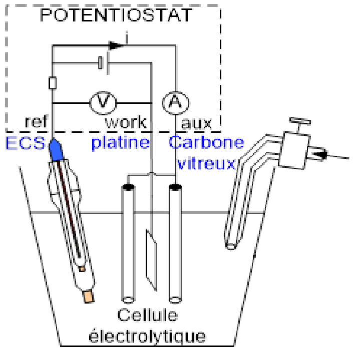
Exercice 2: electrodeposition rate and current efficiency

The quantity of reduced cations is linked to the quantity of coulombs by the

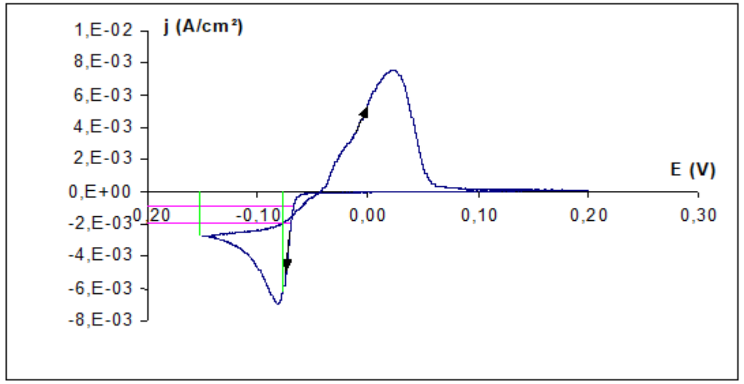
Faraday law: $Q = \int i(t)dt = znF$ Quantity of charge (coulomb) ∝ quantity of matter

Faraday constant $F = q\mathcal{N}_A = 96485\ C.mol^{-1}$

Bismuth is electrodeposited from a degased aqueous electrolyte ($[Bi^{3+}] = 10^{-2}$ mol.L^{-1}, $[HNO_3]$ = 1 M) on an 1 cm^2 working electrode at a sufficiently large overpotential



Argon



1) Propose a protocole to measure the diffusion coefficient of Bi^{3+}.

2) Knowing that $D_{Bi^{3+}} = 10^{-5}$ cm^2.s^{-1}, express the deposition rate of bismuth in mol.s^{-1} as a function of time under purely mass limiting regime and in the absence of convection.

3) Calculate the thickness of the deposit obtained after 1000 s of electroplating (M_{Bi} = 208.98 g.mol^{-1} and ρ_{Bi} = 9.79 g.cm^{-3}).

4) After an electrodeposition of 1000 s, a total of 0.4 C was integrated from the chronoamperometry data. Calculate the electrodeposition efficiency.

5) What could have happened to the other electrons? How could you improve the efficiency?

6) What parameters could allow you to tune the growth rate? What could be the trade-offs?

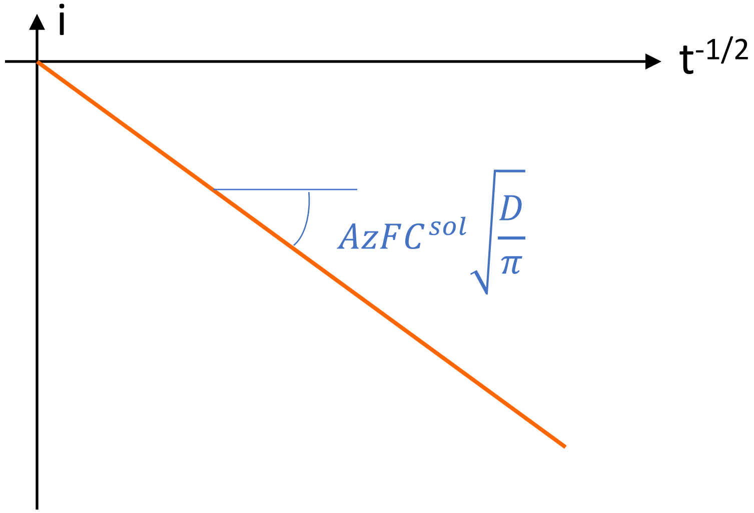
Exercise2: electrodeposition rate and current efficiency

1) Propose a protocole to measure the diffusion coefficient of Bi^{3+}.

The Cottrell law can be used to measure the diffusion coefficient of Bi^{3+}

Let us apply a sufficiently large cathodic overpotential to the cathode so that the reaction $Bi^{3+} + 3e^- \rightharpoonup Bi^0$ is only limited by mass transfer.

Now, let's plot the recorded current versus $t^{-1/2}$



We should obtain a straight line crossing the origin of the plot.

$D_{Bi^{3+}}$ can be calculated from its slope s:

$$D_{Bi^{3+}} = \pi\left(\frac{s}{zFC^{sol}}\right)^2$$

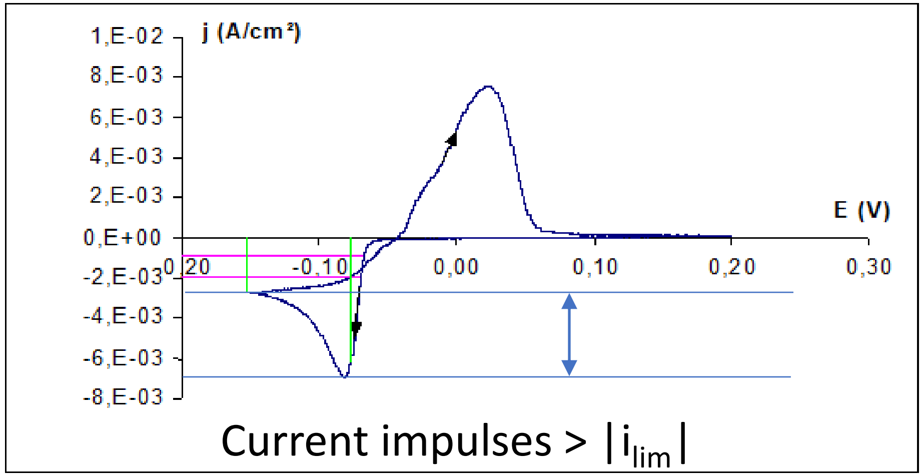
Cottrell law: $j_{lim} = zFC^{sol}\sqrt{\frac{D}{\pi t}}$

Exercise2: electrodeposition rate and current efficiency

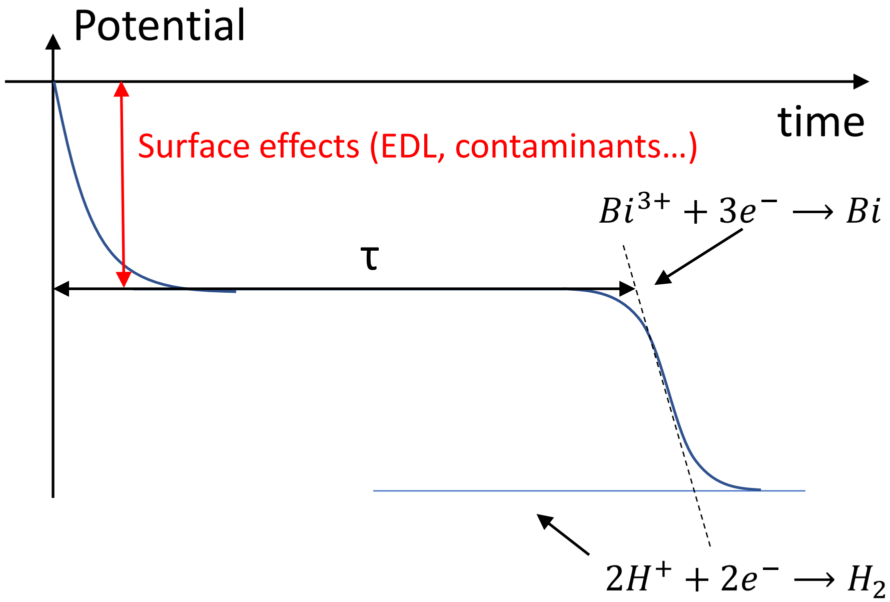
1) Propose a protocole to measure the diffusion coefficient of Bi^{3+}.

In electrochemical deposition, no steady state is reached !!!

A better protocole is the Sand-Bard method that corrects surface modifications



Current impulses > $|i_{lim}|$



At the transition time τ, the flow of Bi^{3+} becomes insufficient to sustain the current

→ The potential jumps to the next reduction potential

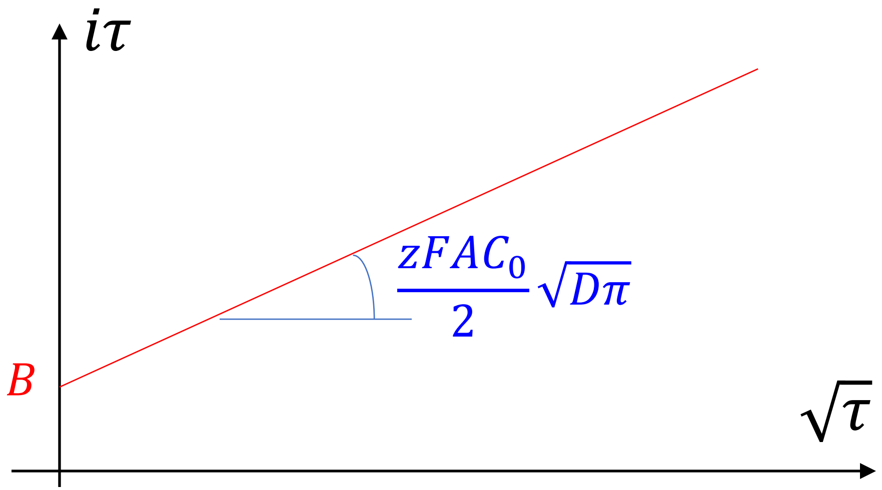
Sand equation: $$\sqrt{\tau} = \frac{zFA}{i}\frac{C_0}{2}\sqrt{D\pi} + \frac{B}{i\sqrt{\tau}}$$ Bard surface correction

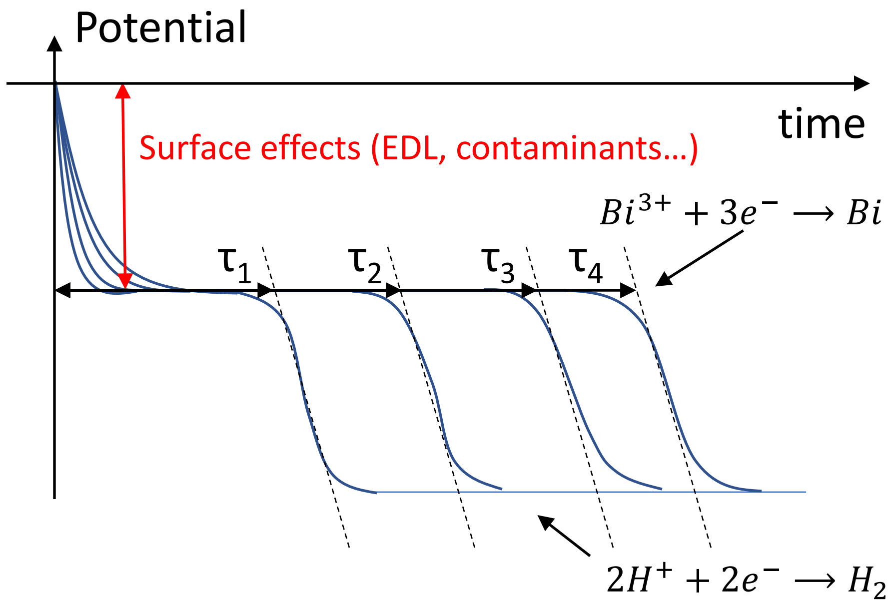
Exercise2: electrodeposition rate and current efficiency

1) Propose a protocole to measure the diffusion coefficient of Bi^{3+}.

In electrochemical deposition, no steady state is reached !!!

A better protocole is the Sand-Bard method that corrects surface modifications





At the transition time τ, the flow of Bi^{3+} becomes insufficient to sustain the current
→ The potential jumps to the next reduction potential

Sand equation: $$i\tau = \frac{zFAC_0}{2}\sqrt{D\pi\tau} + B$$ Bard surface correction

Exercise2: electrodeposition rate and current efficiency

2) Knowing that $D_{Bi^{3+}} = 10^{-5}$ cm^2.s^{-1}, express the deposition rate of bismuth in mol.s^{-1} as a function of time under purely mass limiting regime and in the absence of convection.

[Bi^{3+}] = C^{sol} = 10^{-2} mol.L^{-1} = 10^{-5} mol.cm^{-3}, A = 1 cm^2, and $D_{Bi^{3+}} = 10^{-5}$ cm^2.s^{-1}

$$\int i(t)dt = zn_{Bi}F \quad \rightarrow \quad \frac{dn_{Bi}}{dt} = \frac{i(t)}{zF} = \frac{j(t)}{zF}A$$

Faraday law: $Q = \int i(t)dt = znF$

Cottrell law: $j_{lim} = zFC^{sol}\sqrt{\frac{D}{\pi t}}$

Exercise2: electrodeposition rate and current efficiency

2) Knowing that $D_{Bi^{3+}} = 10^{-5}$ cm^2.s^{-1}, express the deposition rate of bismuth in mol.s^{-1} as a function of time under purely mass limiting regime and in the absence of convection.

[Bi^{3+}] = C^{sol} = 10^{-2} mol.L^{-1} = 10^{-5} mol.cm^{-3}, A = 1 cm^2, and $D_{Bi^{3+}} = 10^{-5}$ cm^2.s^{-1}

$$\int i(t)dt = zn_{Bi}F \quad \rightarrow \quad \frac{dn_{Bi}}{dt} = \frac{i(t)}{zF} = \frac{j(t)}{zF}A$$

$$\frac{j(t)}{zF}A = AC^{sol}\sqrt{\frac{D}{\pi t}} \quad \rightarrow \quad \frac{dn_{Bi}}{dt} = 1 * 10^{-5} * \sqrt{\frac{10^{-5}}{\pi}} * t^{-1/2}$$

Faraday law: $Q = \int i(t)dt = znF$

Cottrell law: $j_{lim} = zFC^{sol}\sqrt{\frac{D}{\pi t}}$

Exercise2: electrodeposition rate and current efficiency

3) Calculate the thickness of the deposit obtained after 1000 s of electroplating (M_{Bi} = 208.98 g.mol^{-1} and ρ_{Bi} = 9.79 g.cm^{-3}).

[Bi^{3+}] = C^{sol} = 10^{-5} mol.cm^{-3}, A = 1 cm^2, $D_{Bi^{3+}}$ = 10^{-5} cm^2.s^{-1}, M_{Bi} = 208.98 g.mol^{-1}, and ρ_{Bi} = 9.79 g.cm^{-3}

$$\int i(t)dt = zn_{Bi}F \rightarrow \frac{dn_{Bi}}{dt} = \frac{i(t)}{zF} = AC^{sol}\sqrt{\frac{D}{\pi t}} = 1 * 10^{-5} * \sqrt{\frac{10^{-5}}{\pi}} * t^{-1/2}$$

Let us integrate: $\Delta n_{Bi} = AC^{sol}\sqrt{\frac{D}{\pi}} \int_0^t t^{-1/2}\,dt = 2AC^{sol}\sqrt{\frac{D}{\pi}}\left[\sqrt{t_2} - \sqrt{t_1}\right]$

$$\Delta n_{Bi} = 2 * 1 * 10^{-5} * \sqrt{\frac{10^{-5}}{\pi}} * \left[\sqrt{1000} - \sqrt{0}\right] \approx 1.128 \cdot 10^{-6} \text{ mol}$$

$$d = \frac{\Delta n_{Bi} \cdot M_{Bi}}{A \cdot \rho_{Bi}} \approx 2.41 \cdot 10^{-5}\ cm = 241\ nm$$

Faraday law: $Q = \int i(t)dt = znF$

Cottrell law: $j_{lim} = zFC^{sol}\sqrt{\frac{D}{\pi t}}$

Exercise2: electrodeposition rate and current efficiency

4) After an electrodeposition of 1000 s, a total of 0.4 C was integrated from the chronoamperometry data. Calculate the electrodeposition efficiency.

$[Bi^{3+}] = C^{sol} = 10^{-2}$ M, A = 1 cm^2, $D_{Bi^{3+}} = 10^{-5}$ $cm^2.s^{-1}$, $M_{Bi} = 208.98$ $g.mol^{-1}$, and $\rho_{Bi} = 9.79$ $g.cm^{-3}$

$$Efficiency = \frac{Q_{ECD}}{Q_{Meas}} = \frac{zn_{Bi}F}{\int i(t)dt}$$

$$n_{Bi} =\approx 1.128 \cdot 10^{-6} \text{ mol}$$

$$Efficiency \approx \frac{3 * 1.128 \cdot 10^{-6} * 96485}{0.4} \approx \frac{0.3266}{0.4} \approx 0.8165$$

Only 81.65 % of the electrons participated to the ECD of bismuth.

Faraday law: $Q = \int i(t)dt = znF$

Cottrell law: $j_{lim} = zFC^{sol}\sqrt{\frac{D}{\pi t}}$

Exercise2: electrodeposition rate and current efficiency

5) What could have happened to the other electrons? How could you improve the efficiency?

Capacitive current (double layer charging) but negligible for long DC electroplating

Uncontrolled side reactions:

→ Reduction of dissolved oxygen $O_2 + 2H^+ + 2e^- \rightharpoonup H_2O_2$

$H_2O_2 + 2H^+ + 2e^- \rightharpoonup 2H_2O$

→ Hydrogen evolution $2H_3O^+ + 2e^- \rightharpoonup H_2 + 2H_2O$

→ Co-deposition of other metals $M^{z+} + ze^- \rightharpoonup M^0$

→ Partial reduction of metal ions $M^{z+} + ye^- \rightharpoonup M^{(z-y)+}$

→ Reduction of surface oxides $M_xO_y + 2yH_3O^+ + 2ye^- \rightharpoonup xM + 3yH_2O$

→ Partial redissolution or detachment of the deposit (corrosion)

Solutions: Argon degassing, optimize the bath formulation (pH, precursors, concentrations), optimize electroplating conditions (electrode potential, temperature, convection), optimize the surface state of the substrate