

Nonlinear oscillations in electrochemical growth of Zn dendrites

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Electrochemical deposition can produce interesting patterns ranging from random fractals to orderly dendrites. We have studied the electrical signals due to the deposition of Zn ions in a cell with ZnSO₄ electrolyte. In the dendritic regime, the current (voltage) exhibits periodic oscillations with constant applied voltage (current). The frequency is proportional to the applied voltage V and the electrolyte concentration n . We relate this behavior to the side-branching nature of the dendrites.

Electrochemical deposition has been found to produce a variety of intriguing patterns.¹⁻⁷ Brady and Ball¹ and Matsushita *et al.*,² first studied the fractal character of the deposits and found them to be *similar* to those obtained by diffusion-limited aggregation (DLA).⁸ Subsequent studies by Grier *et al.*³ and Sawada *et al.*⁴ have found other patterns depending on the applied voltage V and the electrolyte concentration n . Both groups studied the deposition of Zn in a thin cylindrical cell with ZnSO₄ electrolyte and constructed a morphology diagram according to n and V . Fractal structures are observed at low values of n and V , and dendrites at higher values of n and V . Between them is a so-called "dense-radial"³ or "homogeneous"⁴ pattern which has a fractal character at short-length scales and a smooth outer envelope for the whole structure. Sawada *et al.* have found additional patterns labeled "open" and "stringy" at the highest values of n and V . The boundaries between these different regimes are quite vague and their locations are different for the two studies. The reason is not well understood.

To improve the understanding of this interesting problem, we have chosen to study the fluctuations (noise) of the associated electrical signals. We reason that since the growth of the deposit is determined by the current-density field at the cathode, it would be revealing to study how the total current fluctuates for different n - V conditions. In particular, different noise power spectra might be associated with different morphologies. This paper reports our main results: We find that whenever dendrites are formed, the cell current I exhibits periodic oscillations even though the applied voltage V is held constant. Similarly, V oscillates when a constant I is applied. For increasing orderliness of the dendrites, the magnitude of oscillation is larger (up to 10% of the average signal) and the coherence time is longer (up to several minutes). The frequency f ranges from below 1 Hz to above 50 Hz, and it is roughly proportional to the product nV . We also suggest an explanation for the phenomenon and discuss how the different patterns might be related.

Similar to Refs. 3 and 4, we use a thin cylindrical cell made of lucite, with a diameter of 9 cm and a thickness of 0.13 mm. ZnSO₄ solutions of different concentrations are used as electrolytes. A Zn foil lining the cylindrical wall serves as a ring anode and a 1-mm diameter Zn wire inserted along the cylinder's axis is used as a cathode (other electrodes were tried but the results were less reproducible). A small resistor in series with this two-electrode cell is used to monitor the deposition current. Either a constant V or a constant I can be applied to the circuit, and the conjugate quantity (I and V , respectively) is recorded digitally as a function of time. The typical sampling rate is 512 sec⁻¹. Power spectra ($|V(\omega)|^2$ or $|I(\omega)|^2$) are obtained by fast Fourier transform. After confirming that oscillations occur in both the constant- V and the constant- I experiments for a wide range of concentrations, we made systematic measurements using constant V .

Figures 1(a)-(d) show typical time domain data obtained for various n - V conditions. The current fluctuation δI is normalized by the estimated average cell current \bar{I} . Figure 1(a) shows the behavior for high values of nV . There are sharp downward *spikes* at frequencies well above 10 Hz but the coherence time is no more than a few cycles. The morphology of the deposit is similar to what Sawada *et al.* called "open." An example of such pattern is shown in Fig. 2(a) [see also, Fig. 3(a) in Ref. 4]. For lower values of nV , the waveform is more symmetrical, the frequency is lower, and the coherence time is much longer (can be of order 10 min), as seen in Fig. 1(b). The deposit pattern associated with such oscillations is characterized by long straight three-dimensional dendrites, as depicted by Fig. 2(b) (see also, Fig. 4 in Ref. 4 and Figs. 2(c) and 2(d) in Ref. 3). As one further lowers either n or V , the frequency continues to decrease and the waveform evolves to that shown in Fig. 1(c), which is characterized by sharp upward *spikes*. The deposit pattern is still dendritic as in Fig. 2(b). Upon further lowering of nV , the current fluctuations become more like random noise, as shown in Fig. 1(d). Correspondingly, the

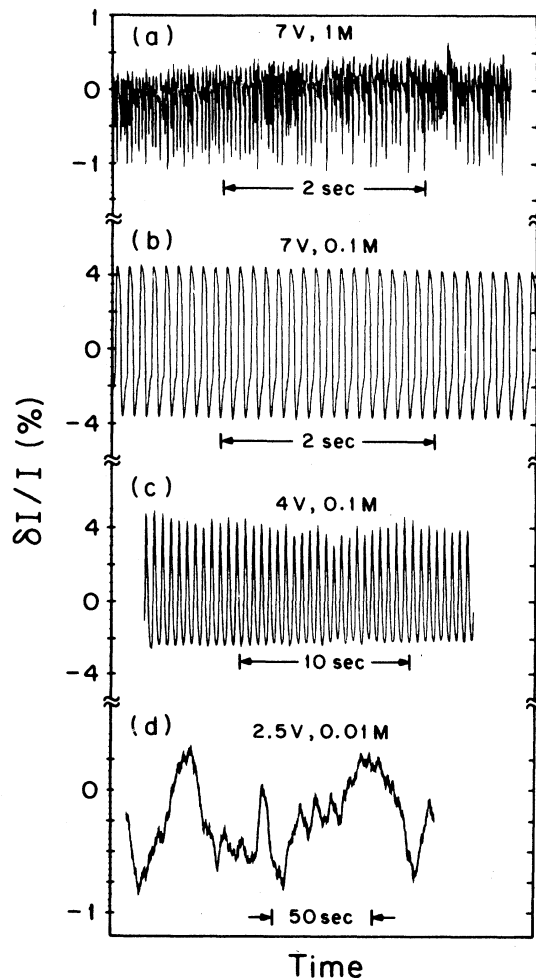


FIG. 1. Current oscillations observed at various concentrations and voltages, as noted. ΔI is the current fluctuation relative to a smoothly varying average current I .



FIG. 2. Patterns associated with (a) incoherent and (b) coherent oscillations. (a) corresponds to $n=0.5$ M, $V=5$ V, after 800 sec of growth and (b) corresponds to $n=0.05$ M, $V=10$ V, after 300 sec of growth.

deposit pattern evolves into what Sawada *et al.* called "homogeneous" (cf. Fig. 2 in Ref. 4) and Grier *et al.* called "fractal" and "dense radial" [cf. Figs. 2(a) and 2(b) in Ref. 3]. Isolated small dendrites are still observed in these structures [cf. Fig. 2(b) in Ref. 4].

Figure 3 shows how the power spectrum changes with nV . Figure 3(a) corresponds to the data in Fig. 1(a). It shows a broad band between 20 and 100 Hz. The sharp peaks come from the pulses in a particular time window, and they are not statistically significant. Figure 3(b) corresponds to the coherent oscillations in Figs. 1(b) and 1(c). The highly nonsinusoidal waveforms lead to a large number of observable harmonics. The (fundamental) oscillation frequency decreases as the structure grows, as depicted in Fig. 4. Figure 3(c) shows the power spectrum corresponding to Fig. 1(d). There is roughly an ω^{-2} decay, which is probably due to the fact that the average current \bar{I} fluctuates and contains a linear variation with t in an arbitrary time window where we perform the Fourier transform. This behavior has also been observed by Sawada.⁹

To investigate how the fundamental frequency f depends on n and V , we performed two series of measure-

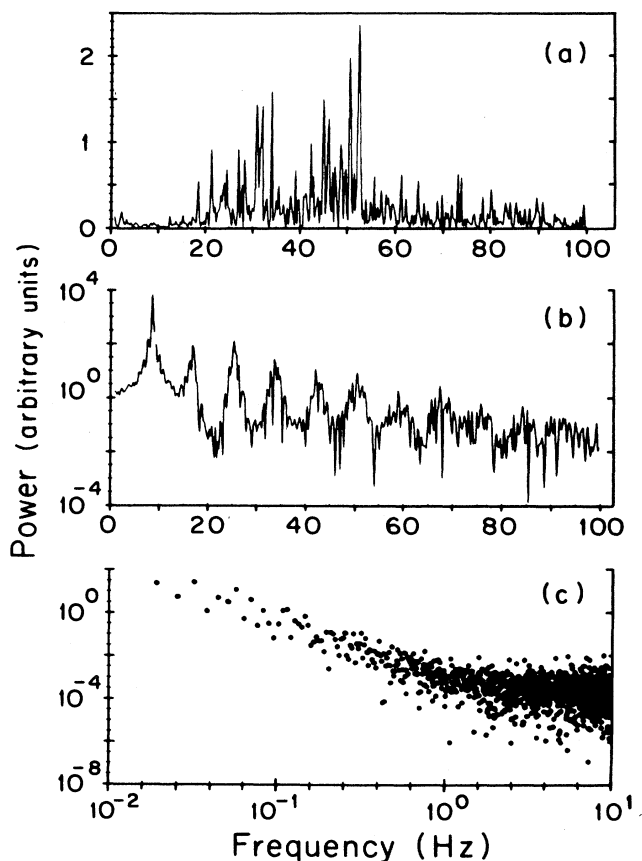


FIG. 3. Power spectra corresponding to Figs. 1(a), 1(b), and 1(d). Note the different horizontal and vertical scales.

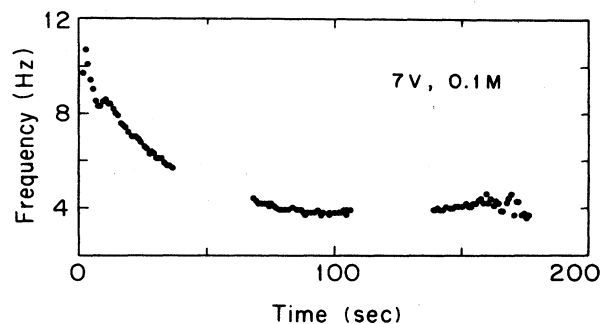


FIG. 4. Example of the decrease of oscillation frequency with time.

ments to probe all the patterns suggested by Refs. 3 and 4. The first series has $V=7$ V and n between 0.01 and 1 M. The second has $n=0.1$ M and V between 2 and 25 V. Oscillations are observed above 0.075 M in the first series, and above 3 V in the second series. Compared with the n - V diagram in Ref. 3, both values fall in the transitional region between "fractal" and "dendrite." In most of these measurements, the oscillations are coherent over many cycles, and the first few millimeters of growth is a ring of radially directed dendrites as shown in Fig. 2(b). Although f changes continuously with time, its range is quite reproducible. At later times, different global structures develop and large variations occur from run to run. Consequently, we use the frequencies during the first 3 min to characterize the dendritic growth for each set of n - V conditions. Figure 5 shows a log-log plot of f versus nV . The large vertical bars are due partly to the time dependence of f , and partly to the broad band behavior shown in Fig. 3(a). We note that both the constant- n and the constant- V data can be approximated by the same straight line with unity slope, which suggests that $f \propto nV$.

Since we have observed a strong correlation between the coherence time of the oscillations and the orderliness of the dendrites, it is reasonable to hypothesize that the oscillation frequency is the side-branching frequency. Ideally, one would like to confirm this hypothesis by direct visual observation. Unfortunately, this proved to be a formidable task. The charge transfer in one oscillation corresponds to about 10^{15} Zn atoms which have a volume of several cubic microns, and it is distributed over many dendrites. A microscope with enough magnifying power does not have a field of view large enough to locate the fast growing tips which advance with typical velocities of 1-100 $\mu\text{m}/\text{sec}$. Trying to determine the side-branching wavelength alone was impossible because the branches thicken as they grow and the smallest features at the micron level could not be preserved. A simple indirect test was to reverse the applied voltage to dissolve the dendrites. We found that they thinned out uniformly without current oscillation. This shows that the oscillation and the dendritic growth are related. Since we also know that there are no oscillations at low current density, the oscillations must be associated with a deposition reaction at high current density. We suggest a plausible ex-

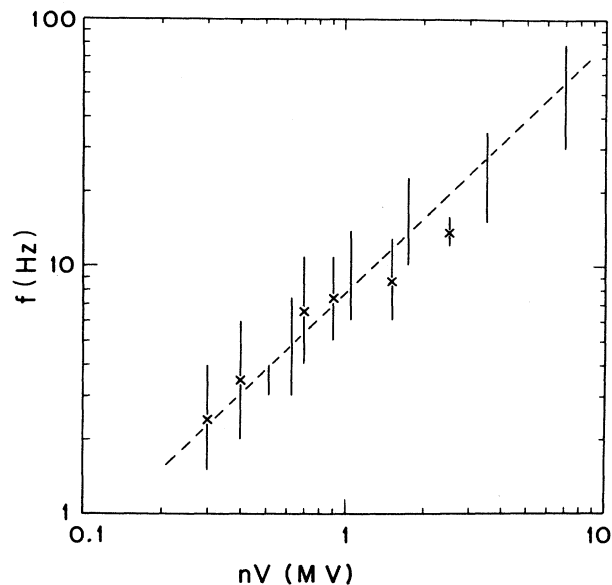


FIG. 5. Oscillation frequency vs the product nV . The dashed line indicates a linear dependence. \times indicates data obtained at fixed concentration $n=0.1$ M, the other data are obtained at fixed voltage $V=7$ V.

planation below.

We note that the electrode-electrolyte interface is a double layer in which the cations and the negatively charged electrode are separated by water molecules.¹⁰ A voltage V_s exists across this microscopic capacitor. In the absence of an applied voltage, the deposition-ionization reactions $\text{Zn}^{2+} + 2e \leftrightarrow \text{Zn}$ take place at equal rates with an exchange current density j_0 of order 1 mA/cm^2 or less. In the experiment, the applied voltage V brings cations to the cathode which increases the interfacial voltage V_s and causes a net deposition to occur. The cell is roughly *ohmic* in the limit of small V . However, because of the small diameter of the cathode, a typical cell current of 1 mA corresponds to a very large current density $J \approx 250 \text{mA}/\text{cm}^2$ at the cathode. The fact that $J \gg j_0$ means that a large amount of charge is piled up across the double layer and the interfacial voltage V_s is far above its equilibrium value. Under such conditions, it is likely that the double layer is driven into a *nonlinear* regime and a dielectric breakdown can deplete the charge. The repeated charging and discharging of the interfacial capacitor will thus lead to current oscillations. Since the resistance between different dendrites is very small, their oscillations can be phaselocked to give a large observable effect. In addition, one would expect each burst of discharge to nucleate a new set of side branches, thereby coupling the electrical oscillation to the side-branching morphology.

The above picture is consistent with all our observations: (i) The oscillations occur only for large deposition current density J or nV ; (ii) since the breakdown threshold should be roughly the same for all concentrations, the time to reach the threshold is inversely proportional to J ,

and hence $f \propto J \propto nV$; (iii) as the dendrites grow longer, more current flows into their sides and less to the tips, thus f decreases with time (Fig. 4); (iv) for very large J or nV , new dendrites are nucleated rapidly, the pattern becomes more disordered, and coherent oscillations cannot be sustained.

Implicit in the above discussion is the assertion that the driving field Δ for dendritic growth is the applied voltage, i.e., the system obeys the Laplace equation $\nabla^2\Phi=0$ where Φ is the Coulomb potential. Since the Laplace equation is equivalent to a diffusion equation with an infinite diffusion length,^{7,11} the problem is similar to the standard diffusion-controlled growth problems, such as solidifications from supercooled liquids or super-saturated solutions.¹¹ The difference is that in those problems, there is a "true" diffusion length l_D ($\equiv D/v$ where D is the diffusion constant and v the tip velocity) that characterizes the distance over which the driving field decays. In the electrochemical problem, however, the long-range nature of the Coulomb potential fixes an "effective" diffusion length l_ϕ equal to the distance between the electrodes, because that is the distance over which the potential falls off. In either case, the side-branching wavelength λ is proportional to $\sqrt{ld_0}$ where l is the diffusion length appropriate for the system and d_0 , the capillary length, is a material dependent constant of order 1 Å.¹¹ For electrochemical growth, $l=l_\phi$ is of order 10^8 Å, so λ should be of order 1 μm. A side branching frequency f in the range of 1–100 Hz would imply a tip velocity in the range 1–100 μm/sec, consistent with what we observed. Furthermore, since $v \propto J \propto nV$, we should expect the $f \propto nV$ behavior shown in Fig. 5. It is interesting to note that in those problems with a true diffusive length, $l=l_D=D/v$ implies $\lambda \propto 1/\sqrt{v}$ and $f \propto v^{3/2}$. The three-dimensional Ivantsov formula¹¹ predicts that $\Delta \propto p \log p \approx p \equiv \rho/l_D$ in the limit of small Peclet number p , where ρ ($\propto \lambda$) is the tip radius, and hence $\Delta \propto \sqrt{v}$ and $f \propto \Delta^3$. This is in contrast to the $f \propto \Delta$ behavior of electrodeposition in the dendritic regime.¹²

While the above discussion can explain the dendritic growth behavior, we may wonder why other patterns such as the DLA and the "dense-radial" structures are also observed. The reason, we believe, is that the equation $\nabla^2\Phi=0$ only describes one limit of the problem where true diffusion effects can be ignored. It is well known that because the cation and anion concentrations (n_\pm) in the double layer are nonuniform, the flow of an electric current alters the concentration gradients (∇n_\pm) and gives rise to diffusion currents. If the electrode surface has a feature of size R , the resulting n_\pm would vary exponentially over the distance R , making the electrode-electrolyte interface much thicker than the original double layer.¹³ The relaxation time τ needed to develop this diffusive layer is just the diffusion time R^2/D .¹³ Howev-

er, since the electrode surface is continuously growing, it may not allow enough time for the concentrations to equilibrate. Specifically, if the surface grows a feature of size R in time t , n_\pm can relax around it only if $\tau \ll t$. Since $R=vt$, this implies $R \ll D/v \equiv l_D$. Hence, for any growth velocity v , l_D defines a crossover length scale: true diffusion is relevant for structures smaller than l_D but not for those larger than l_D . For the former regime, Kessler *et al.*¹¹ and Sander⁷ have shown that the system is described by two Laplace equations $\nabla^2\mu_\pm=0$, where $\mu_\pm=k_B T \ln n_\pm + q_\pm \Phi$ are the chemical potentials of the cations and anions, and q_\pm are their respective charges. The $\ln n_\pm$ term gives the diffusion currents. In the latter regime, the diffusive layer is out of equilibrium and, therefore, has associated with it a higher free energy. This is equivalent to having a high effective surface tension between the electrode and the electrolyte. In the bulk of the cell, away from the diffusive layer, the system is simply described by $\nabla^2\Phi=0$. An important difference between the two regimes is the effect of the diffusive layer. Clearly, when the concentration gradient is spread out over a distance as large or larger than the surface features, the interfacial energy associated with the growth is small and insensitive to the crystalline anisotropy. This would lead to DLA-like patterns. Conversely, if the concentration gradient does not have enough time to equilibrate and spread out, the interfacial energy becomes larger and more sensitive to the anisotropy. In this case, the growth pattern should be dendritic.¹¹ In other words, we expect the $\nabla^2\mu_\pm=0$ regime to have a fractal structure and the $\nabla^2\Phi=0$ regime to have a dendritic structure. For high enough tip velocity v , l_D becomes comparable to the tip radius, and only dendritic growth can take place. This expectation is in agreement with the recent observations by Sander *et al.*¹⁴ For smaller values of v , we would expect a crossover between the $\nabla^2\mu_\pm=0$ problem and the $\nabla^2\Phi=0$ problem, characterized by the length l_D . This may indeed explain the "dense-radial" pattern because, according to Sawada *et al.*,⁴ fractal behavior in such a pattern occurs below a length scale (they called δ) which increases for decreasing n . So we may identify this length as l_D . In addition, the smooth outer envelope of the "dense-radial" pattern may be just the "solid" phase in the $\nabla^2\Phi=0$ problem. (Grier *et al.*³ have also suggested that the finite resistance of the deposit helps stabilize the smooth envelope.)

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