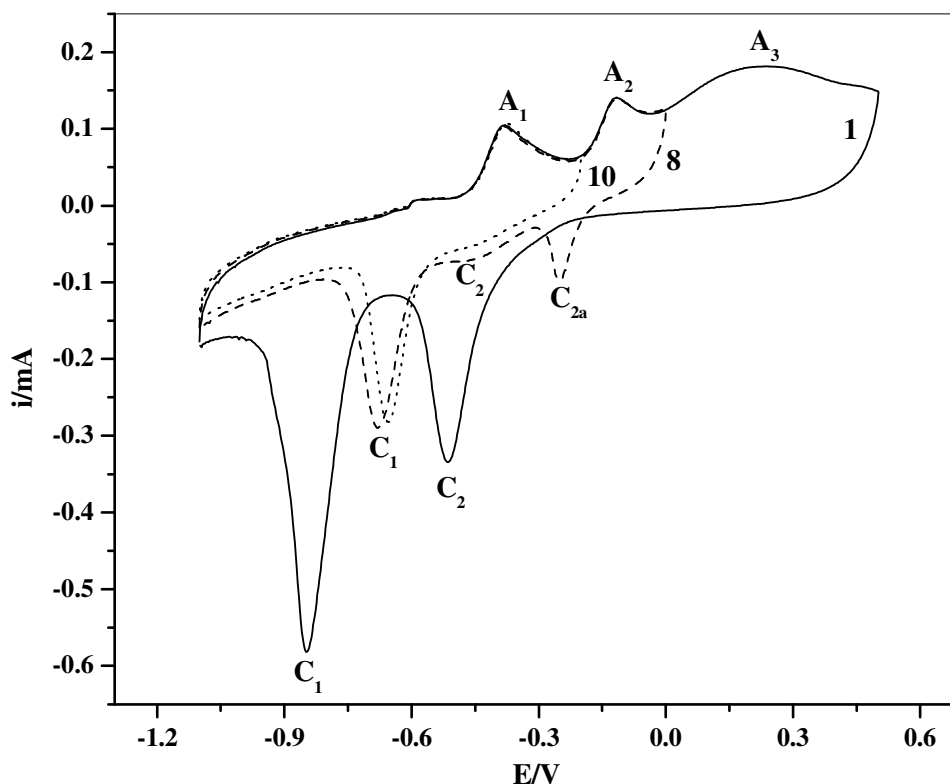

Figure 5. Comparison of CVs of Cu powder immobilized on PIGE electrode in 0.1 M KOH solution with different upper positive potential limits.

Fig. 5 shows the comparison of CVs (curves 1, 8, 10) in order to have a clear visualization of the role of hydrous oxide film in the reduction of Cu (I) and Cu (II) oxides. Using equation 2 and 3, the quantity of product formed at the anodic peaks (A_1 and A_2) and cathodic peaks (C_1 and C_2) may be obtained by using the following expression derived from Faraday's laws:

$$w = Q \times A / z \times F \tag{8}$$

where w is the weight of product (in grams) of electrochemical reaction, Q ($= i \times t$ in coulombs) the charge under the cyclic voltammetric peaks, z is the number of electrons, F is the Faraday's constant

(96500 couolmbs) and A is the atomic weight (g/mol) of the element/ compound. It could be seen that the oxidative products remain almost unaffected by the upper potential limit manipulation but the reductive products show tremendous change. A basic assumption is made that the Q values calculated from the peaks of CVs relate to the cumulative charge of the redox process. This may be proved by the results from curve 10 where E_u restricts the redox transformation of A_2/C_2 couple; 2.43 µg of oxidant at peak A_1 got reduced to almost a stoichimetric amount of 2.34 µg of Cu at C_1. These results conform to observations in our copper refining electrolysis where we get 95 to 98% efficiency for the process.

4. CONCLUSIONS

In this paper, we have proved that using paraffin impregnated graphite electrode to immobilize copper powder and study its electrochemical behavior was highly informative and useful. Both reduction peaks due to Cu (I) and Cu (II) oxides were well separated, stable and sharp even in dilute alkali solutions. By manipulating the upper positive potential limit in the cyclic voltammograms, it could be shown that the presence of hydrous oxide film was responsible for the higher reduction charges of cathodic peaks as well as the over potentials. Twin peaks formed due to reduction Cu (II) oxide initiated by the partial presence of hydrous oxide confirms the presence of copper oxide species in two states; one regular solid state species and the other surface active species in the double layer of the hydrous oxide and are only indirectly related. In the manipulated absence of hydrous oxide film, the solid state redox transformations were stoichiometrically controlled and quasi reversible.

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