VOLUME 65, NUMBER 24 PHYSICAL REVIEW LETTERS 10 DECEMBER 1990

Interfacial Velocity in Electrochemical Deposition and the Hecker Transition

J. R. Melrose,(1) D. B. Hibbert,(2) and R. C. Ball(3)
(1)*Department of Chemistry, Royal Holloway and Bedford New College, Egham Surrey TW20 0EX, United Kingdom*
(2)*Department of Analytical Chemistry, The University of New South Wales, P.O. Box 1, Kensington, Sydney 2033, Australia*
(3)*Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, United Kingdom*

(Received 7 May 1990)

In the thin-cell electrochemical deposition of metals the interfacial velocity is shown, in the regime dominated by migration transport, to match the drift velocity of the *counterion.* The interfacial velocity is predicted to be independent of concentration to leading order and the deposit density is related to that of the electrolyte by the transport number of the counterion. Hecker-like pattern transitions occur when an acid front migrating in from the anode meets the deposit. The deposit radius at the transition is predicted to depend only on the ratio of ion mobilities.

PACS numbers: 68.70.+w, 05.70.Ln, 64.70.Kb, 81.30.−t

The principles which govern the wide variety of tree patterns formed by growth[1-6] under conditions beyond those of diffusion-limited aggregation[5] are at present unclear. Contemporary models[6] of solidification under full dynamic simulation and weak anisotropy evolve at long times a dense branching pattern with a constant interfacial velocity selected by the morphology. In this work we will argue, and support by experiment, that the interfacial velocity of the dense radial pattern deposited in the migration limit of an electrochemical deposition (ECD) system is determined by the transport of the nondepositing anions. This mechanism is absent from contemporary models.[6] This new principle stems from the existence in the system of two transporting ionic species coupled by electroneutrality, but where only one species has a source and/or sink at the growing surface. We use this principle along with additional information to explain the mystery of the universal location of a recently reported ECD pattern transition.[7]

Deposition experiments[1-5] were performed by two of us in a thin film of electrolyte of thickness δ sandwiched between two Plexiglas disks[1] and confined inside a metal-ring anode of inner radius L_A and thickness δ, where $L_A = 3.0$ cm and $\delta = 0.25 \pm 0.02$ mm. Deposition was made onto the tip of a wire cathode inserted central to the anode. At high voltages (10–25 V) the system was dominated by migration transport, and a dense radial pattern[1,4,8] was deposited. Figure 1 shows an example.

We first propose an expression for the interfacial velocity of a dense radial deposit in the migration limit.

Consider deposition of a metal ion M of charge z_+e from a binary $(M_{v+}A_{v-})$ electrolyte of concentration C_0 with an electrochemically inactive anion of charge $-z_-e$. The electric current I in the electrolyte is carried by both ion species.[9,10] Concentration boundary layers around electrodeposits have been reported previously.[3,4,11] For dense radial deposits the concentration of cations within the deposit interior is negligible and a sharp (over <0.1 mm) concentration profile exists across a boundary layer at the deposit interface.[4] By electroneutrality and in the assumed absence of any other cation, anions must also be absent from the interior of the deposit. The key feature to appreciate is that while a net flow of depositing cations can be taken up by the deposit, there is no such source or sink for the anions. A region of depletion of anions just in advance of the cathodic interface recedes at their ionic drift. At the anode, anions and dissolved cations concentrate in a thin layer. For a stationary electrode the depletion at the cathode is usually balanced by diffusion assisted by convection,[9] but for our cells we propose that this is effective over a limited range and that in the migration limit the interface of the deposit is slaved to the drift of the anions.

We assume that the deposit envelope is circular, of radius L, moves with velocity $V_d(L)$, and that, to a good approximation, a step-function ion-concentration profile migrates in front of the interface at a velocity $V_-(L)$. We propose that

$$V_d(L) = V_-(L) = u_-E(L)\,, \tag{1}$$

where $E(L)$ is the electric field at the electrolyte side of the concentration profile and u_- is the ionic mobility of the anion. The current in the cell $I(L)$ is related to $E(L)$ by

$$I(L) = 2\pi\delta L C_0 F(z_+v_+u_+ + z_-v_-u_-)E(L)\,, \tag{2}$$

where u_+ is the cation mobility, F is the Faraday constant, and a small current due to hydrogen ions is neglected. Substitution of $E(L)$ from (2) into (1) and using $z_+v_+ = z_-v_-$ gives[12]

$$V_d(L) = \frac{dL}{dt} = \frac{t_-I(L)}{2\pi\delta L C_0 F z_+v_+}\,, \tag{3}$$

where $t_- = u_-/(u_+ + u_-)$ is called the transport number of the anion.[9] Consider mass balance of cations across the interface. For a deposit of radius L the mass in mol, M, of deposit varies with the disk area A as

$$V_d(L)\frac{dM}{dA} = [V_+(L) + V_d(L)]v_+C_0\delta\,, \tag{4}$$

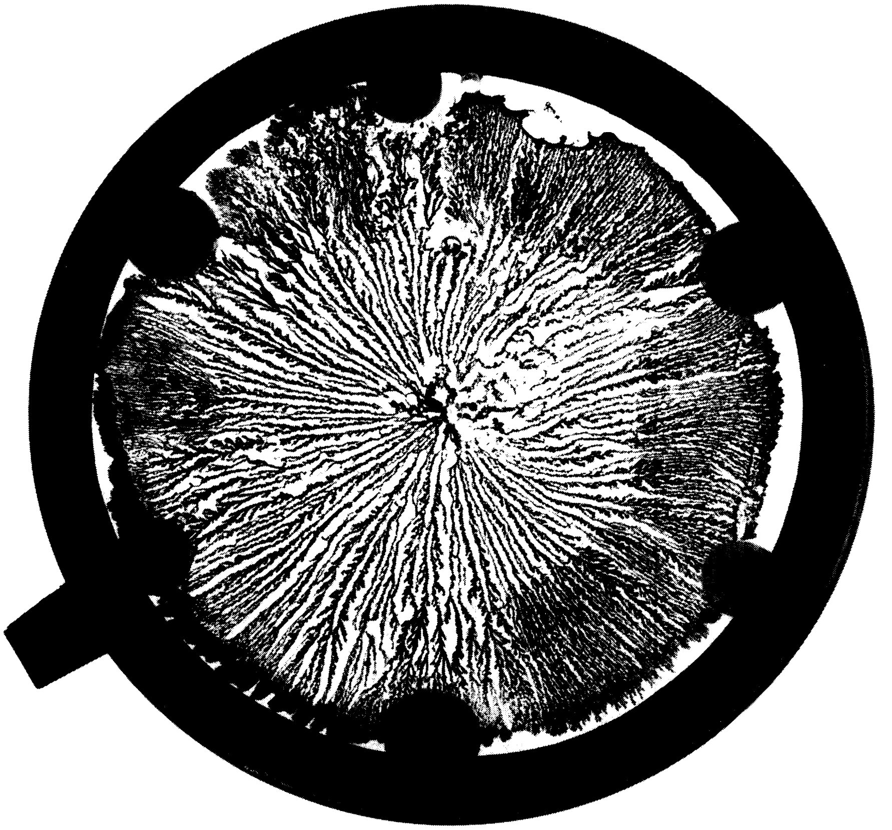

FIG. 1. A deposit within a thin cell of radius 3.0 cm, at an applied potential of 25 V from a 0.05-moldm^{-3} $CuSO_4$ solution. From 12 to 5 o'clock a distinct branching (Hecker) transition is observed at $0.5L_A$. From 4 to 9 o'clock the third transition mentioned in the text is evident at $0.9L_A$.

where $V_+(L)$ is the velocity of the cation just in advance of the interface. Substituting the result $V_d(L)=V_-(L)$ gives $dM/dA=v_+C_0\delta/t_-$; the deposit density is enhanced over that of the electrolyte by the factor $1/t_-$.

An Ohmic model[4,8,11,12] sets the variation of $I(L)$ with L. The cell is modeled as a cathode tip of radius L_0 and resistance R_0, an annulus containing the deposit of inner radius L_0 and outer radius L, an annulus of electrolyte approximated at concentration C_0 of inner radius L and outer radius L_A, and $\eta(L)$ denotes the sum of the voltage drops across the two electrolyte/electrode interfaces. For a potential of V volts applied anode to cathode one finds

$$I(L)=\frac{V-\eta(L)}{(R_c-R_0)[1+R_0/(R_c-R_0)+(\beta-1)\ln(L/L_0)/\ln(L_A/L_0)]}, \tag{5}$$

where R_c is the cell resistance when $L=L_0$ (this is used to substitute for the resistivity of the electrolyte) and β is a ratio of resistivities—that of the region containing the deposit to that of the electrolyte. At the electrode/electrolyte interfaces, the current must simultaneously obey the Butler-Volmer equation of electrode kinetics;[9] in its Tafel regime this latter equation is an exponential relation between I and η. This simultaneous relation allows in (5) the approximation $\eta(L)\cong$const. The interfacial velocity $V_d(L)$ is determined by the substitution of (5) into (3). Although $V_d(L)$ is in principle nonlinear, it is in practice close to constant across much of the cell.[7] With $1/R_c\propto C_0[1+O(C_0^{1/2})]$ (Refs. 9 and 13) the leading-order dependence of (5) on C_0 cancels the C_0 in the denominator of (3). With the assumption of a weak dependence of β on C_0, $V_d(L)$ is predicted, as found in experiment,[7] to be only weakly dependent on C_0.

To test (3) values of $I(L)$ and $L(t)$ were measured for a variety of copper electrolytes. The $I(L)$ results were fitted by (5) by fixing η, using the experimental R_c, and varying β; see Fig. 2. The $I(L)/L$ curve was then substituted into (3) and (3) was numerically integrated to predict $L(t)$. Figure 3 compares with experiment predictions based on the fits of Fig. 2; also shown are predictions for depositions from 0.1 moldm^{-3} $CuBr_2$ and $Cu(CH_3COO)_2$. Ionic mobilities vary with concentration. We show the predictions of (3) with t_- calculated with both infinite-dilution mobilities and mobilities concentration corrected by using the Debye-Huckel-Onsager

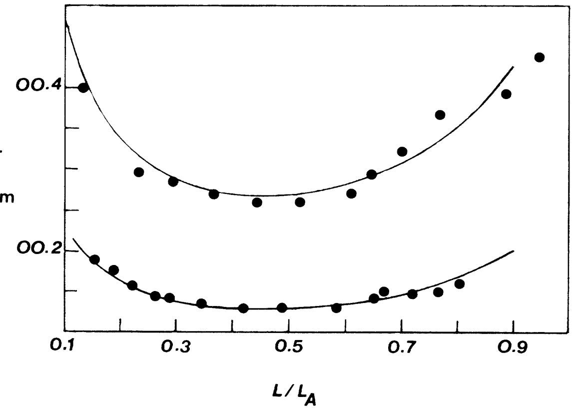

FIG. 2. $I(L)/L$ vs L/L_A, where $I(L)$ is the total current flowing through the cell in the presence of a deposit of radius L. Experimental results (●) are shown for deposition from a 0.1-moldm^{-3} $CuSO_4$ solution at 25 V (upper curve) and 15 V (lower curve). The data are fitted (solid lines) by Eq. (5); typical fit parameters lie in the range 2 kΩ $< R_c <$ 3 kΩ, 0.75 V $< \eta <$ 1.0 V, $0.01 < \beta < 0.1$, $R_0 \cong 10$ Ω, and $L_0 \cong 0.1$ cm.

expression.[13] The predictions appear in good agreement with the experiment; although the Debye-Huckel-Onsager expression at 0.1 moldm^{-3} is not accurate—it overestimates variations in transport numbers.

We now discuss the Hecker transition. This transition (see Fig. 1) involves an increase in branching rate and usually, with copper, a change in deposit color. For $CuSO_4$ and $ZnSO_4$ electrolytes, it occurs at a radius within $(0.4\text{–}0.5)L_A$, universal to a range of applied voltages and electrolyte concentrations.[7] Ourselves and others[14] believe it is due to the confinement of the electrolyte within the cell. A thin cell in which the anode was located externally in a bath of the solution did not show a transition.

We performed experiments with the indicator methyl-orange, which changes color from 90% yellow to 90% red in the pH range 4.4–3.1, added to a 0.1-moldm^{-3} $CuSO_4$ electrolyte. This gave an orange solution consistent with[15] $p\text{H} \cong 4.0$. As the deposit grew out from the cathode we observed a front of red color ending at a sharp red-orange boundary contracting in from the anode. The Hecker transition was, to the eye, exactly coincident with the meeting of the red front and growing interface. The effect was also observed with the indicator bromophenol blue. Addition of the indicator methyl-violet (violet to blue-green, pH 3.0–1.5) showed a Hecker transition prior to any front being observed.

These observations establish that the Hecker transition is due to a chemical front meeting the deposit. We conjecture that the relevant front consists of hydrogen ions at pH 2–3 migrating within the electrolyte[16] (we also injected in advance of a deposit the electrolyte at concentration C_0 but with H_2SO_4 added to pH 2.5; this caused a branching transition). The color changes at transition are explained as the dissolution of black copper oxide by the acid front.

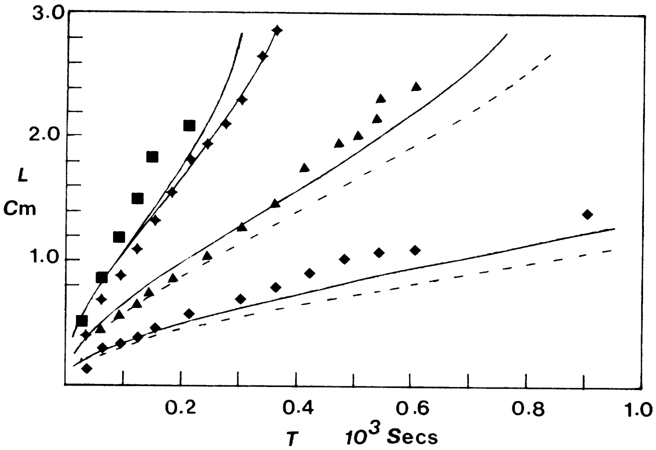

FIG. 3. Prediction (lines) of the growth radius L vs time using the fits for $I(L)/L$ and integrating Eq. (3), compared with experiment (symbols). Results (diamonds) are for 0.1 moldm^{-3} $Cu(CH_3COO)_2$ at 20 V. The dashed curve uses $t_- = 0.433$ calculated from infinite-dilution mobilities; the solid curve uses $t_- = 0.508$ calculated from concentration-corrected mobilities using the Onsager expression. Results (triangles) are for 0.1 moldm^{-3} $CuSO_4$ at 15 V, dashed curve $t_- = 0.598$ (infinite dilution), solid curve $t_- = 0.688$ (concentration corrected). Results (stars) are for 0.1 moldm^{-3} $CuSO_4$ at 25 V, solid curve $t_- = 0.688$ (concentration corrected). Results (squares) are for 0.1 moldm^{-3} $CuBr_2$ at 25 V, top solid curve $t_- = 0.697$ (concentration corrected).

A pH of 4.0 for 0.1 moldm^{-3} $CuSO_4$ is generated by hydrolysis.[15] The H^+ ions of the front are likely to be initiated in the very-high-concentration electrolyte at the anode by this same process.

The acid front advances with the drift of the H^+ ions and the deposit with that of the anions. By use of (2) and (3) we can predict their meeting. Consider at some time the deposit of radius L and the acid front a distance S in from the anode; substituting (2) for the fields at L and S one finds

$$\frac{dL}{dt} = \frac{u_- I(L)}{\delta 2\pi\sigma L}, \quad \frac{dS}{dt} = \frac{u_H I(L)}{\delta 2\pi\sigma(L_A - S)}, \tag{6}$$

where σ is the conductivity of the electrolyte and u_H is the mobility of the hydrogen ion. Equations (6) may be integrated and solved for the radius $L_H = L = L_A - S$ at which the front and deposit meet. We find the universal result

$$L_H = L_A/\sqrt{1+\gamma}, \tag{7}$$

where $\gamma = u_H/u_-$. In the case of the sulfate anion, infinite-dilution mobilities give $\gamma \cong 4$ predicting $L_H = 0.45 L_A$, in close agreement with earlier experiment[7] for both $ZnSO_4$ and $CuSO_4$. Again concentration effects on the u's will alter γ; we find $L_H \cong 0.5 L_A$ and $\gamma \cong 3$.

We speculate for the copper system that three chemical fronts (or layers) exist, that the acid front is the first, and that the other fronts are of electrolyte at concentration $C' > C_0$. With methyl-violet added, a second lower-pH acid front is detected and meets the deposit at $L_2 \cong 0.8 L_A$ [Eq. (7) predicts that $Cu(H_2O)_4{}^{2+}$ migrating from the anode would meet the deposit at $\cong 0.8 L_A$]. There is also a transition[7] at a radius of $0.9 L_A$ (see Fig. 1); this is evidence of a third front. Three fronts may be due to the three species produced at the anode—Cu^{2+} by dissolution (second front), H^+ (first front), and $CuOH(H_2O)_3{}^{1+}$ (third front) by hydrolysis[15] in the thin high-concentration layer at the anode.

We observe evolution of hydrogen in the interior of the deposit and predict for $CuSO_4$ that the interior will have more H^+ than the original solution by a factor $1 + u_H / u_- \cong 5$. Some anions must be incorporated into the interior as counterions to the H^+; this will increase the interfacial velocity.

Previous work by two of us[3,4] observed, in the dense radial regime of a different system, that $L \propto t^{1/2}$. The extension of the above theory to this different system is under investigation.

We conclude that a small change in pH affects the branching rate of dense radial forms. This may be due to increased nucleation in the polycrystalline deposit.[3] We have established that chemical fronts exist in the thin cells and cause the universal branching transition. Our principal conclusion is, however, that in migration-controlled electrodeposition, the interfacial velocity of the deposit is selected by anion transport and not via the growth morphology. We attribute the difference to the breakdown of the quasistatic approximation for the counterions whose recession is crucial.

J.R.M. thanks the Royal Society, Castrol Ltd., and the Levfre Foundation for financial support. We thank the technical staff of the Department of Chemistry, the University of New South Wales, particularly Martin Dudman and Nguyen Than Tron.

---

[1] D. Grier, E. Ben-Jacob, R. Clarke, and L. M. Sander, Phys. Rev. Lett. **56**, 1264–1267 (1986); Y. Swada, A. Dougherty, and J. P. Gollub, Phys. Rev. Lett. **56**, 1260–1263 (1986).

[2] J. H. Kaufman, A. I. Nazzal, O. Melroy, and A. Kapitulnik, Phys. Rev. B **35**, 1881–1890 (1987).

[3] D. B. Hibbert and J. R. Melrose, Phys. Rev. A **38**, 1036 (1988).

[4] D. B. Hibbert and J. R. Melrose, Proc. Roy. Soc. London A **423**, 149–158 (1989).

[5] R. M. Brady and R. C. Ball, Nature (London) **309**, 225–229 (1984); M. Matsushita, M. Sano, Y. Hayakawa, H. Honjo, and Y. Swada, Phys. Rev. Lett. **53**, 286–289 (1984).

[6] F. Liu and N. Goldenfeld, Phys. Rev. A **42**, 895 (1990), and references therein.

[7] P. Garik, D. Barkey, E. Ben-Jacob, E. Bochner, N. Broxholm, B. Miller, B. Orr, and R. Zamir, Phys. Rev. Lett. **62**, 2703 (1989); L. M. Sander, in *The Physics of Structure Formation,* edited by W. Guttinger and G. Danglemayr (Springer-Verlag, Berlin, 1987).

[8] D. Grier, D. A. Kessler, and L. M. Sander, Phys. Rev. Lett. **59**, 2315–2318 (1987).

[9] A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications* (Wiley, New York, 1980).

[10] Previous authors [J. R. Melrose and D. B. Hibbert, Phys. Rev. A **40**, 1727 (1989); T. C. Halsey, Phys. Rev. A **36**, 3512 (1987), T. Nagatani, report, 1989 (unpublished)] have suggested that anion migration may be balanced by diffusion, but we note this would render the cells (Ref. 1) non-Ohmic (Ref. 5).

[11] Melrose and Hibbert, Ref. 10.

[12] D. P. Barkey and D. P. LaPorte, J. Electrochem. Soc. **137**, 1655 (1990); after submission we received a reprint of this paper which contains an analog of Eq. (3) for a linear geometry, but derived under a different concentration model.

[13] D. R. Crow, *Principles and Applications of Electrochemistry* (Chapman and Hall, London, 1973), p. 61.

[14] J. H. Kaufman (private communication).

[15] $Cu(H_2O)_4{}^{2+} \rightleftharpoons CuOH(H_2O)_3{}^{1+} + H^+$. The values of $\ln(k)$ for the hydrolysis of Cu^{2+}, $Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+$, are given in Special Publication No. 17 (The Chemical Society, London, 1964). Using an average value of 7 for temperatures 18–25°C gives pH 4 of H^+ for 0.1 mol dm^{-3} of Cu^{2+}.

[16] We rejected that the first front is a layer rich in electrolyte: $1.5 C_0$ is an upper bound on the concentration of such a layer, thus too small to explain the pH 2–3 of the front; the front velocity is consistent with the drift of H^+; there is evidence for a slower electrolyte rich layer (see text).

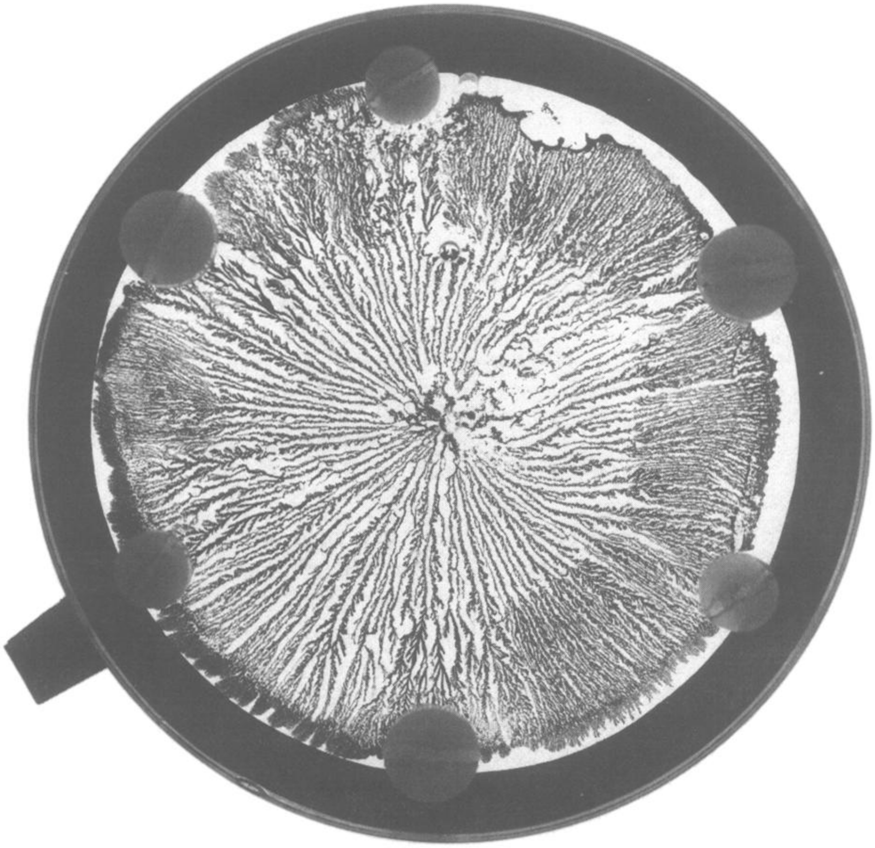

FIG. 1. A deposit within a thin cell of radius 3.0 cm, at an applied potential of 25 V from a 0.05-mol dm^{-3} $CuSO_4$ solution. From 12 to 5 o'clock a distinct branching (Hecker) transition is observed at $0.5L_A$. From 4 to 9 o'clock the third transition mentioned in the text is evident at $0.9L_A$.