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Electrochemical study of Cu_2O in aqueous and non-aqueous solvents in presence of SO_2 using chronopotentiometry

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Abstract
This abstract presents a comprehensive study of electrochemical properties of Cu_2O using chronopotentiometric techniques in different solvent systems. In water, varying current densities were applied to measure potential-time curves, revealing a decreasing trend in potential with increasing current. Analysis at different current ranges illustrated solid-state diffusion behaviour, evidenced by constant transition times. Cu_2O behaviour in water-sulphite and DMSO solvent systems was also investigated, showing similar trends in potential-time curves. Notably, in DMSO, the leaching behaviour of Cu_2O was explored, indicating a significant decrease in potential with increasing current, and confirmed by constant transition times at higher current ranges. Statistical analysis revealed the consistency of results across different experimental conditions. Graphical representation of current versus curve area and slope demonstrated distinctive behaviour displaying higher area values and slightly higher slopes. This research enhances understanding of Cu_2O behaviour in various solvent systems and provides insights into its potential applications.

Keywords: Cu_2O, Chronopotentiometry, SO_2, non-aqueous solvents

Introduction

Leaching [1-3] refers to the process in which there is transfer of solutes from a solid, usually in particulate form, to the contiguous liquid, the extract. It almost invariably involves the diffusion of solutes in the solid to the solvent. The solvent is then subjected to separation process for purification or recovery or both of the desired metals or metal compounds. Electrochemical aspects of different oxides of copper were investigated by using a large number of techniques in various solvent systems. Among the various non-aqueous solvents used DMSO finds a wide spread applications in organic chemistry, biochemistry, industries. [2, 4, 5]. The recovery of copper from ores of carbonate origin has been difficult to achieve by conventional metallurgical techniques. Oxidised copper minerals cannot be effectively separated from carbonate gangue minerals by floatation and direct acid leaching is not economical because of excessive acid consumption. Although the recovery of copper from oxidised copper ores by ammonia or cyanide leaching is technically feasible, problems are often encountered in leachant generation. The leaching of metal oxides is accelerated in the presence of an added reducing agent. Aqueous solution of sulphur dioxide has been used as an efficient leaching agent as it offers rapid and selective extraction of metal values at ambient temperatures and pressure [5-13].

Materials and Methods

All chemicals utilized in these investigations were either of analytical reagent (AR) grade or underwent purification through established methods [14]. 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 [15]. 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.

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Electrode system

Investigations into electrochemical behaviors 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) [16, 17]. 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 WE 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 [21]. 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 [22]. 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.

$$SO_3^{-2} + I_2 + H_2O = SO_4^{-2} + 2H^+ + 2I^-$$
$$HSO_3^- + I_2 + H_2O = SO_4^{-2} + 3H^+ + 2I^-$$
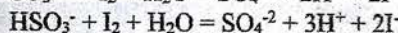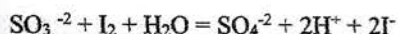
It follows that
1 ml 0.1 N I_2 = 0.0032 gm SO_2

In case of determination of 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 an 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. Chronopotentiometry study of Cu₂O in water

Chronopotentiometry curves were obtained of Cu_2O in water using carbon paste electrode as working electrode.
The potential-time curves were employed by applying a constant potential and varying the current density. A known amount of current was passed in the working electrode and the variation of potential as a function of time was measured.

Table 1: Chronopotentiometric data of Cu_2O in water at various current range

Current (10^{-6}A)	Time (s)	Area (Vs)	Area ($Vs^{1/2}$)	Slope 10^{-3} V/s	Chi-square	Correl
10	10	-1.77	0.21	-11.56	0.05	-0.88
15	10	-1.90	0.29	-58.99	0.11	-0.99
20	10	-2.20	0.38	-66.67	0.74	-0.94
30	10	-2.89	0.55	-75.39	1.51	-0.91
40	10	-2.94	0.84	-103.2	1.76	-0.87

The current densities applied was 1, 1.5, 2, 3 and 4 x 10^{-5} A with a fixed initial potential of 1.0 V. The step time was kept constants at 10 seconds. The transition time (τ) was measured in different current range. A typical plot of t versus E of Cu_2O in water shows that when the current range is increased from 1 to 4 x10^{-5} A, the potential value decreases in an increasing trend. At very high or very low current range, the chronopotentiometry plots are ill-defined.
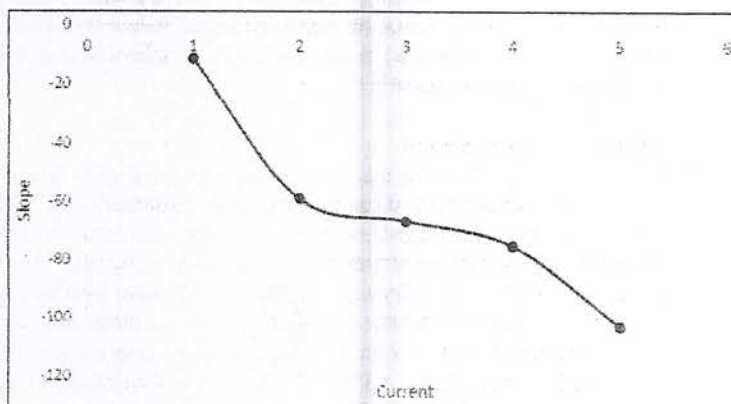

Fig 1: Plot of Slope vs Current for Cu₂O in water

The plot of E versus $\sqrt{t}$ at different current range shows that the $it^{1/2}$ becomes constant with further increase in current density. The transition time also becomes constants with further increase in current density. The term $it^{1/2}$ can be represented as

$$it^{1/2} = \text{constant}$$

The area of the curve for t versus E and $t^{-1/2}$ versus E has been obtained different current range. The data has been shown in Table 1. A gradual increase in area at fixed time period of 10 seconds was observed for both types of plots. The area of curve increased from -1.77 Vs at 1×10^{-5} A to -2.94 Vs at 4×10^{-5} A for t versus E plots at 10 seconds. Similarly in the case of $t^{-1/2}$ versus E plot, the area of the curve increased from 0.21 $Vs^{1/2}$ at 1×10^{-5} A to 0.84 $Vs^{1/2}$ at 4×10^{-5} A at 10 seconds. When the current range was increased to value more than 5×10^{-5} A, the nature of the curve become ill-defined.

Using the chronopotentiometry data, the Sand's equ. [23] can be applied to determine the diffusion coefficient. The Sand's equation can be expressed as follows:

$$it^{1/2} = \frac{\pi^{1/2} n\, FD^{1/2} C}{2}$$

Where symbols have their usual meaning.

The diffusion coefficient values indicate that Cu_2O is controlled by solid state diffusion. Similar studies were carried out with Cu_2S which shows solid state diffusion using carbon paste electrode [24-26].

Table 1 shows the slope values of Cu_2O in water using E versus t plots. It was observed that with the increase in current range, the slope value increases from -11.56×10^{-3} V/s at 1×10^{-5} A to -103.2 V/s at 4×10^{-5}A, The chi-square values increased from 0.053 to 1.76×10^{-3}. The correlation value varied from -0.988 to -0.873. Similar findings were observed for $t^{-1/2}$ versus E plots. The slope increases from -0.035 $V/s^{1/2}$ at 1×10^{-5} to -0.251 $V/s^{1/2}$ at 4×10^{-5} A and 10 seconds. The values are shown in Table 1 along with statistical calculation of chi-square and correlation coefficient. The chi-square value increases from 0.10 at 1×10^{-3} to 1.00 at 4×10^{-3}. The correlation value varies from -0.994 to -0.856.

A graph of current applied versus the area of the curve for t versus E shows that the area increases with an increase in current range However area of Cu_2O becomes constant after certain current value.

The graph of current applied versus the slope for Cu_2O in water. It was seen that with the increase in current range, the slope value increases. At a particular current range of 1.5×10^{-5}A to 3×10^{-5} A, the slope value almost remains constant. As the current increases beyond 3×10^{-5} A, the slope value continues to climb.

2. Chronopotentiometry study of Cu_2O in water-sulphite system: Chronopotentiometry curves were employed to determine the nature of Cu_2O in water-sulphite system. Potential-time curves were obtained by application of constant potential and varying the current density. The E-t curves of Cu_2O were obtained using carbon paste electrode as the working electrode. Here the current passed was varied with the working electrode and the potential response as a function of time was measured.

The current densities applied were 0.5, 1.0, 5.0, 7.5, 10 and 50 μA with the initial potential fixed at 1.0 V. The step time was kept constant throughout the experiment. The E-t plots were obtained at various P^H. It was observed that with the increase in current range from 0.5 μA to 50 μA, the potential value decreases in an increasing trend. The potential value initially decreases upto 0.5 seconds and then almost remains constant at a particular current range. It was seen that at current range lower than 0.5 μA and higher than 50 μA the chronopotentiometric plots are ill-defined. This trend is seen at all the pH values studied.

Table 2: Chronopotentiometric data of Cu_2O in water +sodium sulphite system at various current range and at various P^H

Current (10^{-6}A)	Time (s)	Area (Vs)	Area ($Vs^{1/2}$)	Slope 10^{-3} V/s	Chi-square	Correl.
At pH 8.2						
0.5	10	-4.34	-1.13	-30.41	1.96	-0.682
1.0	10	-5.85	-1.60	-25.11	1.80	-0.627
5.0	10	-8.94	-2.45	-41.05	3.58	-0.682
7.5	10	-9.70	-2.68	-37.11	3.86	-0.630
10.0	10	-11.44	-3.22	-35.31	6.32	-0.517
At pH 3.0						
0.5	10	-1.62	-0.36	-26.49	0.19	-0.933
1.0	10	-2.62	-0.66	-28.84	0.95	-0.678
5.0	10	-5.43	-1.48	-19.53	1.01	-0.623
10.0	10	-6.42	-1.80	-18.96	1.53	-0.550
50.0	10	-12.38	-3.40	-48.81	9.38	-0.565
100	10	-16.94	-4.91	-46.48	18.84	-0.418
At pH 2.2						
0.5	10	-0.34	-0.04	-16.77	0.05	-0.954
1.0	10	-0.32	-0.11	-6.75	0.02	-0.885
5.0	10	-1.53	-0.50	-4.11	0.69	-0.208
10.0	10	-2.12	-0.63	-12.55	0.77	-0.523
50.0	10	-1.38	-0.38	-4.71	0.03	-0.759
At pH 1.8						
0.5	10	-0.67	-0.16	-9.64	0.05	-0.887
1.0	10	-1.16	-0.32	-1.67	0.03	-0.782
5.0	10	-2.05	-0.61	-3.94	0.36	-0.271
10.0	10	-3.57	-1.01	-24.10	1.17	-0.691
50.0	10	-2.60	-0.74	-8.1	0.24	-0.579

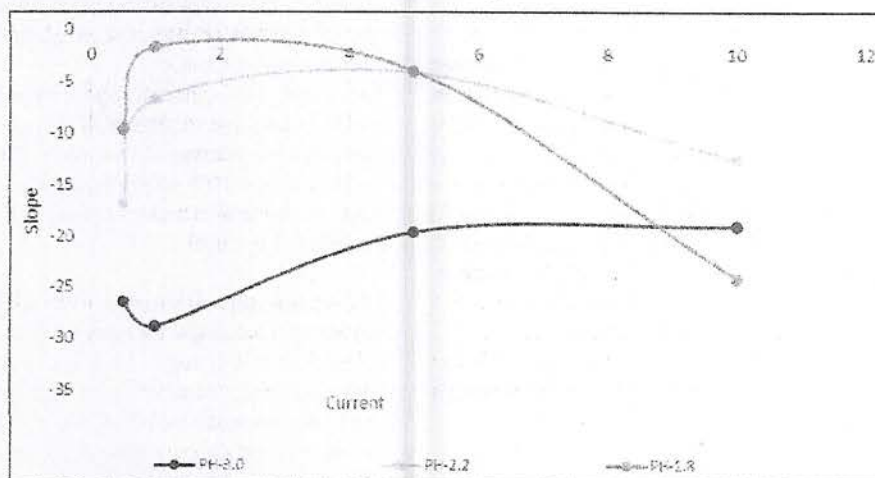| At pH 1.5						
0.5	10	-0.71	-0.22	-6.93	0.05	-0.968
1.0	10	-0.49	-0.09	-13.72	0.09	-0.890
5.0	10	-1.49	-0.47	-1.93	0.38	-0.133
50.0	10	-1.69	-0.47	-3.58	0.06	-0.546
75.0	10	-1.99	-0.56	-4.84	0.13	-0.503

Fig 2: Plot of Slope Vs Current for Cu_2O in water -Sulphite

When we plot E versus $t^{-1/2}$, we found that after certain current value the $it^{1/2}$ term becomes independent of any increase in current density. It was noted the current density and the transition time becomes constant after certain current value. It can be represented by the equation:

$$it^{1/2} = constant$$

The area of the curve for the E vs t plots were calculated at different current range and pH value. The data has been tabulated in Table 3.4-31 to 3.4-35. A gradual increase in area at a fixed time period of 10 seconds was observed at almost all the pH values. However the magnitude of area was lower at pH=1.5 as compared to other pH values.

The slopes, chi-square and correlation value were calculated for Cu_2O in water-sulphite system from the E-t curves. This were obtained at different current range and pH value. Table 2 shows the data calculated for slope, chi-square and correlation value from the E-t curves. The slope value increased with the increase in current range upto 5 µA and then again decreased gradually. This trend is seen in almost all pH value studied. However at pH=1.5, the slope value increased upto 10 µA and then decreased again. It was seen that with further rise in current value, the slope remains constant. The chi-square value increased with increase in current range and decrease in pH value. At pH=1.8, the magnitude of chi-square was comparatively lower than other pH values.

The thee correlation value varied from -0.540 to -0.954 at different pH value.

3. Chronopotentiometry study of Cu_2O in DMSO

Potential time curves were obtained to determine the nature of Cu_2O leaching in DMSO. chronopotentiometry curves were employed for the stud by application of constants potential and varying the current density. Here in this tech current was varied at the we with reference to re and the potential response as a function of time was measured. The E-t curves of Cu_2O were obtained using carbon paste electrode a working electrode.

Table 3: Chronopotentiometric data for area of Cu_2O in DMSO at various current ranges

Current (10^{-6}A)	Time (s)	Area (Vs)	Area ($Vs^{1/2}$)	Slope 10^{-3} V/s	Chi-square	Correl.
5	10	-6.83	-1.88	-28.87	11.37	-0.620
10	10	-8.51	-2.26	-38.79	14.01	-0.691
50	10	-10.43	-2.86	-48.15	8.83	-0.831
75	10	-12.89	-3.67	-46.85	4.76	-0.893
100	10	-17.15	-4.99	-44.68	9.86	-0.796

Table 3 shows the chronopotentiometry data for area of the curve for t versus E and $t^{1/2}$ versus E at different current ranges it was observed a gradual increase in area at fixed time period of 10 seconds. It was seen that at current range higher than 100 µA, the area increases rapidly and later becomes ill-defined.

The initial potential was fixed at 1.0 V and the current densities were varied from 10 µA to 100 µA. The step time was fixed at 10 seconds. The transition time (t) values were obtained in the above range. It was observed that with the increase in the current range ie; 10 µA, 25 µA, 50 µA, 75 µA and 100 µA, the potential value decreases in an increasing trend. At higher current values, the plots are not well defined.
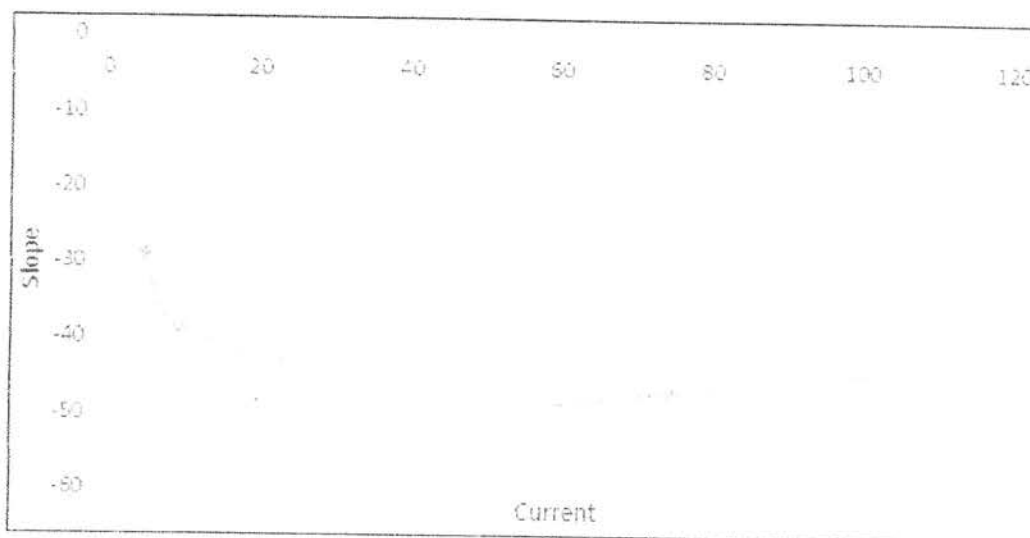
Fig 3: Plot of Slope Vs Current for Cu_2O in DMSO

When we plot E versus $t^{-1/2}$, we found that after certain current value the $it^{1/2}$ term becomes independent of any increase in current density. It was noted the current density and the transition time becomes constant after certain current value. Similar trend was seen previously in the earlier work [25]. It can be represented by the equation.

$$it^{1/2} = constant$$

The slope of the curves were obtained at different current range for Cu_2O in DMSO. The values varied from -28.87 V/s to 44.68 V/s as seen in Table 3. It was observed that at 50 µA current range, the slope becomes maximum value of 48.15 V/s and then again decreases with increase in current value. similar trend was also observed with $t^{-1/2}$ versus E plots. The slope increases from 0.1 V/s at 10 µA to 0.19 V/s at 50 µA. with further increase of current range the slope value decreases to 0.16 V/s at 100 µA current range. The values are shown in Table 3 along with some statistical calculation of chi-square and correlation value.

If we plot a graph of current applied versus the slope of Cu_2O in DMSO, we find that at a particular current range they are constant. In case of Cu_2O slope increases at 5 µA, reaches a maximum at 50 µA and then becomes almost constant with further rise in current.

4. Chronopotentiometry study of Cu_2O in DMSO + SO_2

Chronopotentiometry study of Cu_2O in DMSO + SO_2 solvent system were studied by using carbon paste electrode technique. The chronopotentiometry curves were obtained by applying a constant potential and varying the current range. The E versus t curves were measured by the variation of potential as a function of time.

An initial potential of 1.0 V was fixed and the current range applied was 10, 25, 50, 75, 100 and 200 µA. The step time was kept constant at 10 seconds and the transition time (t) was measured in different current range. It was observed as the current range is increased from 10 to 200 µA, the potential value decreases in an increasing trend. At the beginning potential value decreases upto 0.5 seconds, and then almost remains constant at a particular current range. At lower and higher current value, the plots shows irregular behaviour.

Table 4: Chronopotentiometric data for area of Cu_2O in DMSO+ SO_2 at various current ranges

Current ($10^{-6}A$)	Time (s)	Area (Vs)	Area ($Vs^{1/2}$)	Slope 10^{-3} V/s	Chi-square	Correl.
10	10	-1.56	-0.42	-5.89	0.01	-0.92
25	10	-3.14	-0.86	-9.72	0.21	-0.67
50	10	-4.77	-1.29	-24.59	0.37	-0.86
75	10	-6.22	-1.71	-23.32	1.18	-0.67
100	10	-7.24	-2.03	-21.18	1.88	-0.55
200	10	-9.96	-2.86	-24.18	4.59	-0.63

Table 4 shows the slope, chi-square and correlation value of Cu_2O in DMSO + SO_2 using $t^{-1/2}$ versus E plots. The slope value increases from -19.70 x10^{-3} $V/s^{1/2}$ at 10 µA to 75.80 x 10^{-3} $V/s^{1/2}$ at 50 µA. Later with the increase of current range from 75 µA to 200 µA slope value decreases from 60.83 x 10^{-3} $V/s^{1/2}$ to 17.98 x 10^{-3} $V/s^{1/2}$. The slope value is maximum at 50 µA. The chi-square decreases from 47.43 x 10^{-6} at 10 µA to 7.65 x 10^{-6} at 50 µA. It increases to 99.17 x 10^{-6} at 75 µA and then decreases to 28.89 at 200 µA. The correlation value varied from -0.997 to -0.734.
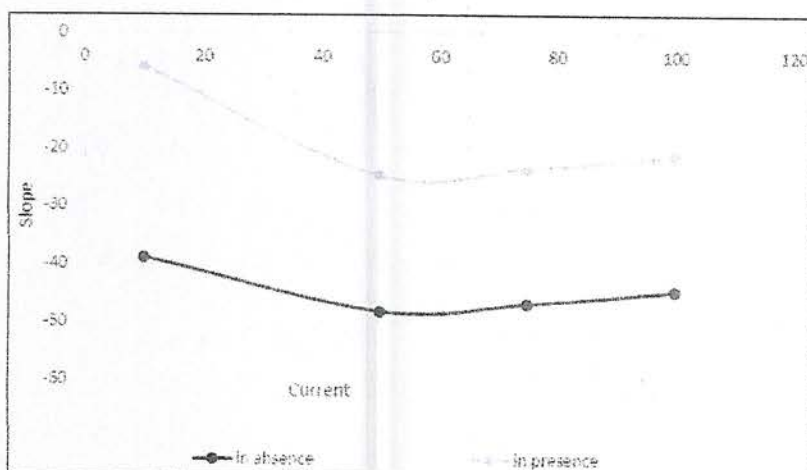
Fig 4: Plot of Slope Vs Current for Cu_2O in DMSO in absence of and in presence of SO_2

We found that after certain time period, the $it^{1/2}$ term becomes independent of any increase in current density. It was noted that the current density and the transition time becomes constant after certain current value. It can be represented by the equation:

$$it^{1/2} = constant$$

The area of the curve for t versus E and $t^{-1/2}$ versus E at different current range has been obtained using chronopotentiometry technique. The chronopotentiometry data has been shown in Table 4. The area of curve increased from -1.56 Vs at 10 μA to -9.96 Vs at 200 μA for t versus E plots at 10 seconds. Similarly in the case of $t^{-1/2}$ versus E plot, the area of the curve increased from -0.42 $Vs^{1/2}$ at 10 μA to -2.86 $Vs^{1/2}$ at 200 μA at 10 seconds. The area of the curve above 200 μA shows irregular behaviour.

The slope were obtained for Cu_2O in DMSO + SO_2 at different current range. Table 4 shows the slope, chi-square and correlation value using E versus t plots. The slope value increased from -5.89 x 10^{-3} V/s at 10 μA to -24.59 x 10^{-3} V/s at 50 μA. The slope value decreased from 24.59 x 10^{-3} V/s at 50 μA to -20.18 x 10^{-3} V/s at 200 μA at 10 seconds. The slope value was maximum at 50 μA. The chi-square and correlation value were calculated using the t versus E plots. The chi-square first decreased from 10.71 x 10^{-3} at 10 μA to 0.21 x 10^{-3} at 25 μA. It further increased from 0.365 x 10^{-3} μA at 50 μA to 4.59 at 200 μA. The correlation value varied from -0.926 to -0.553.

Conclusion

In conclusion, chronopotentiometric studies of Cu_2O in various solvent systems provided valuable insights into its electrochemical behavior. In water, the potential decreases with increasing current density, indicating solid-state diffusion control. The plots become ill-defined at very high or low current ranges. In the water-sulphite system, similar trends are observed, with the potential stabilizing at certain current densities. The area under the curves increases gradually with current density, but the magnitude is lower at pH=1.5. In DMSO, the potential also decreases with increasing current density, and the plots become ill-defined at high currents. The area increases with current, reaching a maximum at 50 μA and then decreasing.

When SO_2 is added to DMSO, similar trends are observed, with the potential decreasing with increasing current density. The area under the curves increases with current density, but the magnitude is slightly higher for Cu_2O Overall, these studies provide important insights into the

behavior of Cu_2O in different solvent systems, which can be valuable for various applications. Further studies could explore the practical implications of these findings in electrochemical applications.

References
1. San Jose MT, Espinosa AM, Tascon ML, Vazquez MD, Batanera PS. Electrochim Acta. 1991;36(7):1209.
2. Raisoni PR, Dixit SG. J Chem. Tech Biotechnol. 1988;42:167.
3. Li Y, Kawashima N, Li J, Chandra AP, Gerson AR. Adv. Colloid Interf. Sci. 2013;197-198:1-32.
4. Parker AJ, Muir DM. Hydrometallurgy. 1980;6:239.
5. Vaisman II, Berkowitz ML. J Am Chem. Soc. 1992;114:7889.
6. Kanungo SB, Das RP. Hydrometallurgy. 1988;20:135.
7. Linkson PB. Aust. Chem. Eng. 1980;8:160.
8. Linkson PB, Nobbs DM. J Chem. Eng., 1981, 107.
9. Linkson PB, Nobbs DM. Inst. Min Metall. UK, 1981, 49.
10. Youzbashi AA, Dixit SG. Metall Trans B. 1993;24B:563.
11. Bertini M, Marezio P, Duby PF. Novel leaching applications of the SO_2/O_2 system, XXI International Mineral Processing Congress, 2000 Jul, Rome (Italy).
12. Miller JD, Wan RY. Reaction kinetics for the leaching of $MnO2$ by sulfur dioxide. Hydrometallurgy; c1983 May.
13. Gill JB, Goodall DC, Jeffreys B. New leaching agents for oxides. Hydrometallurgy; c1984 Dec.
14. Perrin DD, Armarego WLF. Purification of Laboratory Chemicals. New York: Pergamon Press, 1988, 65.
15. Martin D, Hauthal HG. Dimethylsulfoxide. New York: John Wiley & Sons, 1975, 41.
16. Delahay P. New Instrumental Methods in Electrochemistry. New York: Interscience; 1954;72:115-179.
17. Bond AM. Modern Polarographic Methods in Analytical Chemistry. New York: Marcel Dekker; c1980, 169.
18. Chouaib F, Cauquil O, Lamache M. Electrochim Acta. 1981;26:325.
19. Eguren M, Tascon ML, Vazques MD, Batanero PS. Electrochim Acta. 1988;33:1009.
20. Batanero PS. Vazques MD. Quimica Analitica. 1989;8:393.
21. Vogel AI. A Textbook of Quantitative Inorganic Analysis. ELBS & Longman; c1975. p. 370-441.
22. Sand HJS. Phil Mag. 1901;1:45.
23. Gerlach J, Kuzeci E. Hydrometallurgy. 1983;11:345.
24. Price DC. Met Trans B. 1981;231:1213.
25. Choi WK, Torma AE, Ohline RW, Ghali E. Hydrometallurgy. 1993;33:137.