Chronoamperometric study of CuO in aqueous and non aqueous solvents

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Abstract

Chemical techniques have been successfully used for the study of copper oxide leaching, however no attempts have been made so far to electrochemically study the dissolution of copper oxides in non-aqueous solvents. The aim of this investigation is to study the electrochemical behavior of copper oxides in aqueous and non-aqueous solvents and to study the electrochemical behaviour of copper oxide in the presence and absence of sulfur dioxide. We have carried out the recording of the I-t curves of copper oxide using chronoamperometric techniques at different potentials. The diffusion coefficient values were calculated using Cottrell's equation. The values varied from 3.38 to 7.56 x 10^{-7} cm^2/s. Correlation values obtained from statistical calculation varied from -0.993 to -0.989. Area of the curve obtained was between -1.44 to -6.31 mC/cm^2.

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1. Introduction

The vital role played by electrochemical techniques in modern chemical investigation cannot be over emphasized. These techniques have proved to be accurate and precise at trace levels in inorganic and organic analysis. Hydrometallurgy is a relatively recent technology having received wide attention owing to its inherent advantages. There has been a continued interest in copper hydrometallurgy involving low grade ores and secondary sources. There are several hydrometallurgical processes which are electrochemical in nature. The chemistry of copper oxide leaching depends upon various factors among which leachant and the solvent system plays an important role. The leaching of metal oxides is accelerated in the presence of an added oxidizing or reducing agent. The leaching of copper oxides with aqueous solution of sulfur-dioxide is broad commercial interest [1,2]. DMSO was chosen as the non-aqueous solvent for the electrochemical studies due to its unique properties.

In the present work electrochemical properties of CuO were investigated using electrochemical technique. Pure samples of CuO was taken for the fundamental study. Different solvent systems used in the study were 1. CuO in water, 2. CuO in water-Sodium sulphite , 3. CuO in DMSO, 4. CuO in DMSO+ SO₂ system. The electrochemical technique employed in electrochemical dissolution studies are chronoamperometry (CA). 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 an electrode immersed in a non-stirred solution [3]

Materials and Methods: All chemicals used throughout these studies were either of AR grade or were purified using known techniques [4]. CuO was obtained from S.D. Fine chemicals and was used as received. DMSO was of AR grade and was purified by keeping in 3A^0 molecular sieves to absorb water [5]. KCl was AR

grade and was used as such. Sodium sulfite, Iodine, EDTA of AR grade were used and were obtained from S. D. Fine Chemicals. Graphite and paraffin oil used was of reagent grade. Nitrogen gas was obtained from Industrial Oxygen Ltd. with 99% purity. Sulfur 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) [6,7]. 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 the dissolved oxygen gas. The studies were performed in the inert nitrogen atmosphere which was maintained during the run of the experiment. The QRE was placed very near to the WE to eliminate the iR potential drop in the solution. The measurements were taken in an unstirred solution at room temperature.

Estimation of copper: Copper was estimated by EDTA method [8]. About 200 mg of copper oxide was taken in a beaker and then 2 ml of conc. HNO_3, 2 ml of conc. H_2SO_4 and about 1-2 drops of 70% perchloric acid was added in it. The solution was heated strongly to dryness. The decomposed sample 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 near the endpoint. The metal % was calculated as:
1000 ml of 1M EDTA = 63.54 gm of copper.

Determination of Sulfur dioxide concentration : In a conical flask known volume of standard 0.1 N iodine solution (10-25 ml) depending upon the concentration of sulfur dioxide in the solution was taken and diluted with distilled water to about 150 ml and acidified with 5 ml of 2 N HCl [9]. Then the known volume of aqueous sulfur dioxide solution was taken in a pipette was slowly added to the solution in the conical flask and the excess iodine was immediately 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 sulfur dioxide. From the following reaction.
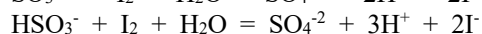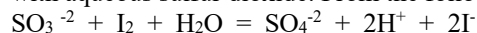
$SO_3^{-2} + I_2 + H_2O = SO_4^{-2} + 2H^+ + 2I^-$
$HSO_3^- + I_2 + H_2O = SO_4^{-2} + 3H^+ + 2I^-$
It follows that
1 ml 0.1 N I_2 = 0.0032 gm SO_2

In case of determination of sulfur dioxide in DMSO, due to high concentration of sulfur 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 pH-Elico instrument. The instrument was standardized 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 to control the instrument. The instrument was hooked to a 386 computer along with a printer.

Result and Discussions:

1. CHRONOAMPEROMETRY STUDY OF CuO IN WATER:
The chronoamperometry technique was used for the study of CuO in water. The i-t curve was recorded in the anodic region with an initial potential of 0.0 V. The potential range was varied from 0.5 V to 1.2 V at different time periods of 10, 20, 40, 60 and 100 seconds. The chronoamperometry curve was obtained using graphite paste as the working electrode. The i-t curve for CuO in water is shown in Fig. 1a at 10 seconds. The curve shows that there is no change in the nature of the curve at lower potential, but at potential higher than 1.0 V the curve becomes irregular. Here the charging current is dominant initially and later on Faradic current dominates.

Table.1. Variation of slope with change in potential for CuO in water using chronoamperometric techniques

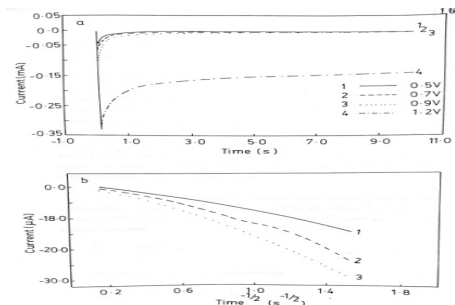| SLOPE ($10^{-6}As^{1/2}$)			
Sr. No.	Time (s)	0.0 to 0.5 (V)	0.0 to0.7 (V)	0.0 to 0.9 (V)
1	10	-13.64	-19.89	-30.72
2	20	-10.73	-16.61	-23.17
3	40	-9.32	-13.44	-17.71
4	60	-9.06	-11.79	-14. 90
5	100	-7.95	-11.33	-13.48

Fig.1.Chronoamperometric plot of CuO in water at various potential range a) time vs current, b) time$^{1/2}$ vs current.

Table 2. Area, Peak current and Peak time data at different potential and time for CuO in water using chronoamperometric techniques.

Table 3. Calculation of slope, diffusion coefficient, chi-square and correlation at different potential and time period for CuO in water using chronoamperometric techniques.

Sr. No.	Volt (V)	Time (s)	Area ($\mu C/cm^2$)	Peak Cur. ($\mu A/cm^2$)	Peak Time (s)
1	0.5	10	-38.16	-48.51	0.10
2	0.5	40	-43.12	-22.00	0.28
3	0.5	100	-39.02	-13.49	0.70
4	0.7	10	-62.31	-73.07	0.12
5	0.7	40	-79.97	-24.41	0.38
6	0.7	100	-87.65	-19.41	0.70
7	0.9	10	-93.50	-115.4	0.11
8	0.9	40	-115.5	-29.69	0.45
9	0.9	100	-137.3	-21.60	0.70
10	1.2	10	-162	-345.0	0.17
11	1.2	40	-491	-224.0	0.52
12	1.2	100	-1020	-198.0	0.70

Sr. No.	Volt (V)	Time (s)	it$^{1/2}$ 10^{-6} As$^{1/2}$	Diff. Coeff. 10^{-7} cm^2	Chi-squ. 10^{-9}	Correl.
1	0.5	10	-13.6	2.02	0.23	-0.979
2	0.5	40	-8.8	1.63	0.02	-0.980
3	0.5	100	-7.95	1.54	0.02	-0.960
4	0.7	10	-19.90	2.44	0.51	-0.978
5	0.7	40	-13.44	2.01	0.06	-0.976
6	0.7	100	-11.33	1.84	0.04	-0.968
7	0.9	10	-30.72	3.04	1.52	-0.973
8	0.9	40	-17.71	2.30	0.08	-0.981
9	0.9	100	-13.48	2.01	0.03	-0.978

The i-t$^{-1/2}$ curve of CuO in water is shown in Fig. 1b. The curve shows a linear relationship between i-t$^{-1/2}$ with decreasing value of current. The current when extrapolated to t=0, represents the Faradic current. The curve obtained with potential higher than 1.0 V shows irregular behavior. The potential range was changed from 0.0 to 0.5 V, 0.7 V, 0.9 V and 1.2 V. The slope value varied with the change in potential at different time periods of 10, 20, 40, 60 and 100 seconds. The variation of slope with change in potential is shown in Table 1. It was observed that at a particular potential range, the slope value decreased with increasing time period i.e.; from -13.64 $\mu As^{1/2}$ at 10 seconds to -7.95

$\mu As^{1/2}$ at 100 seconds. The trend is seen at higher potential range. However, the slope value increased from -13.64 at 0.5 V to - 30.72 $\mu As^{1/2}$ at 0.9 V at given time period of 10 seconds. At potential range of 0.0 to 1.2 V, the slope value shows very high value. The area of the curve, peak current and peak time of CuO in water were obtained from the i-t curve. The data at different potential and time period has been shown in Table 2. The area of the curve increases with increase with increase in potential and time period from -38.16 $\mu C/cm^2$ at 0.5 V and 10 seconds to - 137.30 $\mu C/cm^2$ at 0.9 V and 100 seconds. The peak current decreases in a particular potential range with increasing time period. It however increases with increase in potential at a given time period. It increases from -38.16 $\mu C/cm^2$ at 0.5 V to -93.50 $\mu C/cm^2$ at 0.9 V for 10 seconds time period. The peak time increases from 0.10 seconds to 0.70 seconds and is almost constant at various potential range. The slope, diffusion coefficient, chi-square and correlation values were obtained from the chronoamperometry curves. The data is shown in Table 3. The diffusion coefficient was obtained using the i-$t^{1/2}$ curve according to Cottrell's equation [10, 11]:

$$i \quad = \quad \frac{nFAD^{1/2}C}{\mu^{1/2} \ t^{1/2}}$$

where symbols have their usual meaning

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

The diffusion coefficient decreased from 2.02 x 10^{-7} cm^2/s at 0.5 V and 10 seconds to 1.54 x 10^{-7} cm^2/s at 0.5 V and 100 seconds. At particular potential range, this trend was followed. However, with increasing potential the diffusion coefficient increased at a particular time period from 2.02 x 10^{-7} cm^2/s at 0.5 V to 3.04 x 10^{-7} cm^2/s for 10 seconds time period. The chi-square varied from 0.23 x 10^{-9} at 0.5 V to 1.52 x 10^{-7} at 0.9 V at 10 seconds. The correlation value varied from -0.980 to -0.968. At higher potential, the values are irregular. With increasing time period the diffusion coefficient at particular potential first decreases and then remain constant. With increase in potential the diffusion coefficient also increases. At potential higher than 1.0 V, the diffusion coefficient is very high.

2.CHRONOAMPEROMETRY STUDY OF CuO IN WATER+SODIUM SULPHITE SYSTEM : Chronoamperometry technique was employed for the study of CuO in water and sodium-sulphite system. In this technique a constant potential was applied between the CuO 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 plots were obtained at various pH. Fig.2 and 3 shows the plot at pH of 8.8, 3.0, 2.2, and 1.8.

The area of the curve, peak current and peak time were obtained from the i-t curve using chronoamperometry technique. Table 4 to 5 shows the value at different potential range and time period. It was observed that the area of the curve increases with increase in potential at different pH value. At pH=1.5, the value of area was the lowest (in the μA range) as compared to higher pH (mA range) except at pH=8.8 where it was in the μA range.

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 pH=1.8, the magnitude of the peak current value is higher as compared to other. The peak time increases with increase in time in a particular potential range. The peak time value increases from 0.17 to 0.36 seconds and this trend is seen in almost all the pH values. The chronoamperometry plots above 1.5 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 6 and 7. The slope value were lowest at pH=1.5. From the slope value, the diffusion coefficient values have been calculated using the Cottrell's equation.

The diffusion coefficient value decreases from 2.83 x 10^{-7} cm^2/s at 0.8 V and 10 seconds to 1.99 x 10^{-7} cm^2/s at 20 seconds at pH=1.5. At potential of 1.2 V, it decreases from 2.00 x 10^{-7} cm^2/s and 10 seconds to 1.69 x 10^{-7} cm^2/s at 20 seconds. The diffusion coefficient shows similar trend at various pH. However it was seen at pH=1.5, the diffusion coefficient value is the least. The chi-square value decreased with the increase in time period and potential. The chi-square value varied in the range of 10^{-9} at pH=1.5 and 1.8. However at higher pH, it was in the range of 10^{-12}. The correlation value varied from -0.940 to -0.999.
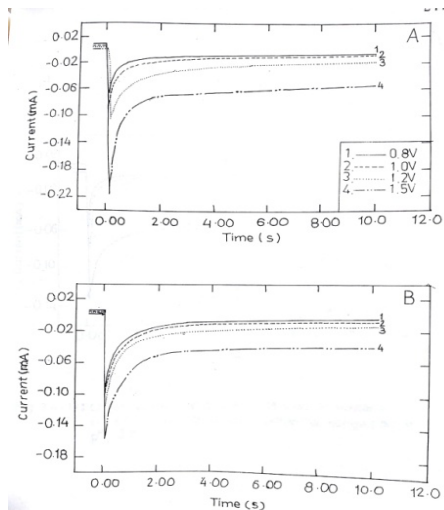
Fig.2.Chronoamperometric plot of CuO in water+ sodium sulphite system at various potential range A) at pH=2.2, B) pH=1.8
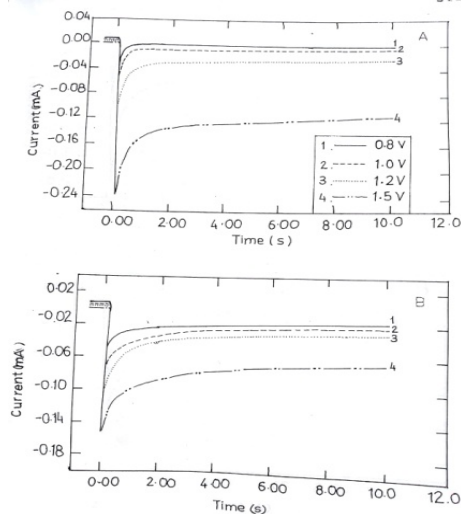

Fig.3.Chronoamperometric plot of CuO in water + Sodium sulphite system at various potential range A) at pH=8.8, B) pH=3.0

Table 4: Area, Peak current and Peak time data at different potential and time period for CuO in water + Sodium sulphite using chronoamperometric techniques at pH 8.8.

Sr. No.	Volt	Time	Area	Peak Cur.	Peak Time
	(V)	(s)	($\mu C/cm^2$)	($\mu A/cm^2$)	(s)
1	0.8	10	-15.13	-17.42	0.17
2	0.8	15	-15.94	-12.68	0.26
3	0.8	20	-17.06	-10.25	0.34
4	1.0	10	-35.92	-30.43	0.22
5	1.0	15	-39.94	-23.95	0.31
6	1.0	20	-43.54	-22.07	0.36
7	1.2	10	-277.8	-104.7	0.18
8	1.2	15	-373.9	-80.19	0.26
9	1.2	20	-440.3	-89.7	0.24

Table 5: Area, Peak current and Peak time data at different potential and time period for CuO in water + Sodium sulphite using chronoamperometric techniques at pH 1.8

Sr. No.	Volt	Time	Area	Peak Cur.	Peak Time
	(V)	(s)	(mC/cm^2)	($\mu A /cm^2$)	(s)
1	0.8	10	-0.115	-94.02	0.12
2	0.8	15	-0.123	-75.62	0.18
3	0.8	20	-0.126	-67.80	0.24
4	1.0	10	-0.143	-104.0	0.12
5	1.0	15	-0.159	-94.00	0.19
6	1.0	20	-0.167	-80.66	0.24
7	1.2	10	-0.230	-121.5	0.12
8	1.2	15	-0.275	-105.8	0.19
9	1.2	20	-0.313	-89.60	0.24

A plot of diffusion coefficient versus time has been shown in Fig. 4 and Fig. 5. 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 pH=1.8 is lower as compared to other pH values.

Table 6: Calculation of slope, diffusion coefficient, chi- square
and correlation at different potential and time period for CuO in
water + Sodium sulphite using chronoamperometric techniques at pH 8.8.

Sr. No.	Volt	Time	$it^{1/2}$	Diff. Coeff.	Chi-square	Correl
	(V)	(s)	$\mu As^{1/2}$	$10^{-7}cm^2/s$	10^{-12}	
1	0.8	10	-5.57	1.29	48.48	-0.966
2	0.8	15	-5.05	1.23	27.21	-0.965
3	0.8	20	-4.79	1.20	17.66	-0.967
4	1.0	10	-12.53	1.94	159.0	-0.973
5	1.0	15	-11.60	1.87	110.2	-0.968
6	1.0	20	-11.20	1.83	74.81	-0.974
7	1.2	10	-27.90	2.89	870.4	-0.975

Table 7 : Calculation of slope, diffusion coefficient, chi- square
and correlation at different potential and time period for CuO in
water + Sodium sulphite using chronoamperometric techniques at
pH 1.8

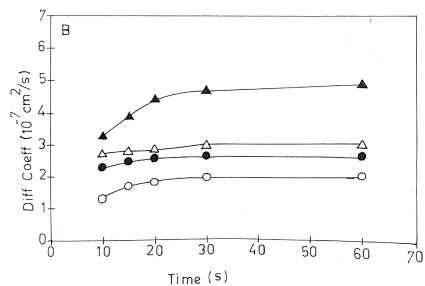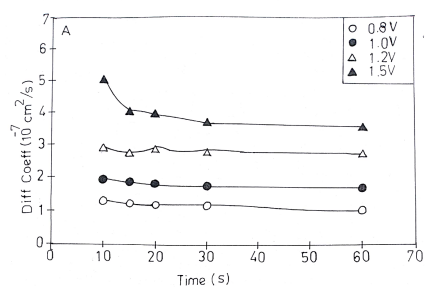| Sr. No.	Volt	Time	$it^{1/2}$	Diff. Coeff.	Chi-square	Correl
	(V)	(s)	$\mu As^{1/2}$	10^{-7} cm^2/s	10^{-9}	
1	0.8	10	-33.91	3.19	0.253	-0.996
2	0.8	15	-31.90	3.09	0.184	-0.995
3	0.8	20	-32.33	3.11	0.454	-0.985
4	1.0	10	-37.79	3.37	0.464	-0.994
5	1.0	15	-39.63	3.45	0.782	-0.987
6	1.0	20	-36.48	3.31	0.719	-0.981
7	1.2	10	-39.00	3.42	0.267	-0.997
8	1.2	15	-38.88	3.42	0.308	-0.995

Fig.4.Chronoamperometric plot of diffusion coefficient versus
Time for CuO in water + sodium sulphite system at various potential
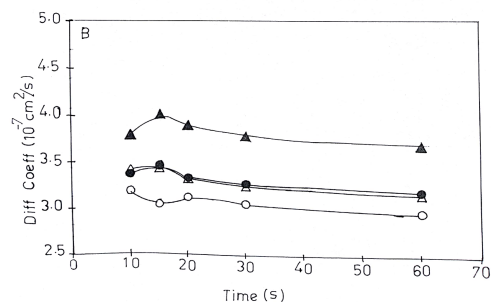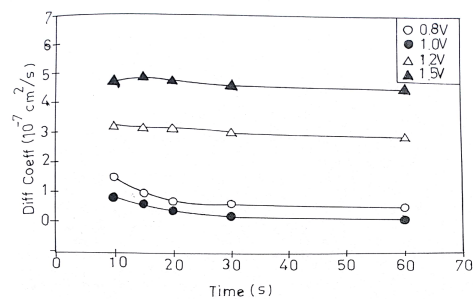Range A) at pH=8.8, B) pH=3.0

Fig.5.Chronoamperometric plot of diffusion coefficient versus
Time for CuO in water + sodium sulphite system at various
potential range A) at pH=2.2, B) pH=1.8

3.CHRONOAMPEROMETRY STUDY OF CuO IN DMSO:

A typical chronoamperometry curve of CuO in DMSO is shown in Fig. 6a. The i-t curve was recorded in the anodic
region at various potential range. The current response as a function of time was recorded. Fig. 6b shows the

chronoamperometry curve of CuO between i and $t^{-1/2}$ at potential of 0.5, 0.7 and 0.9 V. The curve above 0.9 V was not well defined. The chronoamperometry curves of CuO in DMSO were

Table.8. Variation of slope with change in potential for CuO in DMSO solution using chronoamperometric techniques

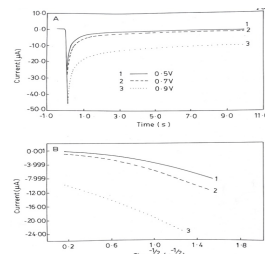| SLOPE ($10^{-6}As^{1/2}$)			
Sr. No.	Time (s)	0.1to 0.5 (V)	0.1to0.7 (V)	0.1to 0.9 (V)
1	10	-7.45	-9.49	-96.30
2	20	-5.99	-7.92	--
3	40	-4.31	-6.16	-115.1
4	60	-3.50	-5.16	--
5	100	-2.71	-4.20	-128.2

Fig.6.Chronoamperometric plot of CuO in DMSO

at various potential range
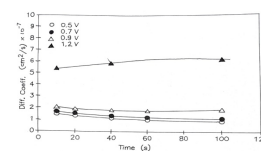
A) time vs current, B) time$^{1/2}$ vs current.

Fig.7.Chronoamperometric plot

diffusion coefficient versus Time

for in CuO- DMSO system

obtained using carbon paste electrode as the working electrode. The curve shows a linear relationship between i and $t^{-1/2}$. The current when extrapolated to t=0, represents the Faradic current. The chronoamperometry curves were measured at different time periods of 10, 20, 40, 60 and 100 seconds with various potential value of 0.5, 0.7, 0.9 and 1.2 V. Table 8 shows the slope obtained at various potential range at time period of 10 to 100 seconds. The slopes obtained at 0.0 to 0.5, 0.0 to 0.7 and 0.0 to 0.9 V shows a decreasing value with increasing time period. However at potential higher than 0.9 V, the slope value increases drastically with increasing time period.

The area of the curve, peak current and peak time were obtained from the i-t curve of the chronoamperometry study. Table 9 shows the value at different potential range with change in time period. The area of the curve increases with the increase in potential and time period from 19.14 $\mu C/cm^2$ to 100.6 $\mu C/cm^2$ from 0.5 V to 0.7 V. After 0.9 V, the area increases from 132.3 $\mu C/cm^2$ to 1606 $\mu C/cm^2$. The peak current decreases with increase in time period for a particular potential. However with increase in potential the peak current increases in a particular potential range. Similar trend is seen in the peak time value. Above 0.9 V, the values are ill-defined.

Table .10. shows the slope, diffusion coefficient, chi-square, and correlation values at different potential and time period. The diffusion coefficient has been obtained from the slope value ($it^{1/2}$).

The diffusion coefficient values were obtained by employing the above equation. The diffusion coefficient values varied from 0.91 x 10^{-7} cm^2/s at 0.5 V and 100 seconds to 6.2 x 10^{-7} cm^2/s at 1.2 V and 100 seconds. The diffusion coefficient values increases with increase in potential value. However in a particular potential range, the diffusion coefficient value decreases with increasing time period of 10 to 100 seconds. Chi-square value varies in a similar trend. It changes from 2.86 x 10^{-12} to 3.89 x 10^{-9}. The correlation coefficient value varies from 0.947 to 0.997. Fig.7 shows the variation of diffusion coefficient value with increasing time period from 10 seconds to 100 seconds. It was seen that at potential value of 0.5 to 0.9 V, the diffusion coefficient almost remained constant with slight decrease with increase in time period. However at potential higher than 0.9 V there is a sudden increase in diffusion coefficient value.

Table 9 Area, Peak current and Peak time data at different potential and time period for CuO in DMSO solution using chronoamperometric techniques

Sr.No.	Volt (V)	Time (s)	Area ($\mu C/cm^2$)	Peak Cur. ($\mu A/cm^2$)	Peak Time (s)
1	0.5	10	-19.14	-22.69	0.14
2	0.5	40	-21.27	-8.50	0.46
3	0.5	100	-24.76	-3.44	1.10
4	0.7	10	-32.98	-27.61	0.16
5	0.7	40	-57.96	-12.38	0.48
6	0.7	100	-100.6	-5.69	1.20
7	0.9	10	-132.2	-47.71	0.17
8	0.9	40	-441.2	-23.40	0.64
9	0.9	100	-1606	-24.86	1.70

Table 10. Calculation of slope, diffusion coefficient, chi-square and correlation at different potential and time period for CuO in DMSO solution using chronoamperometric techniques

Sr. No.	Volt (V)	Time (s)	$it^{1/2}$ 10^{-6} $As^{1/2}$	Diff. Coeff. 10^{-7} cm^2	Chi-squ. 10^{-12}	Correl.
1	0.5	10	-7.45	1.49	83.58	-0.967
2	0.5	40	-4.31	1.14	15.22	-0.947
3	0.5	100	-2.73	0.91	2.86	-0.938
4	0.7	10	-9.49	1.69	107.9	-0.974
5	0.7	40	-6.16	1.36	21.29	-0.962
6	0.7	100	-4.20	1.12	3.84	-0.963
7	0.9	10	-14.62	2.09	52.20	-0.995
8	0.9	40	-11.57	1.86	3.79	-0.997
9	0.9	100	-12.28	1.92	18.96	-0.972
10	1.2	10	-96.30	5.38	3890	-0.987
11	1.2	40	-115.1	5.88	2540	-0.983
12	1.2	100	-128.2	6.20	780	-0.992

4.CHRONOAMPEROMETRY STUDY OF CuO IN DMSO + SO$_2$:

The chronoamperometry plot of CuO in Dimethyl sulfoxide and sulfur dioxide solvent system is shown in Fig.8a. The current-time curve was measured at various potential range in the anodic range and the current response as a function of time was recorded. The chronoamperometry curves was measured using the carbon paste electrode as the working electrode. The chronoamperometry curves were measured at various potential of 1.0, 1.2, and 1.5 V at different time periods of 10, 15, 30 and 60 seconds. It was observed that initially the charging current was dominant and later the Faradic current becomes dominant after 0.01 seconds.The chronoamperometry plot of time$^{-1/2}$ versus current for CuO in DMSO + SO$_2$ system is shown in Fig. 8b. The curve shows a linear relationship between $t^{-1/2}$ and current. The current when extrapolated to t=0, represents the Faradic current. It was observed that the curve above potential of 1.5 V becomes ill-defined.The variation of slope with change in potential value has been shown in Table 11. The slope values shows a decreasing value with increase in time period. The value also goes on increasing when we increase the potential from 1.0 V to 1.5 V. But above 1.5 V , the slope value becomes inconsistent indicating the irregular behaviour at higher potential range.The area of chronoamperometry curve, peak current and peak time were obtained from the current-time curve. Table 12. shows the area, peak current and peak time at different potential and time period. It was seen that the area of the curve increases with increase in potential and time period from 0.184 to 5.45 mC/cm^2. The peak current increases in value from 0.12 to 0.89 mA/cm^2 in similar way. However the peak time increases with increase in time period for a particular potential. The value for all the above parameters shows irregular behaviour above potential of 1.5 V. The calculation of slope value, diffusion coefficient, chi-square and correlation obtained from chronoamperometry curve has been shown in Table 13. The diffusion coefficient value have been calculated from the slope according to Cottrel's equation.The diffusion coefficient value varied from 3.38 to 7.72 x 10^{-7}cm^2/s at 1.0 V to 1.5 V. It increases with increase in potential and time period. The chi-square values shows a similar trend and varied from 0.61 to 3.54 x 10^{-12} at 1.0 V to 1.2 V. At 1.5 V, chi-square inceases drastically to 18.18 x 10^{-12} The correlation value varies from -0.978 to -0.997.The variation of diffusion coefficient with increasing time period of 10 to 30 seconds is shown in Fig. 9. It was seen that as potential increases from 1.0 V to 1.5 V, the diffusion coefficient values increases. At lower time period, the diffusion coefficient value inceases, but at higher time period the diffusion coefficient value almost shows a linear relationship.

Table 11. Variation of slope with change in potential for CuO in DMSO and sulfur dioxide using chronoamperometric techniques.

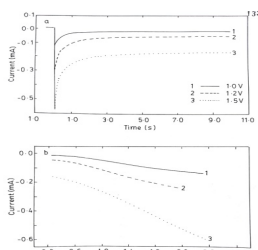| SLOPE ($10^{-6}As^{1/2}$)				
Sr. No.	Time (s)	0.0 to 1.0 (V)	0.0 to 1.2 (V)	0.0 to 1.5 (V)
1	10	-38.16	-89.36	-145.20
2	15	-54.95	-103.10	-171.70
3	30	-76.28	-118.45	-189.60
4	60	-81.15	-127.28	-198.50

Fig.8.Chronoamperometric plot of CuO in DMSO +SO₂ at various potential range A) time vs current, B) time$^{1/2}$ vs current.
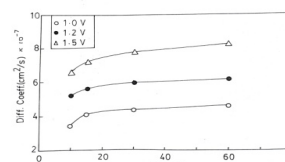

Fig.9.Chronoamperometric plot diffusion coefficient versus Time for CuO in DMSO +SO₂ system

Table .12. Area, Peak current and Peak time data at different potential and time period for CuO in DMSO and sulfur dioxide using chronoamperometric techniques.

Sr.No.	Volt (V)	Time (s)	Area (mC/cm²)	Peak Cur. (mA/cm²)	Peak Time (s)
1	1.0	10	-0.184	-0.120	0.12
2	1.0	15	-0.293	-0.142	0.19
3	1.0	30	-0.360	-0.167	0.23
4	1.0	60	-0.470	-0.192	0.28
5	1.2	10	-0.650	-0.237	0.16
6	1.2	15	-0.917	-0.283	0.24
7	1.2	30	-1.280	-0.356	0.35
8	1.2	60	-1.635	-0.482	0.42
9	1.5	10	-1.925	-0.593	0.12
10	1.5	15	-2.836	-0.615	0.18
11	1.5	30	-3.450	-0.785	0.24
12	1.5	60	-5.445	-0.894	0.48

Table. 13.Calculation of slope, diffusion coefficient, chi-Square and correlation at different potential and time period for CuO in DMSO and sulfur dioxide using chronoamperometric techniques.

Sr. No.	Volt (V)	Time (s)	it$^{1/2}$ 10^{-6} As$^{1/2}$	Diff. Coeff. 10^{-7} cm²	Chi-squ. 10^{-12}	Correl.
1	1.0	10	-38.16	3.38	0.61	-0.993
2	1.0	15	-54.95	4.06	1.63	-0.986
3	1.0	30	-76.28	4.78	1.76	-0.988
4	1.0	60	-81.15	4.93	1.84	-0.978
5	1.2	10	-89.36	5.18	2.08	-0.994
6	1.2	15	-103.10	5.56	3.35	-0.989
7	1.2	30	-118.45	5.96	3.45	-0.978
8	1.2	60	-127.28	6.18	3.54	-0.986
9	1.5	10	-145.20	6.60	3.63	-0.997
10	1.5	15	-171.70	7.18	12.29	-0.989
11	1.5	30	-189.60	7.54	15.78	-0.982
12	1.5	60	-198.50	7.72	18.18	-0.987

Conclusion:

1. The results of the electrochemical investigation showed that as the dissolution potential increases, the anodic current density increases with the increase of copper oxide concentration.

2. Chronoamperometric techniques confirm that the dissolution in copper oxides is under solid-state diffusion control.

3. Diffusion coefficients values were calculated using the chronoamperometric techniques. It varied in different solvent system and it generally depended primarily on the nature of the dissolved substances, the concentration of the diffusing substance, solvent system, pH etc.

4. From the above electrochemical investigation, it is apparent that in the   present analysis, the diffusion rate measured is that of copper oxides through a series of phases of varying composition and structure. It is possible to determine the diffusion coefficient by measurements at low current densities.

5. The dissolution of copper oxides can be classified as an oxidative leaching process. The rate of dissolution is different for different oxidants.

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