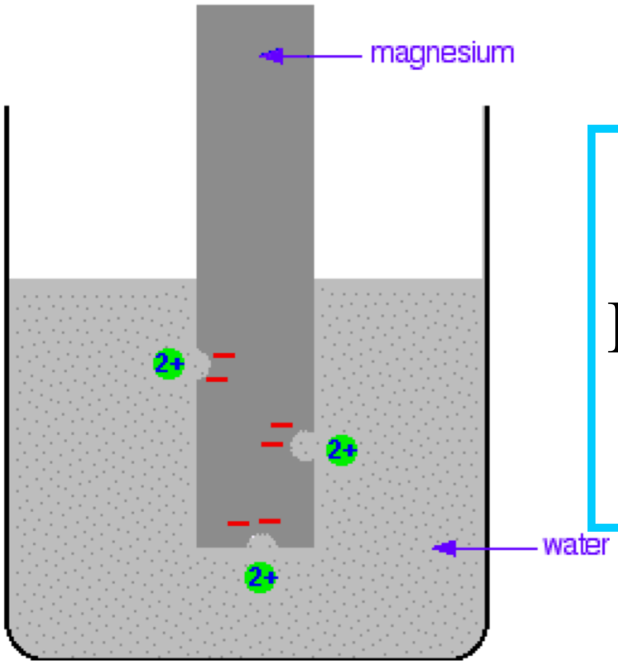
Termodinâmica Eletroquímica

Origem dos potenciais de eletrodo



$$\text{Pode ocorrer} \begin{cases} Mg^{2+}_{(aq)} + 2e^{-}_{metal} \rightarrow Mg \\ Mg \rightarrow Mg^{2+}_{(aq)} + 2e^{-}_{metal} \end{cases}$$

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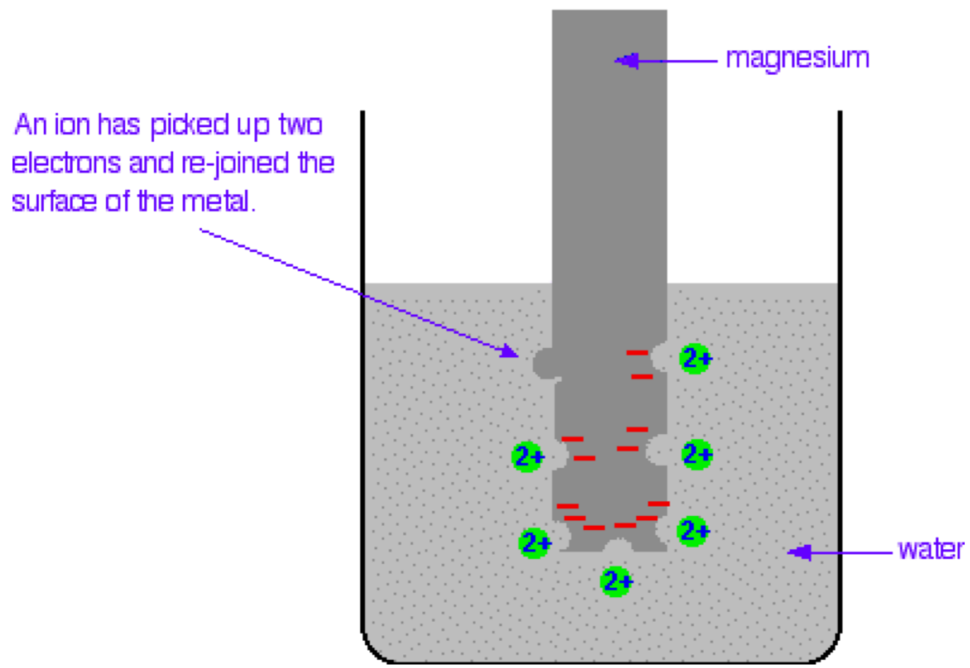
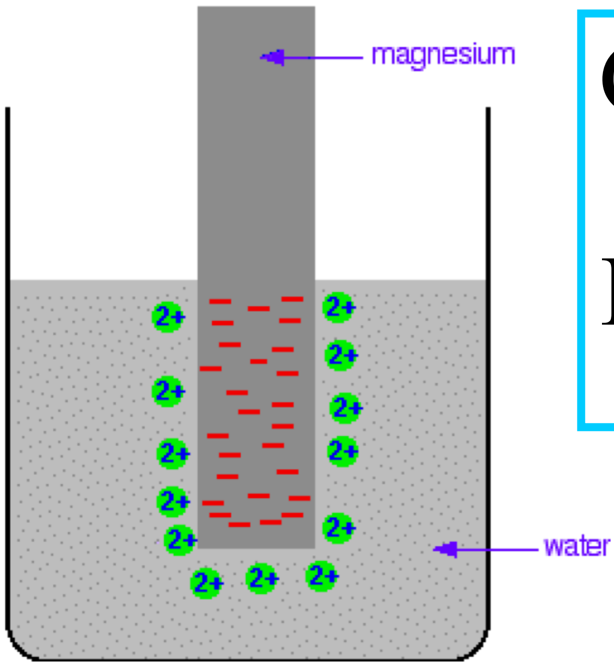


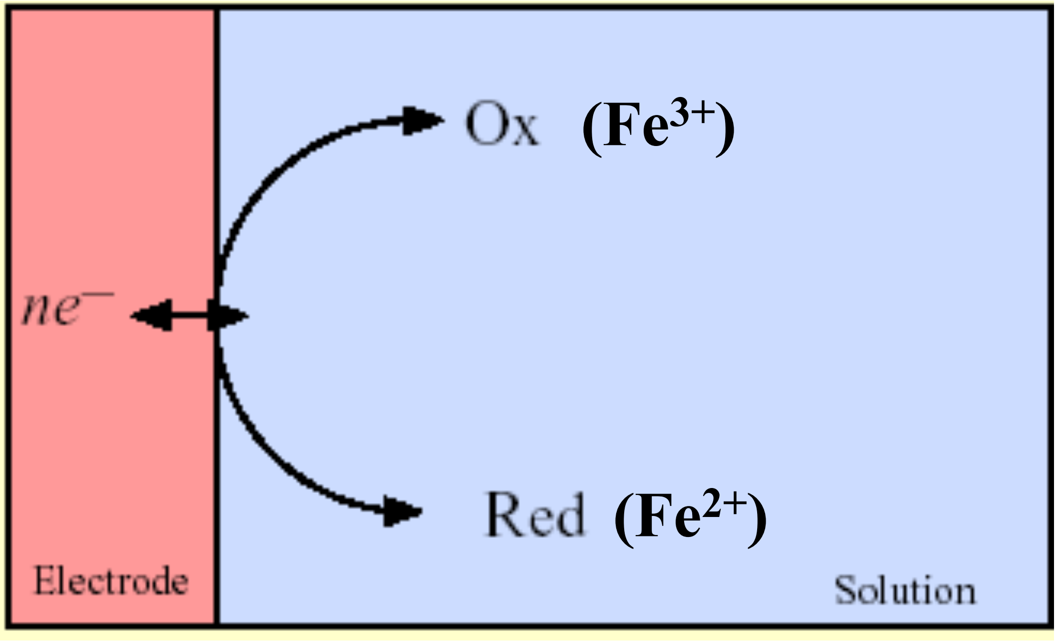


Condição de equilíbrio

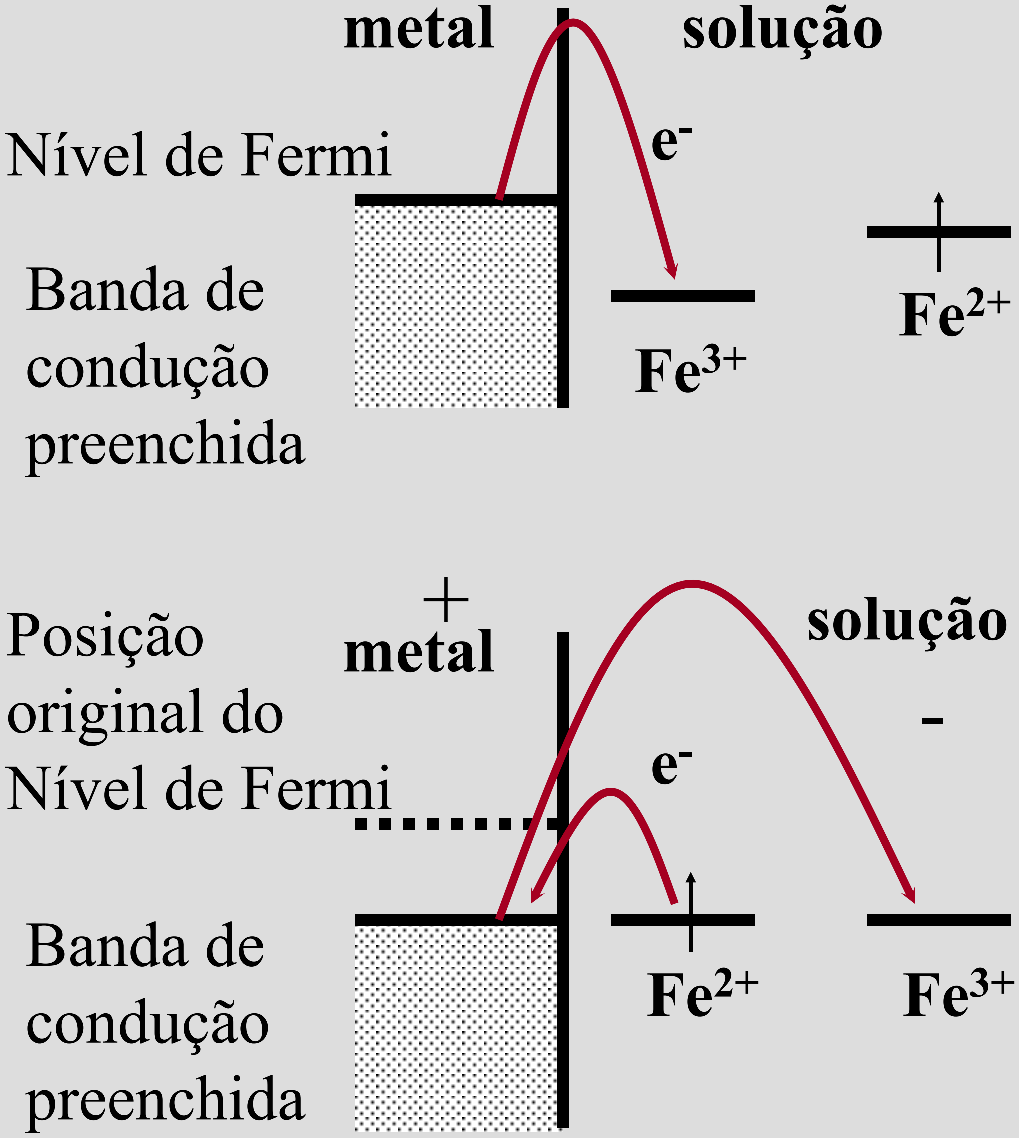
$$Mg^{2+}_{(aq)} + 2e^{-}_{metal} \rightleftarrows Mg$$

Potencial de eletrodo 🡐 diferença de potencial 🡐 separação de cargas

Como é a transferência de cargas na interface eletrodo/solução



$$Fe^{3+}_{(aq)} + e^{-}_{metal} \rightleftarrows Fe^{2+}_{(aq)}$$



Alteração de concentrações muito pequenas. Chega-se a uma situação de **equilíbrio** dinâmico

Se a concentração dos íons é mudada

Deslocamento do equilíbrio

Os íons determinam o potencial

Diferença de potencial (d.d.p) = f(conc. de espécies que determinam o potencial

Equação de Nernst

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{P,T,N_{j \neq i}}$$

$$d\,\overline{G} = -SdT + VdP + \sum_i \mu_i dN_i + F \sum_i z_i \varphi dN_i$$

$$\overline{\mu} = \left(\frac{\partial \overline{G}}{\partial N_i} \right)_{P,T,N_{j \neq i}}$$

Reações envolvendo cargas

Trabalho de manipulação de cargas

Potencial eletroquímico

$$\tilde{\mu}_i = \mu_i + w_e$$

$$\tilde{\mu}_i = \mu_i + z_i F \varphi$$

$$Fe^{3+}_{(aq)} + e^{-}_{metal} \rightleftarrows Fe^{2+}_{(aq)}$$

$$\sum_{produto} G_i = \sum_{reagente} G_i \Rightarrow \sum_{produto} \upsilon_i \tilde{\mu}_i = \sum_{reagente} \upsilon_i \tilde{\mu}_i$$

$$\left(\mu_{Fe^{2+}} + 2\,F\,\varphi_s\right) = \left(\mu_{Fe^{3+}} + 3\,F\,\varphi_s\right) + \left(\mu_{e^-} - 1\,F\,\varphi_M\right)$$

$$\left(\mu_{Fe^{2+}} - \mu_{Fe^{3+}} - \mu_{e^-}\right) = 3\,F\,\varphi_s - 2\,F\,\varphi_s - 1\,F\,\varphi_M$$

$$\left(\mu_{Fe^{2+}} - \mu_{Fe^{3+}} - \mu_{e^-}\right) = 3\,F\,\varphi_s - 2\,F\,\varphi_s - 1\,F\,\varphi_M$$

$$\left(\mu_{Fe^{2+}} - \mu_{Fe^{3+}} - \mu_{e^-}\right) = F\,\varphi_s - F\,\varphi_M$$

$$\mu_i = \mu_i^o + RT \ln a_i$$

$$\frac{1}{F}\left(\mu^o_{Fe^{3+}} - \mu^o_{Fe^{2+}} + \mu^o_{e^-}\right) - \frac{RT}{F}\left(\ln a_{Fe^{2+}} - \ln a_{Fe^{3+}} - \ln a_{e^-}\right) = (\varphi_M - \varphi_s)$$

$$\Delta\varphi^o = E^o_{Fe^{3+}/Fe^{2+}}$$

$$E_{Fe^{3+}/Fe^{2+}}$$

Potencial padrão do eletrodo Pt/Fe^{3+}/Fe^{2+}

$$E_{Fe^{3+}/Fe^{2+}} = E^{o}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

Equação de Nernst

$$Zn / Zn^{2+}_{(aq,a=1)} \| H^{+}_{(aq,a=1)} | H_{2(g,p=1\,atm)} | Pt \qquad E^{o}_{cel} = 0,76\ V$$

$$2\,H^{+}_{(aq)} + 2e^{-} \rightleftarrows H_{2(g)} \qquad E_{d} = EPH = 0V$$

$$Zn^{2+}_{(aq)} + 2e^{-} \rightleftarrows Zn_{(s)} \qquad E_{e} = E^{o}_{Zn^{2+}/Zn}$$

$$2\,H^{+}_{(aq)} + Zn_{(s)} \rightleftarrows H_{2(g)} + Zn^{2+}_{(aq)} \qquad E_{cel} = E_{d} - E_{e} = 0 - E^{o}_{Zn^{2+}/Zn} = 0,76V$$

$$E^{o}_{Zn^{2+}/Zn} = -0,76V$$

metal / metal ion	E° (volts)
Mg^{2+} / Mg	- 2.37
Zn^{2+} / Zn	- 0.76
Cu^{2+} / Cu	+0.34
Ag^{+} / Ag	+0.80

$$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$$

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$$

$$2H^{+}_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

$$Ag^{+}_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$$

Convenção: o potencial da célula é dado pela diferença entre o potencial do eletrodo da direita e o da esquerda

$$\mathbf{E_{cel} = \Delta E = E_d - E_e}$$

$$Pt|H_{2(1\,atm)}|H^+_{(a=1)}||Cu^{2+}_{(a=1)}|Cu$$

$$\Delta E^o_{medido} = E^o_{cel} = E^o_{Cu^{2+}|Cu} - E^o_{H^+|H_2} = 0{,}34V$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftarrows Cu_{(s)} \qquad E_d = E^o_{Cu^{2+}|Cu}$$

$$2\,H^+_{(aq)} + 2e^- \rightleftarrows H_{2(g)} \qquad E_e = E^o_{H^+|H_2} = 0V$$

$$Cu^{2+}_{(aq)} + H_2 \rightleftarrows Cu + 2\,H^+_{(aq)} \qquad E_{cel} = E_d - E_e = E^o_{Cu^{2+}|Cu} = 0{,}34V$$

$$E_{cel} = \left(E^o_{Cu^{2+}|Cu} - \cancel{E_{EPH}}\right) - \frac{RT}{2F}\ln\frac{a^2_{H^+}}{a_{Cu^{2+}}\, f_{H_2}}$$

Potenciais de eletrodo:

Estado padrão:

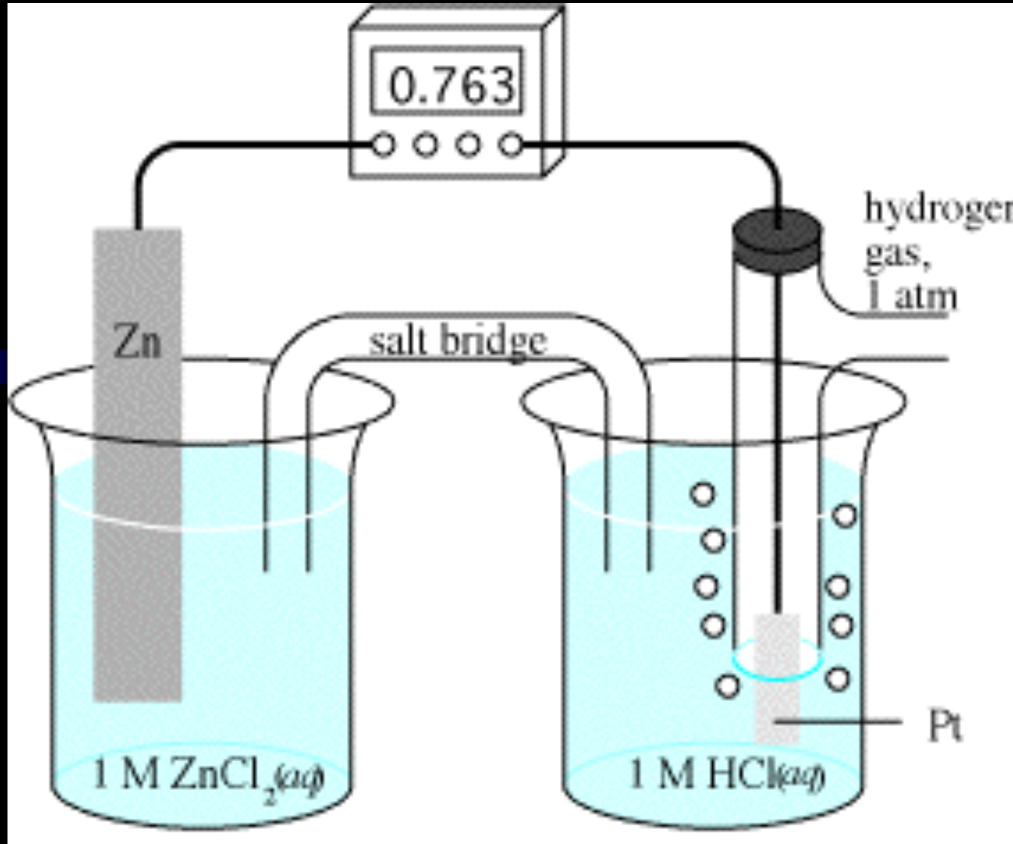
Espécies em solução: a = 1

gases : p = 1 atm

sólidos puros

Os potenciais são referidos ao eletrodo padrão de hidrogênio (EPH):

$$Pt|H_{2(g,1\,atm)}|H^{+}_{(aq,a=1)} \qquad E^{o}_{H^{+}|H_2} = 0V \text{ a } 298\,K$$



$$\text{Deter min ação do } E^{o}_{Zn^{2+}|Zn}$$

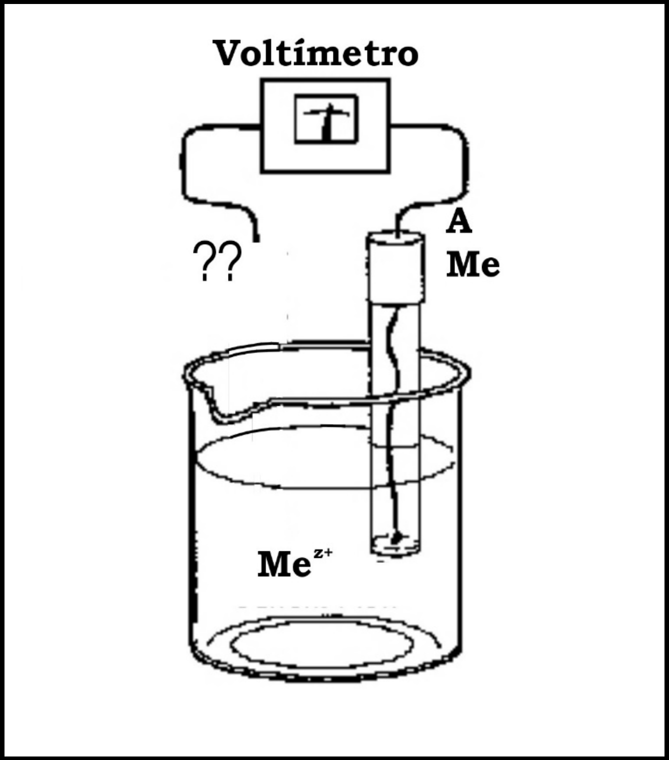
$$Zn^{2+}_{(aq,\ a=1)}\big|Zn\big\|Pt\big|H_{2(1atm)}\big|H^{+}_{(aq,\ a=1)}$$

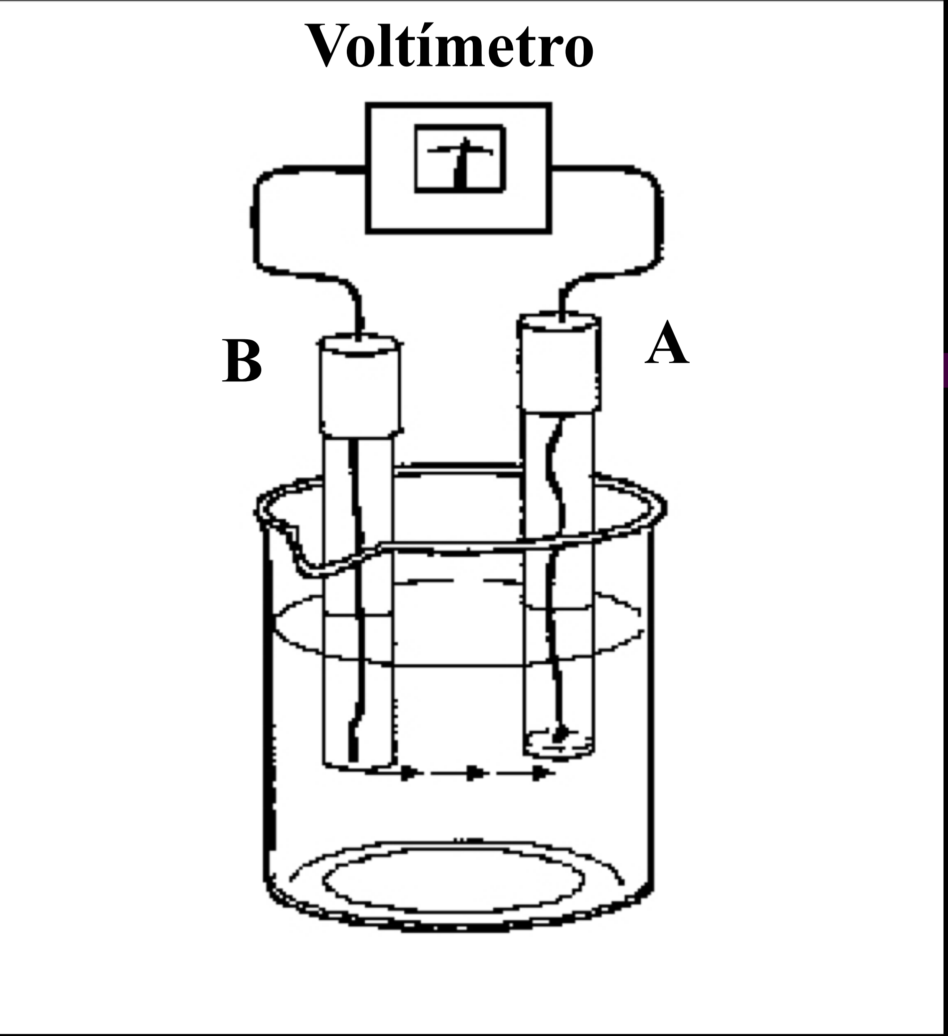
Medida de potenciais de eletrodo: necessidade de um referência

$$E = \Delta\varphi = \varphi_M - \varphi_s$$

Impossível medir

Duas fases distintas





Diferença de potencial entre dois condutores eletrônicos

$$\Delta E = E_A - E_B = (\varphi_A - \varphi_s) - (\varphi_B - \varphi_s) = (\varphi_A - \varphi_B)$$

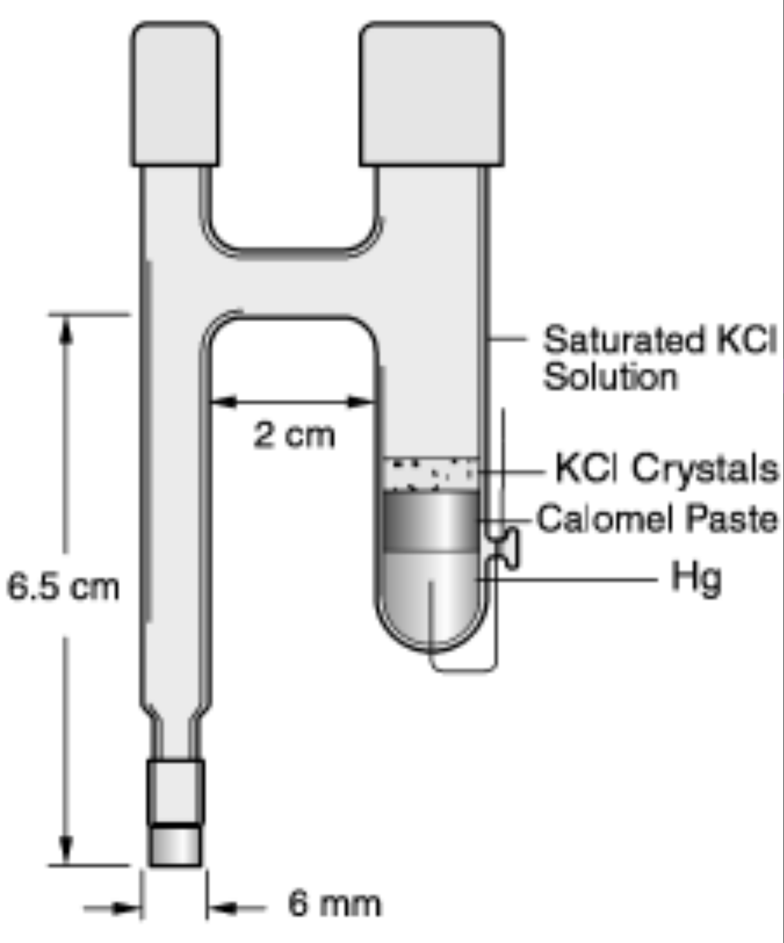
$$\Delta E = E_A - E_B = (\varphi_A - \varphi_s) - (\varphi_B - \varphi_s) = (\varphi_A - \varphi_B)$$

Eletrodo de referência/eletrólito/eletrodo de estudo

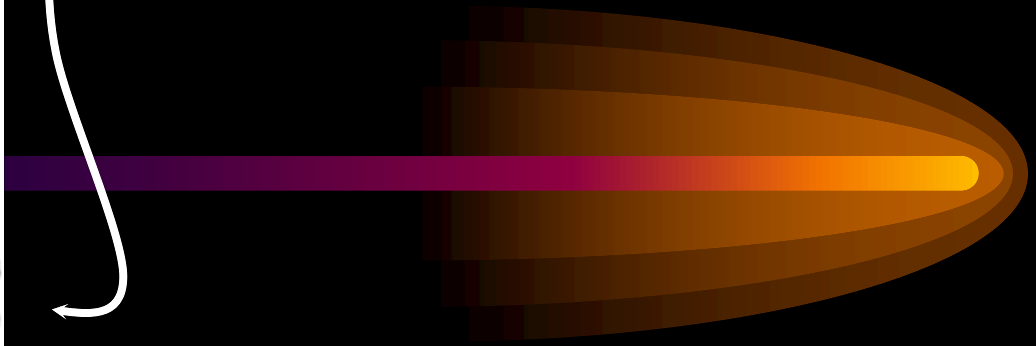
$$\Delta E = E - E_R = \varphi - \varphi_R$$

Tem que ser constante

Composição constante



Pasta de calomelano: Hg/Hg_2Cl_2



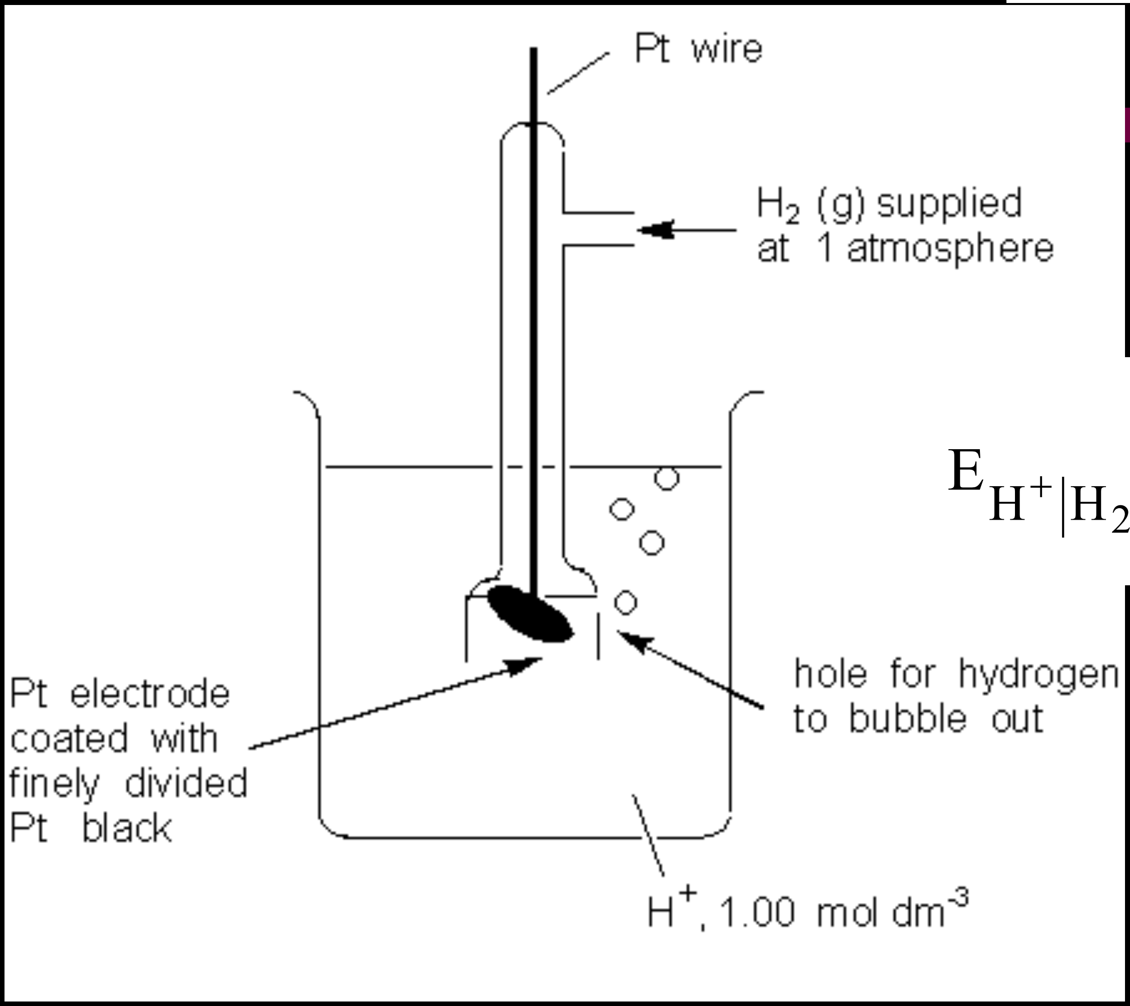
$$Hg_2Cl_{2(s)} + 2e^- \rightleftarrows 2\,Hg_{(l)} + 2\,Cl^{1-}_{(aq)}$$

Eletrodo de calomelano saturado

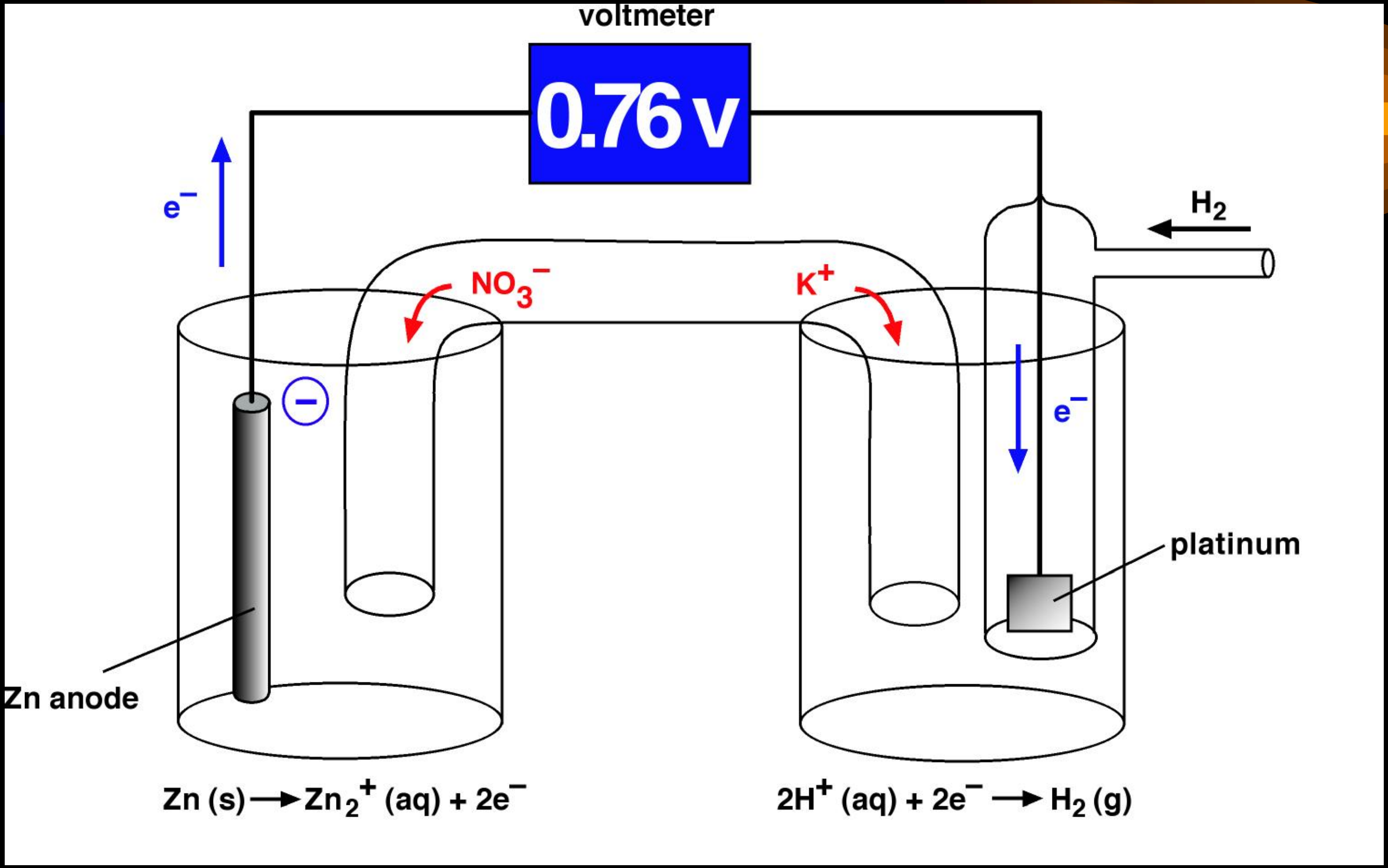
$$E_{Hg_2Cl_2|Cl^{1-}} = E^o_{Hg_2Cl_2|Cl^{1-}} - \frac{RT}{2F}\ln a^2_{Cl^{1-}}$$

Eletrodo padrão de hidrogênio

$$H^+ + e^- \rightleftharpoons \frac{1}{2} H_{2(g)}$$



$$E_{H^+|H_2} = E^o_{H^+|H_2} - \frac{RT}{F} \ln\left(\frac{\sqrt{f_{H_2}}}{a_{H^+}}\right)$$


voltmeter
0.76 v
e⁻
H2
NO3⁻
K+
e⁻
platinum
Zn anode
Zn (s) → Zn2+ (aq) + 2e⁻
2H+ (aq) + 2e⁻ → H2 (g)

Ag/AgCl

Distintos tipos de eletrodos

1 - metal|íons do metal : $M^{z+}|M$

$$Cu^{2+}_{(aq)} + 2e^{-} \rightleftarrows Cu_{(s)}$$

$$E_{Cu^{2+}|Cu} = E^{o}_{Cu^{2+}|Cu} - \frac{RT}{2F} \ln \frac{1}{a_{Cu^{2+}}}$$

Distintos tipos de eletrodos

$$2\text{ - gás}: \mathrm{Pt}\,|\,H^+\,|\,H_2$$

$$H^+_{(aq)} + e^- \rightleftarrows \frac{1}{2} H_{2(g)}$$

$$E_{H^+|H_2} = E^o_{H^+|H_2} - \frac{RT}{F} \ln \frac{\sqrt{f_{H_2}}}{a_{H^+}}$$

Distintos tipos de eletrodos

$$3 \text{ - metal}|\text{sal insolúvel}|\text{ânion comun} : Ag|AgCl|Cl^{1-}$$

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$

$$AgCl_{(s)} \longrightarrow Ag^{+}_{(aq)} + Cl^{1-}_{(aq)}$$

$$AgCl_{(s)} + e^{-} \rightleftharpoons Ag_{(s)} + Cl^{1-}_{(aq)}$$

$$E_{AgCl|Ag} = E^{o}_{AgCl|Ag} - \frac{RT}{F} \ln a_{Cl^{1-}}$$

O potencial do eletrodo

$w_e = n\, e_o\, E$

Em condições de equilíbrio:

$\Delta_r G_{p,T} = -\, w$

$$\Delta_r G_{p,T} = -\, n\, \underbrace{e_o\, N_A}_{F}\, E$$

$$\boxed{\Delta_r G = -\, n\, F\, E}$$

Energy, E, and Spontaneity

Cell potential	Free Energy	Spontaneity
– ***Positive*** $\boldsymbol{E_{cell}}$	$\Delta_r G < 0$	**Spontaneous**
– ***Negative*** $\boldsymbol{E_{cell}}$	$\Delta_r G > 0$	**Not**
– **Zero** $\boldsymbol{E_{cell}}$	$\Delta_r G = 0$	**Equilibrium**

- $\Delta_r G$: free energy of change
- amount of available *(electrical)* work

Equação de Nernst e constante de equilíbrio

$$Ox_1 + Red_2 \underset{}{\overset{ne^-}{\rightleftarrows}} Red_1 + Ox_2$$

$$E_{cel} = E^o_{cel} - \frac{RT}{nF} \ln \frac{a_{red_1}\, a_{ox_2}}{a_{red_2}\, a_{ox_1}} = E^o_{cel} - \frac{RT}{nF} \ln Q$$

No equilíbrio $E_{cel} = 0$

$$0 = E_{cel} = E^o_{cel} - \frac{RT}{nF} \ln \frac{a_{red_1(e)}\, a_{ox_2(e)}}{a_{red_2(e)}\, a_{ox_1(e)}} = E^o_{cel} - \frac{RT}{nF} \ln K$$

$$E^o_{cel} = \frac{RT}{nF} \ln K$$

Connection to work: ΔG^0, E^0, and K

From thermodynamics: $\Delta_r G^0 = -RT \ln K$

From electrochemistry: $\Delta_r G^0 = -nFE^0$

So: $-RT \ln K = -nFE^0$

So:

$$E^0 = \frac{RT \ln K}{nF}$$

At equilibrium: $\Delta_r G^0 = 0$ and $K_{eq} = Q$

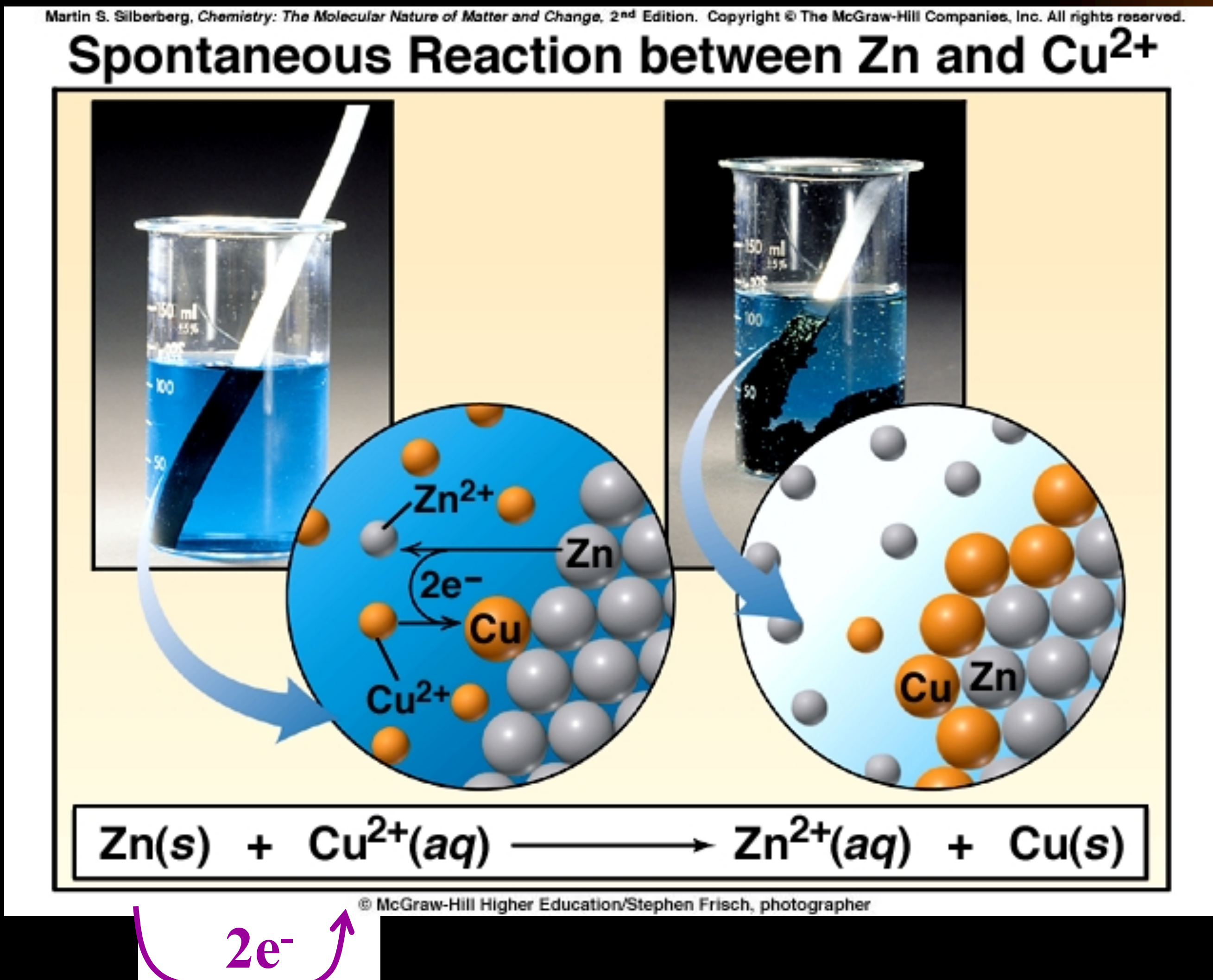
$$E^0_{cell} = \frac{0.0591V}{n} \log \frac{[\,products\,]}{[\,reactants\,]} = \frac{0.0591V}{n} \log \frac{[\,M^{x+}_{ox}\,]}{[\,M^{y+}_{red}\,]}$$

n = #moles of e^- transferred

Redox reactions and spontaneity

- Spontaneity is determined by thermodynamics
- Ex. Cu/Cu^{2+} // Zn/Zn^{2+} system
  - **What will be oxidized (lose e^-)? Cu or Zn**
  - **What will be reduced (gain e^-)? Cu^{2+} or Zn^{2+}**
  - **Will e^- flow from Zn to Cu^{2+} or from Cu to Zn^{2+}?**
  - **What will the energy change be?**
- Current:
  - **"Flow" of e^-**
  - **System's attempt to attain equilibrium (minimum energy state)**

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$



Equação de Nernst e constante de equilíbrio

Corrosão

$$Fe_{(s)} \rightleftarrows Fe^{2+}_{(aq)} + 2e^{-} \qquad E^{o} = 0{,}44V$$

$$4H^{+}_{(aq)} + O_{2(g)} + 4e^{-} \rightleftarrows 2H_2O_{(l)} \qquad E^{o} = 1{,}23V$$

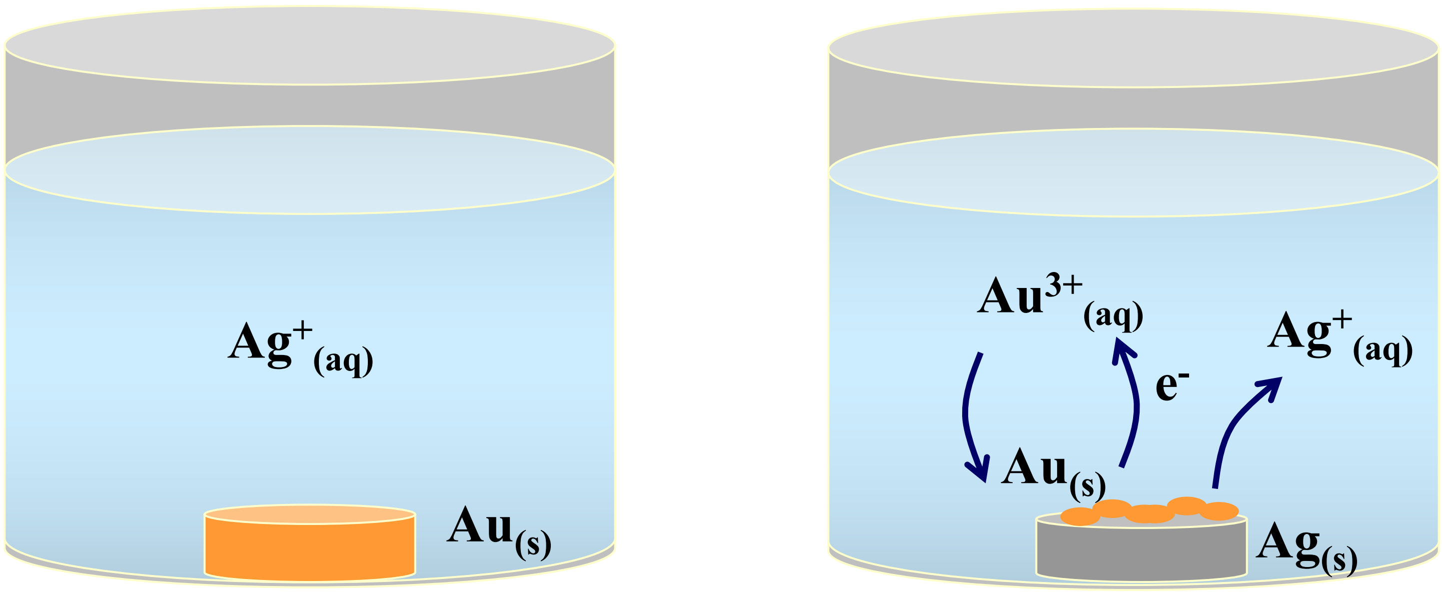
$$4H^{+}_{(aq)} + O_{2(g)} + 2Fe_{(s)} \rightleftarrows 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad E^{o} = 1{,}67V$$

$$E^{o}_{cel} = \frac{RT}{nF} \ln K \qquad K = e^{\frac{E^{o}_{cel}\, n\, F}{R\, T}} = e^{\frac{1{,}67\ V\ x\ 4\ x\ 96487\ C\ mol^{-1}}{8{,}314\ V\ C\ mol^{-1}\ K^{-1}\ 298\ K}}$$

$$K = e^{260}$$

Example

- Gold will plate onto silver (not *vice versa*) – why?



No reaction

$$3Ag + Au^{3+} \rightarrow 3Ag^{+} + Au$$

Example – Au plating on Ag

Spontaneous reaction:

$3Ag + Au^{3+} \rightarrow 3Ag^{+} + Au$

$$E_{cell} = E^0 - \frac{0.0591}{n} log \frac{[Ag^+]^3}{[Au^{3+}]}$$

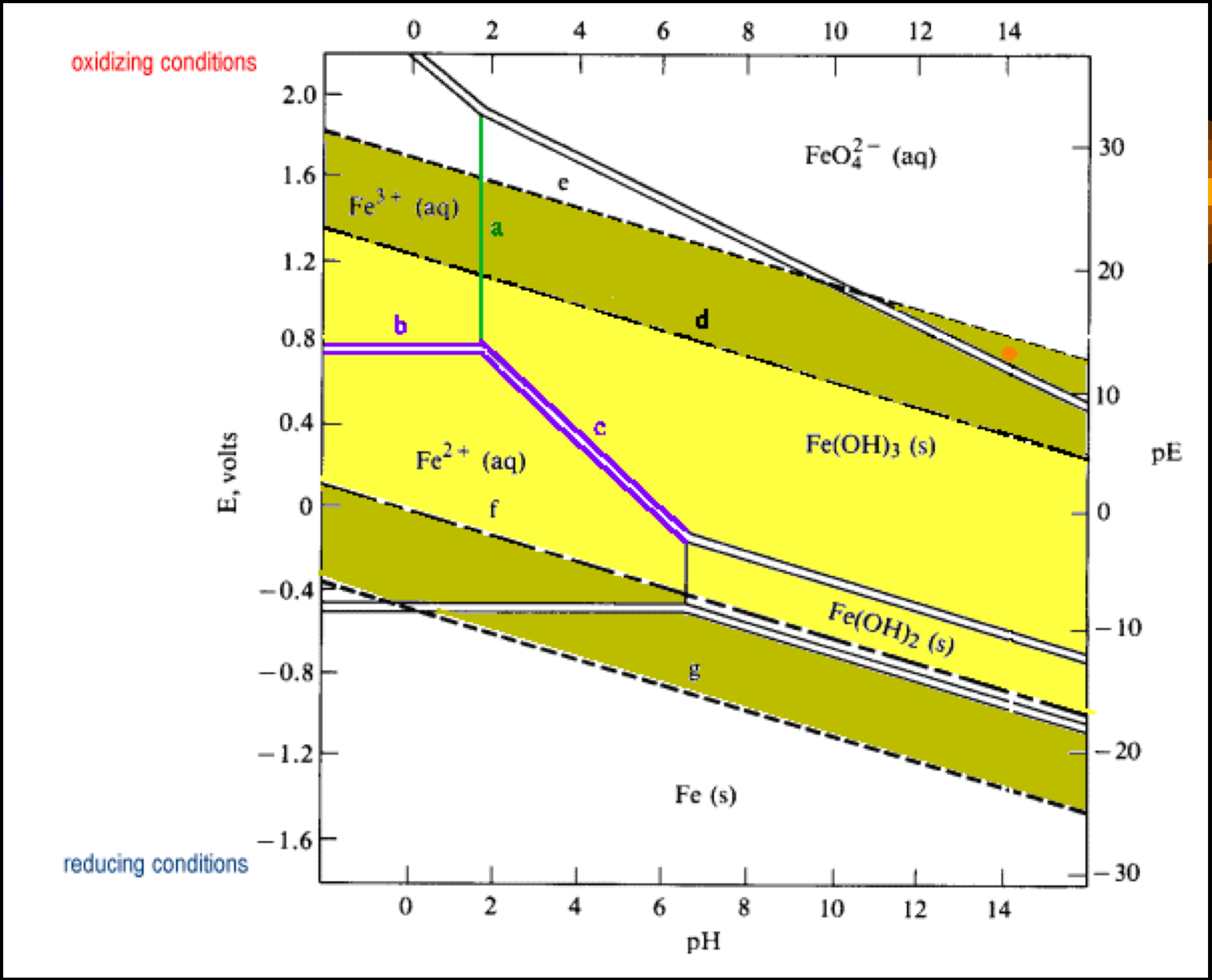
Given (tables):

$Ag^{+} + e^{-}$	$\rightarrow Ag$	$E^0 = +0.80$ V
$Au^{3+} + 3e^{-}$	$\rightarrow Au$	$E^0 = +1.50$ V

$$E^0 = +1.50V + (-0.80V)$$

$$E^0 = +0.70V$$

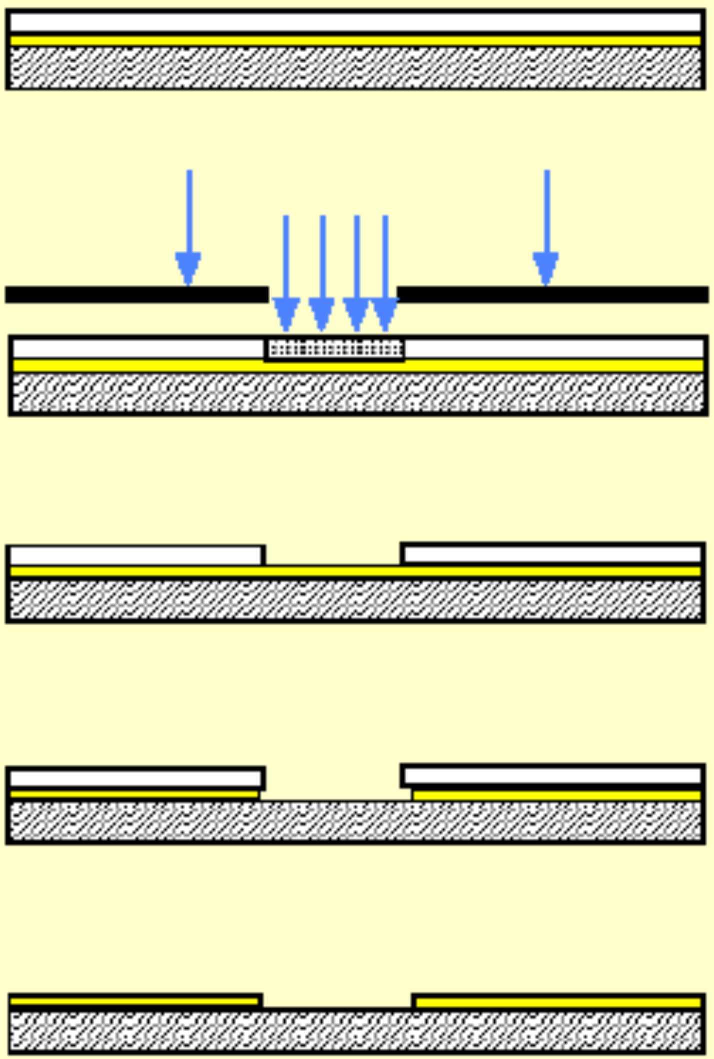
Diagramas de Pourbaix



Aplicações de medidas de potenciais de eletrodo

- Determinação de potenciais padrão
- Determinação de coeficientes de atividade
- Determinação de constantes de equilíbrio
- Titulações potenciométricas
- Equilíbrio em membranas
- Determinação de propriedades termodinâmicas

Foto-litografia



Polymère - Photorésiste
Cuivre
Substrat

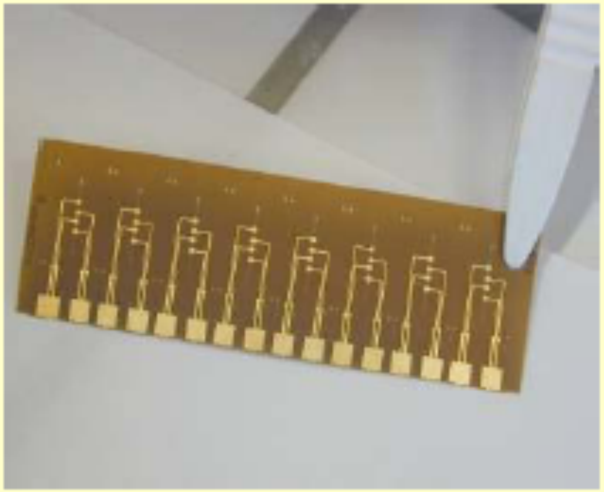
Irradiation

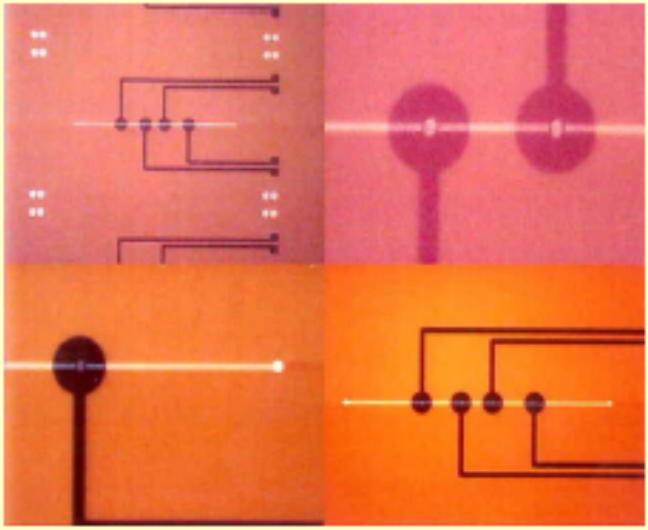
Masque

Dissolution du
polymère irradié

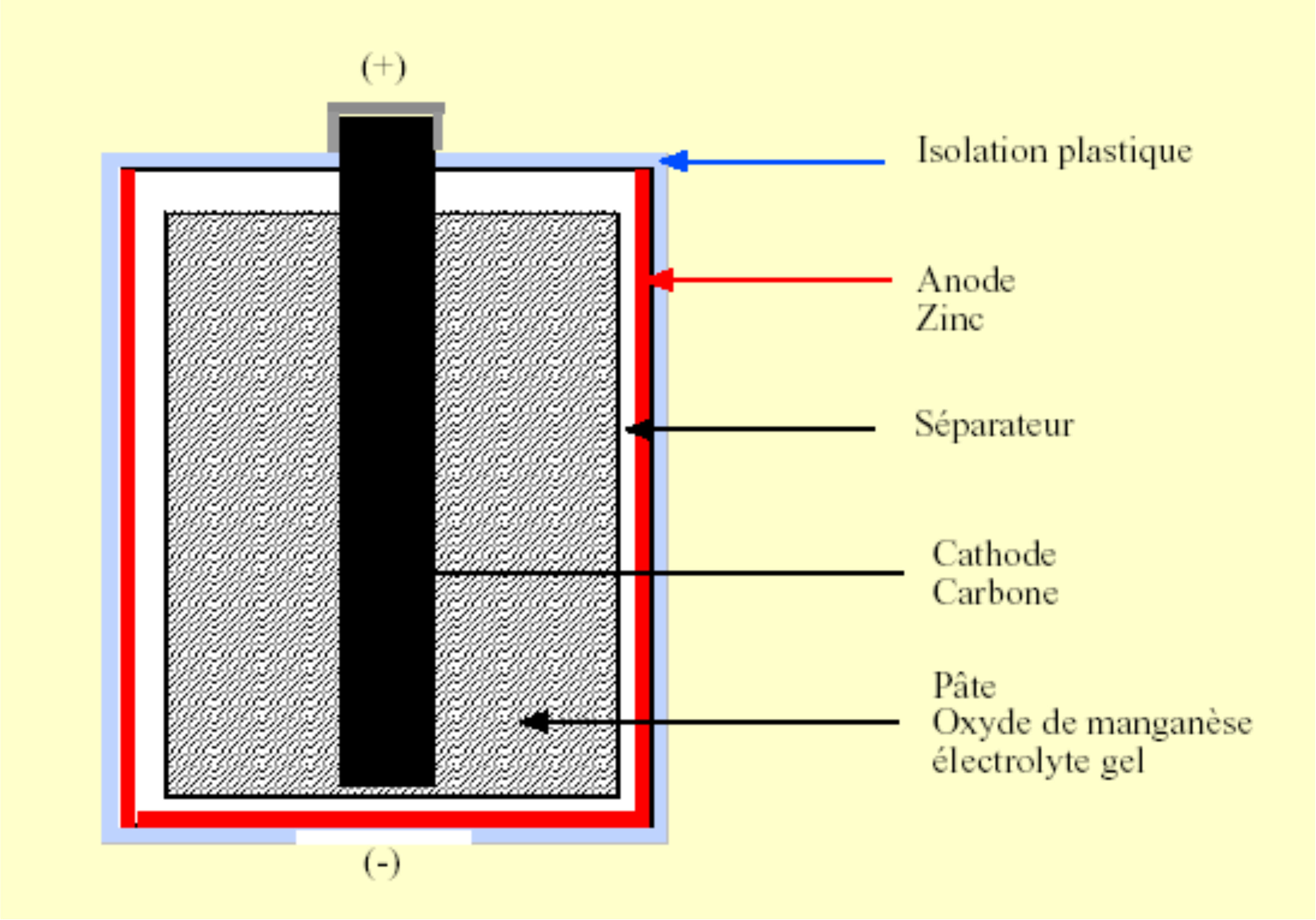
Dissolution rédox
du cuivre

Dissolution du
polymère non-irradié

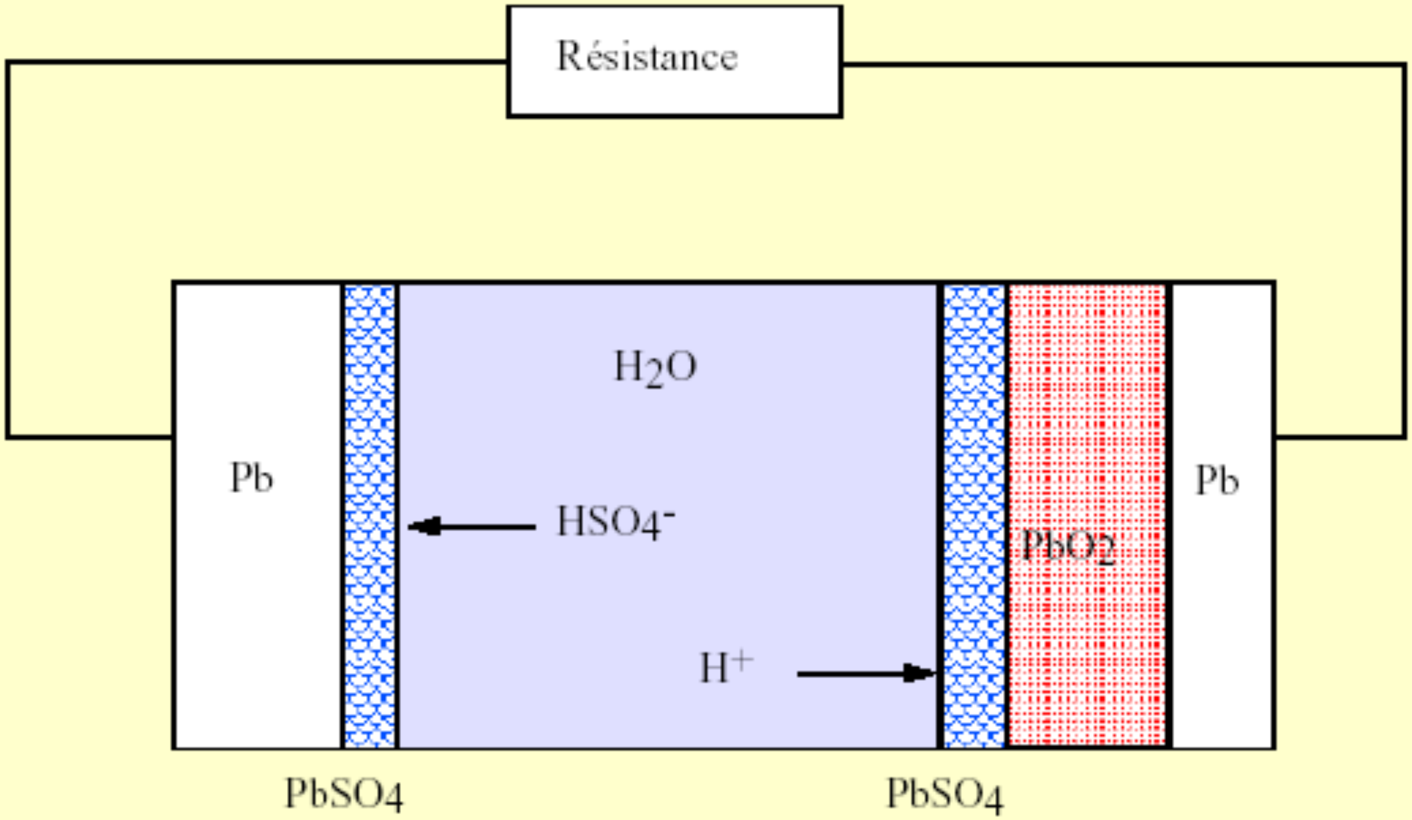




Pilha de Leclanché



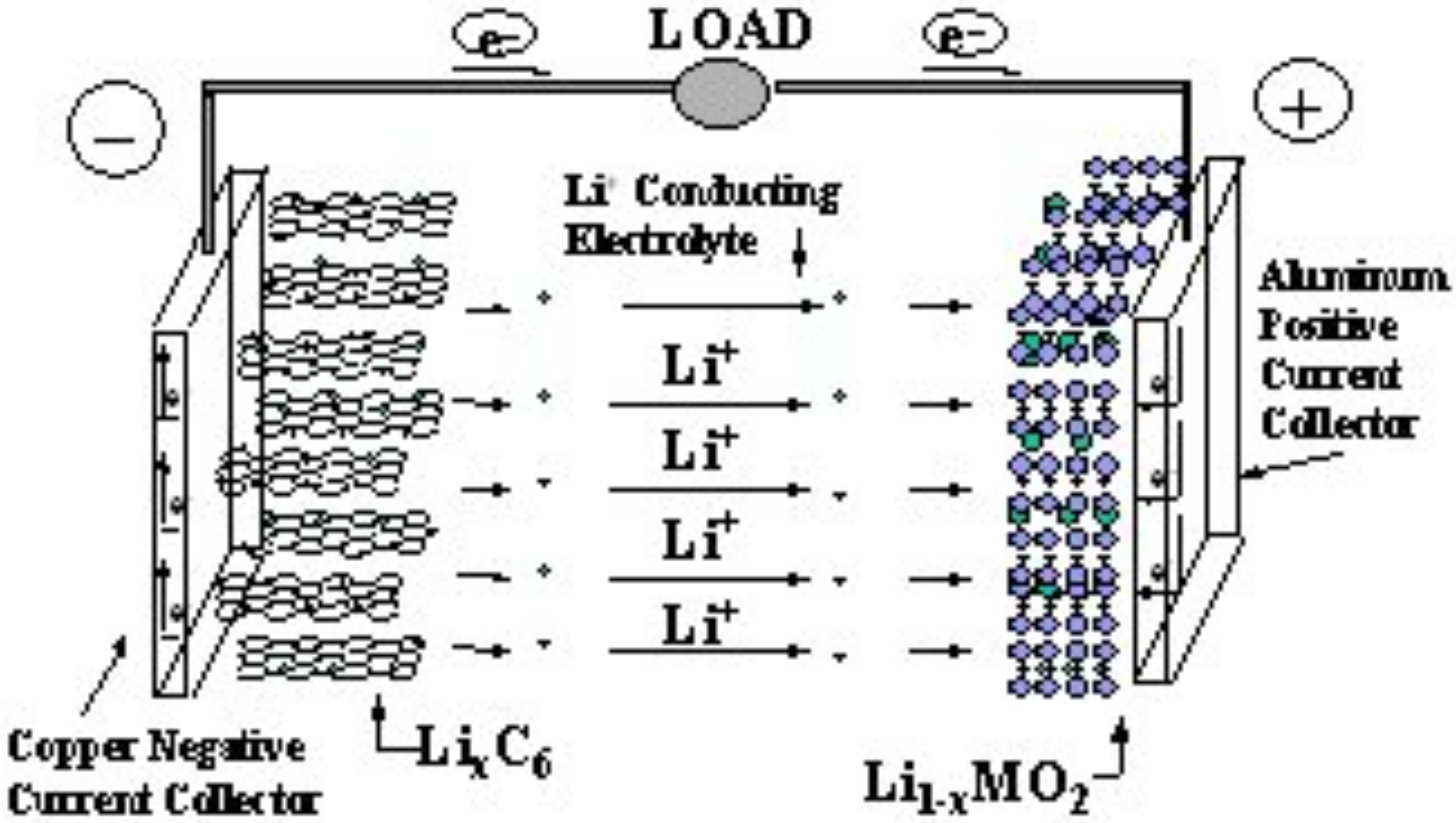
Bateria de chumbo ácido



Décharge : $PbO_2 + 4\,H^+ + SO_4^{2-} + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O$

$Pb + 2\,SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

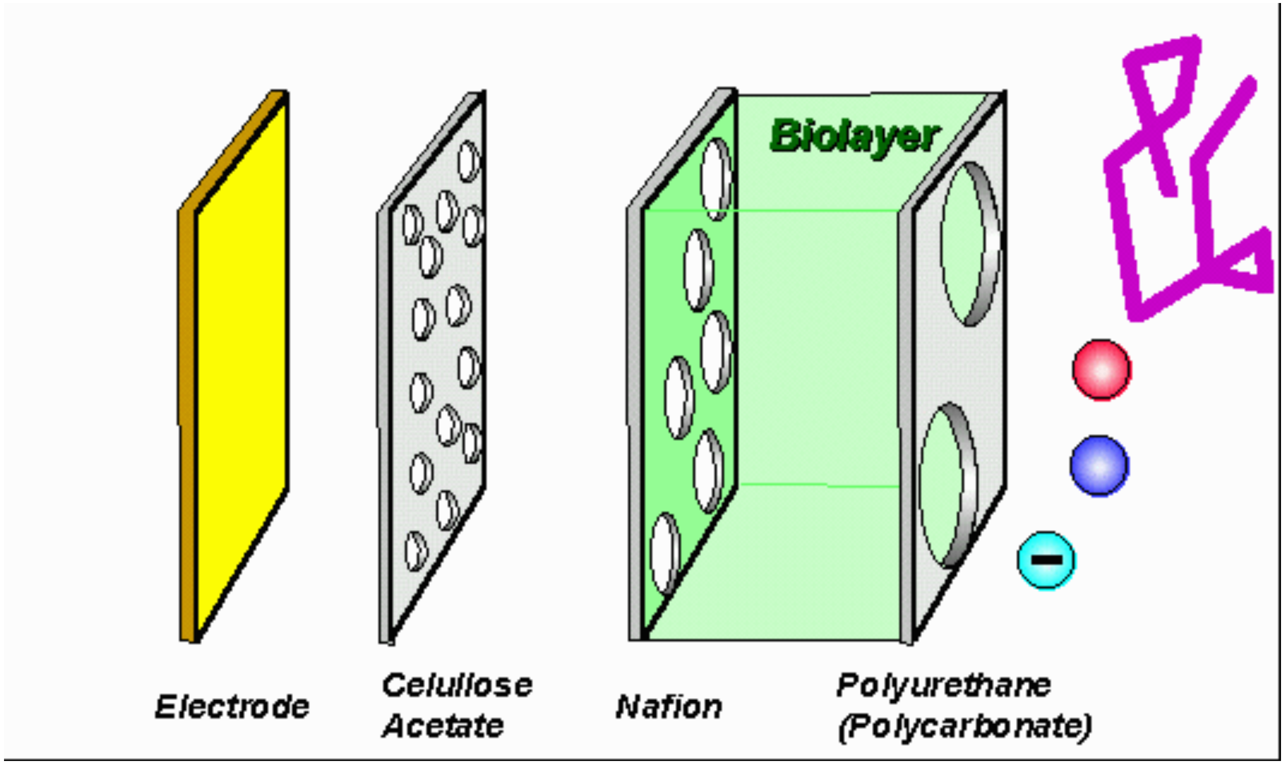
Bateria íon-lítio



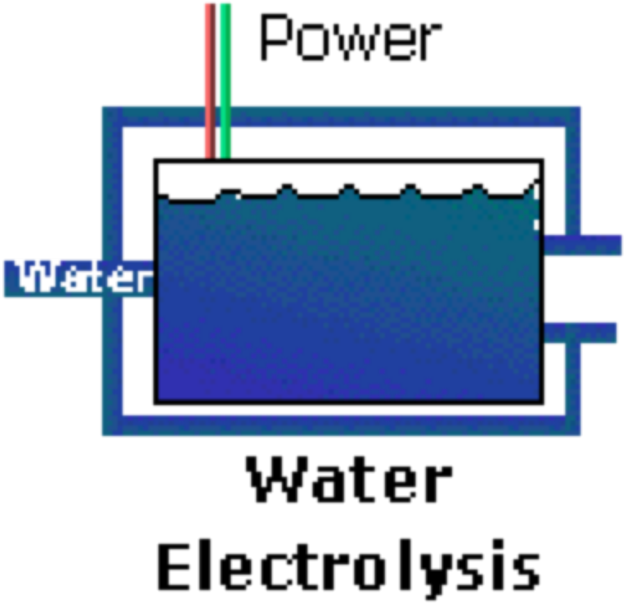
$$C_{6(s)} + xLi^{+} + xe^{-} \longrightarrow Li_{x}C_{6(s)}$$

$$Li_{1}MO_{2(s)} \longrightarrow Li_{(1-x)}MO_{2(s)} + xLi^{+} + xe^{-}$$

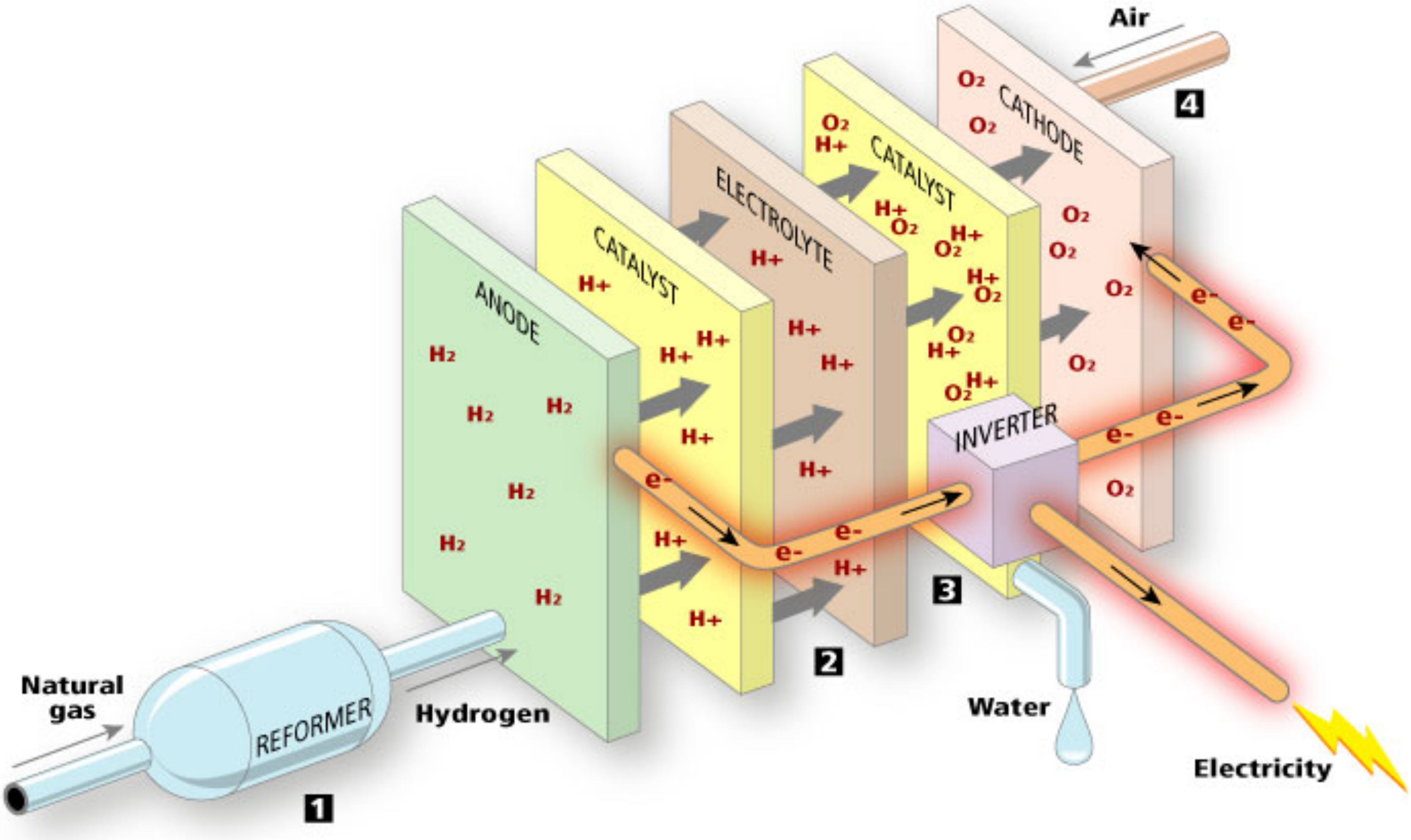
Bio-sensores



Eletrólise



Célula a combustível



Célula a combustível