A Continuous Electroplating Model for Poorly Conductive Substrates

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In order to control the distribution of the current density during continuous electroplating on poorly conductive metal foils and metal foam strips, a mathematical model for this process and a formula for calculating the geometric forms of the anode are described. This model can be applied to the continuous electroplating of nickel on a conductive sponge and can enhance the tensile strength and uniformity of nickel foam.

There are an increasing number of uses for preparing functional materials by electroplating metals or metal oxides on foil. These materials find increasing use in optical, electronic and magnetic applications.[1-3] Porous metal materials produced by coating metals on sponge-like substrates, having the features of a three-dimensional net structure and large specific surfaces, can be used as electrode current collectors and catalyst carriers in rechargeable batteries.[4-6]

Because of the relatively poor conductivity of foil and metal-coated sponge substrates, the current distribution on the surface is not uniform. Thus the goal of this work was to develop a model for continuous electroplating to put the process under constant current distribution control.

Mathematical model

The model configuration for continuous electroplating on a poor conductor is shown in Fig. 1. The model assumes that (1) the poorly conductive strip moves at a uniform velocity during the electroplating process and (2) in order to eliminate the edge effect, the width of both of the anodes and the solution container must be the same as that of the strip. The two anodes must be placed in symmetry and two plastic baffles placed at the bottom. The poorly conductive strip moves vertically into the electrodeposition zone during the process. The direction of electron flow is opposite to the direction of strip motion. Assuming that the electron flow direction is along the x axis, $x = 0$ is at the top of the solution and the distance between the strip and both anodes is $D(x)$ in this section.

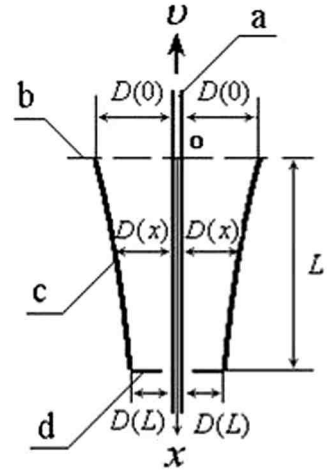

Figure 1—Configuration of the equipment for continuous electrodeposition: (a) the strip after electroplating, (b) top of the solution, (c) anode and (d) plastic baffle.

To insure the quality of the products, the current density must be at an optimum value. Based on the amount of metal that is deposited on the cathode per unit area, this value can be calculated from

Nuts & Bolts: What This Paper Means to You

We are used to thinking of continuous plating as processing a continuous, conductive metal strip. These researchers have dealt with something beyond that, in the form of a continuous conductive strip in the form of a porous sponge. The end-product is a strip of porous metal sponge used in optical, electronic and magnetic applications. Much of this discussion deals with modeling of the plating cell to optimize the shape of the anode. The materials resulting from studies to validate the model are rather interesting, to say the least.

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Faraday's Law and the linear velocity of the moving substrate which was electrodeposited:

$$I = \frac{mH\upsilon}{g\eta} \tag{1}$$

where I is the electric current (A), m is the mass of the metal electrodeposited on the cathode per unit area (kg/m^2), g is the electrochemical equivalent (kg/Coul), η is the current efficiency, υ is the moving velocity of the item being electrodeposited (m/sec) and H is the width of the item (m). If the electrodeposition process is under constant current, then:

$$I = 2HjL \tag{2}$$

where j is the optimum current density (A/m^2). Therefore, the current passing through point x on the strip is:

$$I(x) = I(1-\frac{x}{L}) = 2HjL(1-\frac{x}{L}) \tag{3}$$

where $I(x)$ is the current flux passing through at point x on the strip (A) and L is the projected length of the plating zone.

Because the electrical current flowing at point x corresponds to the mass of metal that is electrodeposited on the strip at point x per unit time, under uniform velocity and constant current, the mass density distribution of the electrodeposited metal in electroplating area is:

$$m(x) = m\left(1-\frac{x}{L}\right) \tag{4}$$

where $m(x)$ denotes the amount of electrodeposited metal per unit area at point x on the moving strip (kg/m^2).

As the current passes, the substrate and its metal coating are connected in parallel. When any part of the strip moves through point x, the total resistance should be:

$$dR(x) = \frac{dR_1 dR_2(x)}{dR_1 + dR_2(x)} \tag{5}$$

$$dR_1 = \frac{K\rho_1}{H\delta}dx \tag{6}$$

$$dR_2(x) = \frac{\sigma K\rho_2}{Hm(x)}dx \tag{7}$$

where $dR(x)$, dR_1 and $dR_2(x)$ are the resistance of the whole strip, the resistance of the substrate and the resistance of the coating layer, respectively, for a length dx at point x (ohms, Ω). δ is the thickness of the foil or the thickness of compact metal which is deposited within the thickness of the nickel foam, ρ_1 is the resistivity of the substrate (Ω·m), ρ_2 is the resistivity of the metal coating (Ω·m), σ is the density of the metal coating (kg/m^3) and K is the resistivity of the porous metal.[7,8] When $K = 1$, the metal is at full density with no porosity. From Equations (4) thru (7), the flowing equation is obtained:

$$dR(x) = \frac{Kdx}{H\left[\frac{\delta}{\rho_1} + \frac{m}{\sigma\rho_2}\left(1-\frac{x}{L}\right)\right]} \tag{8}$$

According to Ohm's Law, the potential difference in the x direction along the strip at point x is:

$$dU(x) = -I(x)dR(x) \tag{9}$$

where $dU(x)$ is the potential difference of the strip for a length dx along the x direction (V). Assuming $y = 1 - \frac{x}{L}$, from Equations (3), (4), (8) and (9) we obtain:

$$dU(x) = \frac{KLIy}{H\left[\frac{\delta}{\rho_1} + \frac{m}{\sigma\rho_2}y\right]}dy \tag{10}$$

The solution of equation (10) is:

$$U(x) = \frac{LI\sigma K\rho_2}{Hm}\left[y - \frac{\sigma\rho_2\delta}{\rho_1 m}\ln\left(\frac{\sigma\rho_2\delta}{\rho_1 m} + y\right)\right] + \overline{C} \tag{11}$$

where $U(x)$ is the potential difference between the anode at point x and the metal foil (V). $\overline{C}$ is a fixed constant.

If $x = 0$ and $U(x) = U(0)$ are set as the boundary conditions, from $y = 1 - \frac{x}{L}$, $\overline{C}$, can be calculated by the following equation:

$$\overline{C} = U(0) - \frac{LI\sigma K\rho_2}{Hm}\left[1 - \frac{\sigma\rho_2\delta}{\rho_1 m}\ln\left(\frac{\sigma\rho_2\delta}{\rho_1 m} + 1\right)\right] \tag{12}$$

where $U(0)$ is the potential difference between the strip and the anode at the top of the solution (V). This can be determined by the applied DC voltage and the potential difference of the strip above the solution. Therefore the solution of equation (10) is:

$$U(x) = U(0) - \frac{LI\sigma K\rho_2}{Hm}\left[\frac{x}{L} + \frac{\sigma\rho_2\delta}{\rho_1 m}\ln\left(1 - \frac{x}{L\left(\frac{\sigma\rho_2\delta}{\rho_1 m} + 1\right)}\right)\right] \tag{13}$$

Because the anode is an equipotential body, $U(x)$ is approximately the potential difference between the anode and the surface of the strip. Meanwhile, the potential decrease along the path anode → solution → foil surface is:

$$U(x) = j\rho_L D(x) + U_r(x) \tag{14}$$

where ρ_L is the resistivity of the solution (Ω·m) and $U_r(x)$ is the polarization potential of the reaction on the electrode at point x (V). Electrodeposition under constant current must meet the condition $U_r(x) \equiv U_r(0)$. Since $I = 2jHL$, from Equations (13) and (14), we obtain the following equation:

$$D(x) = D(0) - \frac{2\sigma K\rho_2 L^2}{\rho_L m}\left[\frac{x}{L} + \frac{\sigma\rho_2\delta}{\rho_1 m}\ln\left(1 - \frac{x}{L\left(\frac{\sigma\rho_2\delta}{\rho_1 m} + 1\right)}\right)\right] \tag{15}$$

When continuous electroplating on poorly conductive substrates, the following parameters can be determined beforehand: the anode length, the optimal current density j and the optimum strip velocity. From all these parameters, together with the resistivity of the solution ρ_L and the distance between anode and strip $D(x)$, which is known from equation (15), the geometric form of the anode can be worked out by calculation.

Continuous electroplating of nickel on a conductive sponge substrate

Materials and methodology

Nickel foam was prepared by soaking a sponge substrate in a conductive gel, drying and then continuously electroplating nickel thereon. The sponge consisted of continuous conductive polyester sponge strip from Japan.** Its width and thickness were 0.65 m (25.6 in) and 1.6 mm (0.063 in) respectively. After a conductive treatment, the conductivity of the conductive gel was 0.48 $\times 10^{-3}$ Ω·m.

The nickel plating electrolyte composition and operating conditions were as follows:

- Nickel sulfate ($NiSO_4 \cdot 6H_2O$) 280 g/L (37.4 oz/gal)
- Nickel chloride ($NiCl_2 \cdot 6H_2O$) 35 g/L (4.7 oz/gal)
- Boric acid (H_3BO_3) 40 g/L (5.3 oz/gal)
- pH 4.1
- Temperature 55°C (131°F)

The conductivity of the solution was measured with a conductivity meter*** in a conductive cell. The morphology of the sample surface was observed by scanning electron microscopy. The tensile strength and elongation of the nickel foam were measured with an electronic material testing machine**** at an elongation velocity of 3.33 mm/sec (0.65 ft/min).

Since the conductivity of the gel is negligible compared with the metal, Equation (15) can be simplified:

$$D(x) = D(0) - \frac{2\sigma K \rho_2 L}{\rho_L m} x \qquad (16)$$

Equation (16) indicates that the distance between anode and cathode is linear with x. If $X = L$, the distance between the bottom of the anode and cathode is:

$$D(L) = D(0) - \frac{2\sigma K \rho_2 L^2}{\rho_L m} \qquad (17)$$

We set the parameters at L = 1 m (3.28 ft), H = 0.65 m (2.13 ft), $D(0)$ = 0.10 m (0.33 ft) and m = 0.45 kg/m^2 (0.092 lb/ft^2), and from the measurements, ρ_L = 0.21 Ω·m and K = 3.58. The density and conductivity of the non-porous compact metal are known, σ = 8.9 $\times 10^3$ kg/m^3 (556 lb/ft^3) and ρ_2 = 9.5 $\times 10^{-8}$ Ω·m. $D(L)$ = 3.6 $\times 10^{-2}$ m was obtained from Equation (17). According to this result, the geometric form of the anode was selected. The equipment layout for continuous electroplating is shown in Fig. 2.

Results

In order to investigate how the electrodeposition process under current control affected the mechanical performance of the nickel foam, the tensile strength of the nickel foam was measured after the material was sintered and reduced. The width and thickness of the sample were 3.0 cm (1.18 in) and 0.16 cm (0.063 in), respectively, and the virtual test length was 0.1 m (3.94 in). The results of the tensile strength tests are shown in Figs. 3 and 4, and the analysis of the data is presented in Table 1. All the results indicate that the tensile strength of the nickel foam prepared by constant current electroplating was enhanced.

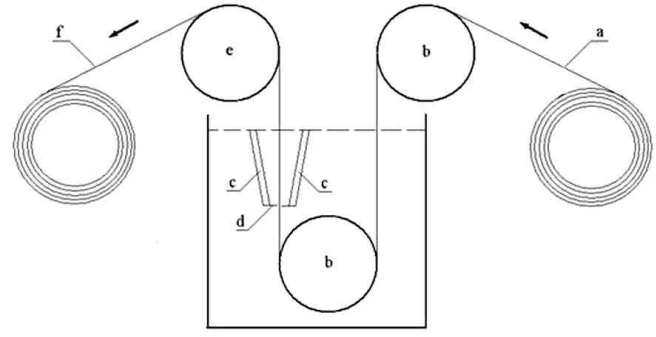

Figure 2—Device for continuous electroplating of nickel foam: (a) conductive sponge, (b) conductive roll, (c) anode, (d) plastic baffle and (e) cathode conductive roll, f-nickel foam.

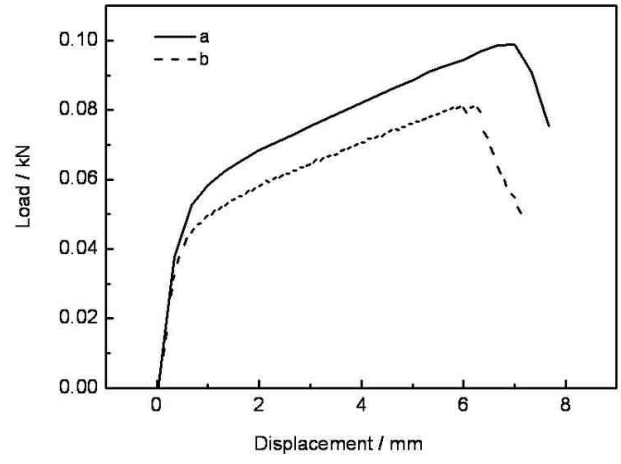

Figure 3—The tensile strength curves for nickel foam in the longitudinal direction: (a) at constant current density and (b) with parallel anodes.

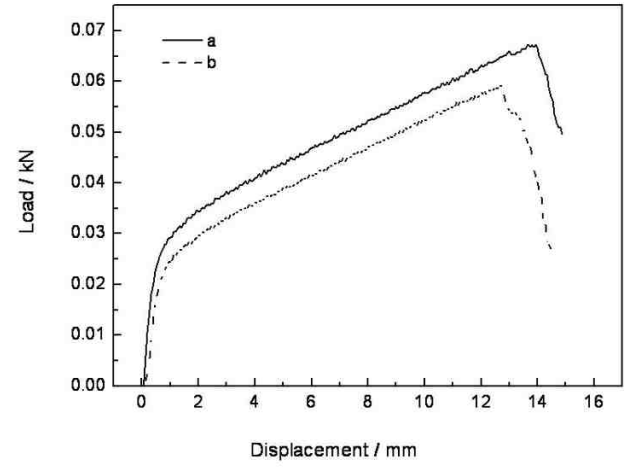

Figure 4—The tensile curves for nickel foam in the transverse direction: (a) at constant current density and (b) with parallel anodes.

** *INOC MF-50LE conductive polyester sponge, Japan.*
*** *DDS-11C conductivity meter, Shanghai LeiCi Instrument Co., Shanghai, P.R. China.*
**** *Instron 5569 electronic material testing machine, Instron Corp., Norwood, MA.*

Figure 5 shows the SEM photographs of nickel foam prepared under constant current control and Fig. 6 shows the SEM photographs of nickel foam that was electroplated under the same current and moving velocity as that in Fig. 5, but with the anodes placed in parallel. It is very clear that the surface of the framework of nickel foam in Fig. 5 is much smoother than that in Fig. 6. The nickel foam produced by using parallel anodes exhibited nodules caused by the asymmetry of the current distribution on the framework. Since the current density is too high when the strip is moved closer to the plating area, such nodules form.

Conclusion

A mathematical model for continuous electrodeposition of metal under constant current density on poorly conductive strip was derived based on Faraday's and Ohm's Laws. A formula for calculating the geometric form of the anodes was developed. This model can be used for the continuous electrodeposition of porous nickel and can enhance the uniformity and tensile strength of such a deposit.

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Table 1
Ultimate tensile strength and percent elongation of nickel foam fabricated in the five-step constant current density electrodeposition process

	Longitudinal		Transverse	
	Electrical	**Parallel**	**Electrical**	**Parallel**
σ_b, MPa (psi)	2.06 (299)	1.69 (245)	1.40 (203)	1.23 (178)
θ, %	8.11	7.91	14.9	14.8

σ_b is the tensile strength and θ is the elongation of the nickel foam.

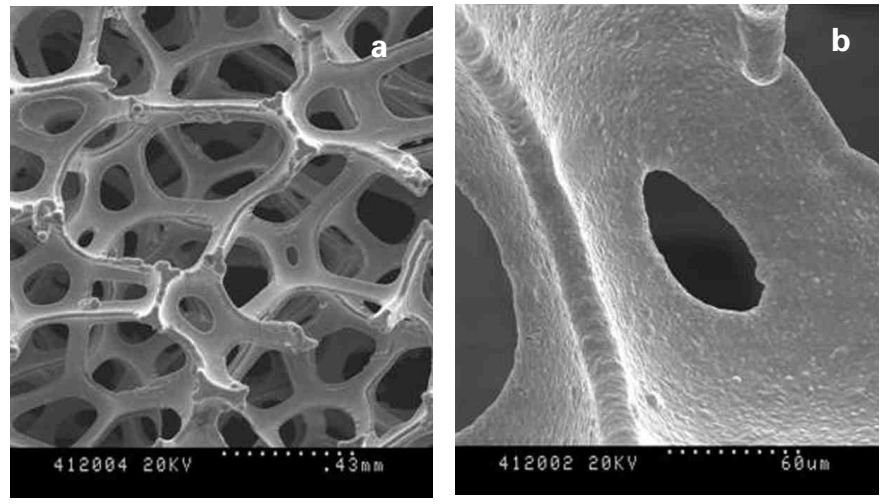

Figure 5—Microstructure of nickel foam fabricated by the five-step constant current density electrodeposition process: (a) net structure and (b) surface morphology of deposited nickel.

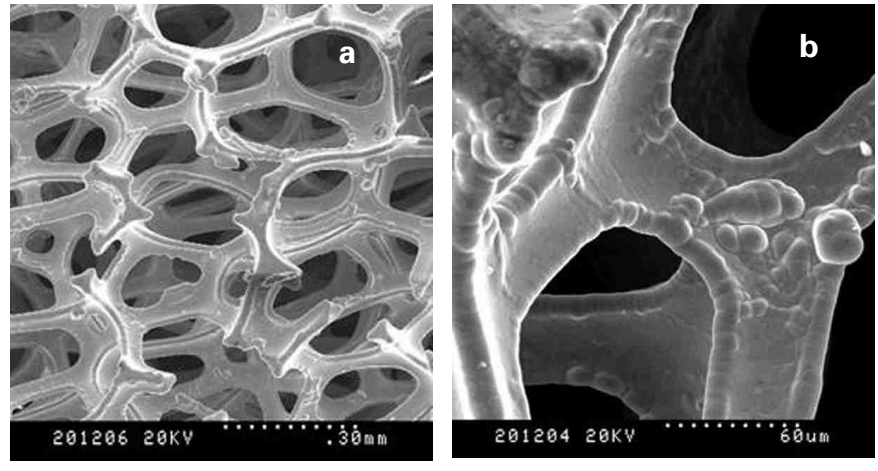

Figure 6—Microstructure of nickel foam fabricated by the non-constant current density electrodeposition process: (a) net structure and (b) surface morphology of deposited nickel.

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