

Local concentration measurements in electrochemical deposition using a schlieren method

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We report local concentration measurements of electrolyte in electrochemical deposition using a schlieren method. The intensity contrast of schlieren images is used to obtain concentration information. The images reveal active regions of the growth and thus provide excellent records to study the dynamics of electrochemical deposition processes. Quantitative results of local concentration measurements in the early stages of the growth agree well with recent model calculations.

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There has been a vast amount of interest in fractal formations from electrochemical deposition of metal in aqueous media in the past decade [1]. This is due to the simplicity of the experiment and the variety of morphologies of deposits formed using different concentrations and applied potentials [2,3]. Despite past efforts, which were limited to global measurements of morphology [4] and current behavior [5], local information has been scarce. Concentration gradients in front of growing tips have been observed but no quantitative results are available [6]. Local measurements of the concentration or the electric field are very desirable because they can provide vital information about the electrochemical deposition processes.

In this Brief Report, we present quantitative measurements of local concentration in electrochemical deposition. A shadowgraphic technique, the schlieren method [7], is used to obtain images of concentration gradients of the electrolyte as intensity contrasts shown in Figs. 1(b)–1(e). Sharp contrasts, corresponding to large concentration gradients, are observed in front of growing regions, while nongrowing regions show no changes. The schlieren images thus provide excellent records to monitor the growth dynamics of electrochemical deposition. Of greater importance, local concentrations can be obtained by a simple integration of the intensity contrasts [7]. Quantitative results of local concentration measurements in the early stages of the growth agree well with one-dimensional model calculations [8,9].

A schematic of the schlieren setup for the electrochemical deposition is shown in Fig. 2. White light from a circular point source (0.18-mm diam) is collimated using a microscopic objective lens to form a 0.8-cm-diam beam.

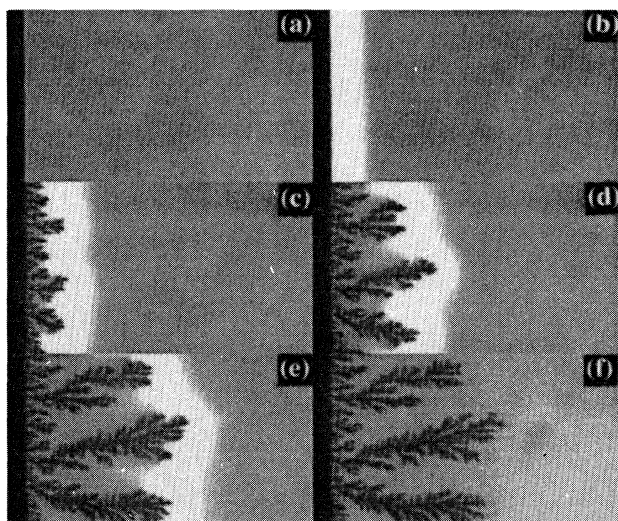


FIG. 1. Sequence of enhanced schlieren images (300×240 pixels, corresponding to an area of $3.23 \times 2.13 \text{ mm}^2$) of copper aggregates in a cell with a 0.102-mm gap using 0.5M CuSO_4 and 6.0-V applied potential. The images are taken at (a) 0, (b) 30, (c) 90, (d) 180, (e) 300, and (f) 1600 s. The current starts at (a) and terminates after (e). Dark pixels represent the cathode and the aggregates. White pixels represent high concentration gradients.

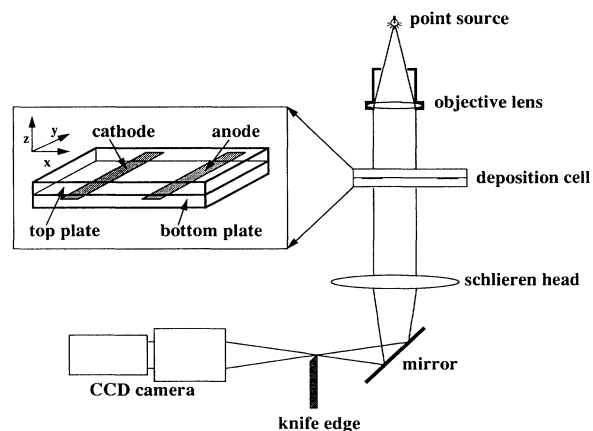


FIG. 2. Schematic of the experimental setup using the schlieren method. The inset is an expanded view of the experimental cell. The cell is 3.69 cm wide with the cathode at $x = 0$ cm and the anode at $x = 2.54$ cm. The axes show the coordinates for the cell.

After passing through the experimental section, the beam is refocused to a focal plane by another lens (the schlieren head). A knife edge made of a razor blade is placed at the focal plane blocking half of the image of the point source for maximum intensity contrast [7]. The knife edge is positioned on the same side as the cathode with respect to the plane symmetry of the cell for positive concentration gradient measurements. An expanded view of the deposition cell is shown in the inset of Fig. 2. Two optically flat rectangular glass plates sandwiching two parallel copper strips form the body of the cell. The gap between the plates is filled with the electrolyte solution that contains the metal ion to be deposited. The gap spacing d (0.025–0.102 mm) is fixed by the thickness of the copper strips that also serve as the electrodes of the system. The edges of the copper strips are polished with fine sandpaper, and new strips are used in every run. A CCD camera captures patterns formed in the cell during deposition. Images of aggregates at the cathode are digitized by an imaging system with a 512×480 pixel resolution (corresponding to an area of 5.5×4.3 mm²). Whole images are recorded for pattern formation studies while only line sections (5.5×0.027 mm²) of the images are used for concentration measurements.

High-purity (99.999%) copper sulfate (0.2–1.0M) and constant applied potentials (2–10 V) between the electrodes are used to grow ramified copper aggregates at the cathode. Figure 1 shows examples of schlieren images at different stages of the growth. Before the current is applied [Fig. 1(a)], the image has uniform intensity across the cell (dark pixels on the left side represent the cathode). A bright halo of high intensity, corresponding to active regions, starts to appear along the cathode as soon as the current is applied. The halo then expands deeper into the cell away from the cathode as shown in Fig. 1(b). It remains uniform and parallel to the cathode until aggregates of copper are formed. Then it is distorted but still covers the envelope of the aggregates. The envelope corresponds to the outermost active growing regions of the aggregate. Inner regions screened by the growing fronts do not show any intensity changes, as is easily seen in Figs. 1(d) and 1(e). Thus the schlieren images are excellent records to visualize the growth dynamics of electrochemical deposition processes. The halo starts to fade away diffusively after the current is terminated indicating that it is not due to some optical effects, such as edge diffractions from the cathode and the aggregates, but is related to some dynamical quantity of the growth. The halo disappears completely after the system has reached equilibrium, as is shown in Fig. 1(f). Runs with different concentrations and applied potentials show similar behavior except for the difference in the intensity contrast of the halo, where it is very dramatic for high concentrations and potentials, and less striking for low concentrations and potentials. Similar results are obtained using zinc sulfate.

The halo observed in the schlieren images can be used to obtain local concentrations of the electrolyte. It can be shown that the intensity contrast of the schlieren image is related to the gradient of the refractive index of the electrolyte by [7]

$$\frac{\Delta I}{I_0} = \frac{f}{an_0} \int_0^a \frac{\partial n}{\partial x} dz, \quad (1)$$

where $\Delta I/I_0 = (I - I_0)/I_0$ is the intensity contrast, I is the intensity during the growth, and I_0 is the intensity before the growth. f is the focal length of the schlieren head, a is a geometrical factor corresponding to the unobstructed portion of the image of the source, n_0 is the refractive index of air [10], and $\partial n/\partial x$ is the gradient of the refractive index of the electrolyte n in the direction normal to the knife edge. The direction of the gradient is also perpendicular to the edge of the cathode (see the inset of Fig. 2). Since the gap spacing of the cell is small, n can be approximated by the averaged value \bar{n} across the gap. Thus, Eq. (1) can be rewritten as

$$\frac{\Delta I}{I_0} = \frac{fd}{an_0} \frac{\partial}{\partial x} \bar{n}. \quad (2)$$

Furthermore, the refractive index of copper sulfate solution is a linear function of concentration [11]; Eq. (1) can be integrated to obtain the averaged concentration $C(x)$ given by

$$\frac{C(x) - C_b}{C_0 - C_b} = \left[\int_0^x \frac{\Delta I}{I_0} dx \right] / \left[\int_0^L \frac{\Delta I}{I_0} dx \right], \quad (3)$$

where C_b is the concentration at the boundary of the cathode ($x = 0$) and L is some distance from the cathode where the concentration has not changed from its initial value C_0 . Corrections to Eqs. (2) and (3) due to absorptions, shadowgraph, diffraction, and temperature effects have been neglected for simplicity.

There is one limitation of the present schlieren setup (Fig. 2): it cannot detect gradients parallel to the knife edge. Despite this limitation, Eqs. (2) and (3) can be used to obtain a qualitative two-dimensional concentration distribution provided that the system is calibrated and proper boundary conditions for the moving boundaries are used for the integration. However, in this report, we will

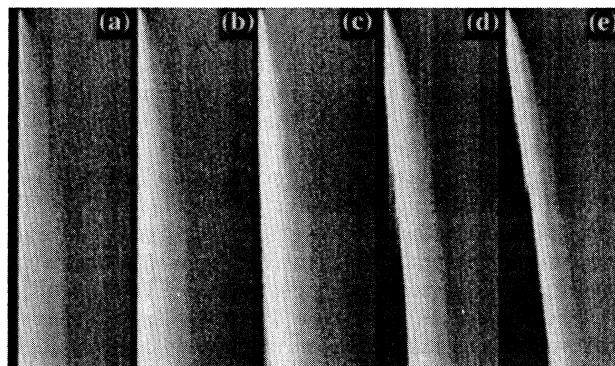


FIG. 3. Time superpositions of enhanced line schlieren images (150×3 pixels, corresponding to an area of 1.617×0.027 mm²) of copper aggregates using the same gap and concentration as in Fig. 1 for (a) 2.0, (b) 4.0, (c) 6.0, (d) 8.0, and (e) 10.0 V applied potentials. Time starts at the top (0 s) and ends at the bottom (79 s). Concentration gradients are represented by gray scales.

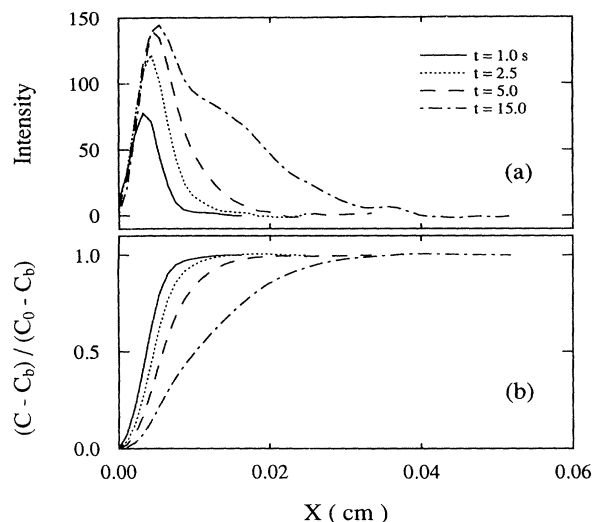


FIG. 4. (a) Intensities (with background subtracted) at different times (see legends) for Fig. 3(c). (b) Normalized concentrations at different times for (a) obtained using Eqs. (2) and (3). Legends in (a) apply to (b).

focus only on the early stages of the deposition where the system is essentially one dimensional and visible growth is absent. Thus Eqs. (2) and (3) can be applied without complications.

Figure 3 shows time superpositions of schlieren images of a narrow section taken in the midplane across the cell in the early stages of growth. Growth of aggregates does not start immediately after the current is applied; instead it starts quite early for high potentials [Figs. 3(d) and 3(e)] and at a much later time for low potentials [Figs. 3(a) and 3(b)]. This indicates that there is an induction period before which no visible growth can occur. This induction period may be caused by the building up of space charges in the diffuse layer near the cathode [8,12]. The induction period increases as the applied potential decreases. Figure 4(a) shows the intensities at different times of Fig. 3(c) before growth appears. The intensity changes sharply in a small region close to the cathode in the early stages and diffuses to a wider region later on [Fig. 4(a) at $t = 15$ s]. Figure 4(b) shows the corresponding normalized concentration for Fig. 4(a) obtained using Eqs. (2) and (3). A sharp gradient of concentration is clearly seen in Fig. 4(b) shortly after the start of the experiment. The width of this gradient is roughly the same in the early stages for all potentials with the same initial concentration (Fig. 3). Similar behavior is observed for runs using different gap spacings. Figure 4(b) gives the first quantitative measurements of concentrations in the early stages of electrochemical deposition and provides a test for recent model calculations [8,9]. Figure 5 shows normalized concentrations obtained from a model calculation using

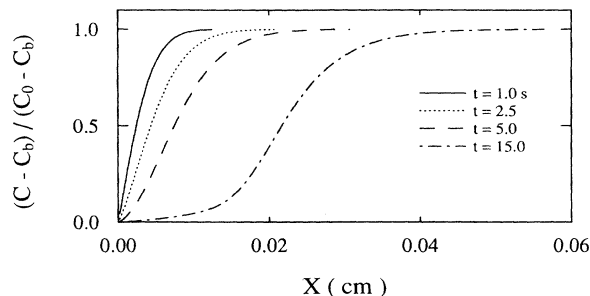


FIG. 5. Normalized concentrations at different times obtained from Ref. [9] using binary electrolytes in a one-dimensional cell of length 2.54 cm using $10^{-10}M$ $CuSO_4$ and 6.0 V applied potential.

binary electrolytes in one dimension [9]. The similarity between Figs. 4(b) and 5 in the early stages is striking. However, the agreement should be cautioned because the model uses an unrealistic initial concentration ($C_0 = 10^{-10}M$) due to prohibitively long calculation at high concentrations [8,9].

In summary, we have measured local concentrations of electrolyte in electrochemical deposition using the schlieren method. The schlieren images of the growth provide excellent records to study the dynamics of electrochemical deposition processes. Quantitative results of concentration measurements in the early stages of the growth agree well with model calculations. The schlieren method can be applied to the anode side of the deposition cell where dissolution of the anode does not cause noticeable changes to the boundary. Thus measurements of concentrations can be obtained at a much later time without complications due to the moving boundary at the cathode. Furthermore, the present setup can be expanded to a two-dimensional schlieren method where gradients of concentration in both normal and transverse directions can be measured simultaneously. Results from such a setup will certainly shed more light onto the processes of electrochemical deposition. The schlieren method can also be applied to other systems that require sensitive concentration measurements, as in convection and solidification experiments.

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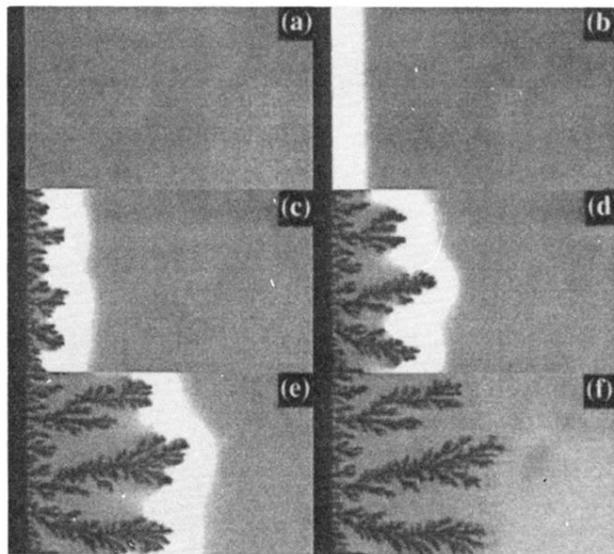


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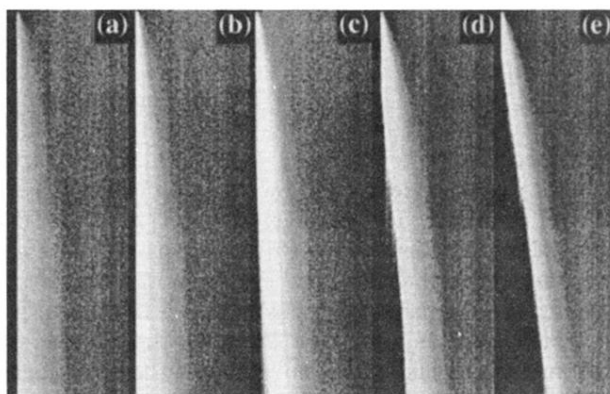


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