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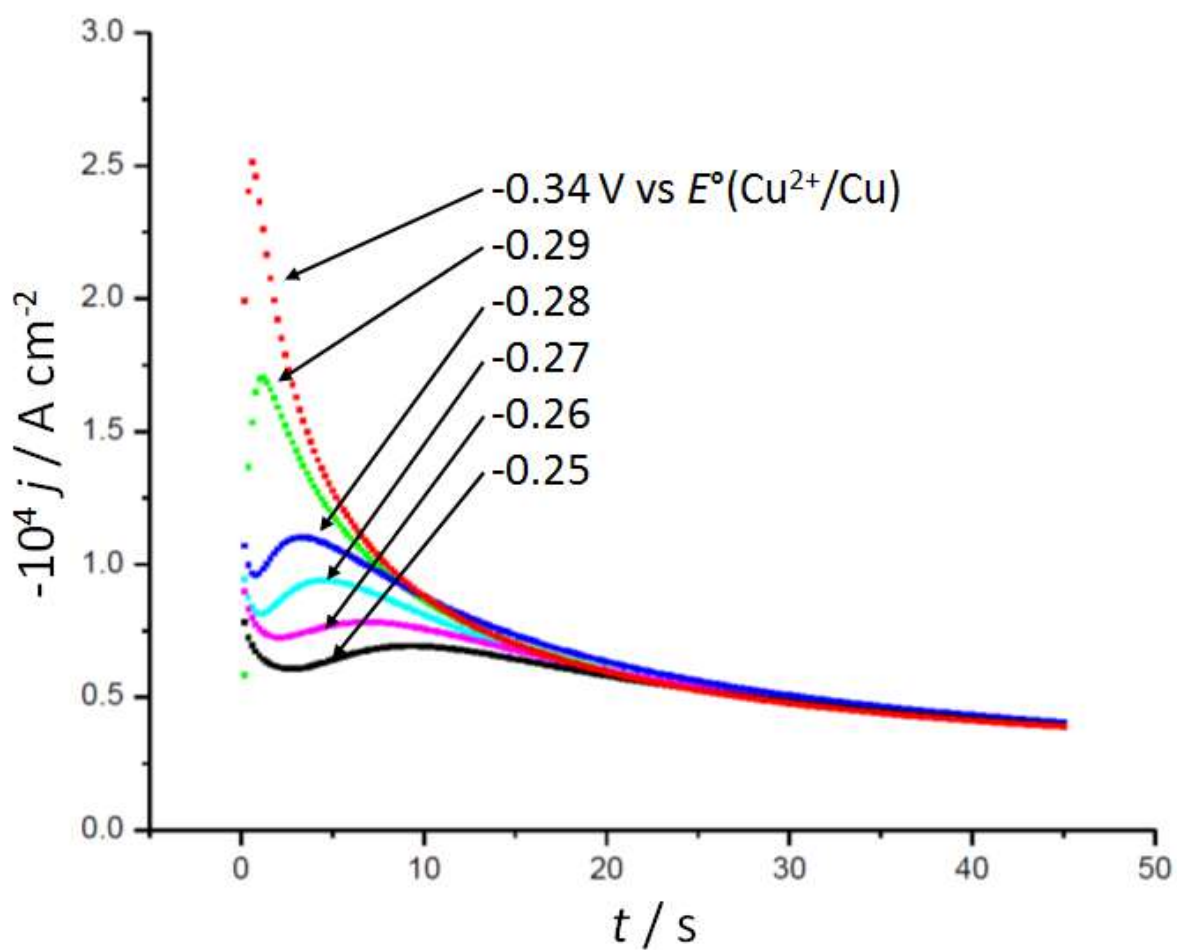
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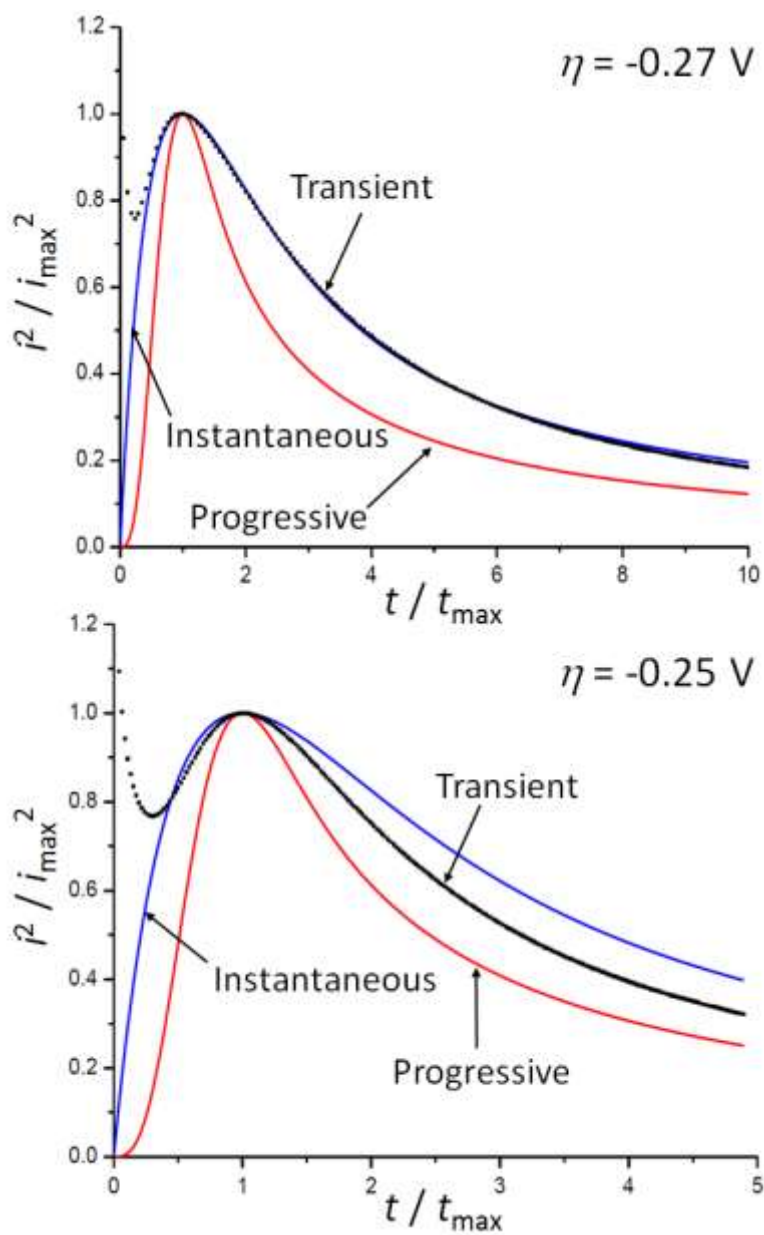
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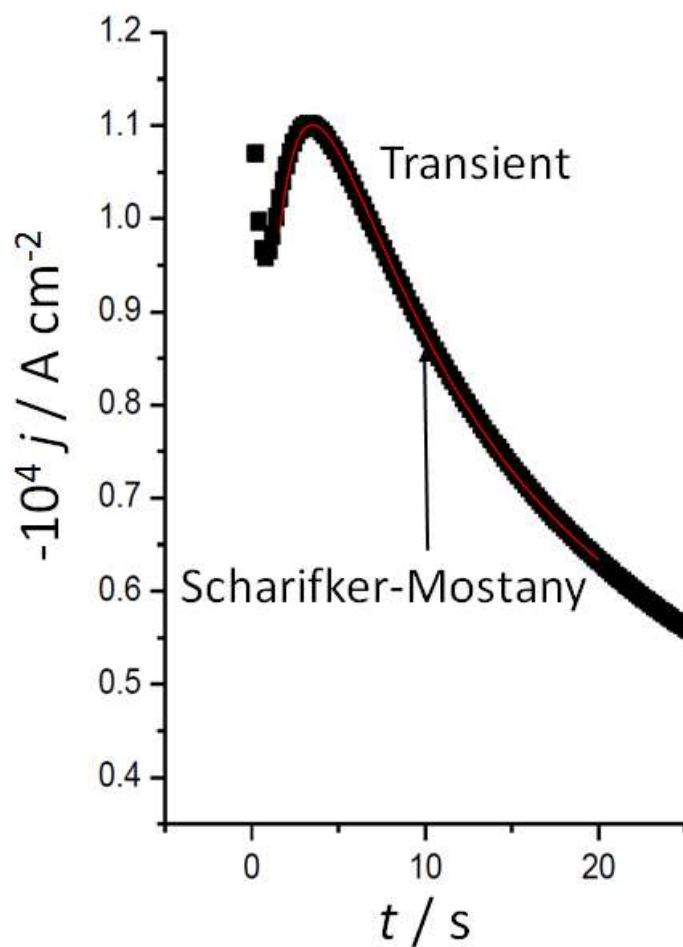
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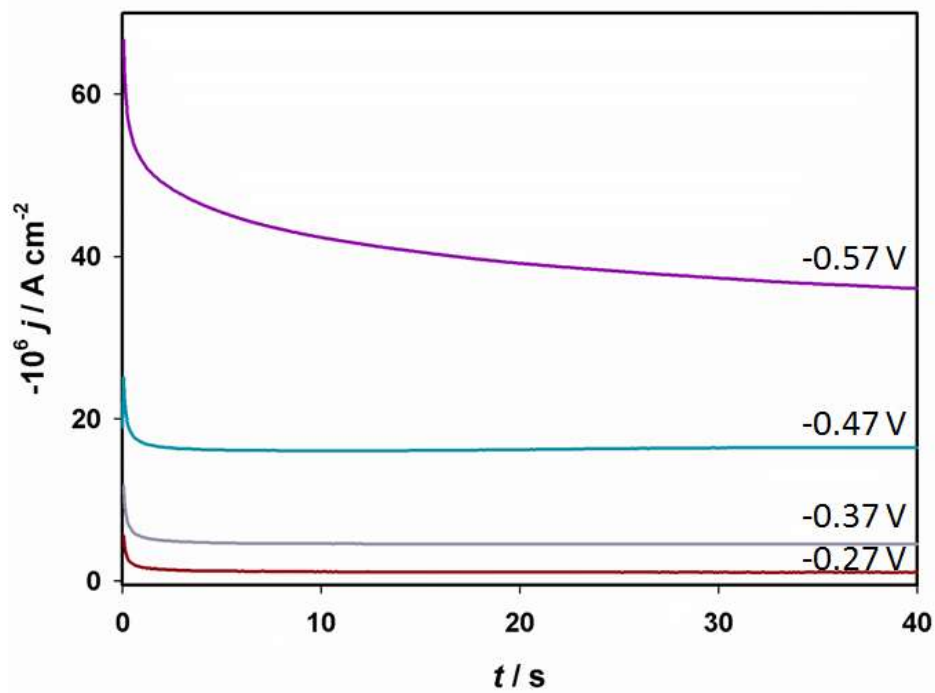
Supplementary Figure 1. Characteristic chronoamperometric transients at ITO electrodes in aqueous solution of CuSO_4 $1.0 \times 10^{-3} \text{ mol} \times \text{dm}^{-3}$ at various overpotentials and room temperature. The electrolyte solution contained $50 \times 10^{-3} \text{ mol} \times \text{dm}^{-3}$ Na_2SO_4 at pH 3.



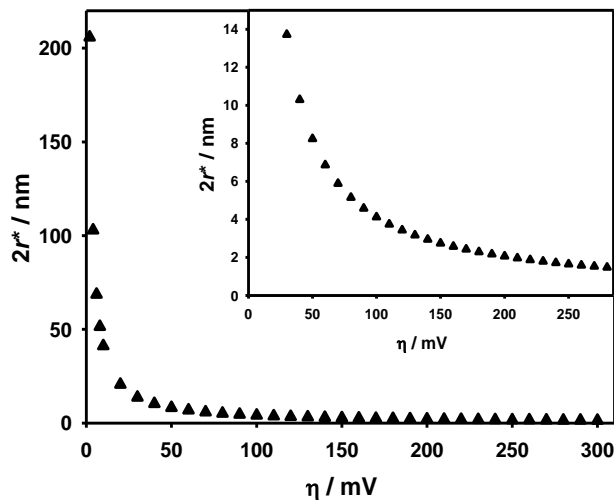
Supplementary Figure 2. Dimensionless plot of the current (i) normalised by the maximum current (i_{\max}) as a function of time (t) at two overpotentials. The experimental conditions are described in the caption of **Supplementary Figure 1**. The *instantaneous* and *progressive* nucleation limits as predicted by the Scharifker-Hills model¹ are indicated.



Supplementary Figure 3. Chronoamperometric transient recorded at -0.27 V fitted to the Scharifker-Mostany model.² Concentration of CuSO_4 is $1.0 \times 10^{-3} \text{ mol} \times \text{dm}^{-3}$. Nuclei number density and nucleation rate of $5.3 \times 10^6 \text{ cm}^{-2}$ and 15 s^{-1} , respectively, were estimated from the fit.



Supplementary Figure 4. Chronoamperometric transients recorded at various overpotentials on ITO electrodes at a CuSO_4 concentration of $1.0 \times 10^{-4} \text{ mol} \times \text{dm}^{-3}$. Other experimental conditions are described in the caption of **Supplementary Figure 1**. The lack of a well-defined current peak and diffusion limiting current suggest a convolution of the dynamics of electron transfer and nucleation.



Supplementary Figure 5. Critical nucleus diameter ($2r^*$) as a function of the overpotential (η), estimated from **equation 1**. In **equation (1)** σ represents the surface tension, M is the atomic weight (M) and ρ is the density.³ This simple relation predicts stable Cu nuclei of 1.5 nm diameter can be formed at overpotentials of -0.27 V. Our experimental observations based on HS-LMFM images revealed stable nuclei of the order of 6-7 nm. Considering that no tip-shape deconvolution routines were applied to these images, our experimental values are close to the thermodynamic limit.

$$r^* = 2\sigma M / \rho zF |\eta| \quad (1)$$

Supplementary References

- 1 Scharifker, B. & Hills, G. Theoretical and Experimental Studies of Multiple Nucleation. *Electrochim Acta* **28**, 879-889 (1983).
- 2 Scharifker, B. R. & Mostany, J. 3-Dimensional Nucleation with Diffusion Controlled Growth.1. Number Density of Active-Sites and Nucleation Rates per Site. *J Electroanal Chem* **177**, 13-23 (1984).
- 3 Scharifker, B. R. & Mostany, J. in *Encyclopedia of Electrochemistry: Interfacial Kinetics and Mass Transport* Vol. 2 (eds A.J. Bard, M. Stratmann, & E.J. Calvo) 512-540 (Wiley, 2003).