ancy between the experimental and calculated curves may come from the fact that  $\theta_{\text{org}}$  changes with the electrode potential whereas in the approximation it was supposed to be constant.

Further studies of the adsorption continue in order to explain the mechanism of the electrocatalytic hydrogenation of organic compounds.

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# A New Electrochemical Method for Determining the Fractal Dimension of the Surface of Rough Metal Electrodeposits

Its Application to Dendritic Silver Surfaces

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# ABSTRACT

The surface of dendritic Ag electrodeposits grown on nearly spherical polyfaceted Pt electrodes from 0.5M Na<sub>2</sub>SO<sub>4</sub> +  $10^{-2}M$  H<sub>2</sub>SO<sub>4</sub> +  $0.5 \times 10^{-2}M$  Ag<sub>2</sub>SO<sub>4</sub> at 0.042 V, has been characterized in terms of fractal geometry by using a new procedure for determining the area (A) and the volume (V) of the electrodeposits. The area was indirectly determined from the Pb and Cd upd voltammetric charge and the volume was evaluated from the Ag electrodeposition charge. The relationship between A and V shows fractal behavior  $A \propto V^{D/3}$  over more than one decade of V with  $D = 2.50 \pm 0.03$ . This figure is consistent with a random Ag dendritic surface growth limited by the electric field on the solution side around the growing tips.

Surface disorder and random roughness can play a determining role in many physical and chemical properties of surfaces and interfaces (1, 2). Highly dispersed metals used in heterogeneous catalysis, thin metal films grown under low mobility conditions and metal electrodeposits exhibit extremely rough and irregular surfaces. Despite the importance of electrodeposited metal surfaces in different chemical and physical processes, the understanding of their structures is at best incomplete. Computer simulations show that both, the internal structure and the surface of several rough metals can be described as fractals (2). However, the demonstration of fractality for real systems is a complex matter as the fractal behavior appears only within a certain scale length. Hence, the choice of the experimental method becomes extremely important for this purpose.

Several ways have been proposed to investigate the fractal nature of electrode surfaces, i.e., to determine the radius of the object through the current decay at a constant potential and the mass (charge) of the electrodeposited material (3); to determine the fractal dimension through diffusion limiting current decay of a redox reaction involv-

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ing soluble species (4); to determine the radius of the object by microscopy and the mass through the electrodeposition charge (5); and to determine the perimeter vs. area relationship of intergranular void patterns through scanning tunneling microscopy (6). Impedance methods (7, 8) have been also considered for this purpose, although it is difficult at present to correlate the constant phase angle exponent to D, the fractal dimension of the object (9).

In this paper, an electrochemical method to determine the fractal geometry of self-similar Ag electrodeposits grown far from equilibrium on polyfaceted nearly spherical Pt electrodes is presented. This is based on the determination of the area (A) vs. volume (V) relationship (10). For this purpose the area of the rough electrodeposited Ag surface is indirectly evaluated through the underpotential deposition (upd) (11) of either Pb or Cd atoms used as yardsticks. The nonfractal volume is obtained from the Ag electrodeposition charge. This method succeeds in proving the fractal geometry of the surface of dendrite Ag electrodeposits and in estimating the corresponding value of D. From the fractal dimension and the electrochemical data an explanation of the kinetics of the Ag dendritic surface development is given in terms of a random process controlled by the local electric field on the solution side around the Ag dendrite tips.

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Fig. 1. SEM micrographs of the surface of Ag electrodeposited dendrites obtained as indicated in the text. (a) 100 (b) 1500 (c) 6000 and (d) 10,000 times. The corresponding length units are indicated.

## Experimental

Each electrochemical run consisted of the preparation of the Ag deposit, and the determination of both the surface area and the volume of the Ag electrodeposits. Runs were made in a conventional Pyrex glass electrochemical cell comprising the usual arrangement of three electrodes.

The initial working electrode was a polyfaceted nearly spherical Pt electrode (apparent area 0.040 cm<sup>2</sup>) where the Ag electrodeposition from 0.5M Na<sub>2</sub>SO<sub>4</sub> +  $10^{-2}M$  H<sub>2</sub>SO<sub>4</sub> +  $5 \times 10^{-3}$  Ag<sub>2</sub>SO<sub>4</sub> takes place. The Ag deposits were grown at a constant potential,  $E_d = 0.042$  V (SHE), *i.e.*, far from the corresponding equilibrium potential ( $E_{rev} = 0.615$  V) (12). The chosen value of  $E_d$  accounted for a sticking probability of depositing Ag<sup>+</sup>-ions sufficiently large to assure the

growth of Ag dendrites (13). The Ag electrodeposition time,  $t_d$ , was conveniently adjusted for producing Ag overlayers of different sizes. The counterelectrode was a large Pt plate, and a saturated calomel electrode was employed as reference. However, in the text all potentials are referred to the standard hydrogen electrode (SHE) scale.

The Ag electrodeposit current transients at  $E_d$  were recorded by first stepping the potential from 0.940 V to 1.49 V to obtain a bare Pt substrate, followed by a second potential step from 1.49 V to  $E_d$  to grow the dendritic Ag deposits.

The surface area of the Ag electrodeposits was determined indirectly through the Pb upd and the Cd upd voltammetric charges obtained at 0.010 and 0.020 V  $\rm s^{-1}$  by





Fig. 2. SEM micrographs of the typical "metal forest" topographies of Ag electrodeposits. (a) 2500 times, lateral view; (b) 1500 times, lateral view; (c) 25,000 times, top view; (d) 40,000 times top view.

using  $10^{-2}M$  Pb (acetate)<sub>2</sub> + 0.5M NaClO<sub>4</sub> +  $10^{-2}M$  HClO<sub>4</sub>, and  $10^{-2}M$  CdSO<sub>4</sub> + 0.5M Na<sub>2</sub>SO<sub>4</sub> +  $10^{-2}M$  H<sub>2</sub>SO<sub>4</sub>, respectively. The procedure employed for the determination of the surface area has been described in detail elsewhere (14).

The nonfractal volume of the Ag electrodeposits was calculated from the electrodeposition charge of  $Ag^+$ -ions considering the bulk Ag density.

Conventional voltammograms related to the Ag electrodeposition/Ag anodic stripping in 0.5M Na<sub>2</sub>SO<sub>4</sub> +  $10^{-2}M$  H<sub>2</sub>SO<sub>4</sub> +  $5 \times 10^{-3}$  Ag<sub>2</sub>SO<sub>4</sub> were also obtained over a wide range of potential sweep rates, *v*. From these data information regarding the rate determining step of the Ag electrodeposition process can be derived.

The electrochemical measurements were made by using a PAR circuitry including Model 173, 175, and 179 units. Fast current transients were recorded with a Model 3091 Nicolet oscilloscope. Solutions were prepared from AR chemicals and MilliQ\*-water. All runs were made under Ar at 25°C.

SEM micrographs of Ag electrodeposits were obtained with a Hitachi S-450 scanning electron microscope (SEM) for beam energies ranging between 20 to 25 kV.



Fig. 3. Photograph of a massive electrodeposit of Ag dendrites separated from the Pt substrate and kept in the electrolyte solution. For size comparison, the picture of the spherical Pt substrate is included. The radius of the Pt sphere is 0.056 cm.

# Results

The SEM micrographs of Ag electrodeposits obtained at different magnifications in the  $1 \times 10^2$  to  $4 \times 10^4$  range are depicted in Fig. 1a-d and 2a-d, together with an *in situ* photograph of a large Ag dendritic deposit (Fig. 3). The morphology shown in these images corresponds to dendritic Ag crystal patterns leading to a "metal forest" display (Fig. 2a-d). Likewise, a large number of dendritic patterns shows V-shaped branched three-dimensional (3D) Ag structures. The scanning electron microscopy (SEM) micrographs (Fig. 2c) also allow one to distinguish the formation of a number of 3D small nuclei in addition to dendrites.

Figure 3 corresponds to a relatively large Ag dendritic deposit immersed in the electrolyte solution, but separated from the Pt substrate. Seemingly, this type of Ag deposit has a relatively poor adherence to the Pt substrate as they can be easily detached by switching the current off or by a gentle mechanical vibration. After detachment the very slow displacement of the Ag deposit in the solution indicates that its density is much lower than that of bulk Ag. It behaves as a highly porous metal impregnated with a large amount of solution, which collapses as one attempts to remove it from the solution.

The voltammograms of Pb upd (Fig. 4a) and Cd upd (Fig. 4b) on the dendritic Ag deposits are comparable, al-





Fig. 4. (a) Voltammogram of Pb upd on a dendrite structured Ag surface run at 0.010 V s<sup>-1</sup>.  $Q_d = 25$  mC cm<sup>-2</sup>. (b) Voltammogram of Cd upd on a dendrite structured Ag surface run at 0.020 V s<sup>-1</sup>.  $Q_d = 35$  mC cm<sup>-2</sup>.

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Fig. 5. Cathodic current transient for Ag electrodeposition at  $E_d = 0.042 \text{ V}$ .

though not equal, to those resulting on smooth Ag electrodes (14-16). From either the Pb upd or the Cd upd voltammetric charge, the value of A, the Ag electrodeposit surface area, was indirectly evaluated using the ratio

$$A = Q_{\rm upd}/q_{\rm m}$$
 [1]

where  $Q_{\rm upd}$  is the voltammetric charge derived from either Pb or Cd upd, and  $q_{\rm m}$  is the monolayer charge density for these metals on a smooth Pt electrode. As the ionic radii (17) of Pb ( $r_{\rm Pb} = 0.120$  nm) and Cd ( $r_{\rm Cd} = 0.097$  nm) are slightly smaller than the ionic radius of Ag ( $r_{\rm Ag} = 0.126$  nm), a common value of  $q_{\rm m} = 0.420$  mC cm<sup>-2</sup> was taken. In this case the value of A becomes independent of the atomic yardstick.

The volume, V, of the Ag electrodeposits was obtained from Faraday's law

$$V = Q_{\rm d} M/z F \rho \qquad [2]$$

where  $Q_d$  is the Ag electrodeposition charge, *M* and  $\rho$  are the atomic weight and density of Ag, respectively. The relationship between *A* and *V* will be used below for charac-



terizing the surface of Ag dendrites and for discussing the most likely growth mechanism related to Ag dendrite formation.

The Ag electrodeposition current transients run at  $E_d = 0.042$  V (Fig. 5) exhibit a rapid initial decay followed by a slower current increase. The latter fits a linear *I* vs. *t* dependence from t = 20 s upwards, *i.e.*, for values of  $Q_d$  greater than 1 mC ( $q_d = 25$  mC cm<sup>-2</sup>). On the other hand, the electrodeposition of Ag at v =

On the other hand, the electrodeposition of Ag at v = 0.001 V s<sup>-1</sup> shows a net cathodic limiting current (Fig. 6) lasting for a certain time. The extent of the current plateau depends on v, the potential scan rate. The limiting current region can be attributed to the induction period required for the beginning of the Ag dendritic growth (18). During this period formation of small 3D Ag crystals is observed. As v is increased a diffusion-controlled cathodic current peak preceding the cathodic current plateau is recorded. The height of the current peak,  $j_p$ , expressed as an apparent current density, fits a linear  $j_p$ , vs.  $v^{1/2}$  relationship (Fig. 7). When the limiting current region has been exceeded, the voltammogram shows a hysteresis which is related to the development of Ag dendrites.

By changing v and the cathodic switching potential systematically, the voltammograms demonstrate that the Ag anodic stripping of 3D Ag crystals formed during the induction period is related to the anodic peak found at 0.780 V (19). In this case, the anodic to cathodic voltammetric charge ratio is equal to one. Otherwise, the anodic stripping of Ag dendrites begins earlier than that of 3D Ag crystals, and it is not complete as it implies the simultaneous detachment of a part of the Ag deposit. Furthermore, the ratio between the amount of dendritic Ag to the amount of 3D Ag crystals changes with both v and the cathodic switching potential (19).

## Discussion

The SEM micrographs of Ag electrodeposits grown at  $E_d$ = 0.042 V exhibit dendritic patterns which behave as those expected of self-similar objects (2, 10). Let us first consider the A vs. V relationship for establishing the fractal geometry of the surface of Ag dendrites. For self-similar fractal objects the following equation holds (10)

$$A = \delta V^{D/3}$$
<sup>[3]</sup>



Fig. 6. Voltammograms of Ag electrodeposition and Ag anodic stripping on Pt. (a) v = 0.001 V s<sup>-1</sup>. (b) v = 0.005 V s<sup>-1</sup>.



Fig. 7. Plot of  $j_0$  vs.  $v^{1/2}$ , resulting from the voltammetric runs.

where  $\delta$  is a constant. Accordingly, the value of *D* is immediate from a linear log *A* vs. log *V* plot (Fig. 8). Thus, within the  $7.9 \times 10^{-8} \le V \le 8.0 \times 10^{-7}$  cm<sup>3</sup> range, the experimental log *A* vs. log *V* plot fits a straight line as predicted by Eq. [3] with a slope  $D = 2.50 \pm 0.03$ . This figure is consistent with the fractal surface of 3D rough metal electrodeposits (3, 5, 20).

We consider now the growth mechanism of Ag dendrites by relating the value of D to data derived from the Ag electrodeposition current transients and voltammetric runs. The initial current decay (Fig. 5) can be attributed to three factors, namely, the relaxation of the electrical double layer which occurs in a very short time, the relaxation of the diffusion layer related to the concentration profiles of reacting ions, and the nucleation and growth of small 3D Ag crystals prior to the initiation of the Ag dendritic growth.

When the decaying portion of the current transient is plotted as  $I vs. t^{-1/2}$ , the linear law predicted by the first term of the radial diffusion equation (21) for  $t \rightarrow 0$  is restricted to the 0.1 s < t < 12 s range (Fig. 5). The deviation resulting for t < 0.1 s can be attributed to specific kinetic

contributions of the initial nucleation and growth of small 3D Ag crystals (18). The radial diffusion equation is obeyed after the buildup of the diffusion layer around the spherical electrode stemming from the overlapping of the local diffusion layers formed around the 3D growing Ag nuclei (22). Henceforth, the rate of increase of the diffusion layer thickness around the spherical electrode becomes about the same or larger than the average rate of thickening of the Ag electrodeposit. Correspondingly, at this stage the increase of surface area due to the electrodeposition of Ag can still be disregarded. This situation is probably maintained up to the time (charge) where the minimum current value is observed (Fig. 5). During this period the current appears to be determined by two main resistance contributions, namely, one due to the diffusion field around the spherical electrode, and one related to the specific kinetics of the initial Ag 3D nucleation and growth.

For t > 30 s the current transient approaches a linear *I* vs. time relationship as it is expected for a linear growth of the Ag dendrites, under either a progressive nucleation and 1D growth or an instantaneous nucleation and 2D growth (23). The formation of Ag dendrites implies that the current at  $E_d$  exceeds the value expected for a radial diffusioncontrolled Ag electrodeposition on the substrate electrode. When such a situation is reached the size of Ag dendrites exceeds the thickness of the diffusion layer built up around the working electrode. As the radius of the dendrites is much smaller than the initial radius of the spherical electrode, and the diffusion layer thickness at the tips of the dendrites depends on the reciprocal of the tip radius, then, the rate of Ag+-ion diffusion towards the tips of the dendrites becomes extremely large. Therefore, the rate of Ag electrodeposition is determined by the rate of migration of ions in the solution.

The Ag electrodeposition/anodic stripping voltammograms obtained at different vs. become particularly relevant in understanding the kinetic aspects concerning the Ag growth modes, particularly the ion migration contribution. For this purpose voltammetric data have been extrapolated to  $V \rightarrow \infty$  in order to make them comparable to data derived from the potentiostatic current transients.

The voltammograms in the first stage of Ag electrodeposition leading to the formation of 3D Ag crystals, fit a linear  $j_p$  vs.  $v^{1/2}$  relationship including the origin (Fig. 7). Therefore, at this stage the Ag electrodeposition occurs under a diffusion-limited mechanism. Otherwise, the voltammograms allow one to estimate  $q_{dl}$ , the apparent charge density involved in the induction period for the Ag dendritic growth. The value of  $q_{dl}$  resulting from the extrapolation  $v \rightarrow \infty$  is 18 mC cm<sup>-2</sup> (Fig. 9). This figure agrees with the lowest charge density required to initiate the Ag dendritic growth in the potentiostatic current transient (Fig. 5). In the log V vs. log A plot (Fig. 8) the value  $q_{dl} = 18$ mC cm<sup>-2</sup> corresponds to log V = -7.1 (inner cutoff). Accordingly, below the inner cutoff no fractal behavior of the Ag electrodeposit surface is observed.





Fig. 9. Plot of  $Q_{di}$ , expressed as apparent charge density, vs. the reciprocal of v.

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The inner cutoff shown in Fig. 8 may be explained in terms of the initial volume of Ag electrodeposit required to start the Ag dendritic growth. It should be noted that when the induction period for the Ag dendritic growth has been exceeded, the voltammogram begins to display a net ohmic behavior (Fig. 6) which extends over a relatively long time period not only during the forward potential scan, but also into a part of the reverse scan. The greater the value of y, the lower the contribution of the ohmic effect in the voltammogram. These voltammetric results indicate that during the potential scan the kinetics of the Ag electrodeposition process has changed. The characteristics of the kinetic transition which also implies a transition in the Ag growth mode, depends on the experimental conditions. As the quasi-steady state conditions are approached  $(v \rightarrow 0)$  the slope of the voltammogram in the ohmic behavior range exhibits an apparent ohmic resistance of about  $7 \times 10^3 \Omega$ . This value can be accounted for by taking the density of growing dendrites equal to  $5 \times 10^{10}$ dendrites  $cm^{-2}$ , the radius of the growing dendrite tip to be estimated as  $10^{-7}$  cm (24), and the specific conductance of the solution to be equal to  $0.1 \ \Omega^{-1} \ \mathrm{cm}^{-1}$ .

In the Ag dendrite formation region, each dendrite behaves as an independent growing center in which a kinetic control by the migration of ions in the electric field built up around the dendrites is approached. The electric field may be determined principally by the resistance of the electrolyte solution, and therefore, the rate of the Ag electrodeposition should be controlled by those ionic species exhibiting the lowest mobility in the solution. Then, the sum of a parallel arrangement of resistances consisting of microtubes of solution interposed between the growing tips and the counterelectrode should approach the experimental resistance value. In fact, taking the current density of Ag dendritic growth as  $0.1 \text{ A cm}^{-2}$  tip area (24), and the dendrite density and average dendrite tip radius already mentioned, the experimental current density which is in the order of  $1 \text{ mA cm}^{-2}$  apparent electrode area is obtained.

According to the preceding discussion the surface development associated with the formation of the Ag dendrites can be explained as a random growth mechanism controlled by the electric field. It should be noted that growth mechanisms controlled by either an electric field or a diffusion limited process predict D = 1.67 for a 2D growth and D = 2.50 for a 3D growth (2, 3, 5).

Finally, we consider the second deviation (outer cutoff) resulting in the log V vs. log A plot (Fig. 8). The outer cutoff would reveal a trend of the system to an increase of the fractal dimension above 2.50 as if the Ag electrodeposits growth pattern for  $q_d > 200 \text{ mC cm}^{-2}$  is changing. This is not actually the case however, since Ag dendritic deposits of relatively large size present, apparently, the same growth pattern (Fig. 3). Otherwise, experiments show that at this stage the shape of the Ag growing deposit has changed, it becomes rather unstable and easily detachable from the substrate. Then, it is possible that in such circumstances the entire resistance of the electrochemical system is out of control and probably the initially uniform potential distribution around the growing Ag dendrites is no longer maintained. This is only a tentative attempt at explaining the appearance of the outer cutoff in Fig. 8.

In conclusion, despite the present limitations on evaluating the fractal dimension of rough surfaces, the method described in this paper appears as promising for application to a number of electrochemical systems.

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