

ELECTROLYTIC COATING OF THE INTERNAL SURFACE OF POROUS MATERIALS

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UDC 621.357.7

In view of the widening technological uses of porous materials, it may become necessary to deposit electrolytic coatings on them. The problem of electroplating the internal surface of a porous material is similar in principle to the problem of deposition of metals on articles of complex configuration.

In electroplating technology the uniformity of a coating is determined mainly by the throwing power of the electrolyte [1]. The throwing power is characterized by the parameter $(1/\rho) \cdot (d\varphi/di)$, i.e., it depends on the specific resistance of the electrolyte and on the polarizability of the electrode.

In the case of porous electrodes the distribution of the deposited metal over the internal surface is influenced, apart from kinetic factors, by the structural characteristics of the electrode. The theory of porous electrodes has now been developed in great detail [2, 3]. However, it is desirable to state its principal points here, as it is being applied to a new object in this case.

When a current passes through a porous electrode, its external surface becomes polarized. Owing to polarization of the external layers, deposition spreads into the electrode. The current I passing through the liquid phase in the electrode pores is gradually consumed, causing deposition of the metal on the pore walls, and enters the solid phase. The rate of deposition decreases with increasing distance from the outer surface owing to the potential drop caused by the resistance of the electrolyte in the electrode pores. The potential drop during flow of current in a pore is given by Ohm's law:

$$\frac{d\varphi}{dx} = -\rho I, \quad (1)$$

where ρ is the effective resistance of the electrolyte in the pores per unit electrode volume; I is the current strength in the electrolyte contained in the pores, in a cross section parallel to the external surface of the electrode.

Moreover, the deposition rate at any point of the internal surface of the electrode is determined by the polarization. In the general form this dependence is represented by a certain function $f(\varphi) = 1$, which is the equation of the polarization curve for a smooth electrode.

At a certain distance from the external electrode surface the change of the current strength in the electrolyte within the pores is determined by the discharge current density (i) and depends on the polarization of the electrode in the given cross section and on the specific surface (S) of the electrode:

$$\frac{dI}{dx} = -Sf(\varphi). \quad (2)$$

An expression representing the process in question is easily obtained from Eqs. (1) and (2):

$$\frac{d^2\varphi}{dx^2} = S\rho f(\varphi). \quad (3)$$

In the simplest case the polarization curve is linear:

$$f(\varphi) = \frac{\varphi}{R}, \quad (4)$$

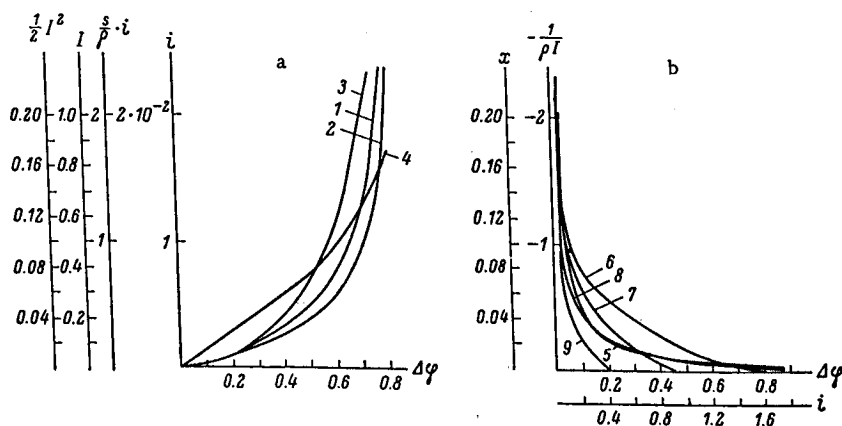


Fig. 1. Successive steps in approximate calculation of the potential and current distribution over the depth of a porous electrode in deposition of tin from an alkaline electrolyte. Electrolyte composition (g/liter): Na_2SnO_3 - 60; NaOH - 20; $t = 80^\circ$; $S \approx 2.5 \cdot 10^3 \text{ cm}^2/\text{cm}^3$, porosity 50%. $\Delta\varphi$ Polarization (V); i true current density (A/cm^2); I geometrical current density (A/cm^2). x Depth (cm), $S/\rho \cdot (i - A/\Omega) \times \text{cm}^4$; $\frac{1}{2}I^2 - \text{A}/\text{cm}^4$, $-\frac{1}{\rho I} - \text{cm}/\text{V}$; the same in Fig. 2. Curves:

- 1) $(i - \varphi)$; 2) $I \frac{dI}{d\varphi} - \varphi$; 3) $\frac{I^2}{2} - \varphi$; 4) $(I - \varphi)$; 5) $-\frac{dx}{d\varphi} - \varphi$; 6 and 7) $(\varphi - x)$; 8 and 9) $(i - x)$.

where $R = d\varphi/di$ is the reaction resistance referred to unit area of the true electrode surface. The distribution of current density and accordingly of the thickness of the deposited metal layer obeys an exponential law:

$$i_x = i \cdot \exp\left(-\frac{x}{x_e}\right), \quad (5)$$

where x_e is the effective penetration depth of the process - a quantity which shows the distance from the external electrode surface at which the true current density decreases by the factor e (2.7); for a linear polarization characteristic x_e can be calculated from the formula

$$x_e = \sqrt{\frac{R}{S\rho}}. \quad (6)$$

It follows that the actual depth to which a porous electrode can be coated corresponds to x_e in order of magnitude. It is seen from formula (6) that the penetration depth of the deposition process increases with the reaction resistance R and decreases with increasing specific surface S and with effective resistance ρ of the electrolyte in the pores.

In practice, for deposition of most metals from various electrolytes on electrodes of various structures the probable values of x_e lie in the range of 10^{-3} to 1 cm.

In many cases the above calculation cannot be used directly, as the polarization curves for real deposition processes are usually nonlinear. For determination of the distribution of the metal within the electrode it is then necessary to solve Eq. (2) in the general form, with the actual form of the $f(\varphi)$ polarization curve taken into account. For a polarization curve of complex form it is preferable to limit oneself to an approximate solution. The approximate solution is found as follows.

Differentiating Eq. (1), we obtain

$$\frac{d^2\varphi}{dx^2} = -\rho \left(\frac{dI}{dx}\right) = -\rho \left(\frac{dI}{d\varphi}\right) \frac{d\varphi}{dx} = \rho^2 I \frac{dI}{d\varphi}. \quad (7)$$

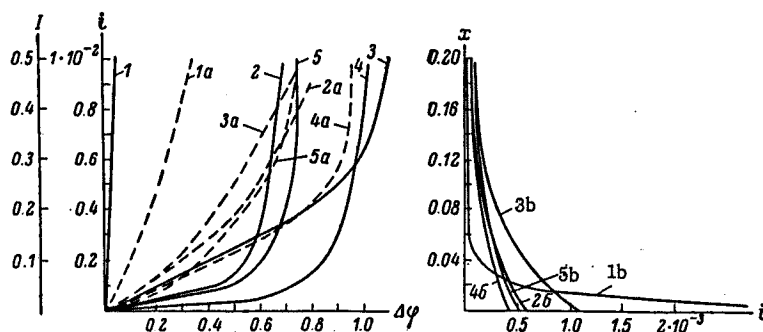


Fig. 2

Fig. 2. Polarization characteristics of smooth and porous electrodes in various electrolytes, and the corresponding current distribution curves. Polarization curves for: 1-5) smooth electrodes; 1a-5a) porous electrodes; 1b-5b) current distribution over the depth of the porous electrodes. All the polarization characteristics of porous electrodes are calculated for electrode No. 4 (see Table 1). Copper electrolytes: 1-1b) acid [4]; 2-2b) ammine (nickel cathode); 3-3b) pyrophosphate (nickel cathode); 4-4b) cyanide [4]; 5) cadmium electrolyte with Trilon B (nickel cathode).

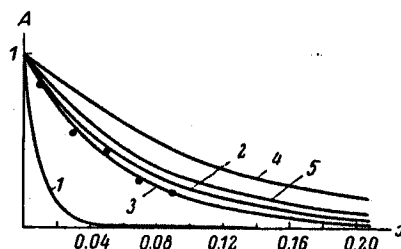


Fig. 3

Fig. 3. Variation of the relative current density with the depth in porous electrodes in different electrolytes. A) Relative current density; x) depth (cm). Copper electrolytes: 1) acid [4]; 2) ammine (nickel cathode); 3) pyrophosphate (nickel cathode); 4) cyanide [4]; 5) cadmium electrode with Trilon B (nickel cathode). The points on curve 3 represent experimental data.

From Eqs. (3) and (7) it follows that

$$IdI = \frac{S}{\rho} f(\varphi) d\varphi. \quad (8)$$

Hence we can find the polarization characteristic of the porous electrode:

$$I(\varphi) = \sqrt{\frac{2S}{\rho} \int_0^{\varphi} f(\varphi) d\varphi}. \quad (9)$$

Substitution of the expression (9) into Eq. (1) and secondary integration gives a function representing the potential distribution over the thickness of the electrode:

$$x = -\frac{1}{\rho} \cdot \int_0^{\varphi} \frac{d\varphi}{I(\varphi)}. \quad (10)$$

With a complex polarization curve for the process it is convenient to solve Eqs. (9) and (10) graphically.

A specimen graphical calculation is shown in Fig. 1. The polarization characteristic $f(\varphi)$ of the smooth electrode (curve 1) is plotted from experimental data. Multiplication of the ordinates of this curve S/ρ gives curve 2, $I(dI/d\varphi)$ versus φ . Graphical integration of curve 2 from 0 to φ gives the $I^2/2$ versus φ relationship (curve 3). Curve 4, the polarization characteristic of the porous electrode, I versus φ , is obtained by taking the square roots of the ordinates of curve 3 and multiplying the results by $\sqrt{2}$ [Eq. (9)]. Curve 5 is plotted from reciprocals of the ordinates of curve 4 multiplied by $-(1/\rho)$. Integration of curve 5 between 0 to φ in accordance with Eq. (10) gives the x versus φ relationship — the potential distribution over the depth (curves 6 and 7). Values of i from curve 1 corresponding to each potential were used for plotting the curves 8 and 9 for current distribution over the depth, x versus i . Curves 6 and 7 in Fig. 1 were calculated for two values of surface polarization: 0.8 and 0.45 V. It is seen in Fig. 1b that in the case of a nonlinear polarization characteristic the uniformity of current and metal distribution depends on the external polarization of the electrode. Lower surface potentials (curves 7 and 9) correspond to more uniform distribution of the deposited metal in the electrode. However, the relationships here are qualitatively the same as with a linear f versus φ relationship: increase of the depth of penetration of the

process is favored by higher polarizability of the electrode (steeper φ versus i polarization curve), low effective resistance of the electrolyte in the pores, and a low specific surface of the electrode. Moreover, the electrolyte should have high covering power (the metal should be deposited at a high current efficiency over a wide range of current densities). These relationships should guide the choice of electrolytes for coating porous materials.

With regard to the above conditions, simple electrolytes are ineffective when it is required to coat the porous material to the greatest possible depth.

Comparative Characteristics of Different Electrolytes

Deposition of certain metals on porous electrodes from solutions of complex salts and from electrolytes with added surfactants was investigated. The former group includes cyanide, ammine, and pyrophosphate electrolytes for copper plating, cadmium electrolyte with Trilon B, and the alkaline electrolyte for tin plating.

Figure 2 shows polarization curves for smooth electrodes in various electrolytes (curves 1 and 5 are based on data in [4]) and the corresponding polarization characteristics of porous electrodes and curves of current distribution over their depth, plotted with the same geometrical current density (0.1 A per cm^2) for each given electrode.

For the initial regions of the polarization curves, where the dependence of current on potential is approximately linear, the effective penetration depth of the process x_e can be calculated from formula (6). For example, for the four copper electrolytes — ammine, pyrophosphate, cyanide, and acid (for comparison) — the calculated values of x_e (for a nickel electrode of a particular structure) are 0.7, 0.55, 1.1, and 0.1 mm. The most uniform distribution of metal over the depth is to be expected with the cyanide electrolyte, and the least uniform with the acid electrolyte.

The differences in the character of deposition from these electrolytes on the internal surfaces of porous electrodes are seen more clearly in Fig. 3. This diagram shows the variations of relative current density with depth. The actual current density on the external surface of the electrode is taken as unity. The penetration depth of the process with a given electrolyte may vary with the geometric current density and the structural characteristics of the electrode. The finer the structure of the porous material, the greater is the specific surface of the electrode and the effective resistance of the electrolyte (which depends on the pore diameter) in it, and consequently the lower is x_e . Conversely, coarse-grained highly porous materials can be coated to a much greater depth.

For electrolytes containing added surfactants the i versus φ curves for the cathode process usually have an adsorption current plateau: there is a considerable shift of potential at a constant small value of the adsorption current (i_{ads}). The greater the shift of potential and the lower the adsorption current, the deeper is the penetration of the process. In the region of the curve corresponding to the adsorption process the current consumed for metal deposition is $i_{\text{ads}} - i_b$, where i_b is the background current. If the action of the additive is very strong, metal deposition may be inhibited almost completely in the region of limiting adsorption current. Moreover, if the additive causes a very large shift of potential (of the order of 1V), hydrogen may be evolved, with a fall in current efficiency. These circumstances restrict the applicability of a number of electrolytes. For example, the current efficiency with cadmium electrolytes containing various additives is low in the adsorption region [5]. The retardation of the reaction is not great in deposition of copper from solutions with added surfactants [6]. The best results in deposition on porous electrodes are to be expected with the use of tinplating electrolytes containing thymol or β -naphthol. They give high current efficiencies in the adsorption region [7]. For example, with an electrolyte of the composition 0.25 N Sn^{2+} , 2 N H_2SO_4 , 1 g gelatin per liter, saturated with thymol ($\Delta\varphi = 0.2$ V, $i_{\text{ads}} = 5 \cdot 10^{-4}$ A/ cm^2) the calculated depth of penetration of the process (for an electrode of 42% porosity, $S = 1500$ cm^2/cm^3 and $\rho = 25$ $\Omega \cdot \text{cm}$) is 1.1 mm.

During metal deposition on a porous electrode it is necessary to ensure an adequate supply of discharging ions to the internal electrode surface. When a metal is deposited from a stationary electrolyte impregnating a porous electrode the pores become impoverished with the electrolyte and are excluded from the process.

TABLE 1. Physical Characteristics of the Test Electrodes, Deposition Conditions, and Experimental Results

Electrode No.	Particle size of the original powder and filler and amount of filler	Physical characteristics of electrode	Current strength (A)	Deposition time (min)	Flow rate (liter/h)	Weight of copper in layers 0.2 mm thick (g)
1	Nickel 6 μ ; (NH ₄) ₂ CO ₃ 40 μ , 30%	Porosity P = 66%, thickness (δ) 0.2 cm, $S \approx 3 \cdot 10^3$ cm ² /cm ³ , electrode diameter d = 0.2 cm	0.2	80	0.5	0.081
						0.040
						0.023
						0.018
						0.012
2	Nickel 200-250 μ ; (NH ₄) ₂ CO ₃ 160 μ , 20%	P = 70%, δ = 0.20 cm, $S \approx 10^3$ cm ² /cm ³ , d = 0.2 cm	0.2	80	1	0.060
						0.046
						0.034
						0.024
						0.018
3	Nickel 6 μ 50%, nickel 65 μ 50%, (NH ₄) ₂ CO ₃ 40 μ , 20%	P = 58%, δ = 0.25 cm, $S \approx 2 \cdot 10^3$ cm ² /cm ³ , d = 0.2 cm	0.2	45	1	0.054
						0.030
						0.018
						0.014
4	Nickel 6 μ ; (NH ₄) ₂ CO ₃ 40 μ , 30%	P = 65%, δ = 0.30 cm, $S \approx 2.5 \cdot 10^3$ cm ² /cm ³ , d = 0.2 cm	0.2	95	0.2	0.121
						0.072
						0.050
						0.035
						0.030
5	Nickel 6 μ 50%, nickel 65 μ 50%, (NH ₄) ₂ CO ₃ 40 μ , 40%	P = 60%, δ = 0.35 cm, $S \approx 2.5 \cdot 10^3$ cm ² /cm ³ , d = 0.2 cm	0.2	70	0.2	0.066
						0.046
						0.012
						0.008
						0.006

With an average specific pore volume of 0.5 cm³/cm³, $S = 2000$ cm²/cm³, and concentration $c_{\text{Cu}^{2+}} = 20$ g/liter the supply of copper ions in the pores is sufficient for deposition of a layer about 0.01 μ thick. It is therefore necessary to provide enforced supply of electrolyte into the electrode pores during the deposition. The necessary flow rate is given by the relation

$$v \geq \frac{I}{cnF}. \quad (11)$$

EXPERIMENTAL

Experiments were carried out on deposition of metals on the internal surfaces of porous electrodes from an alkaline tinplating electrolyte with addition of thymol (on a copper electrode) and from a copper pyrophosphate electrolyte (on a nickel electrode). In the former case the experiments were qualitative in character, with visual estimation of the approximate depth of metal deposition; in the second, the distribution of the metal over the depth of the electrode was studied quantitatively. The electrodes were made by the powder-metal method from nickel or copper powders of definite particle size with addition of ammonium carbonate for pore formation.

The electrode characteristics (composition, grain size of the original powders, porosity, and specific surface) are given in Table 1.

The effective resistance of the electrolyte in the pores was calculated from the conductivity of the solution, with structural characteristics of the electrode taken into account [8].

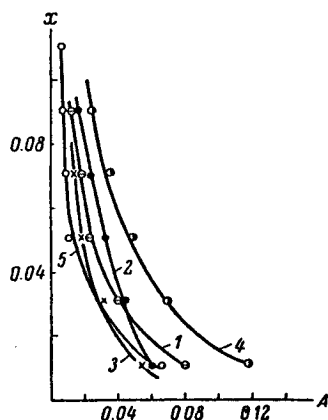


Fig. 4. Experimental curves for metal distribution as a function of depth in deposition of copper from pyrophosphate electrolyte on porous nickel electrodes. x) Depth (cm); A) weight of copper deposited (g). Electrolyte composition (g/liter): CuSO_4 - 30, $\text{Na}_2\text{P}_2\text{O}_5$ - 140; Na_2HPO_4 - 95, Rochelle salt - 35. The electrolyte numbers (see Table 1) are indicated on the curves.

tion through the electrode. The filtration rate was determined by the relation (11). With a tenfold excess of electrolyte in the pore we have

$$V = 10 \cdot \frac{I}{cnF}$$

at $I = 0.2\text{A}$, $C_{\text{Cu}^{2+}} = 0.25\text{ N}$, $V \approx 0.2$ liter/h.

Electrolyte was drawn through the porous electrode by creation of a vacuum on the far side of the electrode. The electrode was mounted with the aid of adhesive in a glass tube connected to the vacuum source and put into the cell with the electrolyte. The deposition was conducted at room temperature.

For determination of the amounts of metal deposited at various depths within the electrode, layers 0.2 mm thick were cut and analyzed for copper. The copper content in the nickel-copper mixture after dissolution of the powder by heating in HNO_3 and H_2SO_4 was determined by the iodometric method.

Experimental Results

The curves in Fig. 4 show the metal contents at different depths in electrodes made from nickel powder (particle size $6\text{ }\mu$, curve 1) and nickel filings (particle size $200\text{--}250\text{ }\mu$, curve 2) with different pore diameters, specific surface, and electrolyte resistance in the pores, and correspondingly with different effective depths of penetration of the process.

The metal distribution over the depth is more uniform for electrode 2 (calculated $x_e = 1\text{ mm}$) than for electrode 1 ($x_e = 0.5\text{ mm}$).

Curves for electrodes of similar structural characteristics but for different deposition times are shown in Fig. 4 (curves 3 and 4). With increase of the coating time the deposition of the metal occurs

For example, for a copper electrode of particle size $150\text{ }\mu$ and 42% porosity the effective resistance of the tinplating electrolyte with addition of thymol ($\kappa_0 = 0.177\text{ }\Omega^{-1} \cdot \text{cm}^{-1}$) is $25\text{ }\Omega \cdot \text{cm}$.

The deposition conditions were chosen in accordance with the required characteristics and the properties of the electrolyte. The depth of coating of a porous electrode should not exceed x_e substantially - coating to a greater depth is impossible.

With regard to uniform coating it is usual to operate at low current densities, and therefore a compromise solution has to be adopted: the distribution must be adequately uniform with an acceptable deposition rate. The maximum deposition rate is determined by the current density at the external electrode surface. It must be within limits ensuring deposits of good quality. It should also be taken into account that the maximum thickness of the surface layer must be substantially less than the pore radius.

The i versus φ and x versus i curves are used for finding the polarization on the electrode surface corresponding to the true current density used. The corresponding geometrical current density is found from the I versus φ curve. For example, in deposition of copper from a pyrophosphate electrolyte (Fig. 2; curves 3a, 3b) $\Delta\varphi = 0.25\text{ V}$, $i = 10^{-3}\text{ A/cm}^2$ (the true current density on the electrode surface), $I_{\text{geom}} = 0.08\text{ A/cm}^2$ (with an external electrode area of 2.5 cm^2 the current strength in the circuit should be 0.2 A).

The duration of electrolysis for deposition of a copper layer $1\text{ }\mu$ thick at a depth $x_e = 0.55\text{ mm}$ is 1.5 h. The external surface of the electrode is then covered by a layer $3\text{ }\mu$ thick.

In all the experiments on coating of porous electrodes the electrolysis was conducted with continuous filtration of the solution through the electrode. The filtration rate was determined by the relation (11). With a tenfold excess of electrolyte in the pore we have

mainly in the outer layers. The filtration rate, if it is several times the minimum value, has no significant influence on deposition. If the filtration rate is inadequate virtually no deposition occurs within the pores. Curves 3 and 5 (Fig. 4) correspond to electrodes of similar structure and filtration rates of 1 and 0.2 liter/h respectively. The experimental and calculated data are compared in Fig. 3.

CONCLUSIONS

1. Investigations showed that porous electrodes can be coated to a depth of about 1 mm with a suitably chosen electrolyte.
2. The electrolyte should satisfy the following conditions: high conductivity and covering power, and considerable polarization in the process (a flat i versus φ curve is desirable).
3. Electrodes made from coarse-grained material are coated to a greater depth and more uniformly. The internal surface of a porous electrode can be coated if forced flow of electrolyte through the pores is created.

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