# 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 $\mathrm{N(t)} = N_0(1 - e^{-k_n t})$, express the total current as a function of the time for the 4 scenarios. (no overlapping)

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3D instantaneous

3D progressive

2D instantaneous

2D progressive

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- The nucleation and growth mode?

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- The nucleation and growth mode?
  - The overpotential (controlled)
  - The surface energy variation, hence the adhesion energy of the deposit on the substrate (intrinsic)

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   - The number density of available nucleation sites?
     - The number density of surface defects of the substrate (partially controlled)
     - The overpotential (controlled) because $\Delta G^*_{Red} \propto$ adion coordination

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   - The number density of available nucleation sites?
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     - The overpotential (controlled) because $\Delta G^{*}_{Red} \propto$ adion coordination

   - There exists a special case named « underpotential deposition ». Define it!
     - Strong substrate/deposit affinity → $\Delta\sigma < 0 \iff \sigma_{Ad} > 2\sigma_s$
     - Cations are reduced at $E > E^{eq}$
     - Limited to 1-2 monoatomic layers

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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.

Perfect 3D hemisphere

$$i(t) = Aj = 2\pi R(t)^2 j$$

Perfect 2D cylinder (only lateral growth)

$$i(t) = Aj = 2\pi R(t) h j$$

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The growth rate normal to a surface can be found through the Faraday law:

$$\int i \,.\, dt = znF \quad \Rightarrow \quad n(t) = \frac{V(t)}{V_m} = \int_0^t \frac{i}{zF} dt \; = \frac{A}{zF} \int_0^t j \, dt$$

$$\Longrightarrow R(t) = \frac{V(t)}{A} = \frac{V_m \, j \, t}{zF}$$

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$$i(t) = 2\pi \left(\frac{V_m}{zF}\right)^2 j^3 t^2$$

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3.2. Considering that nucleation follows a linear kinetics model $\mathrm{N(t)} = N_0(1 - e^{-k_n t})$, express the total current as a function of the time for the 4 scenarios. (no overlapping)

$$I(t) = N(t) i(t) = N_0\left(1 - e^{-k_n t}\right) i(t)$$

## Intantaneous nucleation

$$k_n \gg 1 \quad \Rightarrow \quad N(t) = N_0$$

$$I_{3D}^{Inst}(t) = 2\pi N_0 \left(\frac{V_m}{zF}\right)^2 j^3 t^2$$

$$I_{2D}^{Inst}(t) = 2\pi N_0 \frac{V_m}{zF} h j^2 t$$

## Progressive nucleation

$$k_n \ll 1 \quad \Rightarrow \quad N(t) = N_0 k_n t$$

$$I_{3D}^{Prog}(t) = 2\pi N_0 \left(\frac{V_m}{zF}\right)^2 j^3 k_n t^3$$

$$I_{2D}^{Prog}(t) = 2\pi N_0 \frac{V_m}{zF} h j^2 k_n t^2$$

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

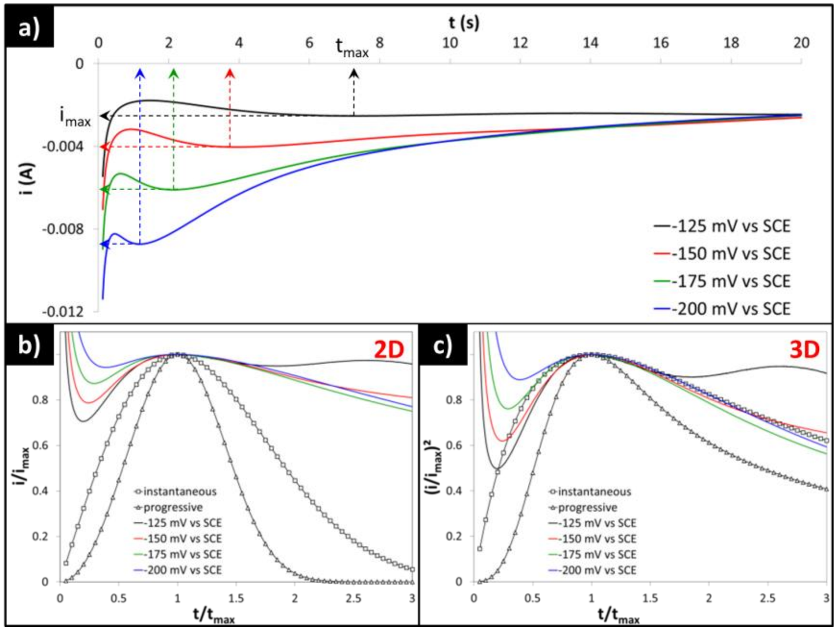
| | **Instantaneous** | **Progressive** |
|---|---|---|
| **3D** | $\left(\frac{i}{i_{max}}\right)^2 = 1.9542\left(\frac{t_{max}}{t}\right)\left[1 - exp^{-1.2564\left(\frac{t}{t_{max}}\right)}\right]^2$ | $\left(\frac{i}{i_{max}}\right)^2 = 1.2254\left(\frac{t_{max}}{t}\right)\left[1 - exp^{-2.3367\left(\frac{t}{t_{max}}\right)^2}\right]^2$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

$$Q_{max} = \int_0^{t_{max}} i(t).dt = \mathbf{0.83545}\, \boldsymbol{i_{max}\, t_{max}}$$

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 $cm^2$ 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 $V_m=7.09\ cm^3.mol^{-1}$)

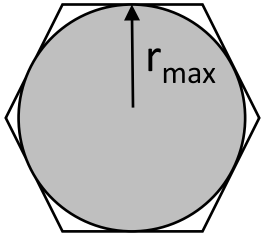
# Exercice 3: Nucleation and growth

## 4) Maximum radius of hemispherical nuclei and nuclei density:

### 4.1. Assumption: Nuclei are ideally packed on the surface (compact hexagonal arrangement)

Hexagonal cell surface area: $\boldsymbol{A_c^{hex} = 2\sqrt{3}.r_{max}^2}$ hence $\boldsymbol{N_0 = \frac{1}{A_c^{hex}} = \frac{1}{2\sqrt{3}.r_{max}^2}}$

Volume of the hemisphere inscribed in the hexagonal cell: $\boldsymbol{V_{max} = \frac{2}{3}\pi r_{max}^3}$



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$Q_{max}$ is related to the electrodeposit volume by the Faraday law: $Q_{max} = zn_{max}F$

$$Q_{max} = z\frac{N_0 V_{max} A}{V_m}F$$

replacing $N_0$ and $V_{max}$

$$Q_{max} = zF\frac{\pi r_{max} A}{3\sqrt{3}V_m}$$

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Hence: $r_{max} = \frac{3\sqrt{3}V_m Q_{max}}{zF\pi A} \approx \frac{1.382\, V_m i_{max} t_{max}}{zFA}$ and $N_0 = \frac{(zF\pi A)^2}{54\sqrt{3}(V_m Q_{max})^2} \approx \frac{0.151\,(zFA)^2}{(V_m i_{max} t_{max})^2}$

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### 4.2. For a 1 cm$^2$ 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?

| | -150 mV / -12.7 mC | -175 mV / -10.5 mC | -200 mV / -8.3 mC |
|---|---|---|---|
| **Maximum radius $r_c$** | 7.72 nm | 6.38 nm | 5.04 nm |
| **Density of nuclei $N_0$** | 4.85E+11 cm$^{-2}$ | 7.09E+11 cm$^{-2}$ | 1.13E+12 cm$^{-2}$ |

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$Q_{max}$ is related to the electrodeposit volume by the Faraday law: $Q_{max} = zn_{max}F$

$Q_{max} = z\frac{N_0 V_{max} A}{V_m}F$ replacing $N_0$ and $V_{max}$ $Q_{max} = zF\frac{\pi r_{max}A}{3\sqrt{3}V_m}$

Hence: $r_{max} = \frac{3\sqrt{3}V_m Q_{max}}{zF\pi A} \approx \frac{1.382\ V_m i_{max} t_{max}}{zFA}$ and $N_0 = \frac{(zF\pi A)^2}{54\sqrt{3}(V_m Q_{max})^2} \approx \frac{0.151\ (zFA)^2}{(V_m i_{max} t_{max})^2}$

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