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

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Abstract

The electrochemical behaviour of Cu₂O in various solvent systems was investigated using chronoamperometry (CA) technique. In water, the chronoamperometry plot revealed a transition from dominant charging current to Faradic current at higher potentials, with irregular behaviour observed above 1.0 V. Diffusion coefficients decreased with increasing potential and time period, exhibiting a linear relationship. In the water-sulphite system, an increase in area of the curve was observed with increasing potential, with the peak current decreasing over time. Diffusion coefficients varied with potential and pH, with lower values observed at pH 1.8 and 2.0. In DMSO, chronoamperometry plots showed a linear relationship between charging and Faradic current, with diffusion coefficients increasing with potential and time period. In DMSO + SO₂, increasing potentials led to higher slope values, indicating a rise in diffusion coefficients. Overall, the study elucidates the electrochemical properties of Cu₂O in different solvent systems, providing insights into its behaviour under varying conditions.

Keywords: Cuprite, chronoamperometry, diffusion coefficient, aqueous solvents, non-aqueous solvents

Introduction

The chemistry of copper oxide leaching [1-4] depends upon various factors among which leachant and the solvent system plays an important role. Copper oxides have got wide industrial applications [5, 6]. The present work is concerned with detailed study of the several hydrometallurgical processes which are electrochemical in nature. Use of electrochemical technique have recently gained importance for the leaching of lean and complex oxide ores [7-11]. Electrochemical techniques have an advantage because of its selectivity, precision and also no pre-preparation is required for analysis. Current work presents investigation of electrochemical properties of Cu₂O using electrochemical technique. Cu₂O in the pure form was taken for the elementary study. The study was carried out at various potential using various solvent systems viz, Cu₂O in water, Cu₂O in water-Sodium sulphite, Cu₂O in DMSO [12-14], and Cu₂O in DMSO+ SO₂ system [15-18]. The electrochemical technique employed in electrochemical dissolution studies are chronoamperometry (CA) [19-23]. Previous work has indicated the above system to be electrochemical in nature, which needed detailed investigations. CA is an electroanalytical technique based on the excitation function of one or more potential steps that are applied to a carbon paste electrode (CPE) [24-27] immersed in a non-stirred solution. The most useful equation in chronoamperometry which is the Cottrell equation, is used to describes the observed current at any time following a large forward potential step in a reversible redox reaction (or to large overpotential) as a function of t^{1/2},

$$i = \frac{nFAv\sqrt{DC}}{\sqrt{\pi t}}$$

Where

n = stoichiometric number of electrons involved in the reaction;
 F = Faraday's constant (96,485 C/equivalent),
 A = electrode area (cm²),

C = concentration of electroactive species (mol/cm^3), and
D = diffusion constant for electroactive species (cm^2/s).

Materials and Methods

All chemicals utilized in these investigations were either of analytical reagent (AR) grade or underwent purification through established methods [28]. Cu_2O sourced from S.D. Fine Chemicals was employed as received. DMSO, of AR grade, underwent purification by exposure to 3A molecular sieves to remove water content [29]. AR grade TBAP procured from Fluka underwent oven drying at 100°C for 1 hour prior to experimentation. AR grade KCl was utilized without further treatment. Sodium sulfate, iodine, and EDTA, all of AR grade, were obtained from S.D. Fine Chemicals. Reagent grade graphite powder and paraffin oil were employed. Nitrogen gas, with 99% purity, was supplied by Industrial Oxygen Ltd. Sulphur dioxide gas, provided by INOX Ltd. in small volume capacity, was used as supplied.

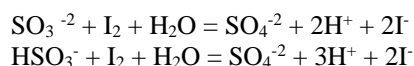
Electrode system: Investigations into electrochemical behaviours were carried out in a round-bottom flask equipped with five necks. The electrochemical analyses utilized a tri-electrode setup comprising a working electrode (WE), a counter electrode (CE), and a reference electrode (RE) [30, 31]. Graphite paste formed the WE [18-20], while the CE was constituted by platinum wire, and the standard calomel electrode (SCE) was employed as the RE for aqueous solutions. In non-aqueous solutions, a silver wire functioned as a quasi-reference electrode (QRE). Prior to each experimental run, the solution underwent a nitrogen gas purge for approximately one hour to expel any dissolved oxygen. The experiments were conducted under a nitrogen atmosphere to maintain inert conditions. The QRE was positioned in close proximity to the us to mitigate any potential iR drop in the solution. Room temperature conditions were maintained for the solution, which was not stirred during measurements.

Copper Estimation: The estimation of copper was performed using the EDTA titration method [32]. Approximately 200 mg of copper oxide was placed into a beaker, to which 2 ml of concentrated HNO_3 , 2 ml of concentrated H_2SO_4 , and 1-2 drops of 70% perchloric acid were added. This mixture was then heated until dry. The resultant substance was dissolved in 5 ml of 2N HCl, followed by the addition of 10 ml of concentrated ammonia solution. The mixture was titrated with a 0.01 M EDTA solution, employing Fast Sulphon Black F as an indicator, until a color transition from blue to pale green indicated the endpoint. The metal % was calculated as:

1000 ml of 1M EDTA = 63.54 gm of copper.

Sulphur Dioxide Determination: To determine sulphur dioxide concentration, a pre-measured volume of 0.1 N iodine solution (10-25 ml) was taken in a conical flask, diluted with distilled water to approximately 150 ml, and acidified with 5 ml of 2 N HCl [33]. A measured volume of aqueous sulphur dioxide solution was then gradually added from a pipette into the flask, with the excess iodine being titrated with a standard 0.1 N sodium thiosulfate solution using starch as an indicator. The calculation of the sulphur dioxide amount was based on the initial volume of iodine

solution used minus the volume indicated by the burette, following the reaction equations provided. From the following reaction.



It follows that

1 ml 0.1 N I_2 = 0.0032 gm SO_2

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 Measurement: The pH of solutions were measured using an Elico pH meter. Prior to each use, the instrument was calibrated with standard buffer tablets to ensure accuracy.

Potentiostat Operations: Electrochemical measurements were conducted with the use of a E.G & G Princeton Applied Research Corporation 273 Potentiostat/Galvanostat. The M270 electrochemical software suite facilitated various instrument functions. This setup was interfaced with an IBM computer and printer for data acquisition and analysis.

Result and Discussion

1. Chronoamperometry study of Cu_2O in water: The chronoamperometry plot of Cu_2O in water was carried out in different potential ranges. The i - t curve was recorded in the anodic region with graphite paste as the working electrode. The current response as a function of time was recorded. The chronoamperometry curve were obtained at a constant potential of 0.5, 0.7 and 0.9 V with an initial potential of 0.0 V. The i - t plot of Cu_2O in water were measured in different time periods of 10, 20, 40, 60 and 100 seconds.

It is seen that there is no change nature of the curve at lower potential but at higher potential than 1.0 V, the curve becomes irregular. Here initially the charging current is dominant, later the Faradic current dominates.

The curve between i - $t^{1/2}$ shows a decreasing value of current with a linear relationship. At lower potential the current value is lower as compared to higher potential. When we extrapolate time to $t=0$, it represents the Faradic current. It was seen that the curve above 1.0 V was irregular in behaviour.

As the potential value was increased from 0.0 V to 0.5, 0.7, 0.9 and 1.2 V, the slope value varied with change in potential range and time period. The slope value decreased from -16.98 at 0.5 V to -106.7 $\mu\text{As}^{1/2}$ at 1.2 V. Similarly, the slope value increased from -9.58 to -163.3 $\mu\text{As}^{1/2}$ at 1.2 V for 100 seconds.

The chronoamperometry plots provided the area of the curve, peak current and peak time. The area of the curve increased from -42.84 $\mu\text{C}/\text{cm}^2$ at 0.5 V and 10 seconds to -194.5 $\mu\text{C}/\text{cm}^2$ at 0.9 V and 100 seconds.

The peak current decreases in value from -58.41 $\mu\text{A}/\text{cm}^2$ at 0.5 V and 10 seconds to -16.90 $\mu\text{A}/\text{cm}^2$ at 0.9 V and 100 seconds.

But with higher potential range, the peak current decreases from -70.90 $\mu\text{A}/\text{cm}^2$ at 0.7 V at 10 seconds to -21.37 $\mu\text{A}/\text{cm}^2$ at 0.7 V and 100 seconds.

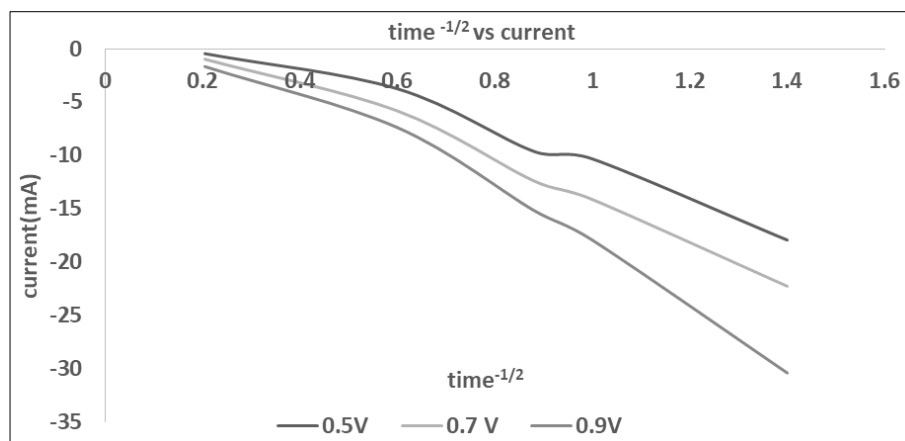


Fig 1: Chronoamperometric plot current vs $\text{time}^{-1/2}$ in Cu_2O in water at various potential

The peak current increases with increase in potential at a given time period. The peak time increases from 0.1 seconds to 0.7 seconds at a particular potential range and remains constant with higher potential range.

Table 1: Area, Peak current, Peak time data and calculation of slope, diffusion coefficient, chi-square and correlation at various potential and time period for Cu_2O in water using chronoamperometric techniques.

Volt (V)	Time (s)	$i^{1/2} \cdot 10^{-6} \text{ As}^{1/2}$	Diff. Coeff. 10^{-7} cm^2	Chi-squ $\chi^2 \cdot 10^{-9}$	Correl.	Area ($\mu\text{C}/\text{cm}^2$)	Peak Cur. ($\mu\text{A}/\text{cm}^2$)	Peak Time (s)
0.5	10	-16.98	2.26	0.35	-0.97	-42.84	-58.41	0.10
0.5	40	-11.14	1.83	0.09	-0.95	-55.33	-21.43	0.32
0.5	100	-9.58	1.70	0.05	-0.94	-65.42	-16.90	0.70
0.7	10	-20.95	2.51	0.36	-0.98	-64.97	-70.90	0.12
0.7	40	-14.29	2.07	0.11	-0.96	-96.49	-24.64	0.40
0.7	100	-12.32	1.92	0.07	-0.95	-119.0	-21.37	0.70
0.9	10	-26.39	2.81	0.36	-0.99	-89.53	-87.80	0.12
0.9	40	-18.18	2.34	0.19	-0.96	-137.5	-33.65	0.44
0.9	100	-13.06	1.97	0.06	-0.93	-194.5	-22.50	0.70

The $i-t$ curves obtained from the chronoamperometry plots provided the diffusion coefficient, chi-square and correlation values as shown in Table 1. From the slope value, the diffusion coefficient values have been calculated using the Cottrell's equation which is –

$$i = \frac{nFA\sqrt{DC}}{\sqrt{\pi t}}$$

$$\text{Or, } \sqrt{D} = 3 \times 10^7 \times i t^{1/2}$$

Where symbols have their usual meaning.

The diffusion coefficient value decreased at 0.5 V from $2.26 \times 10^{-7} \text{ cm}^2/\text{s}$ at 10 seconds to $1.70 \times 10^{-7} \text{ cm}^2/\text{s}$ at 100 seconds. Similarly at higher potential range i.e.; 0.9 V, the diffusion coefficient decreased from $2.81 \times 10^{-7} \text{ cm}^2/\text{s}$ at 10 seconds to $1.97 \times 10^{-7} \text{ cm}^2/\text{s}$ at 100 seconds. The diffusion coefficient however increased from 2.26×10^{-7} to $2.81 \times 10^{-7} \text{ cm}^2/\text{s}$ from 0.5 V to 0.9 V at fixed time period from $5.66 \times 10^{-7} \text{ cm}^2/\text{s}$ at 10 seconds to $6.99 \times 10^{-7} \text{ cm}^2/\text{s}$ at 100 seconds. The chi-square at 0.5 V decreased from 0.35×10^{-9} at 10 seconds to 0.05×10^{-9} at 100 seconds. The value remained almost constant with further increase in potential and time period.

It was seen that the diffusion coefficient value decreases on increasing the potential and time period. At lower time period, the diffusion coefficient decreases, but at higher time period it almost shows a linear value.

2. Chronoamperometry study of Cu_2O in water-sulphite system:

Chronoamperometry technique was employed for the study of Cu_2O in water and sodium-sulphite system. In this technique a constant potential was applied between the Cu_2O sample which served as the working electrode and the reference electrode. CPE was used as the working electrode for the measurement of the $i-t$ curves. The $i-t$ curve was recorded in the anodic region and the current response as a function of time was measured.

The chronoamperometry curves were obtained at constant potential of 0.8 V, 1.0 V, 1.2 V and 1.5 V with an initial potential of 0.0 V. They were measured at different time periods of 10, 15, 20, 30 and 60 seconds.

The area of the curve, peak current and peak time were obtained from the $i-t$ curve using chronoamperometry technique. It was observed the area of the curve increases with increase in potential at different pH value. At $\text{pH}=1.8$, the value of area was the lowest and at $\text{pH}=2.0$, the area increased further.

It was also seen that the peak current value decreases with increase in time period in a particular potential range. At higher potential the peak current shows a higher value. This trend is shown in almost at all pH value studied. However, at $\text{pH}=1.5$, the magnitude of the peak current value is higher as compared to other.

The area of the curve increased with further increase in pH except at $\text{pH}=8.2$ where it was lower.

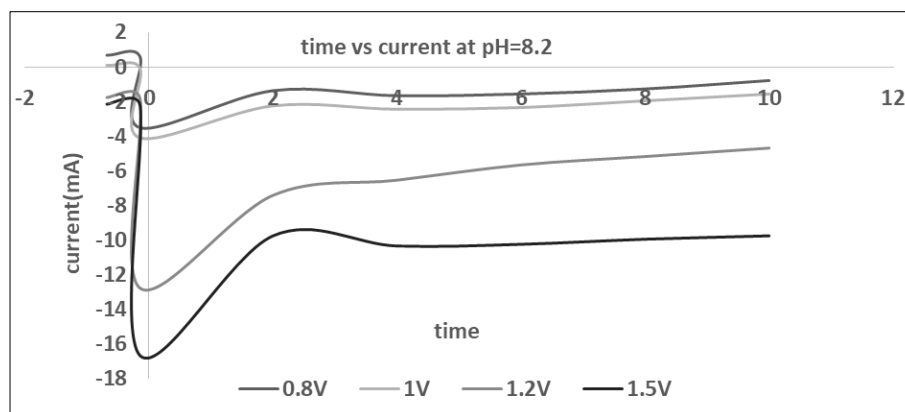


Fig 2: Chronoamperometric plot time vs current in Cu_2O in water-sulphite system at various potential at pH =8.2

Table 2: Area, Peak current, Peak time and calculation of slope, diffusion coefficient, chi- square and correlation data at different potential and time period for Cu_2O in water-sulphite system using chronoamperometric techniques at various pH.

Volt (V)	Time (s)	Area ($\mu\text{C}/\text{cm}^2$)	Peak Current (μA)	Peak time (s)	$it^{1/2}$ ($\mu\text{A s}^{1/2}$)	Diff. Coeff. $10^7 \text{ cm}^2/\text{s}$	Chi-Square 10^{-12}	Correl
At P^H 8.2								
0.8	10	-58.18	-11.55	0.07	-0.67	0.45	0.31	-0.96
0.8	15	-10.28	-2.88	0.25	-0.60	0.44	0.28	-0.96
0.8	20	-4.51	-1.46	0.24	-0.51	0.39	0.22	-0.97
1.0	10	-5.31	-2.15	0.14	-0.68	0.45	0.18	-0.99
1.0	15	-5.89	-2.09	0.18	-0.64	0.44	0.19	-0.98
1.0	20	-5.98	-1.61	0.24	-0.55	0.41	0.15	-0.98
1.2	10	-13.82	-4.05	0.17	-1.14	0.58	0.35	-0.99
1.2	15	-22.47	-4.08	0.26	-1.20	0.60	1.42	-0.96
1.2	20	-34.33	-5.77	0.24	-1.63	0.70	4.12	-0.94
At P^H 3.0								
0.8	10	-50.41	-19.49	0.12	-5.81	1.32	6.75	-0.99
0.8	15	-52.73	-15.99	0.19	-5.91	1.33	1.40	-0.99
0.8	20	-65.63	-15.24	0.25	-6.26	1.37	1.81	-0.99
1.0	10	-95.21	-24.89	0.17	-8.43	1.59	5.61	-0.99
1.0	15	-160.1	-27.27	0.17	-8.93	1.64	10.60	-0.99
1.0	20	-192.0	-25.27	0.23	-9.25	1.64	11.01	-0.99
1.2	10	-194.3	-39.13	0.18	-10.7	1.80	20.08	-0.99
1.2	15	-264.5	-40.53	0.19	-12.3	1.93	30.19	-0.99
1.2	20	-310.3	-34.86	0.36	-14.7	2.11	16.82	-0.99
At P^H 2.0								
0.8	10	-42.88	-22.10	0.13	-6.39	1.39	15.4	-0.99
0.8	15	-62.40	-19.80	0.18	-6.69	1.42	6.01	-0.99
0.8	20	-71.51	-16.18	0.25	-6.00	1.34	5.86	-0.99
1.0	10	-52.96	-22.28	0.13	-6.17	1.36	13.4	-0.99
1.0	15	-70.45	-19.72	0.18	-6.24	1.37	7.59	-0.99
1.0	20	-75.94	-16.33	0.24	-5.85	1.33	7.28	-0.99
1.2	10	-77.37	-25.11	0.16	-8.69	1.62	10.1	-0.99
1.2	15	-88.26	-22.13	0.19	-7.69	1.52	10.4	-0.99
1.2	20	-106.1	-20.31	0.25	-7.69	1.52	6.29	-0.99

The peak time increases with increase in time in a particular potential range. The peak time value increases from 0.11 to 0.36 seconds and this trend is observed in almost all the pH values. The chronoamperometry plots above 1.2 V are not well defined and sometimes the i - t curves fall at a very low value immediately after the run.

The i - t curves obtained from the chronoamperometry plots provided the diffusion coefficient, chi-square and correlation values as shown in Table 2. The slope values were lowest at pH=1.8 and 2.0. From the slope value, the diffusion coefficient values have been calculated using the Cottrell's equation. According to the equation:

$$i = \frac{nFA\sqrt{DC}}{\sqrt{\pi t}}$$

$$\text{or, } \sqrt{D} = 3 \times 10^7 \times it^{1/2}$$

Where symbols have their usual meaning.

The diffusion coefficient value decreases from $1.21 \times 10^{-7} \text{ cm}^2/\text{s}$ at 0.8 V and 10 seconds to $0.97 \times 10^{-7} \text{ cm}^2/\text{s}$ at 20 seconds at pH=1.8. At potential of 1.5 V, it decreases from $1.87 \times 10^{-7} \text{ cm}^2/\text{s}$ and 10 seconds to $1.80 \times 10^{-7} \text{ cm}^2/\text{s}$ at 20 seconds. The diffusion coefficient shows similar trend at various pH. However it was seen at pH=1.8, the diffusion coefficient value is the least. Similar, low value of diffusion coefficient is seen at pH=2.0. The chi-square (χ^2) value decreased with the increase in time period and potential. The chi-square value varied in the range of 10^{-12} at pH=1.5 and 1.8. However, at higher pH, it was in the range of 10^{-9} .

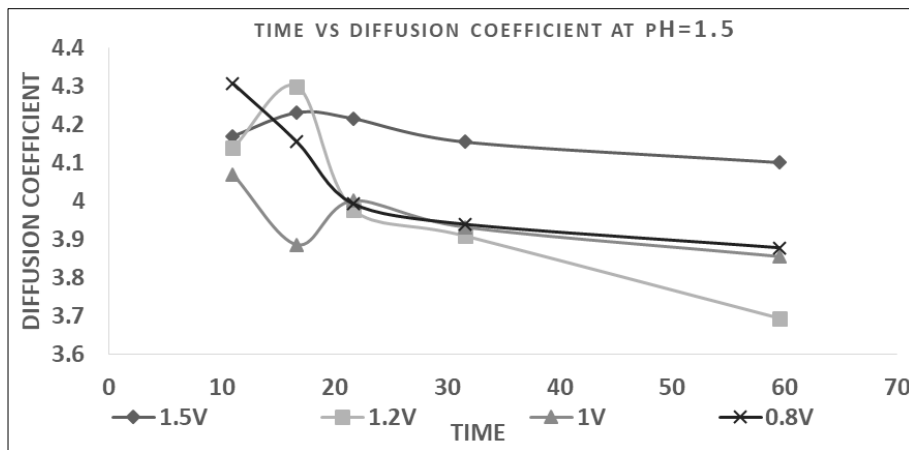


Fig 3: Chronoamperometric plot of diffusion coefficient vs time for Cu_2O in water-sulphite system at $\text{pH}=1.5$

A plot of diffusion coefficient versus time has been shown in Fig. 2.6 to Fig. 2.10. It was seen that the diffusion coefficient value increases with increase in potential and time period. At lower potential, the diffusion coefficient value almost remains constant and shows a linear trend. However, at potential higher than 1.2 V, initially the diffusion coefficient decreases and then remains constant. This trend is similar in all pH values with slight deviation at higher potential value. The magnitude of the diffusion coefficient at $\text{pH}=1.8$ is lower as compared to other pH values.

3. Chronoamperometry study of Cu_2O in DMSO: In order to study the electrochemical properties of Cu_2O in DMSO, we have carried out the recording of $i-t$ curves at various potential ranges. Chronoamperometry method was

employed for the investigations of the compound. The $i-t$ curves were recorded in the anodic region. In this method, a constant potential was applied between the sample (WE) and the RE and the current response as a function of time was recorded [11]. The $i-t$ characteristic curves of Cu_2O were obtained using carbon paste electrode as the working electrode.

Chronoamperometry curves were obtained at a constant potential of 0.5, 0.7, 0.9 and 1.2 V with an initial potential of 0.0 V. The figure shows both the charging current and the Faradic current clearly. It was observed initially the charging current was dominant up to 0.01 sec, later on the Faradic current predominates. When we plot the value of i against $t^{1/2}$, a linear relationship is observed. The i when extrapolated to $t=0$ represents the Faradic current density.

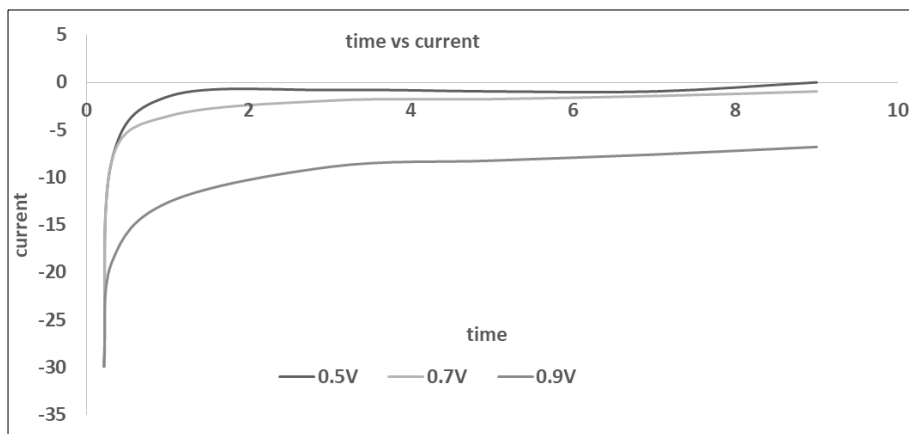


Fig 4: Chronoamperometric plot time vs current in Cu_2O in DMSO system at various potential

The chronoamperometry plots at various potential were measured at different ranges of 10, 20, 40, 60 and 100 seconds. It was observed that in the potential range of 0.0 to 0.5 V and 0.0 to 0.7 V, there is a decrease in slope value

with increasing time period. But at higher potential i.e.; 0.0 to 0.9 V a slightly fluctuating slope values were obtained. At potential of 0.0 to 1.2 V, there is an increase in slope values. These values are shown in Table 3.

Table 3: Area, Peak current and Peak time data, and calculation of slope, diffusion coefficient, chi-square and correlation at different potential and time period for Cu_2O in DMSO solution using chronoamperometric techniques.

Volt (V)	Time (s)	Area ($\mu\text{C}/\text{cm}^2$)	Peak Current (μA)	Peak time (s)	$it^{1/2}$ ($\mu\text{A s}^{1/2}$)	Diff. Coeff. $10^7 \text{ cm}^2/\text{s}$	Chi-Square 10^{-12}	Correl
0.5	10	-7.36	-10.8	0.12	-2.87	0.93	18.61	-0.96
0.5	40	-8.98	-3.07	0.43	-1.64	0.70	1.68	-0.95
0.5	100	-11.51	-2.15	0.70	-1.32	0.63	0.50	-0.96
0.7	10	-17.76	-20.4	0.12	-5.15	1.24	58.69	-0.96
0.7	40	-30.35	-5.91	0.46	-2.99	0.95	3.90	-0.97
0.7	100	-56.23	-2.91	1.10	-2.24	0.82	0.81	-0.97

0.9	10	-84.91	-30.9	0.17	-9.39	1.68	33.63	-0.99
0.9	40	-296.2	-21.6	0.49	-9.14	1.66	3.87	-0.99
0.9	100	-1268	-21.5	0.50	-12.95	1.97	3.52	-0.99

Table 3 shows the chronoamperometry data for area, peak current and peak time data also calculation of slope, diffusion coefficient, chi-square and correlation at different potential and time period for Cu₂O in DMSO solution at various potential at different time periods.

There is observed a gradual increase in area with the increase in time period and potential. However, at potential higher than 0.9 V, the increase becomes drastic. The peak current shows a decreasing trend at a particular potential which increases with higher potential. The value decreases with increasing time period. The peak time value also shows a similar behaviour.

The chronoamperometry plots at potential higher than 1.2 V are not well defined and sometimes current - time curves falls at a very low value immediately after the run. Potential employed for the chronoamperometry runs were chosen from the diffusion limited regions of cyclic voltammetry observed. $i\sqrt{t}$ versus t plots in all the cases did not indicate adsorption in DMSO medium. In order to determine whether Cu₂O undergoes chemical solid state diffusion

coefficient values of Cu₂O at different potential have been calculated. The diffusion coefficient value in DMSO was obtained using Cottrell's equation.

$$i = \frac{nFA\sqrt{D}C}{\sqrt{\pi t}}$$

where symbols have their usual meaning

$$\sqrt{D} = 3 \times 10^7 \times i t^{1/2}$$

The diffusion coefficient values obtained from chronoamperometry technique by using the above equation are given in Table 3. The values varied from 0.63×10^{-7} cm²/s at 0.5 V potential to 4.58×10^{-7} cm²/s at 1.2 V. Statistical calculations based on chronoamperometry plots were also carried out. Chi-square and correlation coefficient values were obtained. Correlation coefficient values varied from 0.963 to 0.998. The chi-square value ranges from 0.50 to 19.2×10^{-12} .

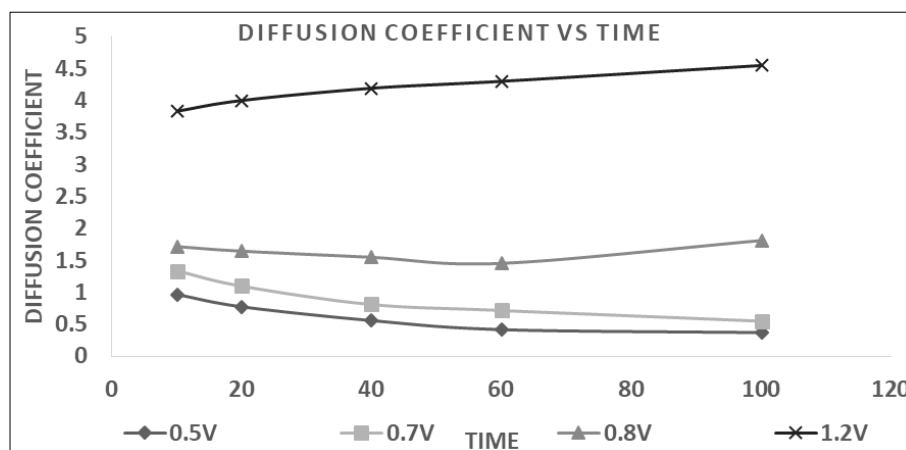


Fig 5: Chronoamperometric plot of time vs diffusion current for Cu₂O in DMSO system for various potential range.

Fig. 3 shows the variation of diffusion coefficient value with increasing time period from 10 seconds to 100 seconds. It was seen that for potential value of 0.5 to 0.9 V, the diffusion coefficient shows marginal decrease with increase in time period. However, at potential above 0.9V i.e.; at 1.2 V there is a sudden increase in diffusion coefficient value.

The values obtained from chronoamperometry studies are typical for reactions which are controlled by solid state diffusion. Similar findings have been reported for copper-sulphide carbon paste electrode.

4. Chronoamperometry study of Cu₂O in DMSO + SO₂:

The chronoamperometry plot of Cu₂O in DMSO + SO₂ solvent system was studied using carbon paste electrode.

The current response as a function of time was recorded at various potential range in the anodic region as shown in Fig. 4 The $i-t$ curves were measured at potential of 1.0, 1.2 and 1.5 V and time periods of 10, 15, 30 and 60 seconds. The charging current was dominant initially and later Faradic current becomes dominant after 0.01 seconds.

The chronoamperometry plot of $1/\sqrt{t}$ versus current for Cu₂O in DMSO + SO₂ shows a decreasing linear relationship between $1/\sqrt{t}$ and current. As the potential increases from 1.0 V to 1.2 V, the current value (in mA) decreases. At potential above 1.5 V, the curve shows a non-linear relationship.

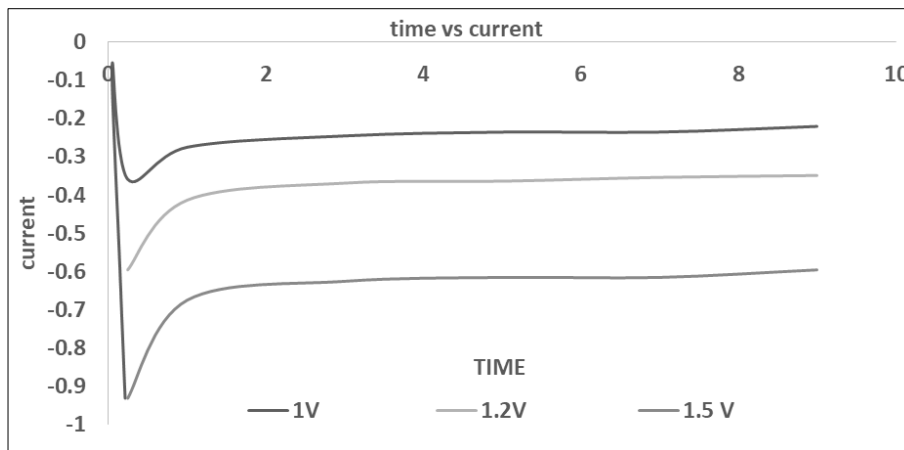


Fig 6: Chronoamperometric plot time vs current in Cu₂O in DMSO+ SO₂ system at various potential range.

The value of slope varied with change in potential is shown in Table 4. The slope value show increasing value with increase in time period from 67.28 to 85.12 As^{1/2} from 10 to 60 seconds. As the potential is increased from 0.0 V to 1.5

V, the slope increases from 67.28 to 101.91 As^{1/2} at 10 secs and 85.12 to 129.45 As^{1/2} at 60 seconds. At potential above 1.5 V, the slope value shows inconsistent data.

Table 4: Area, Peak current and Peak time data and calculation of slope, diffusion coefficient, chi-square and correlation at different potential and time period for Cu₂O in DMSO and sulfur dioxide using chronoamperometric techniques.

Volt (V)	Time (s)	it ^{1/2} 10 ⁻⁶ As ^{1/2}	Diff. Coeff. 10 ⁻⁷ cm ²	Chi-squ. 10 ⁻¹²	Correl.	Area (μC/cm ²)	Peak Cur. (μA/cm ²)	Peak Time (s)
1.0	10	-67.28	4.49	3.24	-0.99	-1.4	-0.25	0.28
1.0	15	-83.77	5.01	3.30	-0.98	-2.2	-0.29	0.34
1.0	30	-84.42	5.03	4.26	-0.98	-2.8	-0.34	0.45
1.0	60	-85.12	5.05	5.45	-0.98	-3.1	-0.39	0.52
1.2	10	-86.96	5.10	6.64	-0.97	-3.4	-0.44	0.23
1.2	15	-94.32	5.32	14.2	-0.95	-3.6	-0.48	0.27
1.2	30	-98.15	5.42	15.8	-0.95	-3.8	-0.56	0.31
1.2	60	-99.72	5.47	17.1	-0.95	-4.0	0.64	0.38
1.5	10	-101.9	5.53	18.6	-0.95	-4.2	-0.70	0.23
1.5	15	-114.4	5.86	24.4	-0.93	-6.3	-0.70	0.35
1.5	30	-121.3	6.03	26.72	-0.92	-7.8	-0.78	0.46
1.5	60	-129.4	6.23	42.1	-0.92	-9.1	-0.86	0.70

The chronoamperometry data for area of the curve, peak current and peak time and calculation of slope, diffusion coefficient, chi-square and correlation at different potential

and time period for Cu₂O in DMSO were obtained from the i-t curves. The values are shown in Table 4 at different potential and time periods.

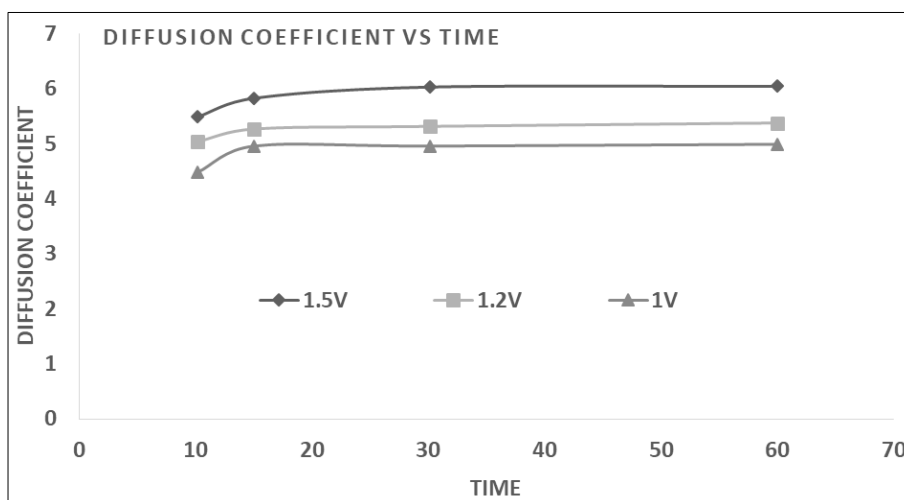


Fig 7: Chronoamperometric plot time vs diffusion coefficient in Cu₂O in DMSO+ SO₂ system at various potential range.

It was observed that the area of the curve increases with increase in potential and time period from -1.45 mC/cm² at 1.0V to 6.36 mC/cm² at 1.5V. The peak current value

increases from -0.25 mA/cm² at 1.0V to -0.70 mA/cm² at 1.5V. The value increases both with the increase of time period and potential. In the case of peak time, it was seen

that at potential of 1.0 V, the peak time increases from 0.28 seconds at 10 seconds to 0.34 seconds at 15 seconds. Similarly with increase in potential from 1.0V to 1.5V, the peak time shows similar trend.

The diffusion coefficient values were calculated from the slope ($it^{1/2}$) according to Cottrell's equation

$$i = \frac{nFA\sqrt{DC}}{\sqrt{\pi t}}$$

Where symbols have their usual meaning

Or, $\sqrt{D} = 3 \times 10^7 \times it^{1/2}$

The diffusion coefficient values increased from 4.49×10^{-7} cm²/s at 1.0V to 5.86×10^{-7} cm²/s. The diffusion coefficient increases with increase in time period and potential. The chi-square value increased from 3.24×10^{-9} at 1.0 V to 24.40×10^{-9} at 1.5 V. The correlation value varied from -0.997 to -0.957. The variation of diffusion coefficient with increasing time period of 10 to 60 seconds is shown in Fig. 4.3. It was seen that at lower time period of 10 seconds to 15 seconds, the diffusion coefficient value increases but at higher time period, i.e.; 20 to 60 seconds, the diffusion coefficient value remains almost linear. With increase in potential, the diffusion coefficient value increases.

Conclusion

In conclusion, the chronoamperometry studies conducted on Cu₂O in different solvent systems provided valuable insights into its electrochemical behaviour. In water, the *i-t* curves revealed a transition from dominant charging current to Faradic current as the potential increased, with irregular behaviour observed at higher potentials. The diffusion coefficient decreased with increasing potential and time period, exhibiting a linear trend at lower potentials.

In the water-sulphite system, the area of the curve increased with pH, while the peak current decreased with time period, yet increased with higher potential. The diffusion coefficient displayed a decreasing trend with increasing time period, particularly at pH=1.8, and the chi-square values varied with both potential and time period.

In DMSO, the chronoamperometry plots indicated a clear distinction between charging and Faradic currents, with the diffusion coefficient values typical for reactions controlled by solid-state diffusion. These values generally increased with potential and time period, with marginal decreases observed at higher potentials initially.

Lastly, in the DMSO + SO₂ system, the chronoamperometry plots showed a linear relationship between $1/\sqrt{t}$ and current, with increasing slope values with both time period and potential. The diffusion coefficient values increased with time period and potential, while chi-square values and correlation coefficients varied accordingly.

Overall, these studies contribute to a comprehensive understanding of Cu₂O's electrochemical properties in different solvent systems, providing valuable data for further research and applications in various fields.

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