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Electroplating of Horizontal Steel Cylinders in Unstirred Copper Sulphate Solutions

ABDEL-MONEM M. AHMED[1,*] and MONA DARWEESH[2]

[1]Department of Chemistry, Faculty of Science, Alexandria University, Ibrahimia, and P.O. Box 426, Alexandria 21321, Egypt
[2]Department of Chemistry, Faculty of Engineering, Tanta University, Tanta, Egypt

*Corresponding author: E-mail: profabdelmonem@gmail.com

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Limiting currents were measured for the electroplating of horizontal steel cylinders in unstirred $CuSO_4$ solutions. Variables studied were $CuSO_4$ concentration, cylinder diameter and temperature. The limiting current was found to increase with $CuSO_4$ concentration over the concentration range from 0.01 to 0.2 M. Cylinder diameter was found to have no effect on the limiting current within the range studied (0.8-3.8 cm diameter). The effect of temperature on the limiting current was found to obey Arrhenius equation. The activation energy for electrodeposition was found to be 15.12-32.5 kJ mol^{-1}. Results were explained in the light of the theory of electrochemical mass transfer.

Keywords: Electroplating, Cylinders, Steel, Mass transfer.

INTRODUCTION

Electroplating has evolved from an art to an exact science. This development is seen as responsible for the increasing number and' widening types of applications of this branch of practical science and engineering. Some of the technological areas in which means and methods of electroplating constitute an essential component are all aspects of electronics: macro and micro, optics, opto-electronics and sensors of most types, to name only a few. In addition a number of key industries such as the automobile industry[1] (that uses for example chrome plating to enhance the corrosion resistance of metal parts) adopt the methods even where other methods, such as evaporation, sputtering, chemical vapor deposition (CVD) and the like are an option.

That is so for reasons of economy and convenience. By way of illustration it should be noted that the modern electroplating equips the practitioner with the ability to pre-design the properties of surfaces and in the case of electroforming those of the whole part. Furthermore, the ability to deposit very thin multilayer's (less than a millionth of a cm) *via* electroplating represents yet a new avenue of producing new materials.

Many metals are deposit in a very rough or powdery form[2], when electroplating is carried out at the limiting current density. The possibility of preventing powder formation at the limiting current by means of a suitable additive of great interest and represent a significant activity in electroplating[3].

Copper electroplating is one of the oldest protective and decorative metallic coating for steel and other basis metals.

Therefore, intensive studies were carried out to obtain copper electroplates. One of the most important baths used for electroplating copper was cyanide bath[4]. But due to the environmental consideration, cyanide baths formulation were replaced non-cyanide formulations as sulphate[5-9] chloride[10], pyrophosphate[11]. The aim of this work is to investigate an effect of dimensional of copper cylinders on the rate of electroplating.

EXPERIMENTAL

Fig. 1 shows the cell and electrical circuit used. The cell was a cylindrical glass container of 11 cm diam. and 15 cm height.

The anode of the cell consisted of a cylindrical copper of 10 cm diameter and 15 cm height placed in outer compartment of the cell and acted in the meantime as a reference electrode by virtue of its high surface area compared to that of the cathode. The cathode were horizontal cylinder made of electrolytic pure steel, each cylinder had a length of 2.5 cm cylinder diameter was varied between 0.8 and 3.8 cm. The electrical circuit consisted of a 6 volt d.c. power, supply, variable resistance and a multi-range ammeter connected in series with the cell.

A high impedance voltmeter was connected with the cell. Five concentrations of $CuSO_4$ were used 0.01, 0.05, 0.1, 0.15 and 0.2 M, all was prepared from A.R. grade $CuSO_4$.

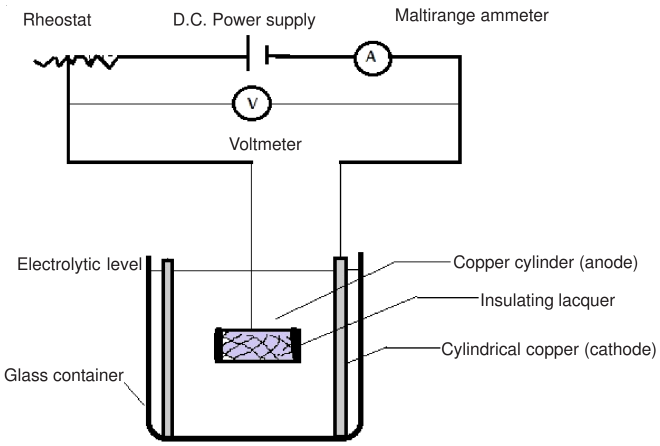

Fig. 1. Cell and electrical circuit

Polarization curves, from which limiting currents were determined, were plotted by increasing the applied current stepwise and measuring the corresponding steady state potential, 1 min were allowed to reach the steady state potential.

Before each run, the ends of the cylinder cathode were insulated by polystyrene lacquer. The surface of the cylinder was degreased by trichloroethylene, polished with fine emery paper and finally, rinsed in distilled water. The cathode was positioned halfway between the top and bottom of the electrolyte. An insulated copper wire (2 mm diameter) brazed to the cylinder anode served to hold the anode in position and to feed it with current. Temperature was regulated by placing the cell in a thermostat.

RESULTS AND DISCUSSION

Fig. 2 shows a set of typical current potential curves obtained at different $CuSO_4$ concentrations. Fig. 2 shows that the limiting current increases with $CuSO_4$ concentration within the range studied (0.01 to 0.2 M). This is in agreement with the finding of previous workers[11-14] within the same range of concentration using other cathode geometries.

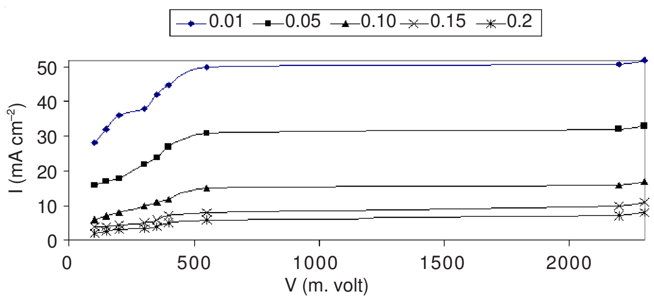

Fig. 2. Typical current pot. curves obtained for different $CuSO_4$ concentration

The effect of $CuSO_4$ concentration on the value of the limiting current can be explained on the basis transfer equation[14].

$$I_l = \frac{ZFD}{\delta C_{Cu^{2+}}} \qquad (1)$$

Table-1 and Fig. 3 show the effect of $CuSO_4$ on the rate of electroplating at 25 ºC using steel cathode. It is obvious that the rate of electroplating increases by increasing $CuSO_4$ concentration.

TABLE-1
EFFECT OF $CuSO_4$ ON I_l (DIAMETER: 3.8, AT 25 ºC)

Conc. of $CuSO_4$	0.01	0.05	0.10	0.15	0.20
I_l (mA cm^{-2})	8	12	16	31	51

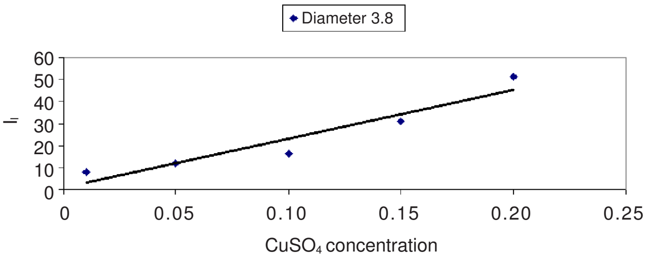

Fig. 3. Effect of $CuSO_4$ concentration on the limiting current density at 25 ºC

Increasing $CuSO_4$ content in the bath decreases the cathodic polarization and consequently increases the limiting current plateau.

These results are expected and could be attributes to be due to an increase in the relative abundance of uncomplexed Cu^{2+} ion in solution.

Fig. 4 shows the effect of cylinder diameter on the value of the limiting current, cylinder diameter has almost no effect on the limiting current within the range studied here. According to the boundary layer theory[14], when the natural convection flow create by density difference between the electrode surface and bulk solution is turbulent, electrode dimension (height or diameter) does not affect the rate of mass transfer or the limiting current. Therefore, it is concluded that the flow in the present case is turbulent. Suchutz[15] who studied natural convection mass transfer at horizontal cylinders presented a useful criterion for testing the nature of flow (laminar or turbulent) at horizontal cylinders. Suchutz[15] found that for turbulent flow the product Schmidt number should be higher than 10^9, where Grashoff number is the Grashoff number and Schmidt number is the Shmidt number. Using the data of Fouad *et al.*[14] for the physical properties of the solutions used in the present work, Schmidt number and Grashoff number were calculated. The product Schmidt number, Grashoff number. for all cylinder diameters studied here was found to be higher than 10^9 *i.e.*, the flow is turbulent. This is consistent with the fact that cylinder diameter has no effect on the limiting current value.

Effect of temperature on the rate of electroplating: It was observed that, the rate of electroplating of steel increases with the rise in temperatures from 25 to 40 ºC.

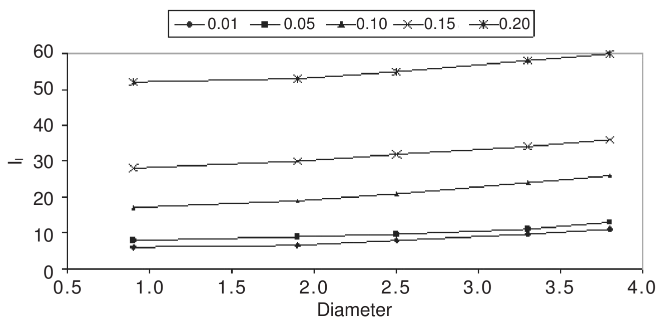

Fig. 4. Effect of cylinder diameter on the limiting current at 25 ºC

TABLE-2
RELATION BETWEEN CYLINDER DIAMETER AND LIMITING CURRENT DENSITY AT DIFFERENT $CuSO_4$ CONCENTRATION

Diameter	Concentration of $CuSO_4$				
	0.01	0.05	0.10	0.15	0.20
	I_l				
0.9	6	8	17	28	52
1.9	6.5	9	19	30	53
2.5	8	9.5	21	32	55
3.3	9.5	11	24	34	58
3.8	11	13	26	36	60

From integrated form of Arrhenius equation:

$$\ln I = -\frac{E_a}{RT} + \ln A \tag{2}$$

where I is the limiting current, E_a is the activation energy, R is the universal gas constant (8.31 kJ mol^{-1}), T is the absolute temperature and A is frequency factor.

Table-3 give effects of temperatures on the limiting current at different diameter of the values of activation energy were calculated from slope of Arrhenius plots of log I and 1/T. where I is the limiting current and T is absolute temperature. The values of E_a are giving in Table-4.

TABLE-3
VALUES OF LIMITING CURRENT AT DIFFERENT TEMPERATURES AND CONCENTRATION OF $CuSO_4$ (DIAMETER 2.5 cm)

Conc. (mol L^{-1})	T (ºC)			
	25	30	35	40
	I_l (mA cm^{-2})			
0.01	50	57	63	70
0.05	60	70	80	90
0.10	80	90	105	120
0.15	153	170	190	210
0.20	250	300	320	360

TABLE-4
VALUES OF E_a AT DIFFERENT CONCENTRATION OF $CuSO_4$

Conc. (mol L^{-1})	0.01	0.05	0.10	0.15	0.20
E_a (kJ mol^{-1})	17.86	18.80	26.53	33.5	39.5

The activation energy for electroplating of copper in $CuSO_4$ was found to be range from 17.8 to 34.5 kJ mol^{-1}.

This value is in agreement with the value reported by Abdel Rahman[16].

F	:	Faraday's constant = 96485 A s mol^{-1}
D	:	Diffusivity of copper ions, cm^2/s
Δ	:	Diffusion layer thickness, cm
$C_{Cu^{++}}$	:	Copper ion concentration
d	:	Cylinder diameter, cm
Gr	:	Grashoff number, $Gr = g\alpha(C_o - C_b)l^3/\nu^2$
Sc	:	Schmidt number, $Sc = \nu/D$
R	:	Universal gas constant = 8.314 J mol^{-1} K^{-1}
T	:	Absolute temperature, K
E_a	:	Activation energy, kJ mol^{-1}
A	:	Arrhenius constant

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