

MONOVALENT COPPER IN AQUEOUS ACIDIC-CHLORIDE ELECTROLYTE: - A CYCLIC VOLTAMMETRIC STUDY

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ABSTRACT

The cyclic voltammetric technique has been employed on a copper electrode in a solution of copper - I/acidic-chloride to investigate the basic aspects of cuprous ion reduction with the particular aim of understanding the role of and arriving at the optimum composition of the bath constituents. It allowed the study of the effects of sodium chloride and hydrochloric acid concentration on copper - I/acidic-chloride system particularly for arriving at the optimum electrolyte composition.

Key words: Cyclic voltammetry, monovalent copper, acidic chloride system.

INTRODUCTION

The electrochemical refining and winning of copper from a cuprous ion complexing electrolyte is attractive, because the involvement of a single electron in the process offers saving in energy or time compared with the conventional two electron process. The advantages of cuprous electrolytes over the conventional cupric electrolytes for electrodeposition of copper have been brought out along with the appropriate process parameters which were arrived at by a study of the electrolysis conditions [1-5]. It has been shown that the cyclic voltammetry technique can be used as a expedient tool to study the steps involved and also to arrive at the optimum electrolyte composition for electrowinning copper from a copper-I-acetonitrile system [6]. It is a more elegant and simple technique for this purpose than the conventional coulometric method. There are two other possible systems viz., copper-I-acidic chloride and copper-I-ammonia electrolytes capable of operating with stable monovalent copper ions. The results obtained with the acidic chloride medium on a cyclic voltammetric study are reported in this communication. The effects of different concentrations of sodium chloride and hydrochloric acid in stabilising the cuprous ion and the sweep rate on the oxidation and reduction of copper ions are covered in this study.

EXPERIMENTAL

A conventional all glass electrolysis cell having a three electrode assembly with provision for inlet and outlet for deaerating the solution with N_2 gas is used. A three electrode

system consisting of (i) a teflon covered copper rod (purity 99.9%) with an exposed circular cross section of 6 mm dia (area 0.283 cm^2) (ii) a platinized platinum counter electrode and (iii) a saturated calomel electrode (SCE) as a reference electrode is employed. Before conducting the experiments, the exposed circular cross section of the copper rod is polished with emery papers down to 4/0 grade, degreased with acetone and finally washed twice with distilled water. All the solutions are prepared from Analar grade reagents and twice-distilled water. A solution of 5 M NaCl in 1 M HCl is employed for studying the copper I-acidic chloride system whereas a solution containing 1 M H_2SO_4 is used for studying the behaviour of conventional bath.

A Wenking (Model LB75M) potentiostat coupled with a Wenking scan generator (Model VSG 72) is used for controlling the potential. Current-potential curves are measured under a potential sweep. The cyclic voltammograms are recorded on an (Digigraphic 2000 series) X-Y recorder. The range of potential covered is -0.6 to $+0.6 \text{ V vs. SCE}$. All the potentials are expressed vs. SCE, and the measurements are made in deaerated solutions at $32 \pm 1^\circ \text{C}$

RESULTS AND DISCUSSION

Comparative cyclic voltammetric experiments for the systems copper/aqueous sulphuric acid and copper/acidic-chloride on copper electrode have been carried out. The effects of scan rate and concentrations of hydrochloric acid and sodium chloride in the electrolyte are studied. These experiments are found to yield reproducible and well defined sharp current-potential curves.

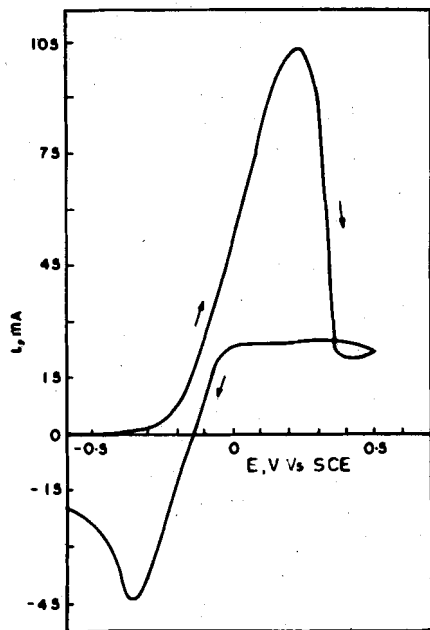


Fig. 1: Cyclic voltammogram obtained for a solution containing 5 M NaCl and 1 M HCl on copper electrode. Sweep rate 100 mV S^{-1} . Range of potential sweep -0.6 to 0.5 V

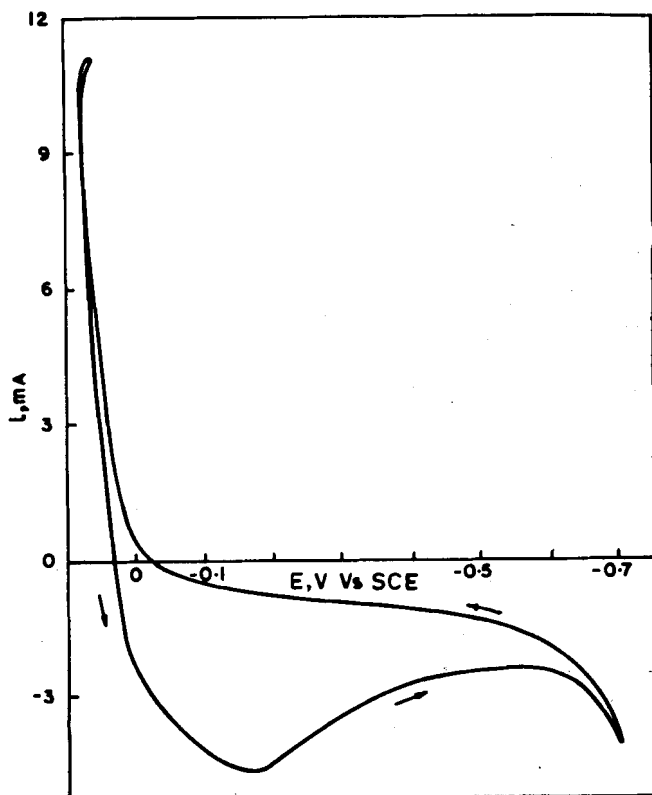


Fig. 2: Cyclic voltammogram obtained for a solution containing 1 M H_2SO_4 on copper electrode. Sweep rate 100 mV S^{-1} . Range of potential sweep -0.7 V to 0.1 V

Fig. 1 represents a typical cyclic voltammogram (CV) obtained for the system copper/acidic-chloride containing 5 M NaCl in 1 M HCl. The CV of the conventional sulphate electrolyte system containing 1 M H_2SO_4 under the identical conditions is given in Fig. 2. It should be noted that the two CV curves are recorded in different sensitivity scale. The amount of charge calculated under the cathodic peak obtained in the presence of chloride is found to be more, when compared with the conventional system under identical conditions.

The effect of sweep rate on the anodic and cathodic peak heights of the cyclic voltammograms on copper electrode in acidic-chloride medium obtained for a solution having 5 M NaCl in 1 M HCl is given in Fig. 3.

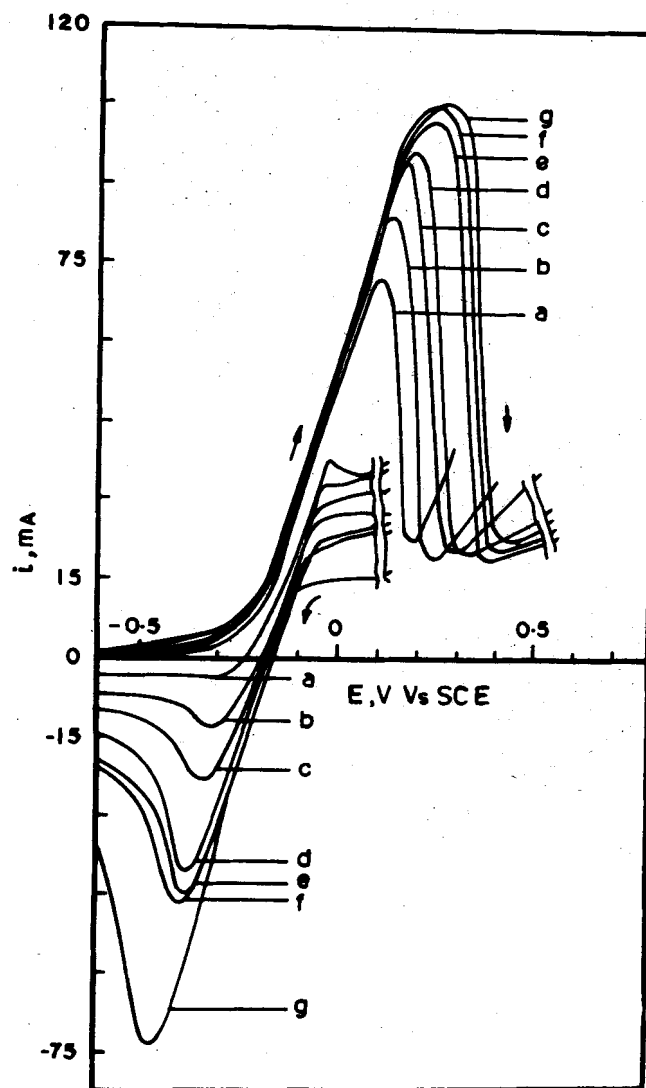


Fig. 3: Effect of sweep rate on CVs on copper electrode of a solution containing 5 M NaCl in 1 M HCl. Range of potential sweep -0.6 to 0.5 V (a) 20; (b) 40; (c) 60; (d) 80; (e) 100; (f) 120 and (g) 140 mV S^{-1}

The corresponding values of cathodic peak potential $E_p(c)$, peak current $i_p(c)$ and current function viz. $i_p(c)/V^{1/2}$ and anodic peak potential $E_p(a)$, peak current $i_p(a)$ and current function viz., $i_p(a)/V^{1/2}$ are given in Table I.

Table I: Cathodic peak potential, $E_p(c)$: peak current, $i_p(c)$ and current functions $\frac{i_p(c)}{V^{1/2}}$ and anodic peak current $i_p(a)$ and the ratio of $\frac{i_p(a)}{i_p(c)}$ values of copper
Electrode obtained for a solution containign 5 M NaCl in 1 M HCl under different sweep rates

Sweep rate V, mV S ⁻¹	Cathodic peak			Anodic peak		
	$-E_p(c)$ (V)	$i_p(c)$ (mA)	$\frac{i_p(c)}{V^{1/2}}$	$E_p(a)$ (V)	$i_p(a)$ (mA)	$\frac{i_p(a)}{i_p(c)}$
10	0.29	0.07	53	...
20	0.30	0.10	64	...
40	0.31	45	7.0	0.13	75	1.66
60	0.32	53	6.9	0.17	86	1.62
80	0.34	60	6.7	0.18	94	1.56
100	0.355	68	6.8	0.23	101	1.48
120	0.38	70	6.4	0.25	105	1.50

The peak potential value of the cathodic peak, $E_p(c)$ is found to shift cathodically, while the anodic peak potential $E_p(a)$ is shifted anodically with increasing sweep rate for a fixed concentration. The data obtained from the difference between $E_p(a) - E_p(c)$ is > 350 mV, which is found to increase with increasing sweep rate. The observation on E_p shift with sweep rate together with the data on the large peak potential difference between $E_p(a) - E_p(c)$ suggest that the anodic and cathodic processes are irreversible under the CV conditions used.

The value of ' αna ' obtained from the slope of the linear plots (viz., $dE_p(c)/d \log V = 30/\alpha na$ mV) resulting from the plot of the cathodic peak potential against the log of sweep rate (see Fig. 4) and equating the shift in the peak potential for a 10-fold increase of V with $30/\alpha na$ mV, is found to be *one* in the case of conventional copper/aqueous sulphuric acid system (where ' α ' is the transfer coefficient and ' na ' is the number of electrons involved in the activation step). This shows that the numbers of electrons involved in the conventional bath is *two*. The value of αna obtained is calculated to be 0.46 in the case of copper/acidic-chloride system indicating the involvement of *one* electron in cuprous ion—excess chloride electrolyte system (assuming $\alpha = 0.5$)

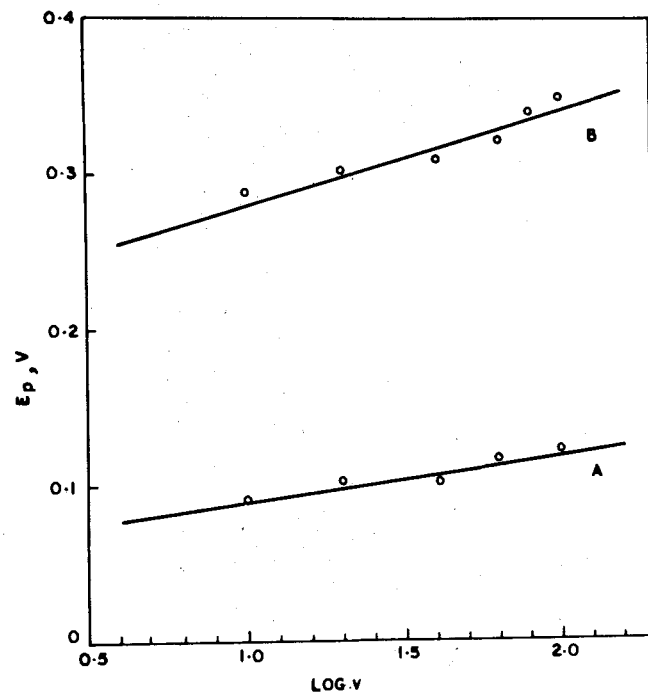


Fig. 4: Plot of peak potential, E_p against log of sweep rate of the cathodic peak obtained

(A) With the conventional bath and
(B) With the NaCl-HCl bath on copper electrode

It should also be noted (see Fig. 3) that the ratio of $i_p(a)/i_p(c)$ obtained for different sweep rate conditions increased from unity with decreasing sweep rate. This suggests that the species generated near the electrode may diffuse away from the electrode surface because of the time effect.

The effect of sodium chloride concentration on the anodic peak height of CVs on copper electrode is shown in Fig 5. The concentration of sodium chloride in 1 M hydrochloric acid varies from 1 M to 5 M. The peak potential value of the anodic peak is found to shift anodically with increasing sodium chloride concentration for a fixed sweep rate and acid concentration. The anodic peak current and the amount of charge calculated under the peak are found to increase with NaCl concentration. It can also be seen that, the rate of increase of amount of charge at higher NaCl concentration viz, above 4 M NaCl is not appreciable. This indicates the optimum sodium-chloride concentration to be about 5 M NaCl.

The effect of hydrochloric acid concentration on the anodic peak height of CVs on copper electrode is given in fig. 6. The range of acid concentration employed varies from 0.1 M to 2.0 M in a solution containing 5 M sodium chloride. The amount of charge calculated under anodic peak is found to increase with increase in HCl concentration and becomes

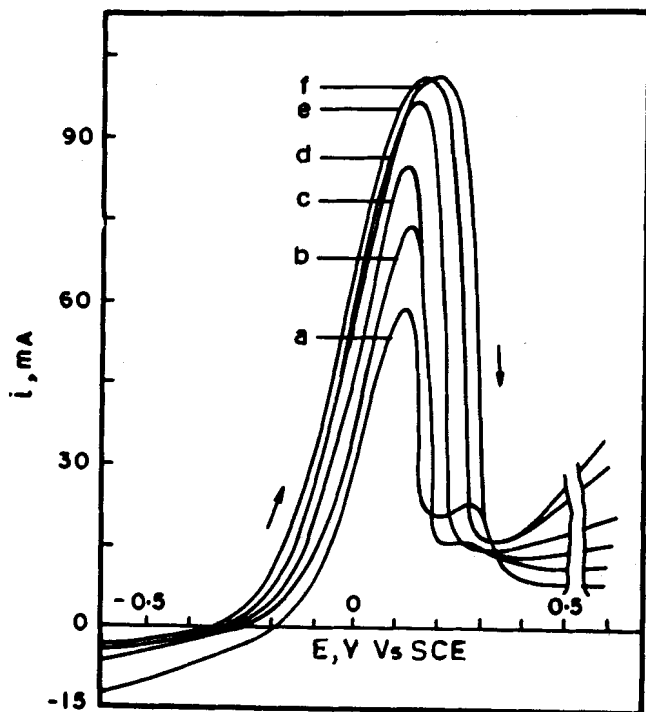


Fig. 5: Effect of sodium chloride concentration on CVs on copper electrode for a solution containing (a) 0; (b) 1; (c) 2; (d) 3; (e) 4; and (f) 5 M NaCl in 1 M HCl

Sweep rate 100 Mv S^{-1}
Range on potential sweep $-0.6 \text{ V to } 0.5 \text{ V}$.

constant beyond an acid concentration of 1 M. This indicates that the acid concentration needed is about 1 M HCl.

The above observations lead to the conclusion that cyclic voltammetry can form the basis for arriving at the optimum electrolyte composition viz. sodium chloride and hydrochloric acid concentration required for copper/acidic-chloride system.

The plot of i_p vs. $V^{1/2}$ shown in Fig 7 for the cathodic process passes through origin and the current function values viz. $i_p(c)/V^{1/2}$ (see Table I) of the cathodic peak are seen to be nearly constant and independent of sweep rate for a fixed concentration, confirming that the process may be diffusion controlled.

The results of these investigations confirm that the cyclic voltammetric technique is an useful tool for understanding the steps of reduction and arriving at the optimum electrolyte composition in the copper/aqueous acidic-chloride system. The method is also more scientific and less time consuming. This technique may also be useful for understanding the other processing parameters temperature, effects of additives etc.

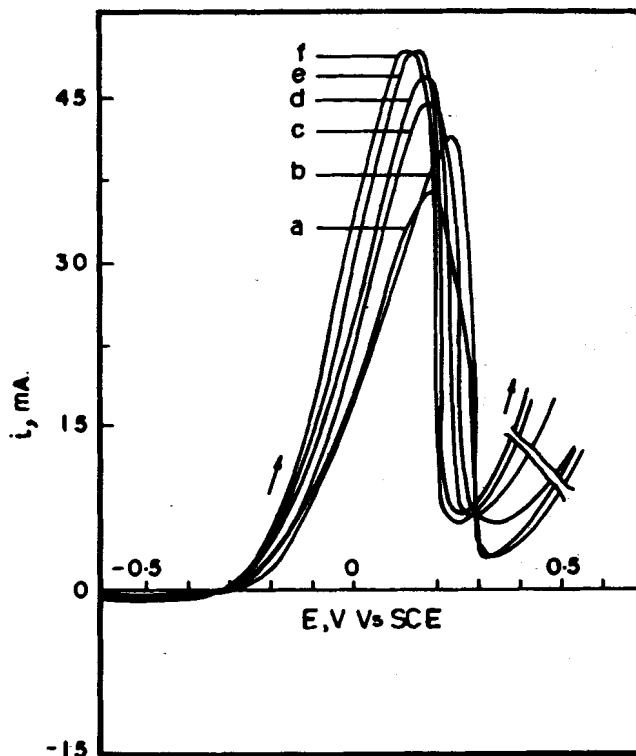


Fig. 6: Effect of hydrochloric acid concentration on CVs on copper electrode for a solution containing (a) 0; (b) 0.1; (c) 0.5; (d) 1.0; (e) 1.5 and (f) 2 M HCl in 5 M NaCl

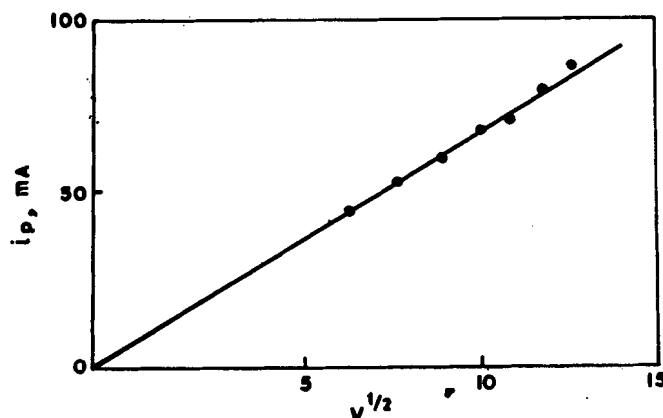


Fig. 7: Plot of peak current, i_p vs. $V^{1/2}$ of copper electrode for a solution containing 5 M NaCl in 1 M HCl.

ACKNOWLEDGEMENT

The authors wish to express their thanks to Shri R. Srinivasan, Head, Electrohydrometallurgy Division, CECRI, Karaikudi for his encouragement and useful discussions.

REFERENCES

1. FA Schimmel, *J Phys and Colloid. Chem.* **54** (1950) 841 and **55** (1951) 2943.
2. SD Gokhale, *J. Sci. Ind. Res. (India)* **108** (1951) 316
3. DM Muir, AJ Parker, JH Sharp and WE Waghorne, *Hydro-metallurgy*, **1** (1975) 155.
4. SD MacLead, DM Muir and AJ Parker, *Aust. J. Chem* **30** (1977) 1423
5. AP Brown, RO Loutfy, GM Cook and Neng Ping Yao, *J Metals* **33** 7, (1981) 49.
6. A Varadharaj, RM Meyyappan and R Srinivasan—Paper presented in "Third International Symposium on Advances in Electrochemical Science and Technology", Dec. (1984) SAEST, Madras.