

Early stages of ramified growth in quasi-two-dimensional electrochemical deposition

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I have measured the early stages of the growth of branched metal aggregates formed by electrochemical deposition in very thin layers. The growth rate of spatial Fourier modes is described qualitatively by the results of a linear stability analysis [D.P. Barkey, R.H. Muller, and C.W. Tobias, *J. Electrochem. Soc.* **136**, 2207 (1989)]. The maximum growth rate is proportional to $(I/c)^\delta$ where I is the current through the electrochemical cell, c the electrolyte concentration, and $\delta=1.37\pm 0.08$. Differences between my results and the theoretical predictions suggest that electroconvection in the electrolyte has an influence on the instability leading to ramified growth. [S1063-651X(96)50506-4]

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Rough surfaces develop in many systems in which the surface grows under far-from-equilibrium conditions [1,2], due to the fact that the smooth surface is unstable to the growth of perturbations over a range of wave numbers. This morphological instability was first treated by Mullins and Sekerka (MS) in the context of solidifying alloys [3]. Metal aggregates grown by electrochemical deposition (ECD) in quasi-two-dimensional geometries display a variety of qualitatively different branched growth morphologies [4,5], and there has been considerable study of the basic instability of the straight electrode which leads to the initial development of branched growth [6–14].

To understand this instability qualitatively, assume that the cations are transported by migration in an applied electric field to the cathode, where they are deposited. The electric field will be uniform along the length of a straight cathode, but will be enhanced near the tip of a small bump. This will lead to an increased current of cations, and so a higher deposition rate, at the tip of the bump. Thus the bump will grow exponentially. A similar argument applies if the transport is diffusive. At very high spatial frequencies, however, the straight interface is stabilized by surface tension. This picture leads to an instability of the straight electrode analogous to the Mullins-Sekerka instability — perturbations within a band of wave numbers k from $k=0$ up to a cutoff wave number k_c will grow, while perturbations with $k>k_c$ will be damped out. The exponential growth rate β of spatial modes with wave number k has the form [3]

$$\beta(k) = qk(1 - rk^2), \quad (1)$$

with $k_c = r^{-1/2}$.

Experimentally, Kahanda *et al.* [14] studied growth by electrochemical deposition in the limit of very low currents. In this case [14], the deposition of metal onto the cathode is limited by the activation of cations in the double layer. Kahanda *et al.* used a Fourier analysis technique to study the growing aggregate front. They determined the growth rate of the Fourier modes as a function of wave number and found semiquantitative agreement with the predictions of MS theory.

At higher currents, however, the deposition rate is governed by the transport of ions in the electrolyte. A number of

electrochemical processes contribute to the ion transport and to the current distribution near the cathode, resulting in modifications to Eq. (1) [7–9,11,13]. Barkey, Muller, and Tobias (BMT) [11] have performed a linear stability analysis of a planar electrode in three-dimensional ECD, and, at least conceptually, the results of their work should carry over to the two-dimensional case studied here. They assume mass transport to be due solely to diffusion. Surface tension manifests itself as a reduction in the binding energy of deposited atoms on a curved surface relative to a flat surface (referred to in BMT as the capillary potential shift). The effects of electrode reactions (kinetic overpotential) and of concentration gradients in the diffusion layer close to the cathode (concentration overpotential) both act to smooth out variations in the current density, and thus reduce the growth rate of perturbations. BMT found [see Eq. (41) of Ref. [11]] the growth rate $\beta(k)$ to have the form

$$\beta = \frac{qk(1 - rk^2)}{(1 + sk)}. \quad (2)$$

The coefficients q , r , and s depend on the properties of the electrolyte and the deposited metal, the ion concentration, and the current [15]. Roughly speaking, q incorporates the destabilizing effects of mass transport, qr involves the stabilizing effects of surface tension, and s is a combination of terms involving the kinetic overpotential and the concentration overpotential. As above, there is a range of unstable wave numbers, $0 < k < r^{-1/2}$; the MS result is recovered in the limit that $s \rightarrow 0$.

In this Rapid Communication, I present results from experiments on the very early stages of the ECD of aggregates of metallic copper from solutions of CuSO_4 , in the regime where the growth is limited by mass transport in the electrolyte. Using analysis techniques similar to those of Kahanda *et al.* [14], I investigate the growth rate $\beta(k)$ and find it to be qualitatively described by the dispersion relation of BMT [Eq. (2)] and not by Eq. (1).

In my experiments [16], two copper foil electrodes 5.1 cm long by 0.025 cm thick, separated by roughly 23 mm, were sandwiched between two 5.1 cm square by 0.6 cm thick glass plates and clamped together. The space between the electrodes was filled with aqueous solutions of CuSO_4 with

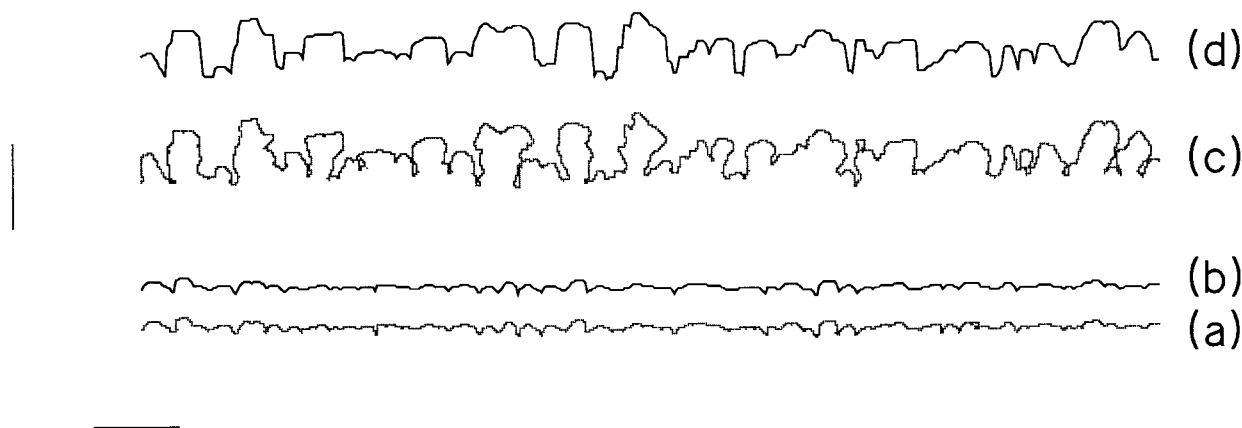


FIG. 1. The edge of the metal aggregate growing on the cathode for a run with $c=0.1M$ and $I=1.4225$ mA. (a) The interface function $p(x)$ at time $t=225$ s, near the end of the exponential growth regime seen in Fig. 2 below. (b) The single-valued function $p_1(x)$ corresponding to curve (a). (c) $p(x)$ at $t=385$ s, well beyond the end of the exponential regime. (d) The single-valued function $p_1(x)$ corresponding to curve (c). The solid bars have length 1mm.

concentrations c in the range $0.02M < c < 0.5M$. A constant current I of from 0.06 mA to 10 mA was passed through the cell, and a branched copper aggregate formed at the cathode. The cell was illuminated from below by a diffuse white light source, and imaged from above with a charge coupled device (CCD) video microscope. Individual images of the aggregate were captured and digitized by a frame grabber in a personal computer, and the growth was also recorded on video tape. The spatial resolution of the digitized images was typically $23 \mu\text{m}/\text{pixel}$.

My data analysis was similar to that of Kahanda *et al.* [14]. The edge of the aggregate (the interface) was located by thresholding the digitized image. Pixels with an intensity lower than a chosen value were deemed to be on the aggregate. Since the aggregate is rough, the interface determined in this way, $p(x)$, will in general not be a single-valued function of the coordinate x along the length of the cathode. For my analysis, I formed a single-valued approximation to the interface, $p_1(x)$, by taking the point on the interface furthest from the original cathode position, i.e., the highest point, at each x value. For a very heavily branched aggregate with many "overhangs," $p_1(x)$ is not a good representation of the true interface. However, for the early times of interest here, the aggregate, although rough, has few overhangs, and $p_1(x)$ is very similar to $p(x)$. The single-valued interface function $p_1(x)$ is then Fourier transformed to give a spatial Fourier power spectrum of the interface [17].

Figure 1 shows the interface functions determined at two different times for a particular run. Curve (a) of Fig. 1 shows $p(x)$ determined from a digitized video image recorded 225 s after the start of the run. The aggregate is rough, but, at least within the resolution of my imaging system, it does not yet contain a large number of overhangs. Curve (b) of Fig. 1 is the single-valued function $p_1(x)$ extracted from curve (a); it is very similar to $p(x)$. Curve (c) shows $p(x)$ at a later time, 385 s after the start of the run. By this time the aggregate is more strongly branched and displays substantially more overhangs. Curve (d) is the corresponding single-valued function $p_1(x)$. In this case there are significant differences between $p_1(x)$ and $p(x)$ and Fourier analysis of

$p_1(x)$ does not provide meaningful information about the true interface.

By Fourier analysing the single-valued interface functions obtained from a time sequence of images, one can extract the Fourier power $|A(k)|^2$ of a mode of wave number k as a function of time. Figure 2 shows $|A(k)|^2$ vs time for three different values of k , from the run illustrated in Fig. 1. In this particular run the growth at the cathode first became visible about 100 s after the start of the run. The Fourier power grows exponentially with time between this time, and about 230 s. The dotted lines in Fig. 2 are fits of the data to a growing exponential over this time range. The growth rate depends on k . At times beyond the region of exponential growth, the growth rate generally decreases. In this regime, however, $p_1(x)$ is not a good approximation to the true interface and quantitative analysis is not possible using this technique. The interface shown in curves (a) and (b) of Fig. 1 corresponds to a time near the end of the exponential growth phase of Fig. 2, while that of curves (c) and (d) of

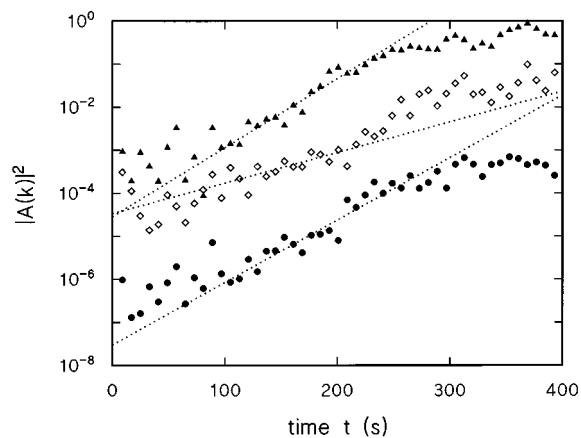


FIG. 2. The Fourier power as a function of time for three values of wave number k , for the same run as shown in Fig. 1. Triangles: $k=27.2 \text{ mm}^{-1}$, circles: $k=75.3 \text{ mm}^{-1}$, diamonds: $k=113 \text{ mm}^{-1}$. The lines are fits to the data in the exponential growth regime.

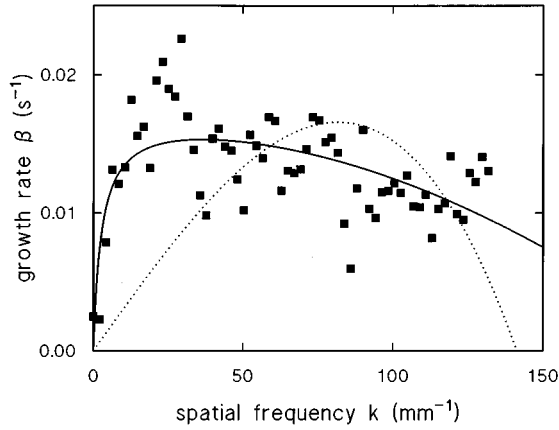


FIG. 3. The growth rate $\beta(k)$ of the Fourier amplitude $|A|$, for the same run as the previous figures. The dotted curve is a fit to Eq. (1), and does not describe the data well. The solid curve is a fit to the form predicted by BMT, Eq. (2).

Fig. 1 is well beyond the end of this phase.

As can be seen from the data in Fig. 1(b), the interface is only of order 10 pixels high by the time the single-valued approximation breaks down. To confirm that the resulting ‘‘digitization steps’’ in the data did not affect the results, the data were numerically smoothed by application of a Savitzky-Golay smoothing filter [17], and then reanalyzed. The results were essentially identical to those obtained from the raw data. Furthermore, data recorded at a higher magnification agreed with the data presented in the wave number region where they overlapped.

Figure 3 shows the exponential growth rate β of the Fourier amplitude $|A(k)|$ as a function of k . The dotted curve is a least-squares fit to Eq. (1), which does not describe the data well. Rather, the growth rate increases more rapidly for small k , displays a weak maximum, and then decreases more slowly for larger k . The solid curve plotted in Fig. 3 is a least-squares fit of the data to a dispersion relation with the form of Eq. (2). The fit is quite good, although, as in Fig. 3, most data sets show perhaps a bit more of a peak in the data than the theoretical curve would indicate. Although fits to the experimental data to Eq. (2) looked satisfactory to the eye, the uncertainties in the parameters were in many cases quite large. This was due to the fairly large scatter in the $\beta(k)$ data; that in the data shown in Fig. 3 is typical.

From fits of Eq. (2) to the data from a number of runs, I determined the growth rate β_{max} of the fastest growing mode. Figure 4(a) is a plot of β_{max} against the cell current I for two values of the concentration c . Although the scatter in the data is considerably larger than the error bars, the trend of the data is well described by the power law $\beta_{max} \propto I^{\delta_1}$ with an exponent $\delta_1 = 1.52 \pm 0.19$ for $c = 0.02M$ and $\delta_1 = 1.28 \pm 0.06$ for $c = 0.1M$. Figure 4(b) shows β_{max} as a function of c for a fixed current. In this case a power law fit to the data gives $\beta_{max} \propto c^{-\delta_2}$, with $\delta_2 = 1.40 \pm 0.16$. The similarity between the values of the exponents δ_1 and δ_2 suggests that β_{max} may be a function of the ratio I/c alone. In Fig. 4(c) the same three data sets are plotted as a function of I/c . With some scatter, the data collapse onto a single power-law function given by $\beta_{max} = (6.8 \pm 2.0)(I/c)^{1.37 \pm 0.08} \text{ s}^{-1}$.

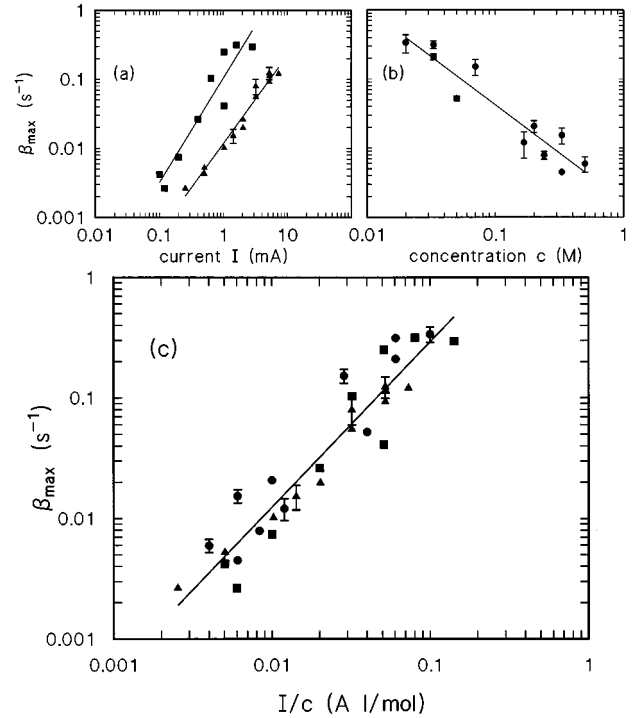


FIG. 4. (a) The maximum growth rate β_{max} as a function of the current I for fixed concentration c . Squares: $c = 0.02M$; triangles: $c = 0.10M$. The lines are fits of the data to power laws in I , as discussed in the text. (b) β_{max} as a function of c for $I = 2.00$ mA. The dashed line is a fit to a power law. (c) The same data as in (a) and (b) plotted as a function of I/c . The symbols are as in (a) and (b), and the line is a fit of all the data to a power law.

I can make a qualitative comparison of my results to the theoretical predictions [11]. Using bulk values for the electrolyte properties involved in the expressions for the coefficients q , r , and s [15], the theory predicts that the coefficients will depend on current and concentration as $q \propto I$, $r \propto c/I$, and $s \propto c/I$. On the other hand, the values of q obtained from fits to the experimental data tend to increase with I at constant c , but decrease with c at constant I ; the fitted values of r show no systematic variation with either I or c and in fact are constant to within a factor of two over the range of conditions studied; and the values of s , while they have large error bars, also show no systematic variation with either I or c . Under the same assumptions, the theory predicts that $\beta_{max} \propto I^2/c$, while Fig. 4(c) indicates that, experimentally, β_{max} behaves as a power law in I/c .

The coefficients q , r , and s depend on the quantity $\Gamma = 1 - i/i_L$, where i is the current density and i_L the limiting current density [18]. Branched growth occurs when i is at or near i_L [19], so this quantity is small. Taking $c = 0.1M$ and $I = 2$ mA as an example, and again using bulk values for the electrolyte properties, the value of q obtained from fits to the experimental data is equal to the predicted value for $\Gamma \approx 5 \times 10^{-4}$, i.e., for $i = 0.9995i_L$. For the same value of Γ , the fitted value of r is roughly five orders of magnitude smaller than the predicted value, but it is worth noting that the quality of the fits to the data (i.e., the χ^2 values) is quite insensitive to the value of r . Finally, the fitted values of s are of order 100 times the predicted values.

The fact that the shape of the experimental dispersion

relation can be fitted by Eq. (2) suggests that the basic ingredients of the theory — that is, that the instability is driven by mass transport, stabilized by surface tension, and modified by electrochemical processes — are correct. However, the quantitative differences between experiment and theory outlined above suggest that either the assumptions made by me in calculating the coefficients are invalid, or that effects not accounted for in the theory play an important role in these experiments.

It is quite likely that the use of the bulk value of the electrolyte conductivity in evaluating the coefficients is a poor approximation, since in an unsupported electrolyte a diffusion layer depleted of ions, and with a correspondingly low conductivity, develops near the cathode. Using a conductivity of zero would make q independent of Γ and give a theoretical value roughly three orders of magnitude smaller than the experimental value for the conditions discussed above, while r and s would go to zero [15].

The theory of BMT assumes that ion transport is due to diffusion only. In an unsupported binary electrolyte, migration will also be important. This can be accounted for by a correction factor which would result in a decrease of the theoretical value of q by about 20–40 %, depending on Γ [20].

A physical effect known to be present in this system, but

not accounted for in the theory of BMT, is hydrodynamic flow near the electrodes. High electric fields in the diffusion layer cause electroconvective flow in quasi-two-dimensional ECD experiments [21,22], which has an influence on ion transport and on the deposition process. Natural convection, driven by density gradients in the electrolyte [23–26] may similarly play a role. These flows may provide at least a partial explanation for the quantitative differences between my experimental results and the theoretical predictions.

In summary, I have measured the growth rate of spatial modes as a function of wave number during the early stages of the growth of metal aggregates in thin-layer electrochemical deposition. The dispersion relation is not well described by a MS-type theory [3], but can be fitted to the form predicted by the stability analysis of Ref. [11]. Quantitative differences between my results and the predictions of the theory of Ref. [11] suggest that convection in the electrolyte driven by electric fields or by density gradients modifies the ion transport substantially and plays an important role in determining the growth rate. A more detailed account of this work will appear elsewhere [19].

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