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Manisha Bhattacharya
Department of Chemistry,
R.J. College, Ghatkopar,
Mumbai, Maharashtra, India

Pintu B
Merck Life Sciences Pvt. Ltd.,
Mumbai, Maharashtra, India

SG Dixit
Merck Life Sciences Pvt. Ltd.,
Mumbai, Maharashtra, India

Electrochemical study of Cu₂O in aqueous and non-aqueous solvents using cyclic voltammetric technique

Manisha Bhattacharya, Pintu B and SG Dixit

Abstract

Cyclic voltammetry investigations were conducted on Cu₂O in water-sodium sulphite and dimethyl sulfoxide (DMSO) solutions. In the water-sodium sulphite system, pH variations influenced the shape and position of anodic and cathodic peaks, indicating the involvement of different copper species. The reversibility of Cu₂O was confirmed, with successive scans revealing the transition of copper species between oxidation states. pH adjustments were found to impact peak potentials, suggesting potential for enhancing selectivity. In the DMSO system, initial cycles exhibited absence of anodic peaks followed by their emergence, accompanied by shifts in peak potentials and sharper cathodic humps. Scan reversal potentials influenced the appearance of anodic peaks, elucidating the oxidation of Cu₂O to CuO and subsequent reduction processes. As cycles progressed, peak heights increased, indicating favored reduction of Cu⁺² to Cu⁺¹ and metallic copper. Overall, the electrochemical reaction of Cu₂O proceeded via a two-electron process, with pH and concentration manipulation offering avenues for optimizing electrochemical properties.

Keywords: Cyclic voltammetry, DMSO, Cu₂O

Introduction

One of the most harmful types of pollution are heavy metals. They can be separated and recovered using a variety of procedures, including electrolysis, hydrometallurgical process, and other processes [1]. In hydrometallurgical processes, the treatment of leach liquor for solution concentration and/or purification prior to metal recovery is an important feature [2-4]. Precipitation can be used to recover metal ions in their metallic state, as oxides or hydroxides, or both, with the potential to be employed again in the future and recoup their market value [5]. Electrochemical techniques are being used more frequently in environmental remediation because they are highly adaptable and can be used to remove polluting solids, liquids, and gases. The most common carbon electrode used in electrochemical analysis is Carbon paste electrode (CPE) [6-10]. Recovering back heavy metals from aqueous solutions is one of the examples of the use of electrochemical methods. In fact, several metal ions in solution can be recovered in the metallic form by reduction at a cathode under specific conditions [11]. Using cyclic voltammetric technique (CV), the potential at which current can be passed anodically and cathodically can be studied. Cyclic voltammetry is the most extensively used technique for acquiring qualitative information about electrochemical reactions [12-20]. It tenders the rapid identification of redox potentials distinctive to the electroactive species, providing considerable information about the thermodynamics of redox process, kinetics of heterogeneous electron transfers reaction, and analysis of coupled electrochemical reactions or adsorption processes. The chemistry of copper oxide leaching [21] depends upon various factors of which leachant and solvent system plays an important role. Water is a substance that is abundant in nature and has several great qualities as a solvent [22]. The use of SO₂ as a leaching agent for the recovery of various metals from their oxidized ores is of much interest [23]. In the chemical industry, dimethyl sulfoxide (CH₃SOCH₃, DMSO) is a common aprotic polar solvent [24-26]. Many inorganic salts can be dissolved by DMSO, which also has other benefits such low toxicity, low vapour pressure at room temperature, and resistance to oxidation and reduction [27].

Materials and Methods

All chemicals used throughout these studies were either of AR grade or were purified using

Correspondence

Manisha Bhattacharya
Department of Chemistry,
R.J. College, Ghatkopar,
Mumbai, Maharashtra, India

known techniques [28]. Cu₂O was obtained from S.D. Fine chemicals was used as received. DMSO was of AR grade and was purified by keeping in 3A° molecular sieves to absorb water [29]. AR grade TBAP was obtained from Fluka and was oven dried for 1 hour at 100 °C before the experiment. KCl was AR grade and was used as such. Sodium sulphate, Iodine, EDTA of AR grade were used and were obtained from S. D. Fine Chemicals. Graphite powder and paraffin oil used were of reagent grade. Nitrogen gas was obtained from Industrial Oxygen Ltd. with 99% purity. Sulphur dioxide gas was supplied by INOX Ltd. in small volume capacity and was used directly.

Electrode systems

Electrochemical studies were conducted using a five necked round bottom flask. Electrochemical measurements were carried out using a three electrode system i.e., working electrode (WE), an auxiliary or counter electrode (CE) and a reference electrode (RE) [30, 31]. The WE was made up of graphite paste, platinum wire served as a CE and the RE electrode used was SCE for aqueous solution and a silver wire which served as a quasi-reference electrode (QRE) in non-aqueous solution. The solution was purged for about 1 hour before each experiment with pure nitrogen gas to remove any dissolved oxygen. The studies were performed in the inert nitrogen atmosphere which was maintained during the run of the experiment. The QRE was placed very close to the WE to eliminate any iR potential drop in the solution. An unstirred solution at room temperature was used for the measurements.

Estimation of copper

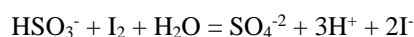
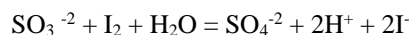
Copper was estimated by EDTA method [32]. About 200 mg of copper oxide was taken in a beaker and then 2 ml of conc. HNO₃, 2 ml of conc. H₂SO₄ and about 1-2 drops of 70% perchloric acid was added in it. The solution was heated strongly to dryness. The sample treated above was dissolved in 5 ml of 2N HCl, then 10 ml of conc. Ammonia solution was added. The resulting solution was titrated against 0.01 M EDTA solution using Fast Sulphon Black F as an indicator. The colour changed from blue to pale green in the vicinity of endpoint. The metal % was calculated as.

1000 ml of 1M EDTA = 63.54 gm of copper

Determination of Sulphur dioxide concentration

In a conical flask known volume of standard 0.1 N iodine solution (10-25 ml) depending upon the concentration of sulphur dioxide in the solution was taken and diluted with distilled water to about 150 ml and acidified with 5 ml of 2 N HCl [33]. Then the known volume of aqueous sulphur dioxide solution was taken in a pipette and was slowly added to the solution in the conical flask and the excess

iodine was titrated against standard 0.1 N sodium thiosulfate solution, using starch as an indicator. The total volume of standard iodine solution taken minus the burette reading gave the amount of iodine which has reacted with aqueous sulphur dioxide. From the following reaction.



It follows that

1 ml 0.1 N I₂ = 0.0032 gm SO₂

In case of determination of sulphur dioxide in DMSO, due to high concentration of sulphur dioxide very low volume of the solvent mixture i.e.; 0.1 ml was taken for iodometric analysis.

pH Meter

The pH of the solution was measured with the Elico pH-meter instrument. The instrument was standardised using buffer tablets before each experiment.

Potentiostat

Electrochemical measurements were performed using a E.G & G Princeton Applied Research Corporation 273 Potentiostat / Galvanostat model. M270 electrochemical software was used for various functions of the instrument. The instrument was connected to a IBM computer along with a printer.

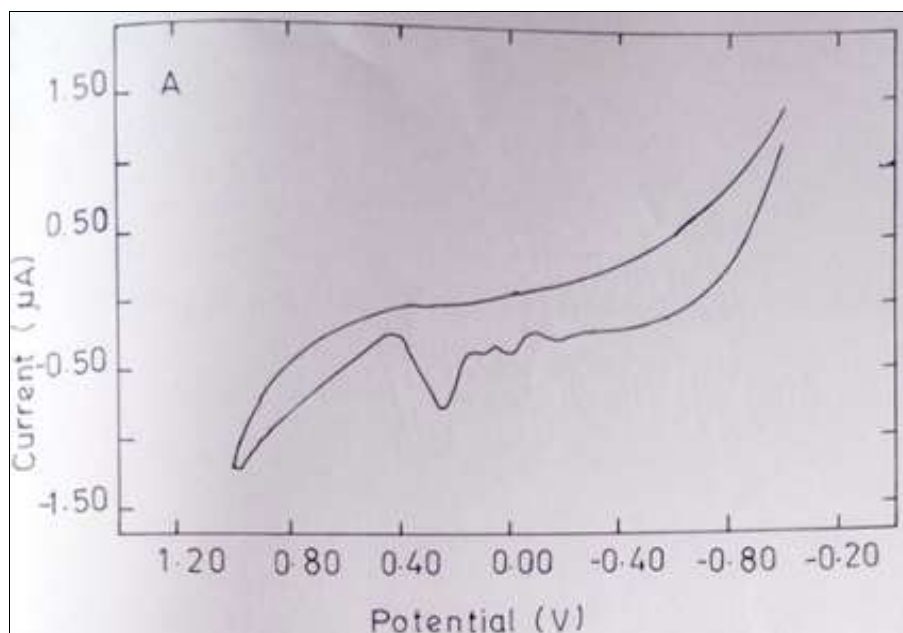
Results and Discussion

Cyclic voltammetry of Cu₂O in water-sodium sulphite system

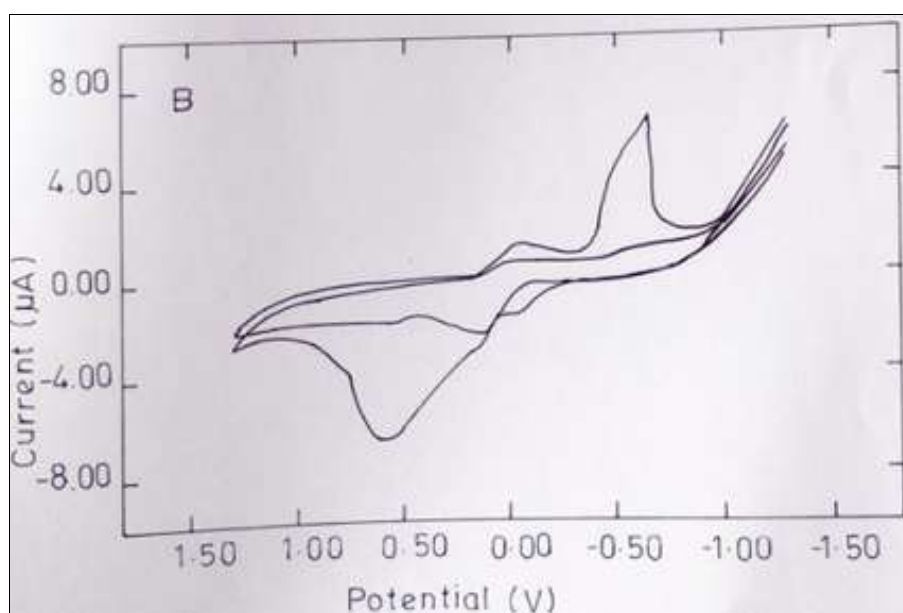
A series of cyclic voltammograms were recorded of Cu₂O in water-sodium sulphite system. The anodic and cathodic peak potential and peak currents were studied at different scan rates, concentration, potential scan reversal, pH, etc.

Cyclic voltammograms were measured at different pH values of 8.2, 3.0, 2.0, 1.8 and 1.5. The effect of pH on the nature of the curve were studied. Cyclic voltammograms were recorded at a fixed scan rate of 20 mV/s with a known concentration of Cu₂O. The area of the working electrode was kept constant throughout the experiment. The range of the potential was changed from 1.0 V to 1.3 V and their effect were also studied.

In the first cycle, one anodic peak appears but there is no cathodic peak in the reverse cycle. In the next cycle the anodic peak height increases and there appears a cathodic hump. There also occurs a shift in the peak potential. The anodic peak shifts towards a more positive potential and the cathodic peak potential towards a more negative potential.



a)



b)

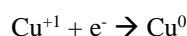
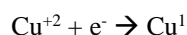
Fig 1: Cyclic voltammogram of Cu_2O in water-sulphite system at $\text{pH}=8.2$ (A) upto 1.0V, (B) upto 1.3V

The reversible nature of Cu_2O was studied by first running the cyclic voltammogram from -1.0 V to 0.0 V and then again from 0.0 V to 1.0 V. From the studies it was found that the anodic peak appears around 0.3 V and the cathodic hump around 0.0 V. It was observed that at pH around 2.0, the peaks are broad in nature. However, at pH 1.8, both the anodic and the cathodic peak are very distinct. If the peaks are either reduced or increased the peaks are not well defined.

From the nature of the peaks obtained we can conclude that Copper (II) species are first formed on the positive going scan. On consequent negative going scans, corresponding cathodic peaks appear on the voltammograms due to the reduction of Copper (II) species to Copper (I) species. When the potential is reversed, the Copper (I) species are further reduced to metallic Copper ions which further gets oxidised in the positive scan. Thus we can say that in the positive scan



and in the negative scan



Based on the above studies, we can conclude that the electrochemical reaction of Cu_2O is a two electron species. Hydrogen ions are involved in the reduction of most organic/inorganic species. It was seen that the potential is dependent on the hydrogen ion concentration, that is pH of the solution. The Nernst equation applies only to thermodynamically reversible system but an equivalent expression involving hydrogen ion concentration applied to

all reduction and oxidation. It was seen that the anodic/cathodic peak potential of Cu_2O shifts at a constant rate and is dependent on the number of hydrogen ions and electrons. It was observed that in multicyclic voltammograms, there is not much effect on the potential with change in pH, but merely the height of the wave varies. It was seen that at lower concentration and higher pH causes the peak potentials to shift which results in a poorly formed wave. At lower pH and higher concentration the peak potentials are stable and forms a well formed wave. The choice and control of pH can be used to enhance the selectivity. A pH range may be chosen such that there is no overlapping in the wave nature.

Cyclic voltammetry of Cu_2O in DMSO

The cyclic voltammetry of Cu_2O with graphite paste was recorded in DMSO solution. The first initial anodic

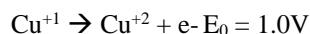
polarization scan was recorded in the anodic direction at 20 mV/s scan rate. The scan was started from -1.0V and reversed at +1.2V. There was no anodic peak in the first cycle in the anodic scan but a straight line. In the reverse cathodic scan, there appears two cathodic humps.

In the second anodic cycle, there appears a small anodic peak in the forward scan. In the reverse cathodic scan, the cathodic humps become sharper. In the subsequent cycles both the anodic and the cathodic peaks become sharper and also increase in peak heights as compared to previous cycles. As seen in Fig. 2a. With the increase in the number of cycles, there occurs a shift in peak potentials. The anodic peak shifts towards more positive potential and the cathodic peak shifts towards more negative potential as seen in Fig. 2 b. The peak anodic and cathodic potential and currents are given in Table 1.

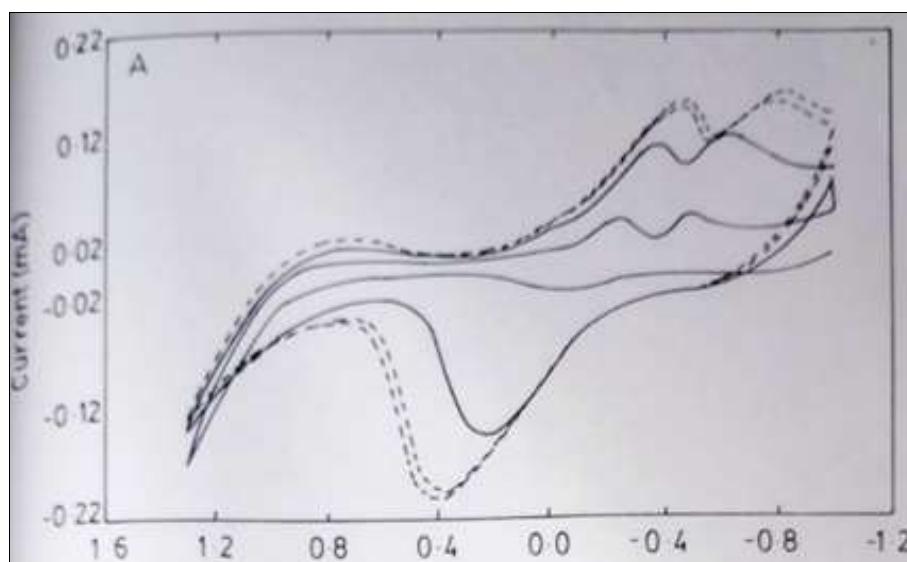
Table 1: Peak Potentials and current values of Cu_2O in Dimethyl sulfoxide

Peak Anodic Potential and current values				
Cycle No.	$I_{pa1} 10^{-2} \text{ A}$	$E_{pa1} \text{ (V)}$	$I_{pa2} 10^{-2} \text{ A}$	$E_{pa2} \text{ (V)}$
1	-	-	-	-
2	-9.05	0.016	-6.4	0.116
3	-10.70	0.048	--	--
4	-14.99	0.196	--	--
5	-20.90	0.392	--	--
Peak Cathodic Potentials and current values				
Cycle No.	$I_{pc1} 10^{-2} \text{ mA}$	$E_{pc1} \text{ (V)}$	$I_{pc2} 10^{-2} \text{ mA}$	$E_{pc2} \text{ (V)}$
1	1.96	-0.144	2.3	-0.45
2	2.92	-0.236	6.9	-0.57
3	4.70	-0.240	8.3	-0.60
4	11.76	-0.392	12.7	0.63
5	15.98	-0.488	16.8	-0.82

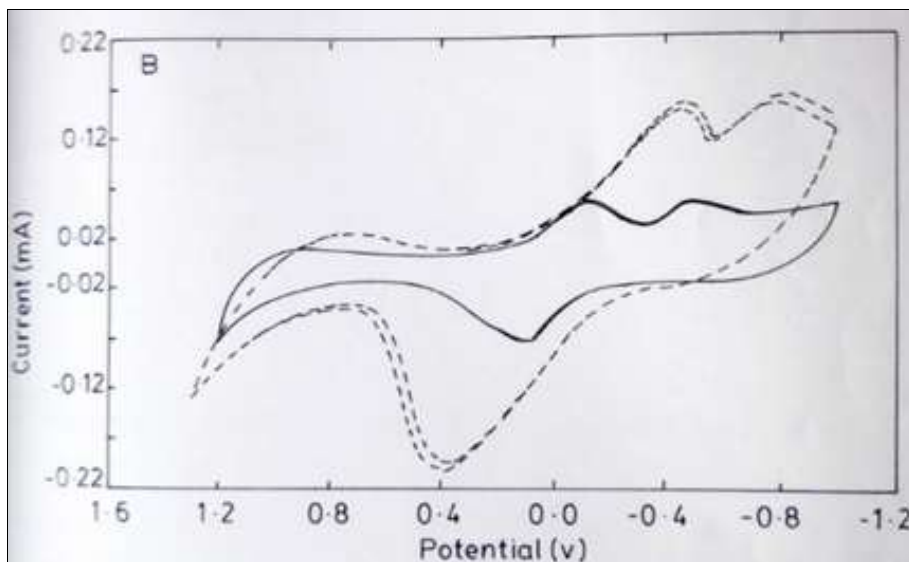
An attempt was made to determine the relation between oxidation and reduction peaks. It was observed that if the scan reversal potential is decreased, there appears only one cathodic peak and with subsequent cycle, the peak height decreases. This means that it is the reverse reaction of the above process. Thus, we can conclude that at this potential, Cu_2O is oxidised to CuO . Hence



On further study, it was observed that when the scan potential was reversed, the cathodic peak formed might be of the reduction of Cu^{+2} ion to Cu^{+1} ion. In the subsequent cycle, the cathodic peak height goes on increasing indicating more of Cu^{+2} ion are reduced. The peak potential value almost matches with the peak assigned by Gerlach *et al.* [14] and other workers [15, 16].



a)



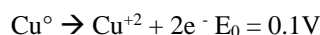
b)

Fig 2: Cyclic voltammogram of Cu₂O in DMSO (A) multicyclic, (B) beyond 1.2V

It was further observed that the potential at which the first cathodic scan is reversed for the beginning of the second cycle is also important. If the potential was reversed before -0.8V, there appears no anodic peak in the second cycle. It indicates that copper ions are reduced to metallic copper. The potential value at which it is reduced agrees with the value obtained by Gerlach^[14]. Thus we can conclude that.



Further in the second cycle, there appears two anodic peaks. The first anodic peak is of graphite paste which was observed earlier when the blank graphite paste was run. The second small anodic peak might be of the metallic copper which was formed previously getting oxidised to Cu⁺² ion. Thus.



As the number of cycle is increased, the second anodic peak merges with the first anodic peak which are very close to each other. This might also be due to the increase in the peak height of the two anodic peaks resulting in the disappearance of the second anodic peak.

The cathodic peak potential move towards more negative potential as the number of cycles is increased. Similarly the anodic peak potential move towards more positive potential values, indicating the increase in Cu⁺² species. There is an increase in both the anodic and the cathodic peak heights indicating that the cathodic process is reduction of Cu⁺² to Cu⁺¹ and then to metallic copper is favoured and the corresponding reduced products are further oxidised in the cathodic scan i.e., oxidation of Cu⁰ to Cu⁺¹ and then to Cu⁺². Based on the results obtained, the electrochemical reaction of Cu₂O is found to proceed through a two electron process.

Conclusion

In this study, cyclic voltammetry was employed to explore the electrochemical behavior of Cu₂O in a water-sodium sulphite system and DMSO system. The investigation revealed significant insights into the effect of pH, concentration, and potential scan reversal on the peak

potentials and currents. Distinctive features were observed in the cyclic voltammograms, such as the emergence of anodic peaks and cathodic humps in successive cycles, accompanied by shifts in peak potentials. The reversible nature of Cu₂O was confirmed, highlighting its transition between different oxidation states during cyclic scans. The findings suggest that Cu₂O undergoes a two-electron process, with potential applications in selective electrochemical processes. Overall, this study contributes valuable insights into the electrochemical behavior of Cu₂O, paving the way for further exploration and utilization in various fields.

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