

Predicting the coverage ratio of copper electrodeposits obtained on mesh cathodes

L. Cifuentes *, G. Crisóstomo, M. Mella

Departamento de Ingeniería de Minas, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Tupper 2069, Santiago, Chile

Abstract

The physical quality of electrodeposits obtained on mesh cathodes may be characterized by a coverage ratio which reflects the homogeneity of the deposit over the electrode surface. On the basis of experimental results, an expression is proposed to predict this ratio for copper electrodeposits obtained in arsenic-containing electrolytes.

Keywords: Electrometallurgy; Electrorefining

1. Introduction

1.1. Objectives

This work aims to quantify the relationship between the cell current density, cathodic kinetic parameters and the coverage ratio of the electrodeposits obtained in a reactive electro dialysis (RED) cell which uses copper mesh cathodes.

1.2. Previous work

The physical quality of a copper electrodeposit is mainly determined by its microstructure, smoothness and continuity (absence of porosity, cracks and voids). The effect of operation parameters on the physical quality of copper electrodeposits obtained on mesh cathodes in a RED cell was recently investigated (Cifuentes and Mella, in press). The main conclusion was that the physical quality can be explained in terms of current density distribution on the cathode surface, kinetic controls for the copper electrode-

position reaction and a coverage ratio. The physical quality of the electrodeposit increased with increasing cell current density, decreasing electrolyte temperature and decreasing copper concentration in the catholyte, whereas variations of the catholyte's recirculation flowrate had a less pronounced effect.

Impurities and additives strongly influence the electrodeposit quality. In the present work the only studied impurity is arsenic and no additives were added to the electrolyte.

2. Experimental

In normal operation, the RED cell is made up of two compartments, the first one containing the cathode and the catholyte and the second one containing the anode and the anolyte. The compartments are separated by an anion membrane, meant to prevent cation transport between the electrolytes. A current, provided by a rectifier, is passed through the cell in order to obtain chemical species at one or both electrodes. The electrolytes are recirculated to ad hoc tanks.

In the present work, in order to approximate conditions in an operating RED cell (cell geometry, electrolyte composition and hydrodynamics), a similar cell was used to carry

* Corresponding author. Tel.: +562 978 4510; fax: +562 672 3504.
E-mail address: luicifue@ing.uchile.cl (L. Cifuentes).

Nomenclature

A	constant in Eqs. (3) and (4) (V^{-1})
A_{cov}	electrode surface area covered by deposit (m^2)
A_{total}	total electrode surface area (m^2)
B	constant in Eqs. (3) and (4)
C	constant in Eqs. (3) and (4)
c_b	reactant concentration in the bulk solution (mol/m^3)
D	diffusivity (m^2/s)
F	Faraday's constant, C/eq
i	current density (A/m^2)
i_{cell}	cell current density (A/m^2)
i_L	limiting current density (A/m^2)

i_{mc}	current density for a cathodic reaction under mixed control, (A/m^2)
i_0^b	exchange current density (A/m^2)
Q	flowrate (mL/min)
R	gas constant (J/mol K)
T	temperature (K)
z	charge number

Greek symbols

α_c	cathodic charge transfer coefficient
η	overpotential (V)
ρ_{cov}	coverage ratio

out a potentiodynamic sweep with the aim of characterizing the cathodic kinetics. A schematic of the RED cell and photographs of the produced copper mesh cathodes can be found elsewhere (Cifuentes et al., 2003; Cifuentes and Mella, in press). In the present work, rectifier, cathode and anode were absent, but the working, reference and counter electrodes were connected to a Solartron 1286 electrochemical interface. The working electrode was placed in the catholyte compartment. It was made of four sheets of $4\text{ cm} \times 4\text{ cm} \times 0.06\text{ cm}$ copper mesh. The counter electrode was a $4\text{ cm} \times 4\text{ cm} \times 0.01\text{ cm}$ platinum sheet and it was placed in the anolyte compartment. A Hg/Hg_2SO_4 electrode with Luggin capillary was used as reference. The sweep rate was 1 mV/s .

The catholyte composition was 4.8 g/L Cu (from cupric sulphate), 50 g/L sulphuric acid and 1.6 g/L arsenic. This composition approximates that of a copper electrorefining electrolyte (without additives or impurities other than arsenic) at 1:4 dilution after it has been subject to 4 h of copper recovery in an RED cell. The source chemicals were of analytical grade. The anolyte composition was 50 g/L sulphuric acid. The electrolytes were separately recirculated at a flowrate of 450 mL/min and their temperature was kept constant at $50\text{ }^\circ\text{C}$ as described in previous publications (Cifuentes et al., 2004; Cifuentes and Mella, in press). The cell was made of acrylic plates. Construction details, as well as membrane properties and pretreatment have been given elsewhere (Cifuentes et al., 2003, 2004; Cifuentes and Mella, in press).

3. Results and discussion

3.1. Determination of kinetic parameters

The kinetic parameters for the copper electrodeposition reaction were obtained from a potentiodynamic sweep and calculated by a method described elsewhere (Cifuentes et al., 2003). The experimental conditions were: $[Cu] = 4.8\text{ g/L}$, $[As] = 1.6\text{ g/L}$, $T = 50\text{ }^\circ\text{C}$ and $Q = 450\text{ mL/min}$. The resulting parameter values were: exchange current den-

sity = 25 A/m^2 ; charge transfer coefficient = 0.34; limiting current density = 696 A/m^2 .

3.2. Quantifying and predicting electrodeposit quality

Cifuentes and Mella (in press) proposed a quantification of the physical quality of electrodeposits obtained on mesh cathodes by means of a coverage ratio (ρ_{cov}). This ratio is defined as the fraction (%) of the apparent cathode surface area covered by the electrodeposit after 2 g of copper have been deposited

$$\rho_{\text{cov}} = \frac{A_{\text{cov}}}{A_{\text{total}}} \times 100 \quad (1)$$

Results for the dependence of the coverage ratio on the cell current density and the corresponding cathodic overpotential values are presented in Table 1. Both the coverage ratio and the absolute value of the overpotential for copper electrodeposition increase with increasing cell current density.

In normal industrial operation, the copper electrodeposition reaction takes place under mixed control. In this case, the overpotential of the cathodic reaction is

$$|\eta| = \frac{RT}{\alpha_c F} \ln \left(i_0^b \left| \frac{1}{|i_L|} - \frac{1}{|i_{\text{cell}}|} \right| \right) \quad (2)$$

The same authors demonstrated that, when the electrodeposit is obtained at a cathode potential near the charge

Table 1

Coverage ratio and cathodic overpotential as functions of cell current density^a

Cell c.d. i_{cell} (A/m^2)	Coverage ratio ^b ρ_{cov} (%)	Overpotential ^c for Cu^{2+}/Cu^0 (V)
290	94	-0.20
225	80	-0.17
150	65	-0.12

^a Experimental conditions: $[Cu] = 4.8\text{ g/L}$, $[As] = 1.6\text{ g/L}$, $T = 50\text{ }^\circ\text{C}$ and $Q = 450\text{ mL/min}$.

^b Data taken from Cifuentes and Mella, in press.

^c Data from Fig. 1.

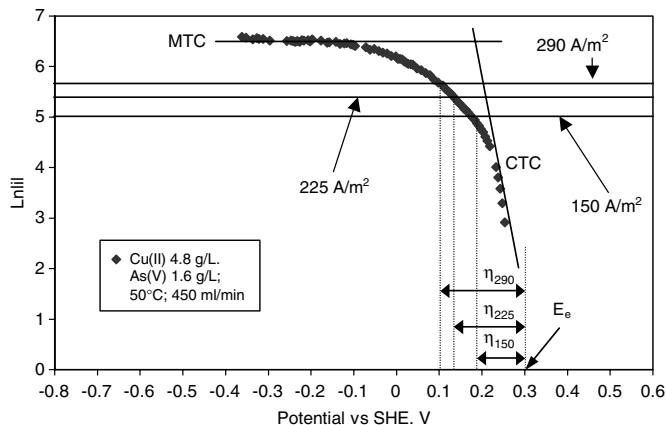


Fig. 1. Evans diagram for the $\text{Cu}^{2+} + 2e \rightarrow \text{Cu}^0$ reaction. Condition: $[\text{Cu}] = 4.8 \text{ g/L}$, $[\text{As}] = 1.6 \text{ g/L}$, $T = 50^\circ\text{C}$ and $Q = 450 \text{ mL/min}$. MTC = mass transfer control; CTC = charge transfer control; E_e = equilibrium potential; η_{290} , η_{225} , η_{150} = cathodic overpotentials at $i_{\text{cell}} = 290$, 225, and 150 A/m^2 respectively.

transfer control range (i.e. in the mixed control range dominated by charge transfer) its physical quality is low. On the other hand, when the cathode potential is near the mass transfer control range (i.e. in the mixed control range dominated by mass transfer) the physical quality of the electrodeposit is high. This means that the physical quality depends on the overpotential of the cathodic reaction.

A graphic representation of the relationship between kinetic parameters, kinetic controls, cell current densities and cathodic overpotentials is shown in Fig. 1 as an Evans diagram. Straight lines have been drawn to coincide with the mass transfer control (MTC) and charge transfer control (CTC) sections of the potentiodynamic curve, respectively. The central section of the curve, which does not coincide with the MTC and CTC lines, represents the mixed control range. The horizontal lines indicate three cell current densities (150, 225 and 290 A/m^2) and their intersections with the potentiodynamic curve determine the corresponding cathodic overpotentials (η_{150} , η_{225} and η_{290}).

A relationship between coverage ratio and cathodic overpotential can be given as

$$\rho_{\text{cov}} = A|\eta|^B + C \quad (3)$$

where A , B and C are constants.

Substituting η from Eq. (2) in Eq. (3), an expression for the coverage ratio as a function of the kinetic parameters (i_0 , α_c and i_L) and of the applied cell current density (i_{cell}) is obtained

$$\rho_{\text{cov}} = A \left| \frac{RT}{\alpha_c F} \ln \left(i_0^b \left| \frac{1}{|i_L|} - \frac{1}{|i_{\text{cell}}|} \right| \right) \right|^B + C \quad (4)$$

From the kinetic parameters given above and data in Table 1, the following values for the constants in Eq. (4) have been determined: $A = 54.81 \text{ V}^{-1}$; $B = 3.405$; $C = 0.529$. When Eq. (4) is used with these constant values, the correlation coefficient between measured and calculated coverage ratios is $R^2 = 0.999$.

It must be kept in mind that the physical quality of the copper electrodeposit also depends on other variables, such as the concentration of impurities other than arsenic (e.g. antimony) and additives (e.g. glue and thiourea). Further work is required in order to obtain a full quantification of mesh cathode quality as a function of physico-chemical variables.

Acknowledgements

This work was funded by the National Committee for Science and Technology (CONICYT, Chile) via FONDECYT Project No. 101 0138. Thanks are due to Rodrigo Ortiz for his help with the calculation of kinetic parameters. Financial support from Placer Dome is also acknowledged.

References

- Cifuentes, L., Mella, M., 2005. The effect of operation parameters on the physical quality of copper electrodeposits obtained on mesh cathodes in a reactive electro dialysis cell, *Canadian Metallurgical Quarterly*, in press.
- Cifuentes, L., Glasner, R., Casas, J.M., 2003. Aspects of the development of a copper electrowinning cell based on reactive electro dialysis. *Chemical Engineering Science* 59, 1087–1101.
- Cifuentes, L., Mondaca, C., Casas, J.M., 2004. The effectiveness of membrane systems for the separation of anolyte and catholyte in a lab-scale copper electrowinning cell based on reactive electro dialysis. *Minerals Engineering* 17, 803–809.