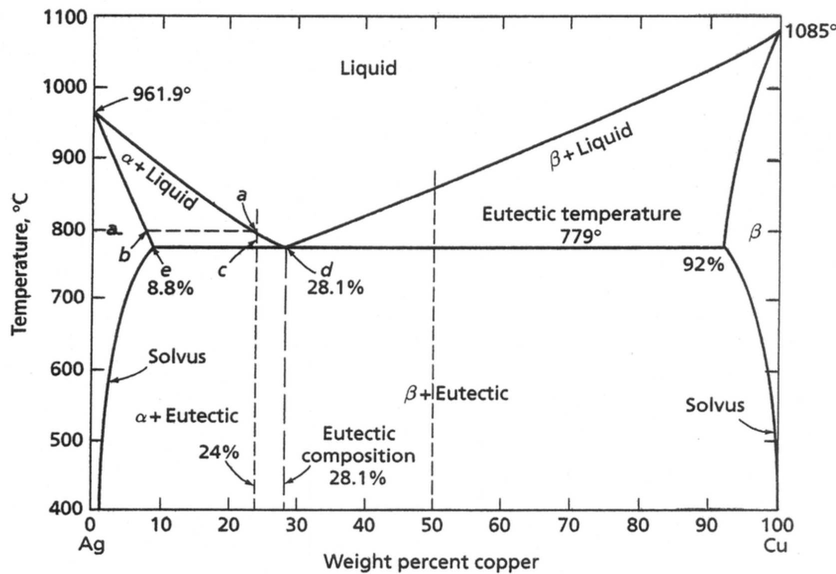
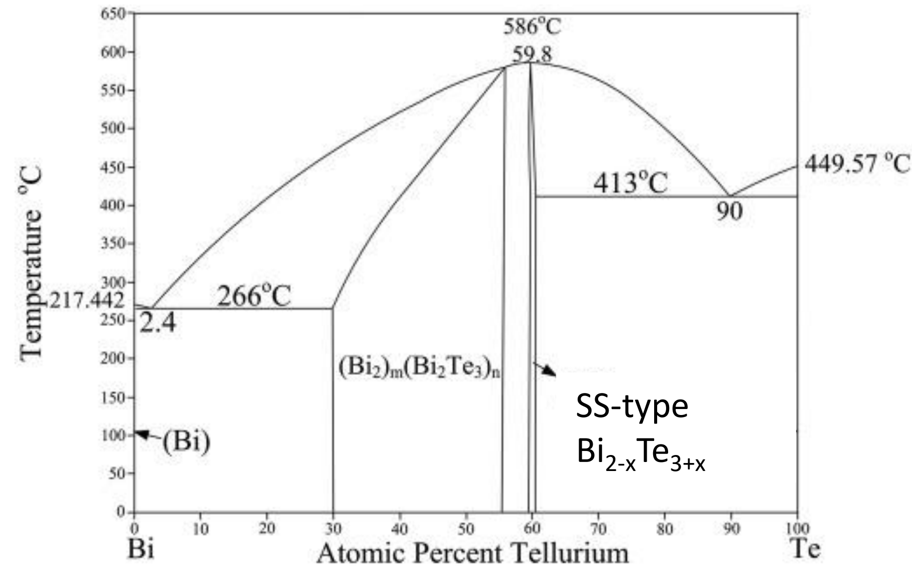
6 – Electrodeposition of alloys and solid solutions

Some examples of electrodeposited alloys

Protective & decorative	Corrosion resistant	Magnetic alloys	Heat resistant allloys	Electronic & jewelry	Antifriction
NiZn	ZnCd	NiCo	CrMn	PdNi	PbAg
NiAu	ZnSn	NiFe	CrW	AuNi	InPb
NiCd	CrNi	CoW	CrMo	AuCo	PbCu
NiSn	CrRe	CoPt	WFe		AgSn
AuCu		FePt			
AuAg					
CuSn					

I) Alloys and solid solutions

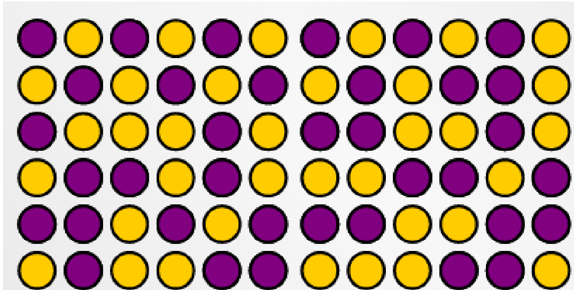




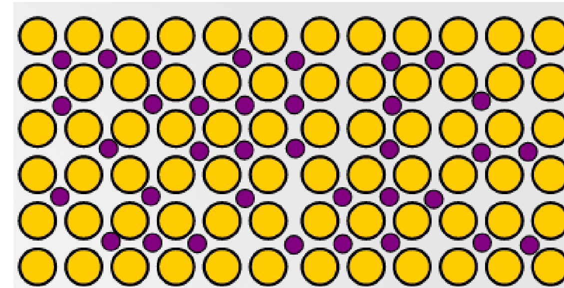
- Phase diagram for metallurgy only useful for predicting the phase-type
- Localized electrocrystallization enables single phases with wider composition range
- Highly dispersed supersaturated solid solutions can be electroplated Metastable: decompose upon annealing

I) Alloys and solid solutions

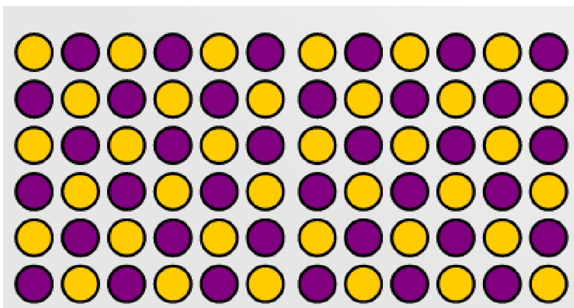
Substitutional solid solution:
B randomly replace A



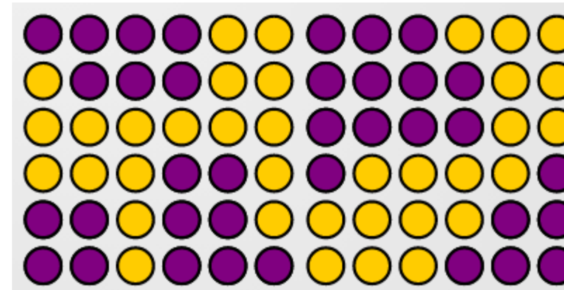
Interstitial solid solution:
Smaller atoms in random interstitial sites



Intermetallic alloys:
A and B form a new lattice



Bimetallic:
No mixing of A and B

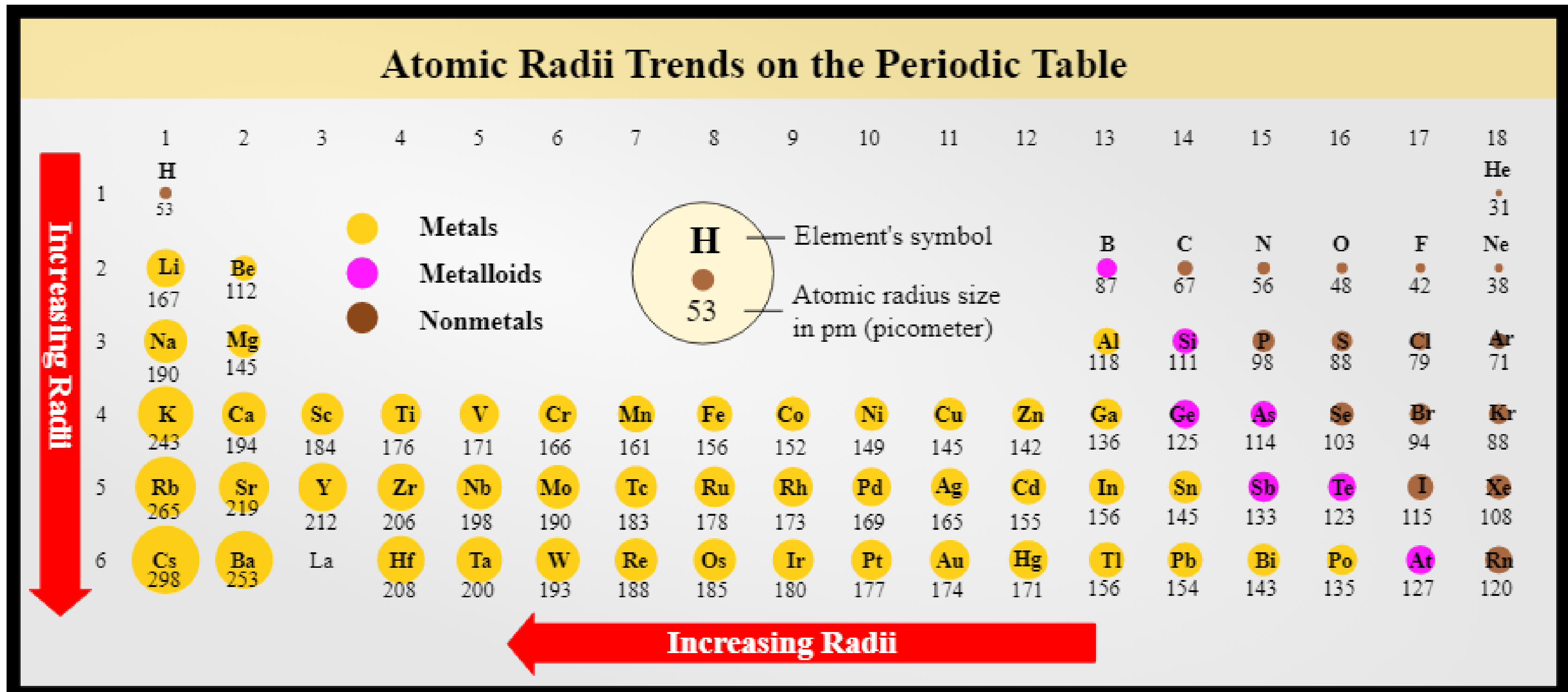


I) Alloys and solid solutions

Intrinsic internal stress due to differences of atom radii

Interstitial atom: B_i^* → compressive stress

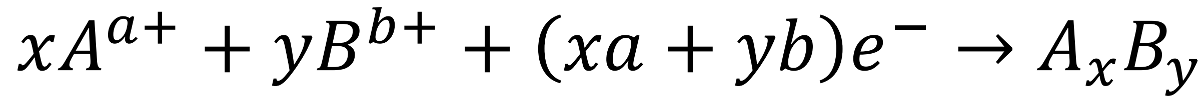
Substitution: B_a^x → compressive if $r_B > r$ tensile if $r_B < r_A$



II) Electrodeposition of several elements

1) Direct deposition process

Both metal cations are reduced in a single step:



$$xA^{a+} + yB^{b+} + (xa + yb)e^{-} \rightarrow A_xB_y$$

Particularity of direct electrodeposition mechanism:

$$E^0\left(xA^{a+}, yB^{b+}\middle|A_xB_y\right)\ may\ be\ \ higher\ than\ both\ E^0(A^{a+}|A^0)\ and\ E^0\left(B^{b+}\middle|B^0\right)$$

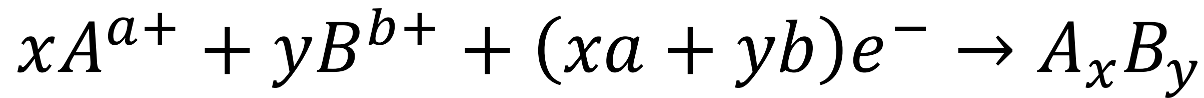
Not possible to deposit only one cation selectively

x and y still depend on the overpotential and the mass transfer of individual species

II) Electrodeposition of several elements

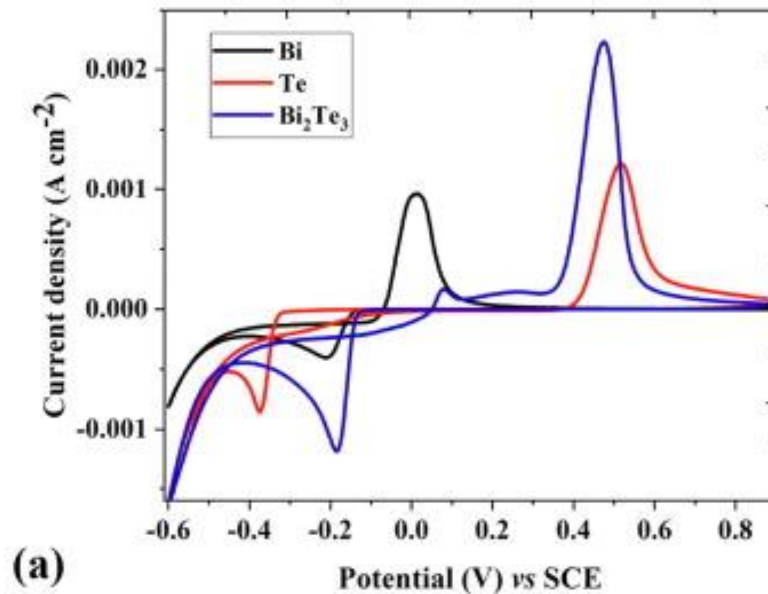
1) Direct deposition process

Both metal cations are reduced in a single step:



$$xA^{a+} + yB^{b+} + (xa + yb)e^{-} \rightarrow A_xB_y$$

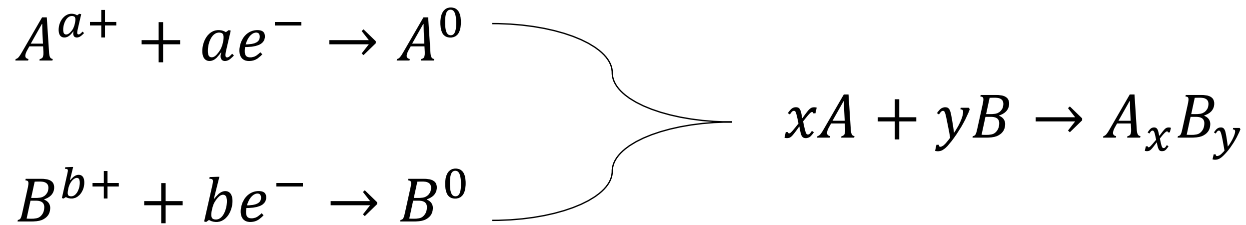
Indications by cyclic voltammetry

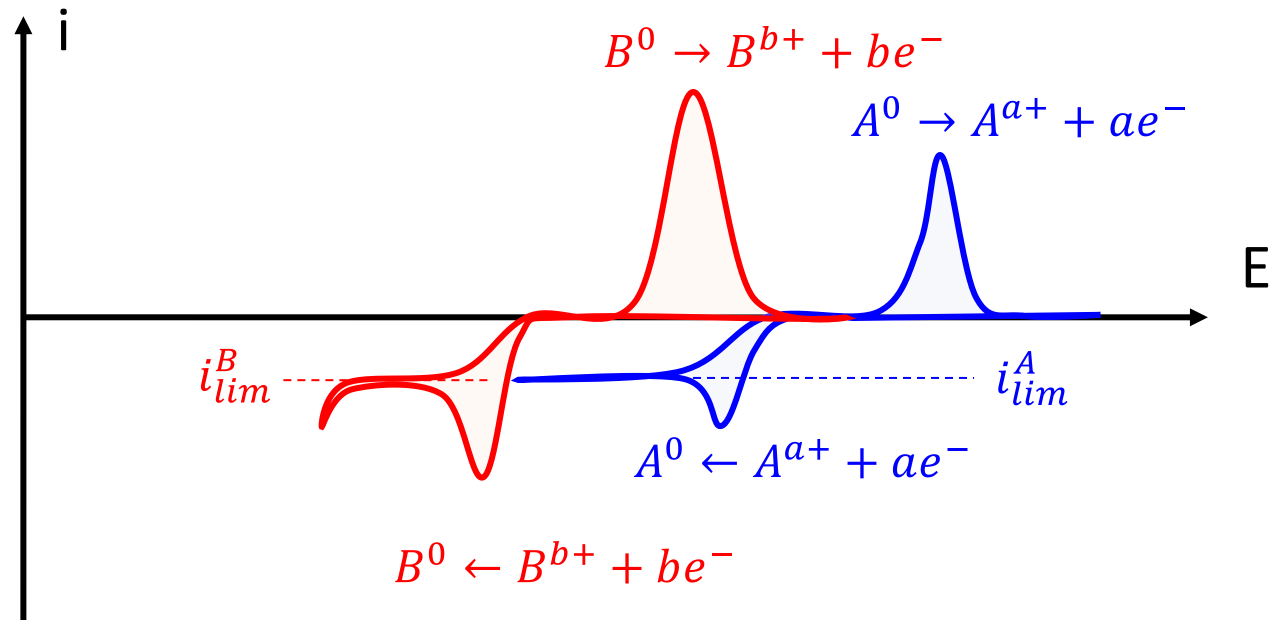


II) Electrodeposition of several elements

2) Co-deposition process

Both metal cations are reduced independently:





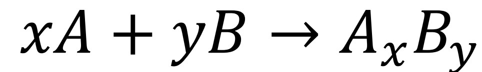
II) Electrodeposition of several elements

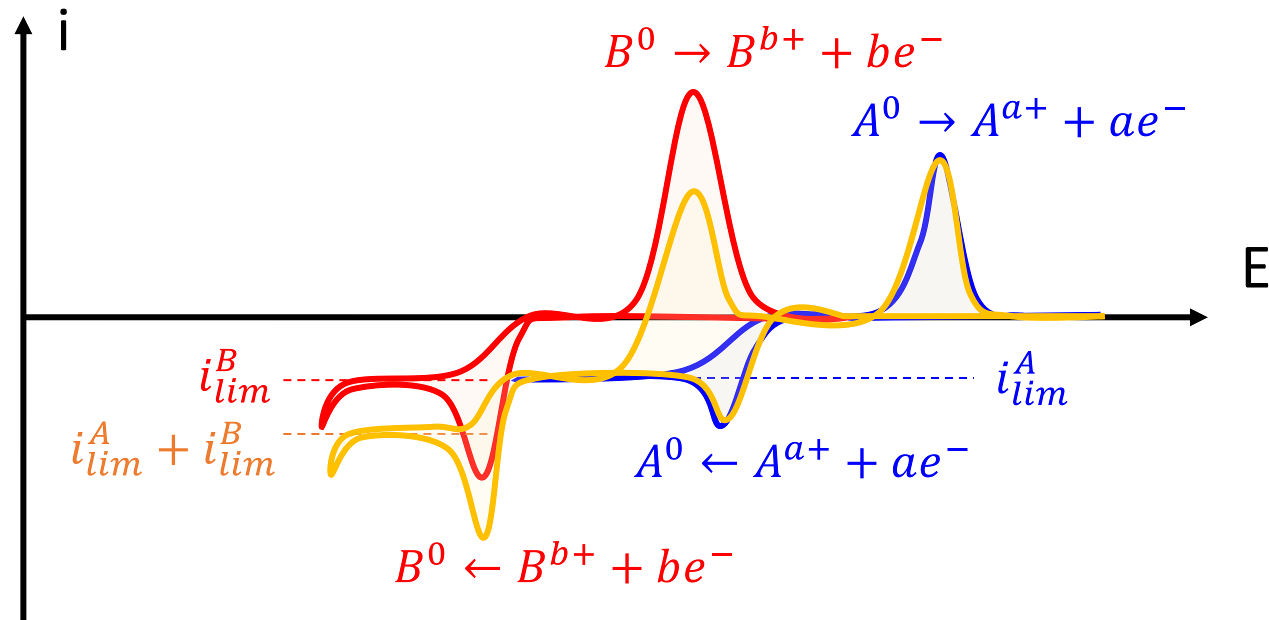
2) Co-deposition process

Both metal cations are reduced independently:

$A^{a+} + ae^- \rightarrow A^0$

$B^{b+} + be^- \rightarrow B^0$


$xA + yB \rightarrow A_xB_y$



II) Electrodeposition of several elements

2) Co-deposition process

Both metal cations are reduced independently:

The deposit composition will depend on partial currents $i_A(t)$ and $i_B(t)$:

Express the general equation that gives molar ratio $\frac{n_a}{n_b}$!

II) Electrodeposition of several elements

2) Co-deposition process

Both metal cations are reduced independently:

The deposit composition will depend on partial current $i_A(t)$ and $i_B(t)$:

$$a n_A F = \int i_A(t)dt \quad \text{and} \quad b n_B F = \int i_B(t)dt$$

$$\boldsymbol{\frac{n_A}{n_B} = \frac{b}{a}\frac{\int i_A(t)dt}{\int i_B(t)dt}}$$

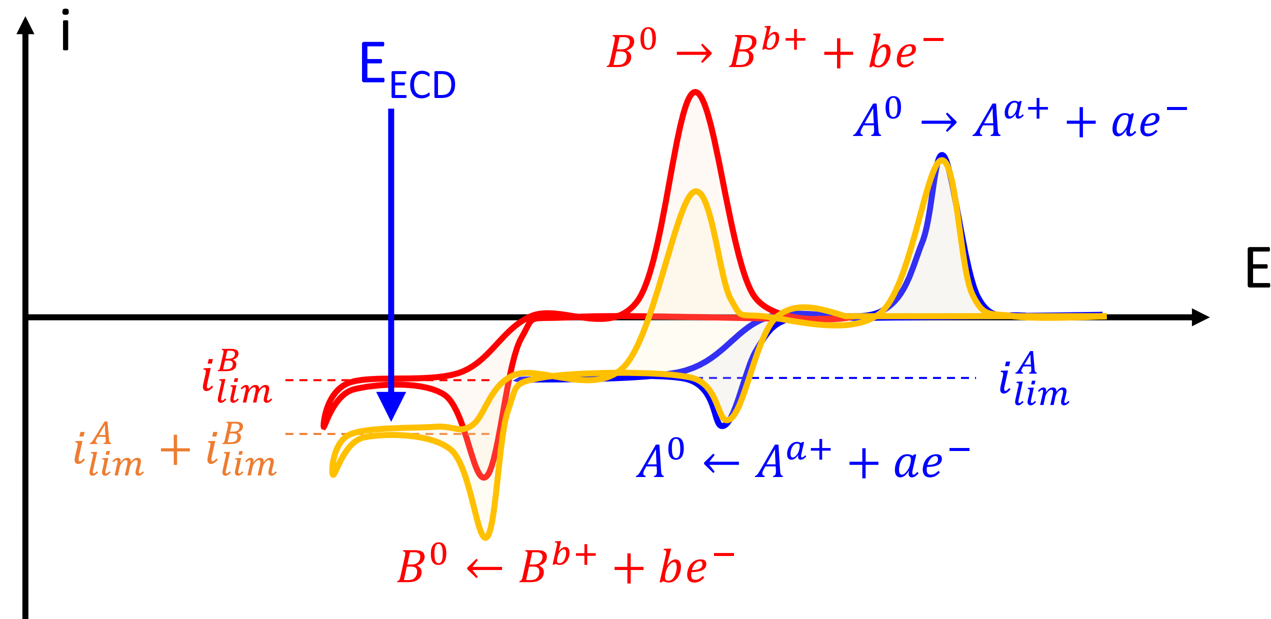
II) Electrodeposition of several elements

2) Co-deposition process

Both metal cations are reduced independently:

Co-deposition of A and B is carried out at overpotentials sufficiently high so that only mass transfer controls the kinetics.

What parameters will allow you to tune the composition?



II) Electrodeposition of several elements

2) Co-deposition process

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The deposit composition will depend on partial current $i_A(t)$ and $i_B(t)$:

$$a n_A F = \int i_A(t)dt \quad \text{and} \quad b n_B F = \int i_B(t)dt$$

$$\boldsymbol{\frac{n_A}{n_B} = \frac{b}{a}\frac{\int i_A(t)dt}{\int i_B(t)dt}}$$

Case 1: high overpotentials

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

$$\boldsymbol{\frac{n_A}{n_B} = \frac{C_A^0}{C_B^0}\sqrt{\frac{D_A}{D_B}}}$$

Composition can only be tuned via concentrations

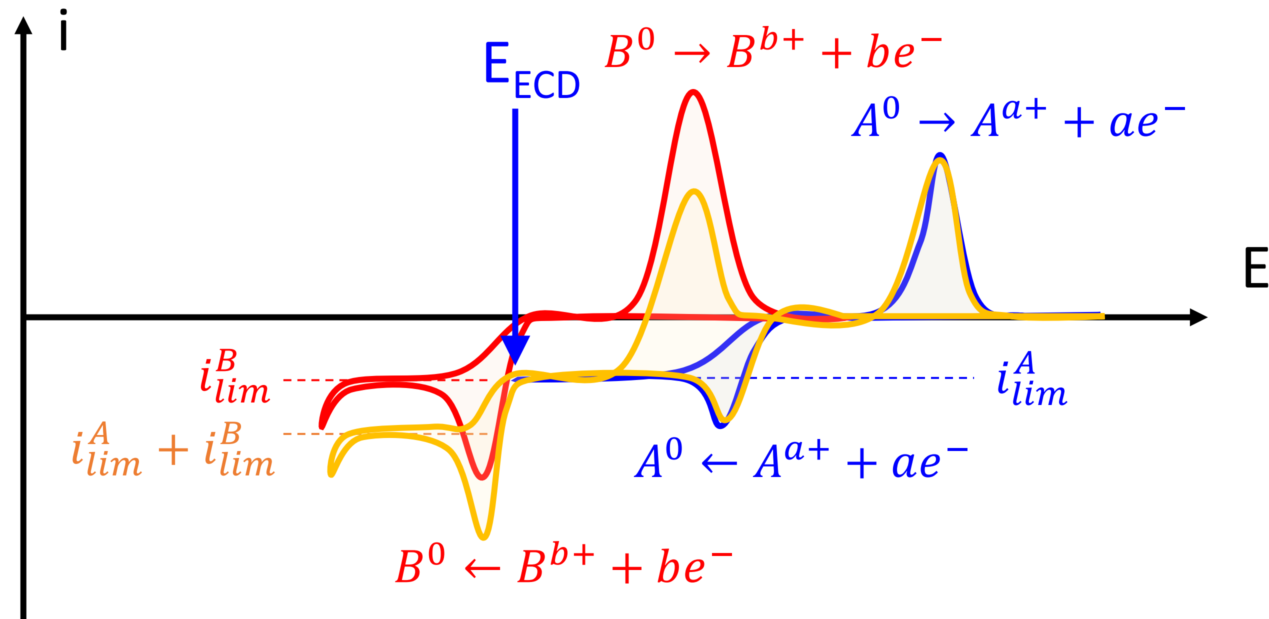
II) Electrodeposition of several elements

2) Co-deposition process

Both metal cations are reduced independently:

Co-deposition of A and B with $\eta_A >> \eta_B$ so that:
- ECD of A is purely limited by mass transfer
- ECD of B is in the linear Butler-Volmer region

Find the equation that predicts the coating composition!



II) Electrodeposition of several elements

2) Co-deposition process

Both metal cations are reduced independently:

The deposit composition will depend on partial current $i_A(t)$ and $i_B(t)$:

$$an_A F = \int i_A(t)dt \quad \text{and} \quad bn_B F = \int i_B(t)dt$$

$$\boldsymbol{\frac{x}{y} = \frac{n_A}{n_B} = \frac{b}{a}\frac{\int i_A(t)dt}{\int i_B(t)dt}}$$

Case 3: $\eta_A \gg \eta_B$

$$j_A = aFC_A^0\sqrt{\frac{D_A}{\pi t}} \quad \text{and} \quad j_B \approx j_0^B \cdot \frac{bF\eta_B}{RT}$$

$$\boldsymbol{\frac{n_A}{n_B} = \frac{2}{\pi}\frac{C_A D_A}{j_0^B \eta_B} RT t^{-0.5}}$$

Depends on concentrations, η_B, and time ⇒ **composition gradient**

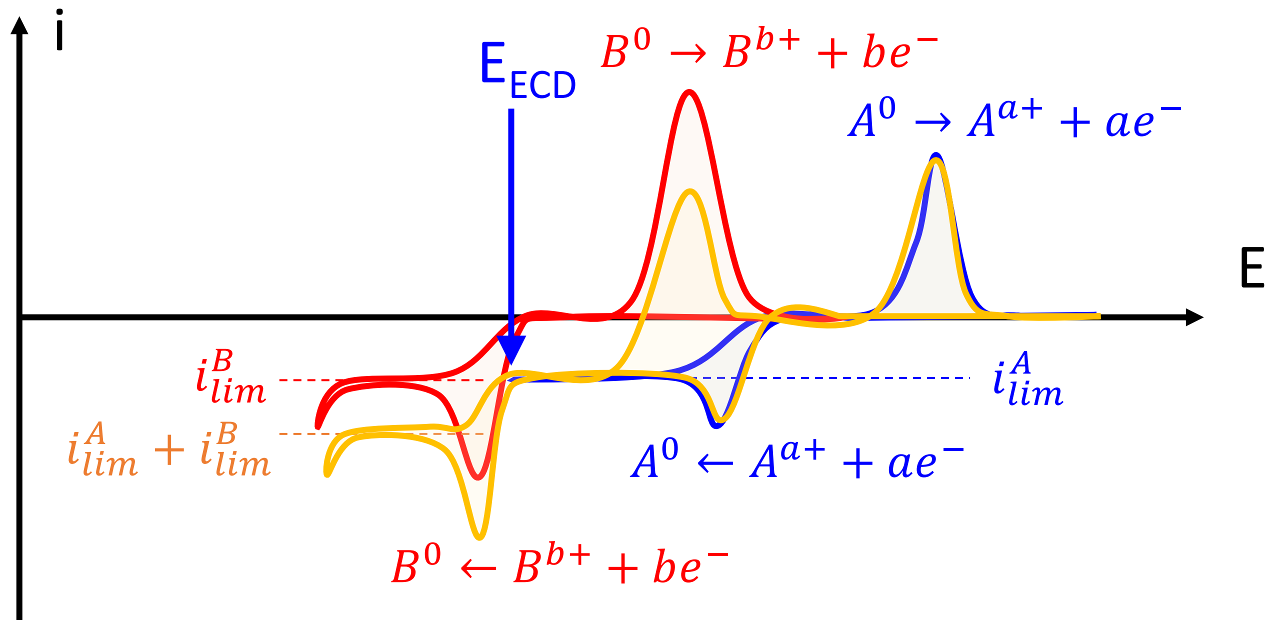
II) Electrodeposition of several elements

2) Co-deposition process

Both metal cations are reduced independently:

What morphology may you expect?

How could you correct it?



II) Electrodeposition of several elements

3) The use of ligands

Let us consider cations A^{a+} and B^{b+}, both complexed by Ligands $L^{\alpha-}$.

Starting from the Nernst equation for each cation, can you find what parameter will affect the difference between their equilibrium potentials?

II) Electrodeposition of several elements

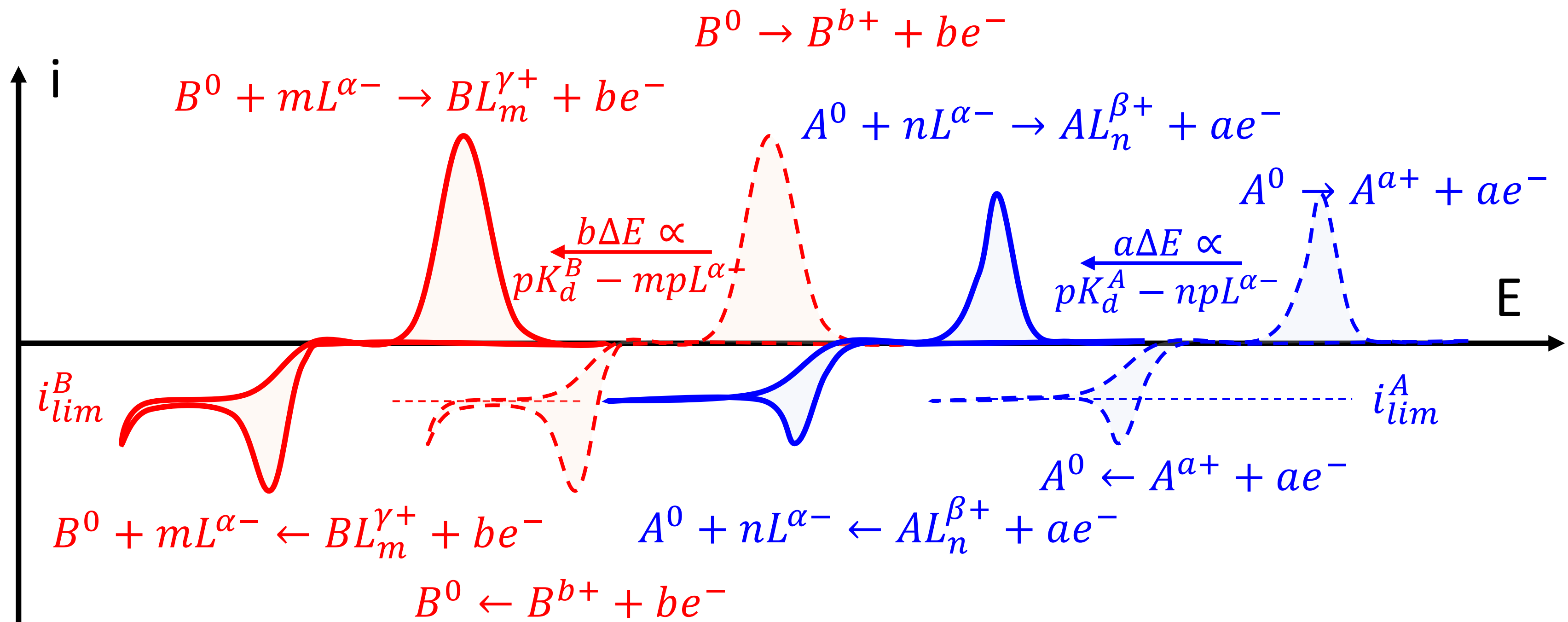
3) The use of ligands

$$E^{eq} = E^0(M^{z+}/M^0) + \frac{RT}{zF}\ln[M^{z+}] \qquad K_d = \frac{[M^{z+}][L^{\alpha-}]^n}{[ML_n{}^{\beta+}]} \rightarrow [M^{z+}] = K_d\frac{[ML_n{}^{\beta+}]}{[L^{\alpha-}]^n}$$

$$E_A^{eq} = E_A^0 + \frac{RT}{aF}\ln\left(\frac{K_d^A[AL_n^{\beta a+}]}{[L^{\alpha-}]^n}\right)$$

and

$$E_B^{eq} = E_B^0 + \frac{RT}{bF}\ln\left(\frac{K_d^B[BL_m^{\gamma+}]}{[L^{\alpha-}]^m}\right)$$



II) Electrodeposition of several elements

3) The use of ligands

$$E^{eq} = E^0(M^{z+}/M^0) + \frac{RT}{zF}\ln[M^{z+}] \qquad K_d = \frac{[M^{z+}][L^{\alpha-}]^n}{[ML_n{}^{\beta+}]} \rightarrow [M^{z+}] = K_d\frac{[ML_n{}^{\beta+}]}{[L^{\alpha-}]^n}$$

$$E_A^{eq} = E_A^0 + \frac{RT}{aF}\ln\left(\frac{K_d^A\left[AL_n^{\beta+}\right]}{[L^{\alpha-}]^n}\right) = E_B^{eq} = E_B^0 + \frac{RT}{bF}\ln\left(\frac{K_d^B\left[BL_m^{\gamma+}\right]}{[L^{\alpha-}]^m}\right)$$

$$E_A^{eq} + \frac{2.303RT}{aF}\left(pK_d^A + pAL_n^{\beta+} - n.pL^{\alpha-}\right) = E_B^{eq} + \frac{2.303aRT}{bF}\left(pK_d^B + pAL_m^{\gamma+} - m.pL^{\alpha-}\right)$$

$$pL^{\alpha-} = \left\{\frac{abF}{2.303RT}\Delta E^0 - b\left(pK_d^A + pAL_n^{\beta+}\right) + a\left(pK_d^B + pM_2L^{\beta_2+}\right)\right\}\frac{1}{ma-nb}$$

If both metals form complexes, then $E_1^{eq} - E_2^{eq}$ only depends on dissociation constants and stoichiometry numbers

A feasible solution may exist only if the less noble metal has higher K_d or Ox state

Often necessary to find a selective complexing agent

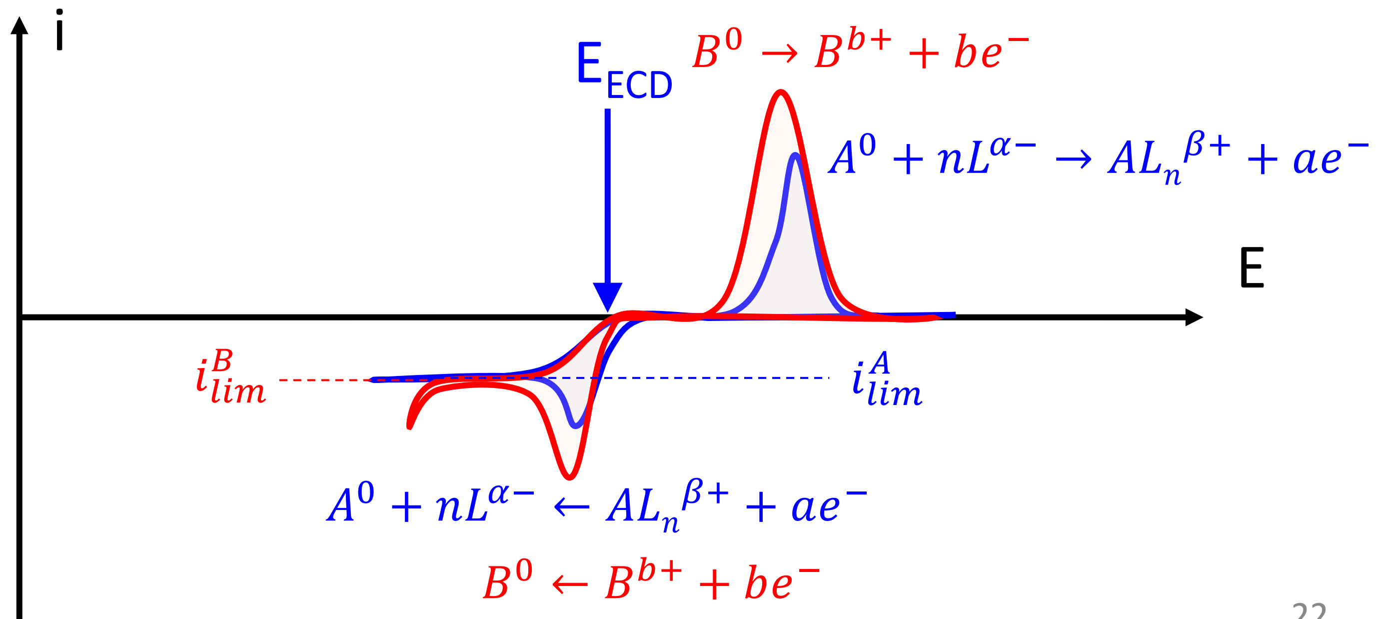
II) Electrodeposition of several elements

2) Co-deposition process

Both metal cations are reduced independently:

Co-deposition of A and B is carried out at:
- low overpotentials for both cations: linearized Butler-Volmer
- No mass limitation: $C_{el} = C^0$.

Express the ratio $\frac{n_a}{n_b}$!



II) Electrodeposition of several elements

2) Co-deposition process

Both metal cations are reduced independently:

The deposit composition will depend on partial current $i_A(t)$ and $i_B(t)$:

$$an_AF = \int i_A(t)dt \quad \text{and} \quad bn_BF = \int i_B(t)dt$$

$$\boldsymbol{\frac{x}{y} = \frac{n_A}{n_B} = \frac{b}{a}\frac{\int i_A(t)dt}{\int i_B(t)dt}}$$

Case 2: low overpotentials $j \approx j_0 \cdot \frac{zF\eta}{RT}$ (Butler-Volmer linear approx.)

$$\boldsymbol{\frac{n_A}{n_B} = \frac{j_0^A}{j_0^B}\frac{\eta_A}{\eta_B}}$$

Composition depends on exchange currents and overpotentials

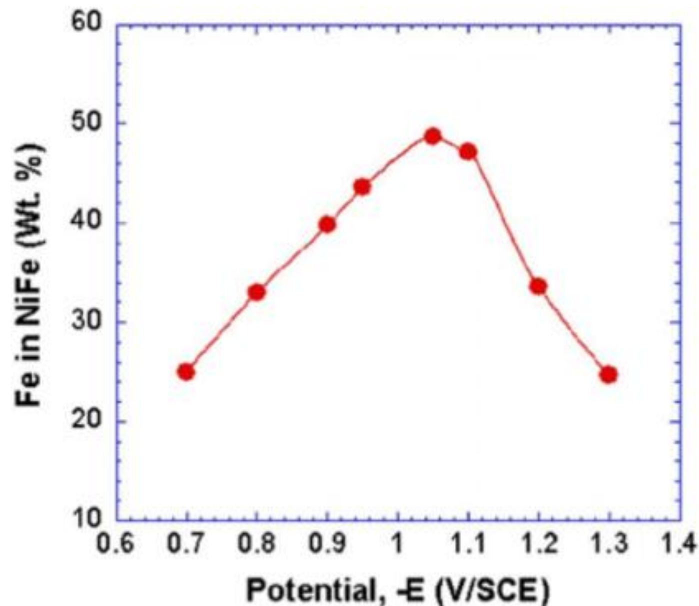
II) Electrodeposition of several elements

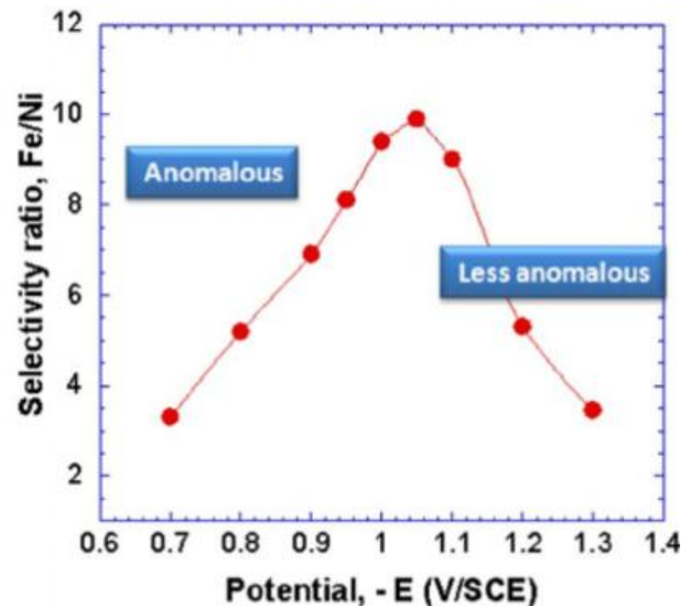
5) Anomalous co-deposition

The less noble metal becomes the more noble metal

The electrodeposit composition tendency towards overpotential reverts

Observed for numerous Ni intermetallic alloys (NiFe, NiCo…)





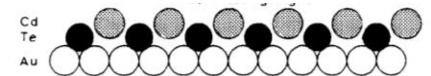
II) Electrodeposition of several elements

6) Consecutive UPD layers

The nucleation of A on substrate S performs with $\Delta\sigma < 0$

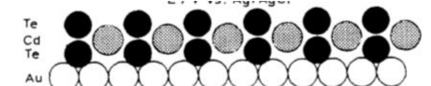
Then a monoatomic layer of A on S can be deposited at $E > E_{eq}$

The nucleation of B on monolayer A occurs with $\Delta\sigma < 0$



Then a monoatomic layer of A on B can be deposited at $E > E_{eq}$

The nucleation of B on monolayer A performs with $\Delta\sigma < 0$



Then a monoatomic layer of B on A can be deposited at $E > E_{eq}$

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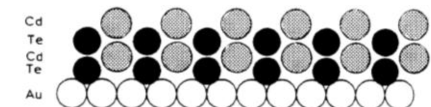
Repeat as many time as necessary to reach the desired thickness



III) Quick ECD optimizations

1) The Hull cell

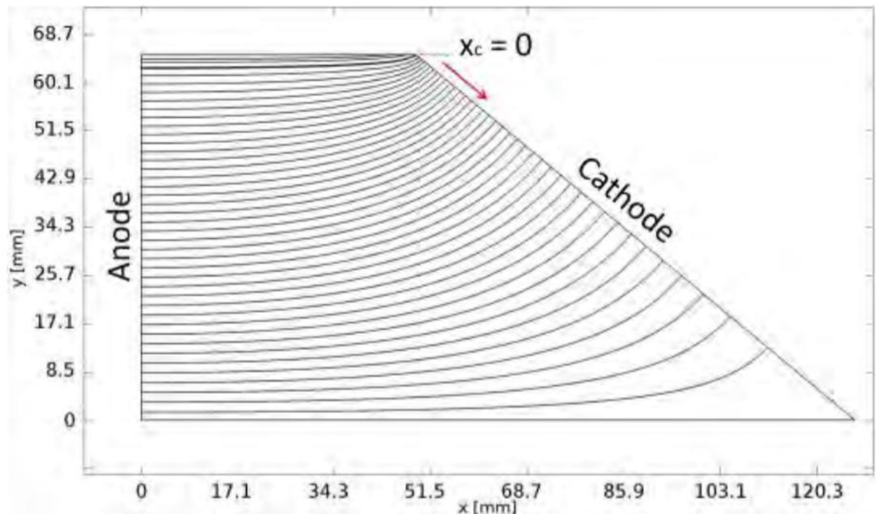


Figure 2. 250 ml Hull cell current density streamlines

Cathode surface area = 66.3 cm^2

$$I_c = I(5.1 - 5.24 \log x_c)$$

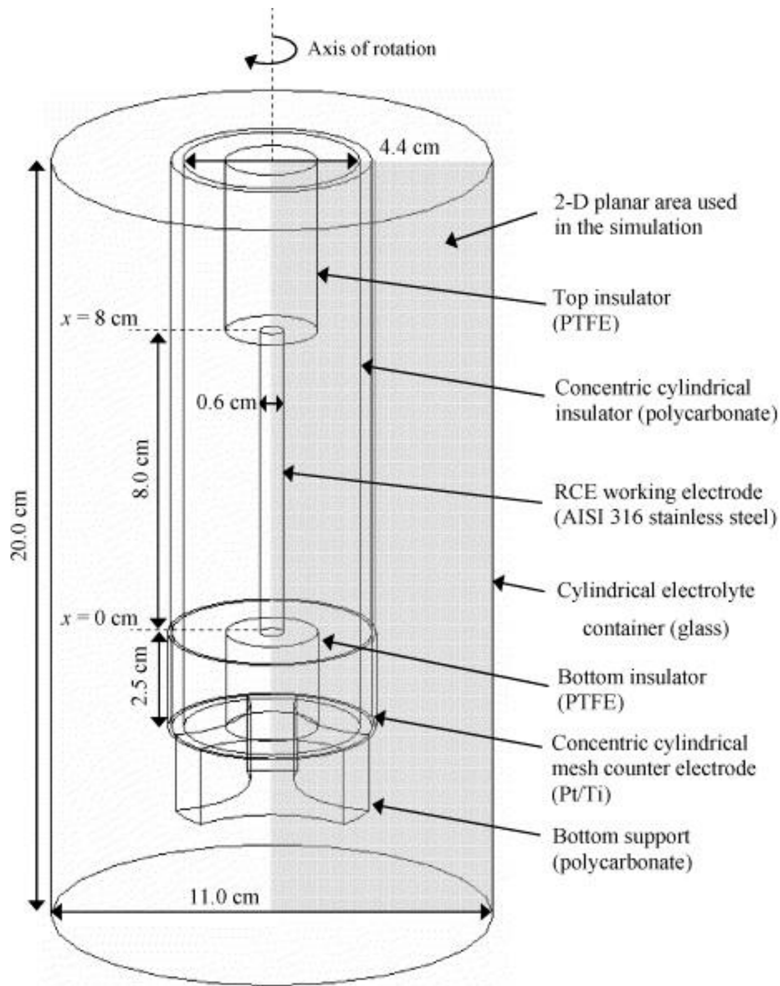
I_c - cathode current density [A/dm^2]
I - total current in the cell [A]
x_c - coordinate along the cathode [cm]

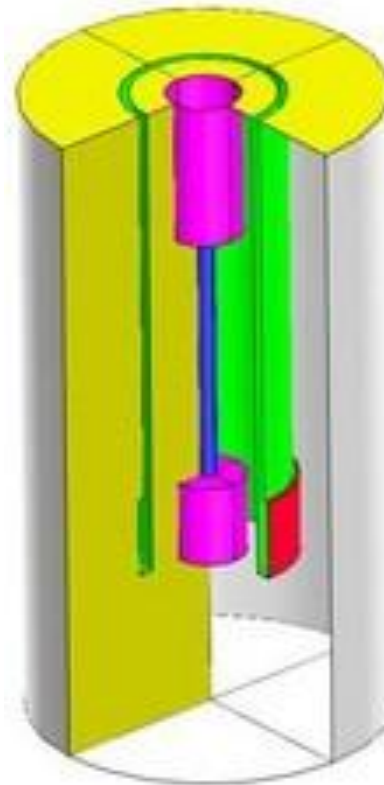
The composition and growth rate of the electrodeposit may vary with the position x_c
The deposit morphology and microstrucure may vary with the position x_c

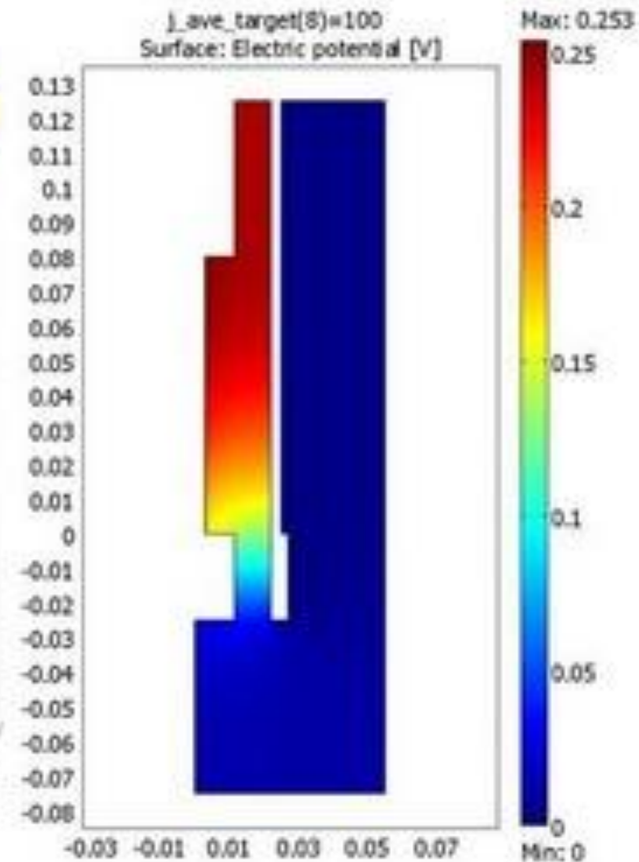
Quick optimization of the current density
Assessment of the macrothrowing power
Difficult to apply ideal agitation: studies normally performed under natural diffusion

III) Quick ECD optimizations

2) The rotating cylinder Hull cell

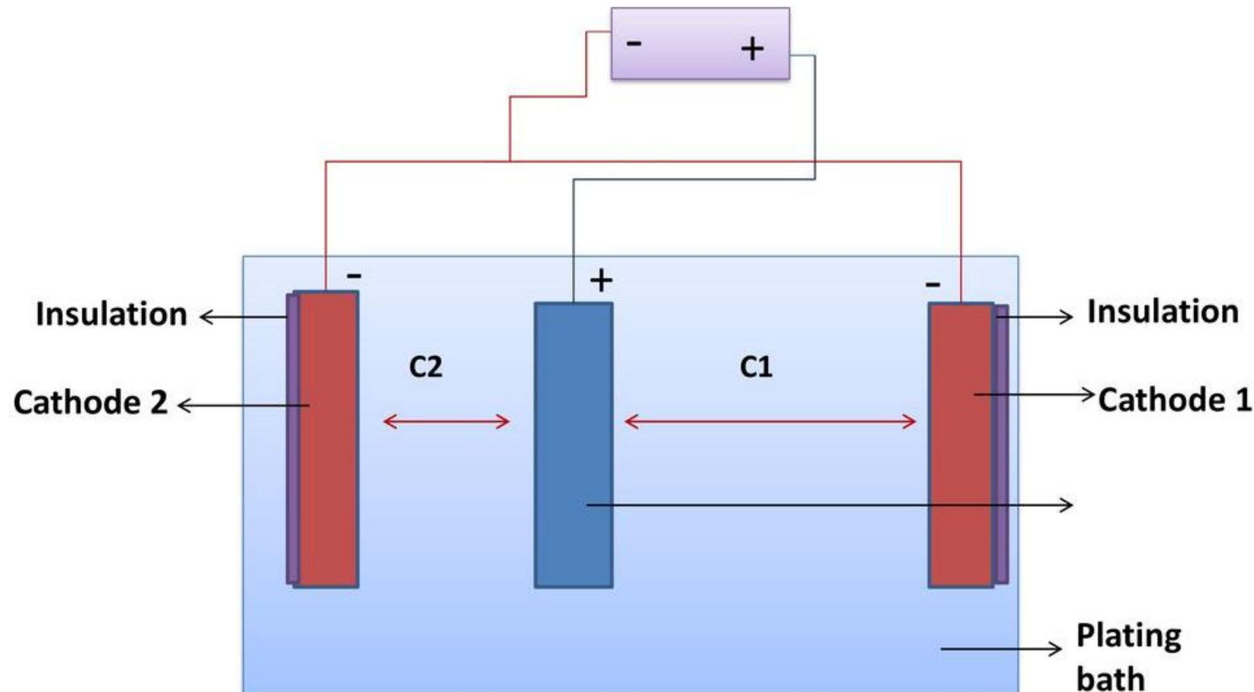






III) Quick ECD optimizations

3) The Haring-Blum cell



Used to evaluate of the macrothrowing power:
Optimization of levellers!

II) Electrodeposition of several elements

7) The Hull cell

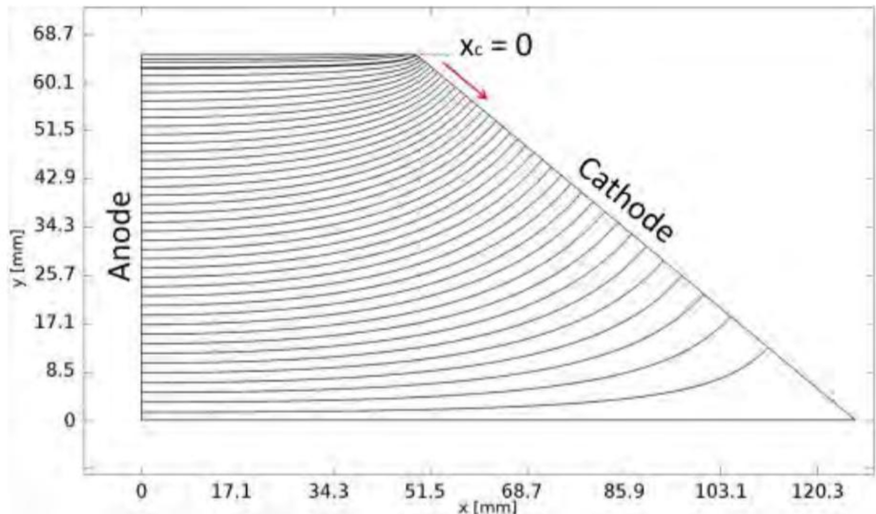


Figure 2. 250 ml Hull cell current density streamlines

$$I_c = I(5.1 - 5.24 \log x_c)$$

I_c - cathode current density [A/dm^2]
I - total current in the cell [A]
x_c - coordinate along the cathode [cm]

Cathode surface area = 66.3 cm^2

Cu and Ni are codeposited at pH 9 in a Hull cell with a total current of 1 A

$E^0(Cu^{2+}/Cu)$ = 0.16 V vs NHE, $[Cu^{2+}]$ = 0.05 M, j_{lim} = 275 mA.dm^{-2}
$E^0(Ni^{2+}/Ni)$ = -0.23 V vs NHE, $[Ni^{2+}]$ = 0.2 M, j_{lim} = 555 mA.dm^{-2}

Can you estimate the composition profile along x_c?
Can you predict the current efficiency?
We consider that only HER occurs as a side reaction and that $j_{HER} = j_{tot} - j_{lim,Cu} - j_{lim,Ni}$

II) Electrodeposition of several elements

7) The Hull cell

Let us define limit conditions:

1) There exist a value x_c above which $5.1 – 5.24 \log x_c \leq 0$

$$x_c^{(1)} = 10^{(5.1/5.24)} = 9.403 \text{ cm}$$

2) $E^0(Cu^{2+}/Cu) >> E^0(Ni^{2+}/Ni)$: if $I_C \leq j_{lim}(Cu)$ then only copper is deposited

$$x_c^{(2)} = 10^{((5.1-0.275)/5.24)} = 8.333 \text{ cm}$$

3) $E^{eq}(H^+/H_2) = E^0(H^+/H_2) – 0.059 \text{ pH} = 0.531 \text{ V vs NHE} << E^0(Ni^{2+}/Ni)$

HER only occurs when $I_C > j_{lim}^{(Cu)} + j_{lim}^{(Ni)}$

$$x_c^{(3)} = 10^{((5.1-0.275-0.555)/5.24)} = 6.530 \text{ cm}$$

II) Electrodeposition of several elements

7) The Hull cell

$x_c > x_c^{(1)}$: no deposition

$x_c^{(1)} > x_c > x_c^{(2)}$: only copper is deposited at the rate

$$\frac{dn_{Cu}}{dt} = \frac{I_c}{2F}$$

$x_c^{(2)} > x_c > x_c^{(3)}$: copper and nickel are codeposited:

$$\frac{dn_{Cu}}{dt} = \frac{j_{lim}^{Cu}}{2F} \quad \text{and} \quad \frac{dn_{Ni}}{dt} = \frac{I_c - j_{lim}^{Cu}}{2F}$$

$$\frac{n_{Ni}}{n_{Cu}} = \frac{I_c - j_{lim}^{Cu}}{j_{lim}^{Cu}} = \frac{I(5.1 - 5.24 log\ x_c) - j_{lim}^{Cu}}{j_{lim}^{Cu}} = 17,545 - 19.055 \log x_c$$

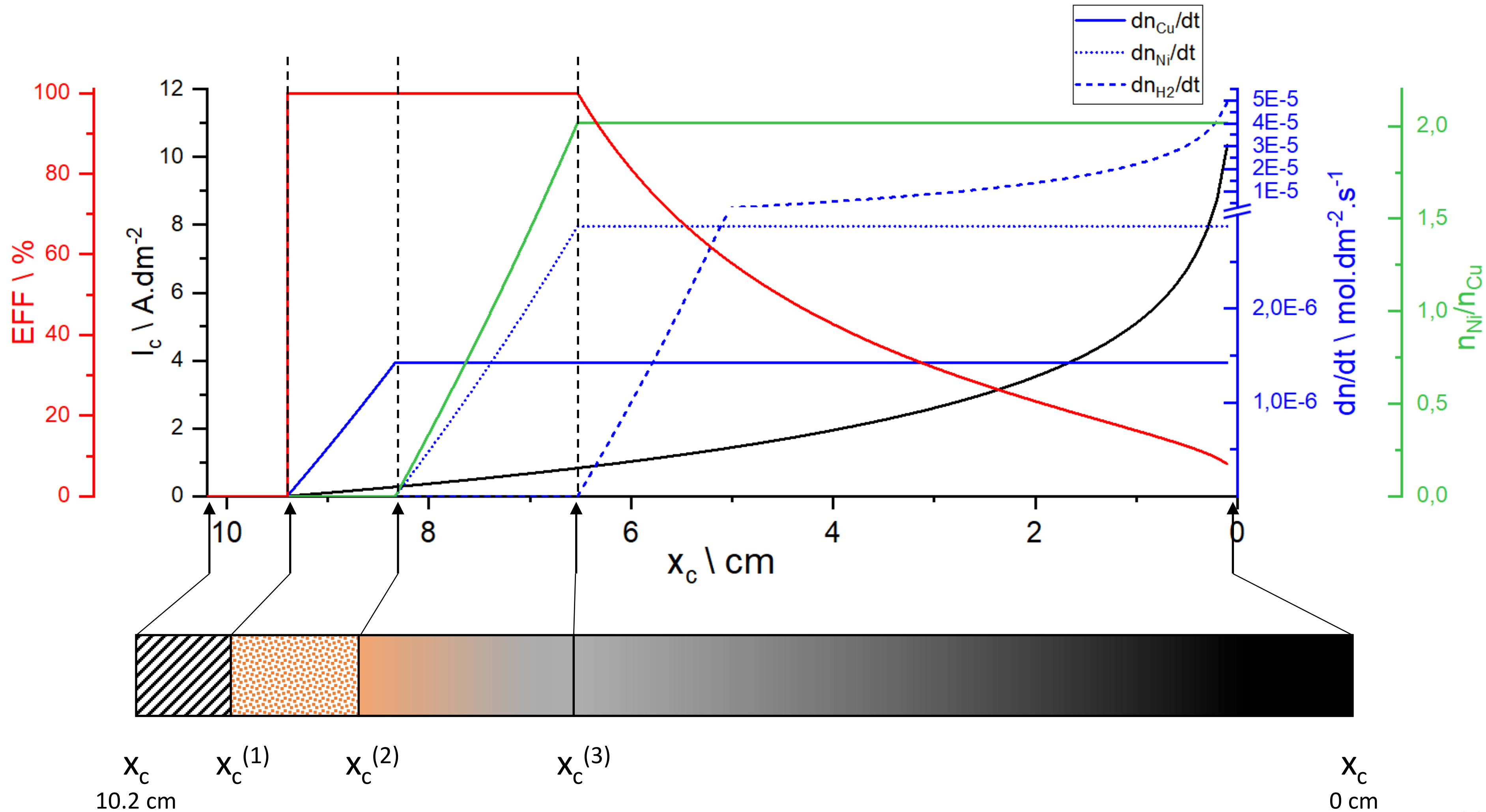
$x_c < x_c^{(3)}$: The deposit composition is constant: $\frac{n_{Ni}}{n_{Cu}} = \frac{j_{lim}^{Ni}}{j_{lim}^{Cu}} = 2.02$

ECD is accompanied by HER: $\frac{dn_{H_2}}{dt} = \frac{I_c - j_{lim}^{Cu} - j_{lim}^{Ni}}{2F} = (2.21 - 2,72 \log x_c) \cdot 10^{-5} mol.s^{-1}$

ECD efficiency = $\frac{j_{lim}^{Cu} + j_{lim}^{Ni}}{I_c} = (6.145 - 6.313 \log x_c)^{-1}$

II) Electrodeposition of several elements

7) The Hull cell



II) Electrodeposition of several elements

7) The Hull cell

In reality, the distribution of the current results from three contributions:

1) The primary current: ionic conduction

Ohm's law of the electric potential through the ionic conductor: $\nabla\phi = -\rho i$

The electrode potentials are constant V_a and V_c

The potential distribution in the electrolyte is a solution of Laplace equation $\nabla^2\phi = 0$

2) The secondary current: reaction kinetics

The overpotential: $\eta = V_c - \phi = f(x_c)$

Butler-Volmer for charge tranfer limitations: $j = j_0(exp^{\frac{-\alpha zF\eta}{RT}} - exp^{\frac{(1-\alpha)zF\eta}{RT}})$

3) The ternary current: mix kinetics and transport

2) Butler-Volmer for mix control: $j = j_0(\frac{[C_{el}]}{[C^0]} exp^{\frac{-\alpha zF\eta}{RT}} - \frac{[A_{el}]}{[A_{el}^0]} exp^{\frac{(1-\alpha)zF\eta}{RT}})$

3) Cotrell for pure diffusion: $j = zF[C^0]\sqrt{\frac{D}{\pi t}}$

Typically, simulations are performed to determine the exact current distribution