

Exercice 3: Nucleation and growth

- 1) What are the 4 nucleation and growth models?
- 2) What property and parameters determine:
 - The nucleation and growth mode?
 - The number density of available nucleation sites?
 - There exists a special case named « underpotential deposition ». Define it!
- 3) The induction time is the formation of critical nuclei and their growth as discrete islands on the substrate.
 - 3.1. Show that the current that crosses a single hemispherical nucleus and a single cylindrical nucleus varies with t^2 and t , respectively.
 - 3.2. Considering that nucleation follows a linear kinetics model $N(t) = N_0(1 - e^{-k_n t})$, express the total current as a function of the time for the 4 scenarios. (no overlapping)

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4) Accounting for overlapping, Scharifker and coworkers established the following equations:

	Instantaneous	Progressive
3D	$\left(\frac{i}{i_{\max}}\right)^2 = 1.9542 \left(\frac{t_{\max}}{t}\right) \left[1 - \exp^{-1.2564\left(\frac{t}{t_{\max}}\right)}\right]^2$	$\left(\frac{i}{i_{\max}}\right)^2 = 1.2254 \left(\frac{t_{\max}}{t}\right) \left[1 - \exp^{-2.3367\left(\frac{t}{t_{\max}}\right)^2}\right]^2$
2D	$\left(\frac{i}{i_{\max}}\right) = \left(\frac{t}{t_{\max}}\right) e^{\left[\frac{1}{2} - \frac{1}{2}\left(\frac{t}{t_{\max}}\right)^2\right]}$	$\left(\frac{i}{i_{\max}}\right) = \left(\frac{t}{t_{\max}}\right)^2 e^{\left[\frac{2}{3} - \frac{2}{3}\left(\frac{t}{t_{\max}}\right)^3\right]}$

Copper depositions below -150 mV vs SCE demonstrated 3D instantaneous nucleations. Integrating the quantity of charge at t_{\max} gives:

$$Q_{\max} = \int_0^{t_{\max}} i(t) \cdot dt = 0.83545 i_{\max} t_{\max}$$

SEM observations showed that the contact angle was 90°, making perfect hemispherical nuclei.

1) Express the maximum radius of nuclei and their density under the assumption that Nuclei are ideally packed on the surface (compact hexagonal arrangement)

2) For a 1 cm² substrate, you integrated Q_{\max} and found 12.7 mC, 10.5 mC, and 8.3 mC at -150 mV, -175 mV, and -200 mV, respectively. What can you conclude? ($z=2$ and $V_m=7.09 \text{ cm}^3 \cdot \text{mol}^{-1}$)

