Fingering Instability of Gravity Currents in Thin-Layer Electrochemical Deposition

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A hydrodynamic instability has been observed in quasi-two-dimensional electrochemical deposition experiments in which the electrochemical cell is inclined with respect to the horizontal. Gravity-driven flows generated at both anode and cathode become unstable and form a pattern of fingers when the anode is uphill from the cathode. I report measurements of the onset wavelength and development of the pattern, and discuss ways in which the growth of the metal aggregate at the cathode interacts with the flow and its instability.

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Growth and aggregation in nonequilibrium systems is a subject of substantial fundamental and practical interest [1]. In particular, the growth of ramified aggregates by electrochemical deposition (ECD) in quasi-two-dimensional geometries has been studied extensively in the last decade [2–22]. Much of the initial interest in this system was due to the analogy between ECD, under appropriate experimental conditions, and the diffusion-limited aggregation growth model [23]. The aggregates grown in ECD experiments are much more diverse in form than predicted by the simple diffusion-limited aggregation model, however, with many different morphologies and morphological transitions having been observed under different experimental conditions [3–10].

ECD experiments are ostensibly simple—two thin electrodes are sandwiched between transparent plates, and the space between them filled with an electrolyte. When a current is passed through the cell, a branched metal aggregate is deposited on the cathode. In fact, this simplicity is deceptive, as many electrochemical and electrohydrodynamic processes affect the morphology of the aggregate [9–14], including convective flows driven by the electric field [15–19] and by buoyancy [19–22].

Buoyancy-driven convective flows arise in ECD experiments due to density variations in the electrolyte which result from ion concentration gradients [19–22]. When a current flows, metal ions come out of solution at the cathode, joining the aggregate. To maintain electrical neutrality, anions migrate away from the cathode with a drift speed equal to the growth speed of the aggregate [7,12]. The fluid near the cathode thus has a lower ion concentration than the bulk electrolyte, and so is less dense. At the anode, cations come into solution, and neutrality is maintained by the arrival of anions migrating in the applied field. Thus near the anode, the ion concentration and the density are higher than in the bulk. These density variations result in "gravity currents" [24] at both electrodes [19–22]. More-dense fluid spreads away from the anode, flowing under the less-dense bulk electrolyte, while lighter fluid flows away from the cathode, over the bulk fluid.

Here I report results from experiments in which an ECD cell was inclined at an angle α with respect to the horizontal, so that one electrode was higher than the other. The gravity-driven flows near both electrodes become unstable and break up into a pattern of fingers if gravity reinforces the natural convective flow. I also show how the aggregate growing at the cathode influences the flow and its instability there, and, conversely, how the presence of the flow influences the growth, through its role in ion transport through the cell.

The ECD cells used had parallel copper electrodes, 0.25 mm thick, separated by 23 mm; similar phenomena were also observed in thinner cells. The electrodes were clamped between two 5.08 cm square glass plates, 5 mm thick. Aqueous solutions of $CuSO_4$ were used as electrolyte. Experiments were performed at constant applied voltage V. The gravity currents were observed using shadowgraphy [22,25]. Collimated light passing through the cell is focused or defocused by refractive index variations in the electrolyte, leading to variations in intensity when the beam is imaged with a charge coupled device video camera. The shadowgraph intensity is proportional to $-\nabla_h^2\langle n\rangle$, the negative Laplacian of the refractive index $n(\mathbf{x})$ in the plane of the cell, averaged over the cell thickness. The shadowgraph data were recorded on video tape. The cell inclination angle α was varied by tipping the entire apparatus; $\alpha > 0$ corresponds to the anode being uphill of the cathode.

Figure 1 shows shadowgraph images recorded during a run with $\alpha = +5.8°$; i.e., the anode (the white line near the top of the images) lies above the cathode (the dark line near the bottom). At the cathode, the growing aggregate complicates the situation, so for now we focus on the flow originating at the anode. When the cell voltage is turned on, higher-density fluid forms and flows away from the anode as described above. After some time, the initially straight front of the gravity current deforms and an approximately periodic pattern of fingers develops. Concurrently, a cross-slope modulation in the shadowgraph intensity develops, indicating a corresponding variation in the thickness of the fluid layers. The finger formation is

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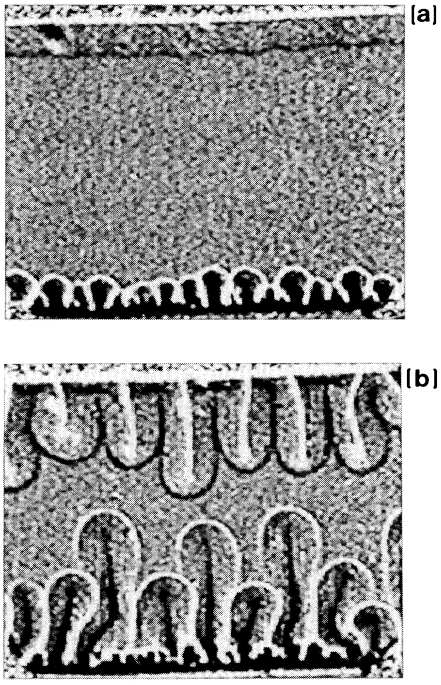

FIG. 1. Shadowgraph images showing the development of the fingering instability in a run using $0.1M$ $CuSO_4$, $V = 10$ V, and $\alpha = 5.8°$. The electrodes are 23.0 mm apart, with the uphill anode at the top of the image. (a) At time $t = 138$ s after the start of the run, a slight periodic variation in the position of the front of the flow originating at the anode has developed. At the cathode, the flow has formed into envelopes around the branches of the growing aggregate. (b) At $t = 331$ s, there are fully developed fingers at both electrodes.

shown at an early stage in Fig. 1(a), and when the fingers are fully developed in Fig. 1(b). The bright lines running down the center of the anode fingers correspond to regions where $\nabla_h^2\langle n\rangle < 0$, indicating that the thickness of the lower, more-dense layer is a maximum there. Similarly, the thickness of that layer is a minimum along the dark lines between the anode fingers. The pattern coarsens as it develops: Some fingers die and the average wavelength increases with time. Eventually, the two sets of fingers meet and interdigitate, with those coming uphill from the cathode sliding in between and above those flowing downhill from the anode.

Experiments were also performed in which the motion of 1 μm diameter latex spheres added to the electrolyte was observed under a microscope. When $\alpha > 0$, flow was observed which, as a function of position along the electrodes, was alternately towards and away from the electrode. The flow became stronger as α was increased.

The formation of fingers was not observed when $\alpha \leq 0$, i.e., when the cell was level, or when the cathode was above the anode. Instead, the regions of high and low concentration spread away from the electrodes uniformly, with their fronts remaining straight. Similarly, the alternating regions of inflow and outflow were not observed under the microscope for $\alpha \leq 0$. Rather, a steady outflowing layer was observed above (at the cathode) or below (at the anode) a steady inflowing layer.

Figure 2 shows the average wavelength λ of the finger pattern at the anode, at the onset of the instability, as a function of $\sin\alpha$. The pattern is not perfectly periodic, and the error bars give the standard deviation over the pattern. The data in Fig. 2 are from runs with $V = 10$ V, with $0.1M$ $CuSO_4$ as the electrolyte. The variation of λ is well described by a power law; a least squares fit gives $\lambda = (0.76 \pm 0.08)(\sin\alpha)^{-0.55\pm0.03}$. The wavelength is independent of V, as illustrated in the inset to Fig. 2, and showed a very weak decrease as the electrolyte concentration was decreased to $0.01M$.

The variations in intensity across the shadowgraph image become more pronounced with time as the fingers develop, indicating that the variations in thickness of the fluid layers are increasing in magnitude. This is illustrated in Fig. 3. Figure 3(a) shows the shadowgraph intensity as a function of position in the direction parallel to the anode, at three different times, for the run illustrated in Fig. 1. The intensity was averaged over roughly ten rows of pixels just behind the finger tips. Figure 3(b) illustrates the development of a strong peak, and its odd harmonics, in the corresponding fast Fourier transform (FFT) power spectra. The amplitude of the fundamental peak in the power spectrum is plotted against time in a semilogarithmic plot in Fig. 3(c). The peak amplitude increases exponentially over a range of times as the finger pattern develops, as would be expected if this quantity could be considered as the growing amplitude of a linearly unstable mode. At later times it saturates and then decreases with time.

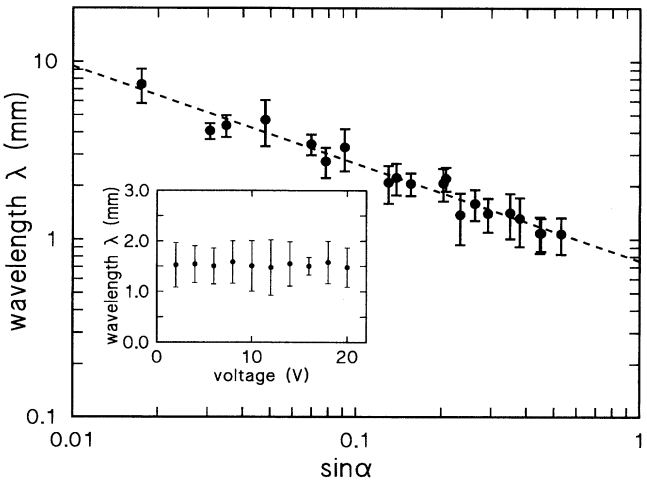

FIG. 2. Wavelength at onset of the anode finger pattern, as a function of $\sin\alpha$, for 0.1M $CuSO_4$ and $V = 10$ V. The dashed line is a fit to a power law giving $\lambda = (0.76 \pm 0.08)(\sin\alpha)^{0.55\pm0.03}$. The inset shows the onset wavelength as a function of V for the same electrolyte at $\alpha = 13.5°$.

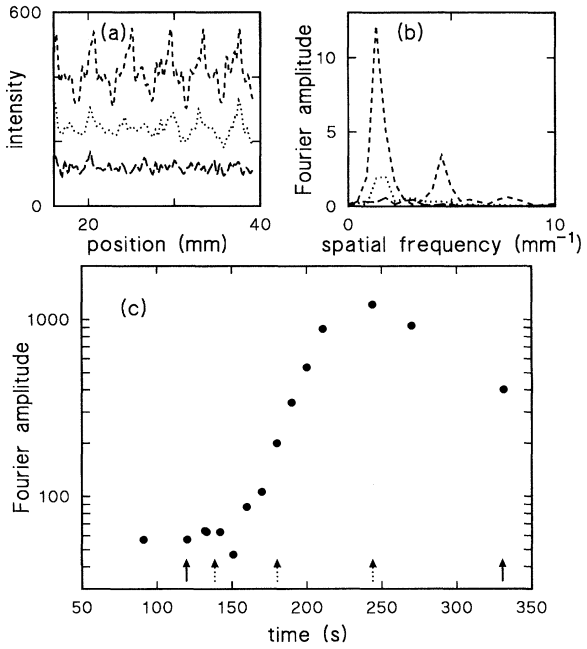

FIG. 3. (a) Shadowgraph intensity, in arbitrary units, as a function of cross-slope position, measured behind the tips of the fingers of the anode flow. The data are from the same run as shown in Fig. 1, at $t = 120$ (bottom), 180 (middle), and 244 s (top), and have been offset vertically. (b) FFT power spectra, also in arbitrary units, for the three sets of intensity data shown in (a). (c) The peak value of the Fourier power spectrum as a function of time. Dashed arrows indicate the times corresponding to the images in Fig. 1; solid arrows the times corresponding to the data shown in (a) and (b).

Fingering instabilities occur at moving fronts in many other systems. For example, fingering driven by surface tension gradients [26] and by gravity [27,28], and viscous fingering due to the Saffman-Taylor instability [29] have all been studied recently. The fluid properties and the phenomenology of the instability observed here suggest that it is not closely related to any of these. Garik *et al.* have observed an instability at the driven interface between two miscible liquids in a horizontal cell, which they attributed to the Marangoni effect [30]. The fluid properties in the present work are similar to those in the work of Garik *et al.*, but the behavior and physical appearance of the instability are quite different. Diffusion of concentration between the higher- and lower-concentration regions is significant in the present system and may play an important role in the observed instability, as may the effective surface tension between them [31].

The flow and instability described above occur here in the presence of the growth taking place at the cathode, and the flow and growth interact with each other. The flow contributes to ion transport in the cell and so can modify the electrochemistry near both electrodes. Conversely, the presence of the electrodeposit affects the flow and instability near the cathode. Three separate effects due to these interactions have been observed.

First, the growth velocity of the cathode aggregate decreases substantially as α is increased, although the current through the cell remains the same. This may be due to a modification of the electrochemical environment near the cathode resulting from the transport of ions by the gravity-driven flow. As the flow becomes stronger, the reduction of metal cations contributes less, and other cathode reactions [10] contribute more to the total current.

The second effect is a morphology transition which occurs when the fingers flowing down from the anode meet the aggregate growing up from the cathode. Since there is very little growth at higher α, this transition is only observable at rather low inclination angles. It is illustrated in Fig. 4; the transition closest to the anode is the one of concern here [32]. This transition has been observed previously in horizontal cells [10,19,22], in which case the flow has a smooth front and the morphology change appears at a fixed distance from the anode. In tilted cells, in which the fingering instability occurs, the flow meets the aggregate at different points across the cell, and so the transition line has a scalloped appearance. This transition can again be attributed to a change in electrochemical environment at the growth front that occurs when the high-concentration flow meets the aggregate.

Finally, the growth can also affect the flow and its instability. At large α, there is little growth on the cathode, and the instability develops there in the same way as at the anode. However, at low values of α, at which the growth is substantial, the region of low

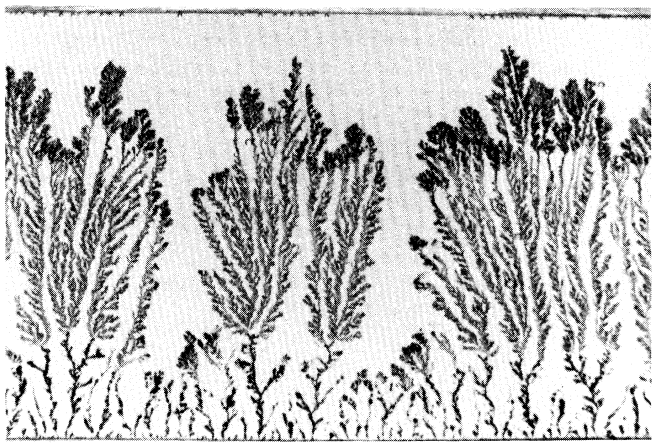

FIG. 4. Copper aggregate grown at 10 V from 0.1M $CuSO_4$ at $\alpha = 5.1°$. A morphology change occurs about one-third of the cell width away from the anode, where the aggregate meets the flow originating at the anode. The growth becomes finer and more dense and appears darker in the figure. The position at which the change occurs varies across the aggregate, reflecting the shape of the fingers making up the flow.

concentration hugs the front of the aggregate. No currents spreading away from the growth, and no fingers, are observed. At intermediate angles, there is less growth. Fingers do appear at the cathode, but not in a regular periodic pattern; the initial formation and spacing of the fingers is governed by the location of branches of the aggregate. In this regime fingers can form in two ways. A gravity current front can form as an envelope around a branch, or group of branches, of the aggregate [22] then spread away from the branch and grow into a finger. The fingers at the cathode in Fig. 1 formed in this way. Alternatively, a region of low concentration between two branches, resulting from electroconvective flow [15], can grow out from the aggregate to form a finger. Both cases lead to fingers forming independently, rather than the formation of a periodic pattern via an instability of the gravity current front. In both cases, as the fingers grow, their position can be pinned by the branches of the aggregate, and coarsening of the pattern does not occur as it does at the anode.

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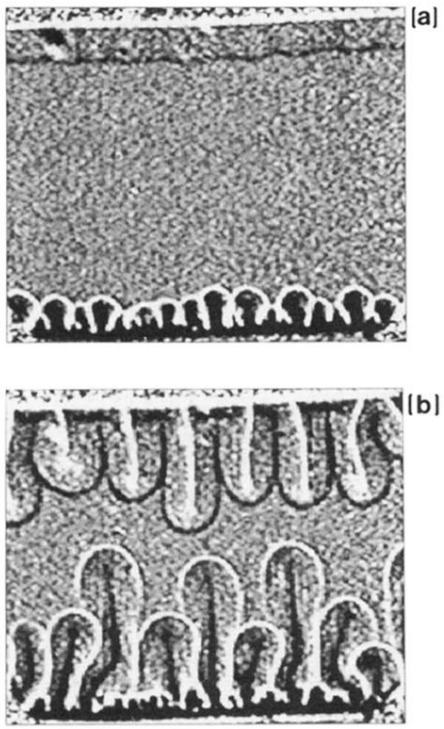
[32] Two morphology transitions are visible in Fig. 4. That closer to the cathode is due to the migration of a front of increased H^+ concentration from the anode [7,9,10,19]. This front was not visible in our shadowgraphs.



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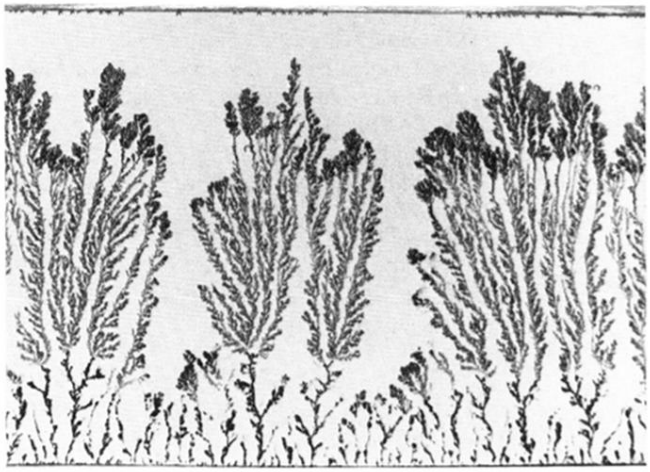

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