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Scale-up of the deposition-threshold voltage in the electrodeposition of bright chromium

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A single nonlinear equation is described whose root yields the minimum potential drop required for the onset of bright chromium deposition as a function of electrode size and separation.

Nomenclature

A_e	active electrode area (cm^2)
d	cathode/anode separation distance (cm)
I_m	current observed at V_m
i_m	current density observed at V_m (I_m/A_e); (A m^{-2})
r^2	linear correlation coefficient
S	slope of the current–potential curve in electrolysis
SSE	sum of the square errors between experimental and regression-predicted values of the dependant variable
V_m	deposition-threshold potential drop (or voltage) between the electrodes (V)

1. Introduction

The electrodeposition of chromium from aqueous acidic electrolytes is characterized by complex reaction mechanisms [1, 2]. On account of various parasitic cathode processes, the cathodic current efficiency is low; in typical cases [3] involving CrO_3/H_2SO_4 concentration ratios in the range of 50:1–300:1 the current efficiency varies between 21 and 27.5% at cathode current densities higher than 15.6 A dm^{-2}. One important parameter is the minimum potential drop between the anode and cathode required for the electrodeposition of chromium. If the potential drop (hence current density) is too low [4] chromic acid is reduced essentially only to Cr^{3+} ions at the cathode and *net* reduction to the zero-valency stage is negligible.

As the potential drop is gradually increased, the reduction of chromate ions to chromium metal according to the stoichiometric scheme

$$Cr_2O_7^{2-} + 14\,H^+ + 12\,e^- \rightarrow 2\,Cr + 7\,H_2O \quad (1)$$

becomes dominant and bright chromium deposits are obtained within a specific potential drop range. Upon an excessive increase in the potential deposition of chromium mat, on the cathodes is accompanied by H_2 evolution. Hence, the minimum potential drop V_m associated with the onset of bright chromium deposition, called the deposition-threshold voltage, is a characteristic cell parameter; its numerical value for a chromium deposition process scaled up from bench-scale laboratory data is an important design quantity. The purpose of this paper is to describe the estimation of V_m based on small-scale experimental observations, for a cell with arbitrary electrode size and separation distance (the electrodes are parallel vertical plates).

2. Experimental procedure

The laboratory-size cell is a facsimile of a 'standard' chromium plating process [5] where the electrolyte contains 250 g dm^{-3} CrO_3 (99.7% pure) and 2 g dm^{-3} H_2SO_4 in doubly deionized water. The Plexyglass cell (16 cm × 2.5 cm × 2.5 cm active volume) was equipped with fifteen vertical grooves in the wall, each groove 1 cm apart, to allow electrolysis to proceed at various electrode distances. The cathodes (active height: 1.46 cm, active width: 2.5 cm) were highly polished pure copper plates and the anodes were made of lead, coated prior to each experiment with a PbO_2 layer in a separate bath containing the same electrolyte, using a current density of

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20 A dm^{-2}. During the chromium deposition runs the potential was increased slowly and the current-potential variation was recorded by a conventional continuous strip chart recorder. Freshly prepared electrolyte was used in each experiment and the electrolyte temperature was kept at 24 ± 1° C during electrolysis. The potential drop was usually not increased beyond the bright deposit region (except in a small number of exploratory experiments). A typical set of experimental results is shown in Table 1.

3. Analysis and scale-up of the deposition-threshold voltage

Regression analysis of the data [6] indicates that V_m and d are related in a strongly linear fashion (the linear correlation coefficient $r^2 \approx 1.0$). Moreover, the quantity $[V_m - (I/S)]$ varied only between 2.879 V ($d = 2$ cm) and 2.973 V ($d =$ 12 cm) in a random manner; the associated linear correlation coefficient is only about 0.35, and the null hypothesis of no correlation between $[V_m - (I/S)]$ and d cannot be rejected at any statistically meaningful significance level. Using the entries in Table 1, it may be assumed that $[V_m - (I/S)] = 2.90$, independent of the electrode separation distance. Carrying out similar analyses of regression, one finds that d and S can also be correlated by various regression models (see Appendix I); the smallest $SSE = 5.9 \times 10^{-3}$, pertains to the regression model $d^S = 1.4774$ (d, cm; S, A V^{-1}). Similarly, i_m and V_m are correlated as

$$i_m = 270.21\, V_m^{1/2} \tag{2}$$

with $r^2 = 0.95$ and $SSE = 5.68 \times 10^{-4}$; for further details see Appendix II.

The estimation of V_m in a cell of arbitrary electrode size and separation distance is based on the generalization of the regression equations related to the laboratory cell. They can be written in general as,

$$V_m - \frac{I}{S} = k \tag{3a}$$

$$d^S = K$$

$$i_m = \beta\, V_m^{1/2}. \tag{3c}$$

Combining the three expressions, the single equation

$$V_m - \frac{\beta A_e \log d}{\log K}\, V_m^{1/2} = k \tag{4}$$

is obtained. Since, β, K and k are known experimentally, V_m may be estimated by solving the reduced variant of Equation 4:

$$F(V_m) = V_m - \frac{\beta A_e \log d}{\log K}\, V_m^{1/2} - k = \epsilon \approx 0 \tag{5}$$

to a predetermined small value ϵ close to zero. Any appropriate root-search technique (e.g. bisection) can be employed. If, for instance, V_m at $d = 5$ cm is to be estimated in the experimental cell, than taking $K = 1.4774, \beta = 0.027\,021$ and $k = 2.9$ (the units here are consistent for separation distance to be expressed in cm), the root of

$$F(V_m) = V_m - 0.4067\, V_m^{1/2} - 2.9 = 0 \tag{6}$$

is $V_m \approx 3.67$ V, which differs by about 2.6% from the experimental value. In this manner, at least a first estimate of V_m may be obtained in the design

Table 1. Summary of a typical set of experimental observations

Electrode separation distance, d (cm)	I_m (mA)	*Slope of the polarization curve, S* (A V^{-1})	V_m (V)	i_m (A dm^{-2})
2	175.2	0.547	3.20	4.80
4	178.8	0.337	3.45	4.90
6	196.9	0.246	3.70	5.39
8	200.0	0.164	3.95	5.48
10	202.9	0.162	4.20	5.56
12	206.2	0.140	4.45	5.65
14	209.1	0.120	4.70	5.73

Table A1. Comparison of models for correlating the variables d and S (see Table 1; d in cm, S in A V^{-1})

Model	*Least-square values of the regression parameters*	*SSE*	*Standard error of estimate*
$S = C(1/d)$	$C = 1.2056$	0.01228	0.0418
$S = a/d^b$	$a = 1.1168$ $b = 0.7893$	0.0157	0.1252
$d^S = K$	$K = 1.4774$	5.89×10^{-3}	0.029

of a plating cell in contrast to a purely trial and error determination.

Appendix I

Correlating the electrode separation distance and the slope of the polarization curve

The variables d and S can be correlated via several models with varying values of SSE, as illustrated in Table A1. Although a sophisticated model discrimination procedure, such as the maximum likelihood ratio technique [7], may not indicate a significant difference between the contending models, the choice of the third regression relationship whose SSE is the smallest, does stand to reason. However, the possible choice of the first regression cannot be excluded inasmuch as its form of Equation 6,

$$V_m - 0.4090 V_m^{1/2} - 2.9 = k \qquad \text{(A1)}$$

yields the root $V_m \approx 3.865$ V whose relative error is only about 0.7% larger than in the case of the third model considered. It follows that the equation

$$V_m - \frac{\beta A_e d}{C} V_m^{1/2} = k \qquad \text{(A2)}$$

is a statistically acceptable alternative to Equation 4.

Appendix II

In order to arrive at Equation 2, the general regression $i_m = p V_m^q$ is assumed with *a priori* unknown parameters p and q. The linearized form is then treated via a conventional least-square analysis. With the data given in Table 1 the numerical estimates $\log p = 2.4351$ and $q = 0.4941$ are obtained ($SSE = 5.58 \times 10^{-4}$; standard error of estimate ≈ 0.009). For the sake of simplification the null hypothesis $H_0: q = 0.5$ is tested [6]; since the computed $t-$ statistic, -0.1083, is appreciably larger than the 5% level ($t = -1.943$) and the 1% level ($t = -3.143$) critical values, the null hypothesis cannot be rejected and $q = 0.5$ is taken in lieu of 0.4941. The adjusted value of $\log p = 2.4317$ yields $p = 270.21$ and Equation 2 is obtained with $SSE = 5.68 \times 10^{-4}$ and an associated $r^2 = 0.954$.

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