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Arresting Dendritic Growth by Additives

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Due to morphological instability associated with surface imperfections, electrodeposits tend to evolve roughness elements which often evolve into nodular or dendritic growth[1,2]. The nodular deposits may cause shorts and loss of active material in batteries, and lead to unacceptable surface properties. The growth rate of the dendrites and their dependence on the system parameters had been quantitatively modeled[3,4], however, despite fundamental understanding, effective practical solutions leading to the elimination of dendrites have not been demonstrated.

We introduce here a method for arresting dendritic growth, based on the use of inhibiting additives which incorporate in the deposit. The approach is based, in part, on earlier work by Roha and Landau[4], however, here we specifically link the effectiveness of the method to the properties of the inhibiting additives and the process conditions, mapping a parameter range for effective dendrite suppression. We provide a quantitative model simulating the growth rate of the dendritic element, and provide experimental data of copper deposition in the presence of inhibiting additives on substrates with well-characterized initial roughness.

The underlying reason for the accelerated growth of the roughness element is the enhanced three-dimensional transport to the small curvature tip as compared to the linear transport to the surrounding flat region of the electrode. By incorporating inhibiting additives, which preferentially cover the tip with a higher surface coverage than the flat region, dendritic growth can be arrested. We show that an essential feature of effective inhibiting additives is their capacity of being occluded within the deposit. Without such incorporation, the relative degree of inhibition between the dendritic tip and the substrate cannot be maintained, and dendritic growth cannot be inhibited.

We model and provide experimental data of copper deposition from acidified copper sulfate electrolyte in the presence of trace amounts (1 – 1000 ppm) of a leveling additive: a high molecular weight (~750,000) polyethylene imine (PEI). Fig. 1 shows the simulated height of a copper nodule, as a function of time. The model clearly indicates that the growth rate slows down, and if the correct concentration of leveling additive is used, the nodule actually diminishes in height over time. By contrast, if we apply polyethylene glycol (PEG), a well-known and highly effective copper inhibiting additive, which, however, does not incorporate within the deposit, no inhibition effect is noticed. Fig. 2 shows the ratio of the current density at the nodular tip to that of the flat surface, corresponding to their relative growth rates. At short times, in the presence of the PEI this ratio is significantly lower than one. At longer times, as the nodule shrinks and merges with the substrate, this ratio approaches unity.

References:

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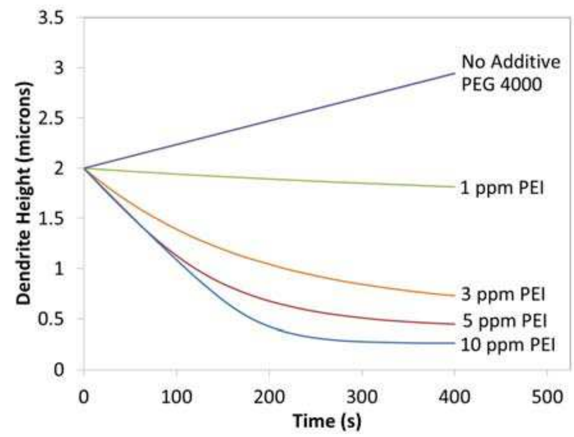

Fig. 1: Simulated height of a nodular element as a function of time when plated in the presence of additives. With no additives, or in the presence of 100 ppm PEG (non- incorporating inhibitor), linear growth is observed. However, in the presence of PEI (leveler) the height of the element above the flat plated surface decreases. Copper plating from acidified copper sulfate solution at a current density of 30 mA/cm^2 on the flat surface is assumed. The initial nodular element height is 2 μm with a tip curvature of 0.1 μm. The copper mass transport boundary layer thickness was 40.5 μm.

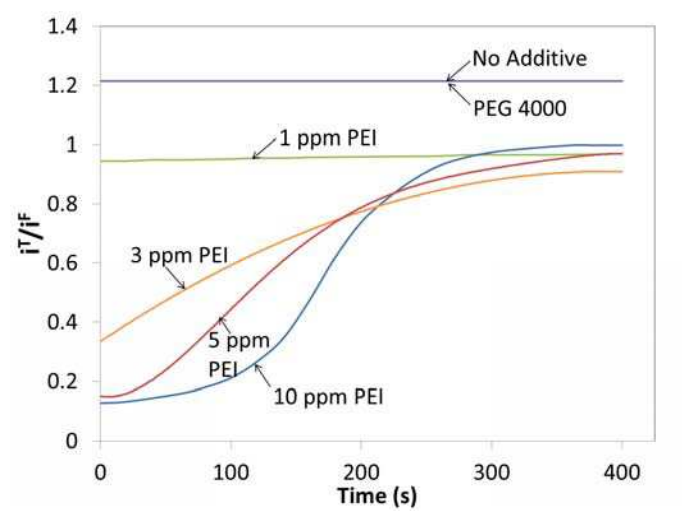

Fig. 2: Current density ratio of a nodular tip to the flat surface in the presence of additives. With no additives or with 100 ppm of PEG 4000, the tip current density is 20% higher than that of the flat region. Incorporating PEI leveler is effective in reducing significantly the current density at the tip. All conditions are the same as in Fig.1.