

Estimation of Nanoscale Current Density Distributions during Electrodeposition

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The control of interfacial morphology in electrochemical processes is essential for various applications. Morphological instability, particularly dendrite formation, can cause potentially catastrophic failure in rechargeable batteries and can lower the quality of electroplated coatings, yet may also be useful in forming porous deposits. Thus, it is important to understand the temporal development of morphology and the nature of the forces that govern the geometry of the electrode-electrolyte interface. Liquid cell electron microscopy allows us to image, in real time and with nanoscale resolution, the evolution of the solid-liquid interface during electrochemical deposition as a function of process conditions [1- 3]. Our nanoscale resolution allows us to infer the current density along the interface.

Here, we use liquid cell electron microscopy to quantify the transient growth of interfaces during galvanostatic deposition of copper from acidic electrolytes. We extract the explicit electrode-electrolyte interface as a function of time, which gives, among other measures, the normal growth velocity at each point along the interface, a measure of the point-wise current density on a time and length scale previously inaccessible. We find that initial stages of growth can be understood through Kinetic Roughening Theory [4, 5]. At longer times, we identify a transition in growth mode consistent with the onset of diffusion limited growth. The non-uniform distribution of current density along the interface ultimately leads to a rapid increase in the amplitude of surface asperities [6].

The experiments were carried out with our custom made liquid cell, the *nanoaquarium* [7], operating in a three terminal configuration with Pt electrodes controlled by a Gamry potentiostat. The interface morphology evolution was imaged at video rate (30 images per second) as a function of current density, current pulsing and solution composition, in a Hitachi H-9000 TEM at 300kV. **Figure 1** presents images of the interface recorded under conditions leading to the onset of a diffusive instability. We apply our in house-developed, unsupervised, non-parametric image processing algorithm [8] to extract the interface location as a function of time. This data is used to compute the point-wise normal speed, which is akin to the current density distribution in space-time as shown in **Figure 2a**. The current density distribution evolves in conjunction with the amplitude of the surface perturbations. **Figure 2b** shows the current density normalized by the average current density as a function of a point's height deviation from the mean. This measure matches well with the solution for a single sinusoid under galvanostatic conditions (solid line overlay) [6]. It therefore appears that the growth regime is dictated by the macroscale diffusion physics, while the morphology is the direct consequence of the nanoscale current density distributions [9].

References:

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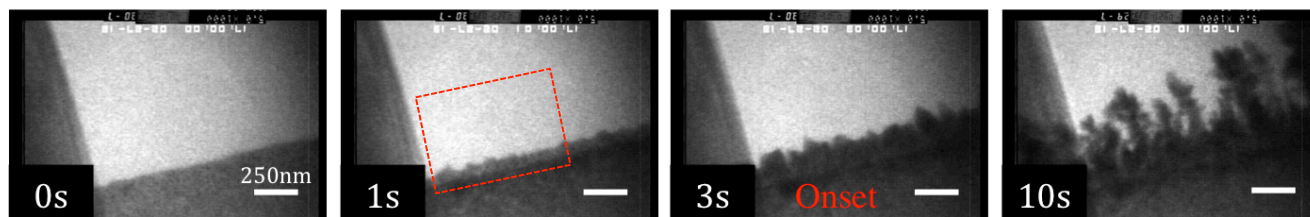


Figure 1. Instantaneous micrographs of the growth interface for Cu deposition from acidified CuSO_4 with an experimentally measured current density of 1500 A/m^2 for galvanostatic conditions with 400 nA total applied depositional current. Red outline represents analyzed region.

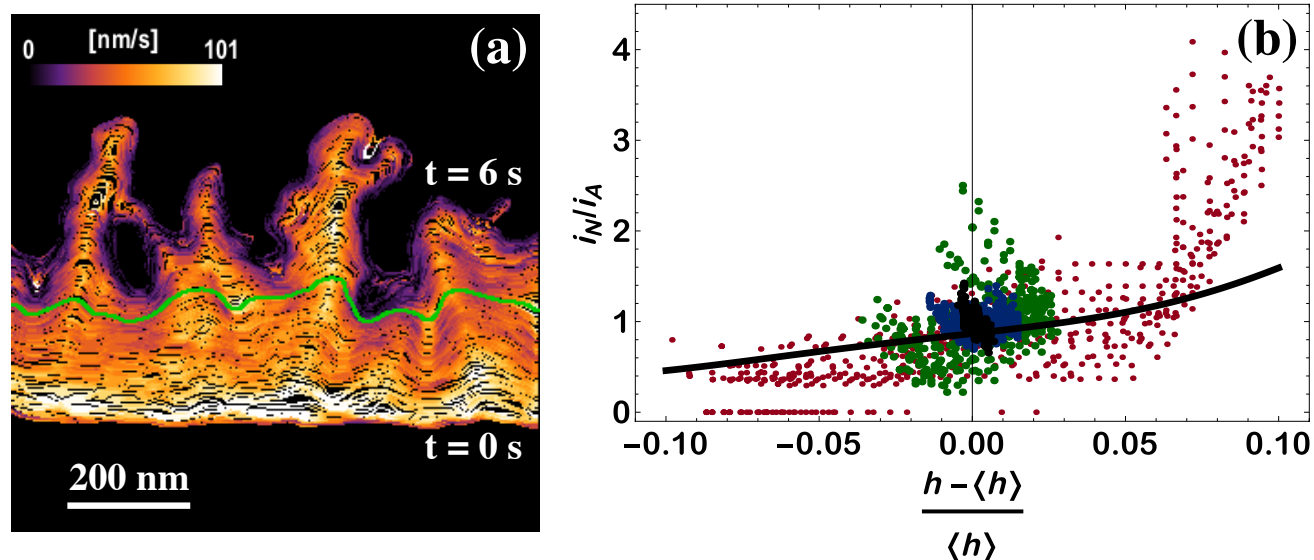


Figure 2. (a) “Heat Map” of normal growth speed (akin to point-wise current density) with the measured transition time overlaid in green. (b) Current density normalized by average current density as a function of deviation from the mean height. Data extracted from the growth of **Figure 1** at $t = 0.0$ (black), 2.0 (blue), 3.0 (green), 3.8 (red) s. Solid line represents sinusoidal solution from [6].