Technical Article

The Effect of Conductivity On Current Distribution in the Hull Cell

By M. Ghorbani, Sh.A. Sharifabadi & M.N. Zahed

In this study, current distribution data were obtained from a controlled variation of electrolyte conductivity, using a 267 mL Hull cell. Current distribution measurement was made using a sectioned electrode. The current density for each strip was calculated by measuring the weight gain of the strips during plating and applying Faraday's Law. Finally, the Hull cell formula was derived by plotting the regression line for current density versus average logarithmic distance along the segmented Hull cell panel.

Three systems were studied: acid sulfate copper, all-chloride nickel, and all-chloride zinc. We found that the solution conductivity affects the current distribution. As the conductivity is increased, the slope of the current distribution regression line increased, and consequently, the current distribution became non-uniform.

Current distribution is a major factor in successful electroplating. The variations of current density on the cathode surface can be measured with a number of simple geometric plating cells. The current distribution is defined as a distance ratio with a Haring cell.¹ The Tena cell is used





Fig. 2—Sample of a current distribution curve produced from the data in Table 2.

to calculate current density on optional points of a cathode.² The familiar Hull cell is commonly used for current distribution studies because of its simple experimental setup.³ Hull derived a formula for current density along the cathode with a general expression as follows:

C.D. = $i(K_1 - K_2 \log L)$ (1)

Where C.D. is the initial current density at the location along the panel, point L, i is the total cell current and K₁ and K₂ are constants which depend on the nature of the electrolyte. In this study, a 267 mL Hull cell was used to investigate the effect of electrolyte conductivity on the current distribution equation (Hull cell formula). To determine current distribution, a cathode panel, consisting of a number of segments placed in series, was used. The current distribution was calcu-

Table 1 Average Logarithmic Distance For Each Strip						
Strip	L	Average log L				
1	0.1 - 1.0	-0.323				
2	1.0 - 2.0	0.167				
3	2.0 - 3.0	0.395				
4	3.0 - 4.0	0.543				
5	4.0 - 5.0	0.652				
6	5.0 - 6.0	0.740				
7	6.0 - 7.0	0.812				
8	7.0 - 8.0	0.875				
9	8.0 - 9.0	0.929				
10	9.0 - 10.0	0.978				

lated from the weight gain of the series of cathode segments and Faraday's law.

Three electroplating solutions were studied, including acid sulfate copper, all-chloride nickel, and all-chloride zinc. The conductivity was characterized as a function of bath composition. One bath constituent was varied in each bath to obtain a range of conductivities. The all-chloride nickel solution consisted of varying amounts of nickel chloride plus 27 g/L boric acid as a buffer. In the case of the zinc chloride solution, the zinc chloride was held constant at 18 g/L, while the concentration of ammonium chloride was varied. The acid copper solution contained a constant 200 g/L of copper sulfate, while the sulfuric acid content was varied.

Experimental Procedure

In the Hull cell test, a mild steel plate was divided into ten strips or segments, each 10 mm wide and 50 mm high, yielding a working area of 500 mm² (5.0 cm²; 0.78 in²). The segmented substrates were previously degreased and pickled. The areas of the plates that were not to be used were isolated with lacquer. The weight of each strip (W_1) was determined, then the strips were placed and fixed in a row within the cell, using clamps as illustrated in Fig. 1. Here, the edges of the complete "panel" are represented by "a" and "b," and any given position along that panel is at point "L."

The weight gain was determined for each strip in each plating run, and a new solution was prepared for each Hull cell test. All tests were carried out twice, and the average weight gain of each strip pair was used in the calculations.

The calculation procedure to plot the current density J vs. log (L) curve was as follows:

By applying Faraday's Law, the average current (i) for electroplating each strip was obtained, by

$$i = \frac{(W_2 - W_1) nF}{Mt}$$
(2)

Using the known current, i and the area of each strip, S, the effective current density for the coating of each strip making up the complete cathode was calculated,

$$\mathbf{J}_{eff} = \frac{i}{S} \tag{3}$$

Actual current density was worked out, considering cathode efficiency (CE), where

$$CE = \frac{i_{eff}}{i_{app}}$$
(4)

where i_{eff} is the total effective current for coating all of the strips, and i_{app} is the total applied current (1.0 A). I_{eff} was calculated by applying Faraday's Law based on the total weight gain of the strips,

$$\mathbf{I}_{\text{eff}} = \frac{\left(\sum W_2 - \sum W_1\right) nF}{Mt}$$
(5)

Next, assuming CE to be constant for all strips, the actual current density J was obtained by dividing the I_{eff} of each strip by CE.

$$=\frac{J_{eff}}{CE}$$
(6)

In order to plot actual current density versus the logarithm of panel position (J vs. log L), the average log L for each strip must be calculated. Since log L is a continuous function along the entire Hull cell panel (i.e., between edges a and b, the average log L will be

$$A = \frac{1}{b-a} \int_{a}^{b} \log L dL = \frac{0.4343}{b-a} \int_{a}^{b} \ln L dL = \frac{0.4343}{b-a} [b \ln b - b - a \ln a + a]$$
(7)

The average log L values for each cathodic segment are shown in Table 1. These values were constant for all experiments.

Finally, after plotting the regression line of the current density of each strip versus the average log L, the equation of resulting linear curve was determined (Hull cell formula).

Results & Discussion

J

The all-chloride nickel solution was first tested. Conventional nickel plating is normally based on a form of the Watts nickel bath, which contains nickel sulfate, nickel chloride and boric acid. For better control of the solution conductivity, however, an all-chloride nickel was used here. A typical data sample and the resultant current distribution curve are shown in Table 2 and Fig. 2, respectively. Table 3 presents the derived equations for the five levels of nickel chloride content, along with the corresponding measured

J

27

1.1

6.95

8.94

conductivities. From this table, the slope of the current distribution curve was found to increase with conductivity (Fig. 3). This figure shows that the uniformity of current distribution decreased with increasing solution conductivity.

From the formulas in Table 3, we plotted current density versus conductivity for each of the segments in the composite Hull cell panel. The results are presented numerically in Table 4 and graphically in Fig. 4. It can be seen that increasing electrolyte conductivity increased the current density in the cathodic region nearer the anode. Therefore, more current is used in this region. Because the applied current in the cell is constant, less current is consumed in the cathodic region, furthest from the anode. Consequently,

the current distribution became less uniform. This figure also demonstrates that the maximum distance from the anode along the cathode that can be covered with nickel from this all-chloride solution is about 9 cm (3.5 in.). At L = 9, the current approaches zero given a sufficient level of conductivity.

The total current density is closely related to the polarization behavior of the electrode. Therefore, increasing the current density through an increase in conductivity can result in an increase in polarization at cathodic areas near the anode, and prevent further increases in current density.



3

ï

6.00

Table 2



NiCl., 6H,O, g/L

240

268

180 200 220

4.6

160

Fig. 4—Current density vs. conductivity for each of the Hull cell segments, as distance L.

4.04

Conductivity, µ S/cm

4.92

11.0

Table 3Current Distribution FormulasFor the All-chloride Nickel Solution

Solution No.		NiCl ₂ •6H ₂ O, g/L	Conductivity, µS/cm	Hull Cell Formula			
i = 1 A	1	180	0.866	$J = i(4.7244 - 4.7231 \log L)$			
t = 5 min	2	200	0.889	$J = i(4.7406 - 4.7513 \log L)$			
$T = 55^{\circ}C$	3	220	0.904	$J = i(4.8190 - 4.8872 \log L)$			
	4	240	0.912	$J = i(4.8428 - 4.9284 \log L)$			
	5	260	0.927	$J = i(4.9956 - 5.1934 \log L)$			

Table 5Test Results for the Acid Copper & Chloride-Zinc Solutions

Type of Solution	Variable	Conductivity,	Current			
	Component	µS/cm	Distribution Formula			
Acid Copper, 200 g/L CuSO ₄ i = 1 A t = 5 min	40 mL/L H ₂ SO ₄ 50 mL/L H ₂ SO ₄ 60 mL/L H ₂ SO ₄ 65 mL/L H ₂ SO ₄ 70 mL/L H ₂ SO ₄	1.132 1.018 1.034 1.041	$J = i(3.9398-3.3630 \log L)$ $J = i(4.2842-3.9600 \log L)$ $J = i(4.3431-4.0621 \log L)$ $J = i(4.5778-4.4690 \log L)$ $L = i(4.5778-4.4690 \log L)$			
$T = 20^{\circ}C$	70 mL/L H ₂ SO ₄	1.338	$J = i(4.0799-3.6059 \log L)$			
Chloride Zinc,	100 g/L NH ₄ Cl	0.937	$J = i(3.1845-2.0536 \log L)$			
18 g/L ZnCl ₂	110 g/L NH ₄ Cl	0.965	$J = i(3.2548-2.1753 \log L)$			
i = 1 A	120 g/L NH ₄ Cl	1.049	$J = i(3.6398-2.8421 \log L)$			
t = 5 min	130 g/L NH ₄ Cl	1.033	$J = i(3.5997-2.7732 \log L)$			
T = 24°C	140 g/L NH ₄ Cl	1.193	$J = i(3.7886-3.1008 \log L)$			

mine the current distribution. The uniformity of the current distribution decreases while the conductivity is increased, and more current will be consumed in the cathode region nearer the anode. In the lower-current-density regions furthest from the anode, calculations show that zero coverage is a possibility with the all-chloride nickel solution.

References

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Table 4										
Values of Current Densities for Different Conductivities with Distance L										
uS/cm	L = 1	L – 2	L = 3	L – 4	L = 5	L = 6	L – 7	L – 8	I. – 9	L – 10
0.886	4.7244	3.3028	2.4709	1.8808	1.4231	1.0491	0.7329	0.4590	0.2174	0.0013
0.889	4.7406	3.3103	2.4737	1.8800	1.4196	1.0434	0.7253	0.4497	0.2067	-0.0107
0.904	4.8190	3.3476	2.4872	1.8766	1.4030	1.0160	0.6888	0.4054	0.1554	-0.0682
0.912	4.8428	3.3592	2.4914	1.8756	1.3980	1.0078	0.6778	0.3920	0.1399	-0.0856
0.927	4.9928	3.4322	2.5177	1.8689	1.3656	0.9548	0.6067	0.3055	0.0398	-0.1978

To properly study current distribution, polarization should be considered in addition to electrical conductivity. Wagner,⁴ Kasper⁵ and Tobias⁶ defined the polarization parameter as the slope of cathodic polarization curve multiplied by the electrical conductivity. Current distribution can therefore be characterized by the polarization parameter. The higher the value of the polarization parameter, the more uniform the current distribution at predetermined geometric parameters.

In this study, the slope of the polarization curve was assumed to be constant along the cathodic segments, and only the effect of conductivity has been considered.

The same procedure was also applied to the other solutions. The results were in accord with what was found for the all-chloride nickel solution. The Hull cell formulas derived for each of these other solutions, the acid copper sulfate and the chloride zinc, are shown in Fig. 5.

Conclusion

At certain linear positions along a Hull cell cathode, the slope of the polarization curve and the specific electrical conductivity deter-