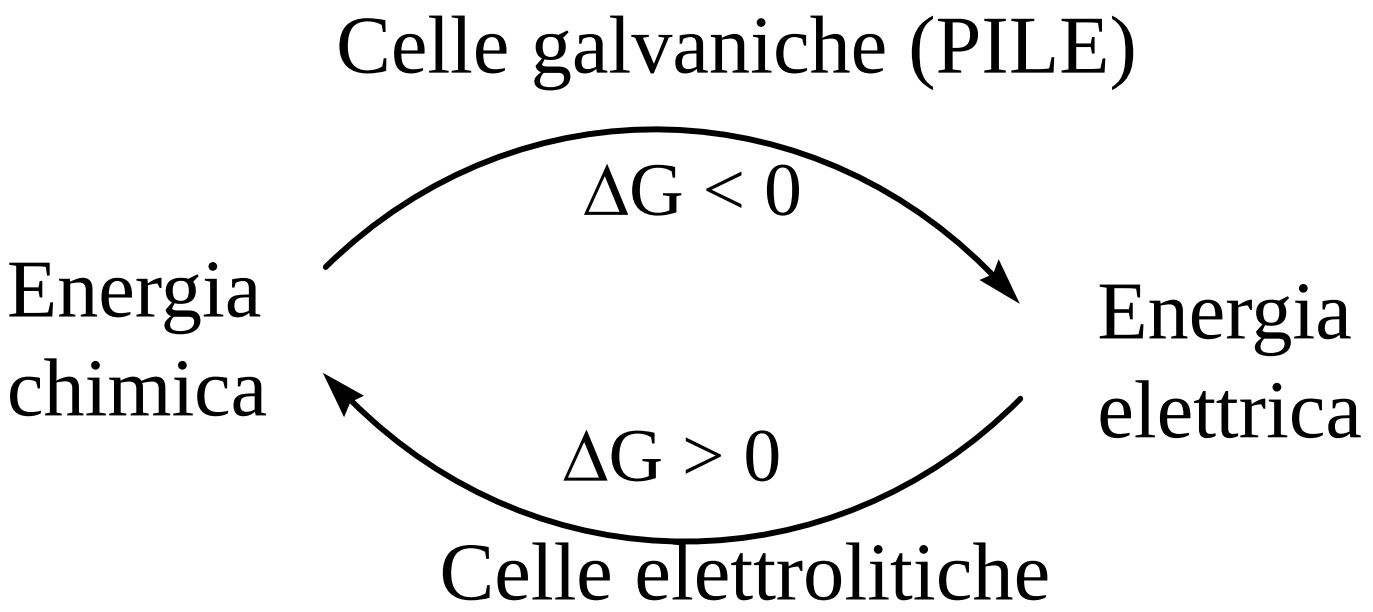
ELETTROCHIMICA



ELETTROCHIMICA

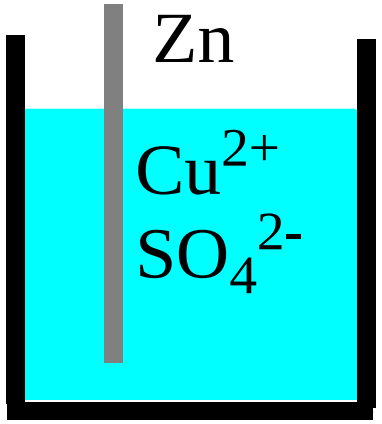
PILA → dispositivo che utilizza una REAZIONE REDOX SPONTANEA per produrre LAVORO ELETTRICO

Energia chimica → Energia elettrica

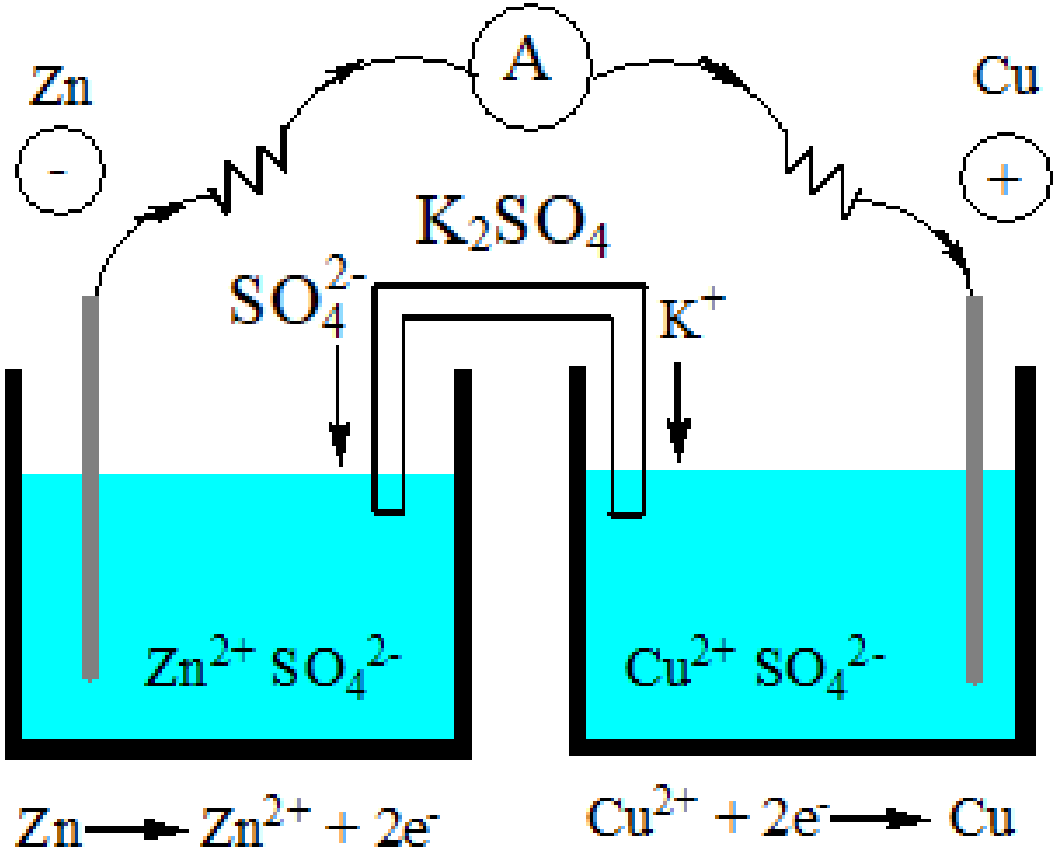
$Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+}$

red $Cu^{2+} + 2\ e^- \rightarrow Cu^0$

ox $Zn^0 \rightarrow Zn^{2+} + 2\ e^-$



$E_{PILA} = E_+ - E_- > 0$



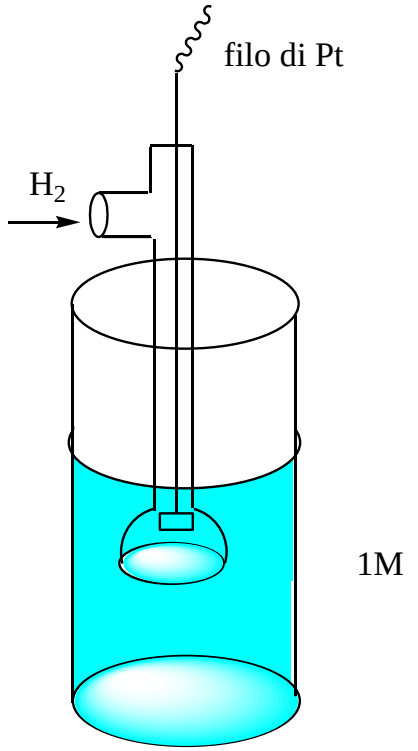
$Zn_{(s)} \mid Zn^{2+}_{(aq)} \mid\mid Cu^{2+}_{(aq)} \mid Cu_{(s)}$

$$E_{PILA} = E_{+} - E_{-}$$

E_{+} , E_{-} dipendono :
- dalla concentrazione delle specie ossidate e ridotte
- dalla loro natura chimica

POTENZIALE STANDARD di un semielemento
→ Tutte le specie hanno concentrazione unitaria
→ Pressione pari ad 1 atmosfera
→ T=25 °C= 298 K E°

Si può misurare la f.e.m. di una pila
non il potenziale dei singoli semielementi



Elettrodo standard a idrogeno

$2\ H^+ + 2\ e^- \rightarrow H_{2\ (g)}$

$2\ H_3O^+ + 2\ e^- \rightarrow H_{2\ (g)} + 2\ H_2O$

$Pt\ (H_{2(g)}, 1atm) \mid H^+\ (1M)$
$[H^+] = [H_3O^+] = 1\ M$

$P_{H_2} = 1\ atm$ $E°_{H^+/H_2} = 0$

specie ossidata	*specie ridotta*	E^0 *(V)*
$F_{2\ (g)} + 2e \leftrightarrows 2F^-_{(aq)}$		+2.87
$H_2O_{2\ (aq)} + 2H^+_{(aq)} + 2e \leftrightarrows 2H_2O_{(l)}$		+1.77
$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e \leftrightarrows Mn^{2+}_{(aq)}$	$+ 4H_2O_{(l)}$	+1.51
$Au^{3+}_{(aq)} + 3e \leftrightarrows Au_{(s)}$		+1.50
$Cl_{2\ (g)} + 2e \leftrightarrows 2Cl^-_{(aq)}$		+1.36
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e \leftrightarrows 2Cr^{3+}_{(aq)}$	$+ 7H_2O_{(l)}$	+1.33
$O_{2\ (g)} + 4H^+_{(aq)} + 4e \leftrightarrows 2H_2O_{(l)}$		+1.23
$ClO_4^-{}_{(aq)} + 2H^+_{(aq)} + 2e \leftrightarrows ClO_3^-{}_{(aq)}$	$+ H_2O_{(l)}$	+1.23
$Pt^{2+}_{(aq)} + 2e \leftrightarrows Pt_{(s)}$		+1.20
$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e \leftrightarrows NO_{(g)}$	$+ H_2O_{(l)}$	+0.96
$Ag^+_{(aq)} + e \leftrightarrows Ag_{(s)}$		+0.80
$Cu^{2+}_{(aq)} + 2e \leftrightarrows Cu_{(s)}$		+0.34
$2H^+_{(aq)} + 2e \leftrightarrows H_{2(g)}$		**+0.00**
$Fe^{2+}_{(aq)} + 2e \leftrightarrows Fe_{(s)}$		-0.44
$Cr^{3+}_{(aq)} + 3e \leftrightarrows Cr_{(s)}$		-0.74
$Zn^{2+}_{(aq)} + 2e \leftrightarrows Zn_{(s)}$		-0.76
$Al^{3+}_{(aq)} + 3e \leftrightarrows Al_{(s)}$		-1.66
$Mg^{2+}_{(aq)} + 2e \leftrightarrows Mg_{(s)}$		-2.36
$Na^+_{(aq)} + e \leftrightarrows Na_{(s)}$		-2.71
$K^+_{(aq)} + e \leftrightarrows K_{(s)}$		-2.93
$Li^+_{(aq)} + e \leftrightarrows Li_{(s)}$		-3.05

$E_{PILA} = E_+ - E_-$ E_+ , E_- dipendono :

- dalla natura chimica delle specie ossidate e ridotte → E°
- dalla loro concentrazione

ox + ne^- → red

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} = E^0 + \frac{0{,}0592}{n} \log \frac{a_{ox}}{a_{red}}$$

R = 0,0821 atm·l·K^{-1}= 8,31 J ·K^{-1} T = 298 K

F= 96500 C Costante di Faraday

Equazione di Nernst

2,3 conversione da ln a log

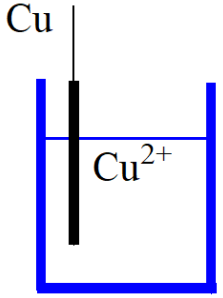
a = attività ↗ per le specie in soluzione: concentrazione (M)
→ per i gas: pressione P
↘ per i solidi puri: 1

a ox + ne^- → b red

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}^a}{a_{red}^b}$$

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}} = E^0 + \frac{0{,}0592}{n}\log\frac{a_{ox}}{a_{red}}$$

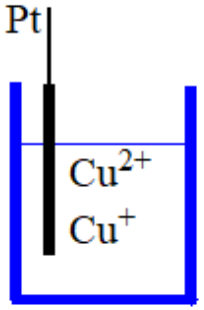
$Cu^{2+} + 2\ e^- \rightarrow Cu^0$ $\qquad E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0{,}0592}{2}\log[Cu^{2+}]$



$Cu \mid Cu^{2+}$

$Cu^{2+} + e^- \rightarrow Cu^+$

$E_{Cu^{2+}/Cu^+} = E^0_{Cu^{2+}/Cu^+} + 0{,}0592\log\frac{[Cu^{2+}]}{[Cu^+]}$

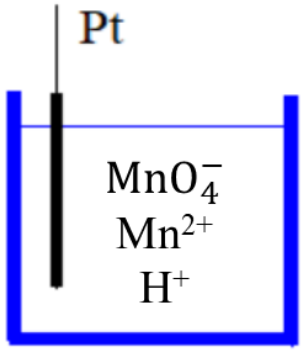


$Pt \mid Cu^{2+}, Cu^+$

$\overset{+7}{MnO_4^-} + 5\ e^- + 8\ H^+ \rightarrow \overset{+2}{Mn^{2+}} + 4\ H_2O$

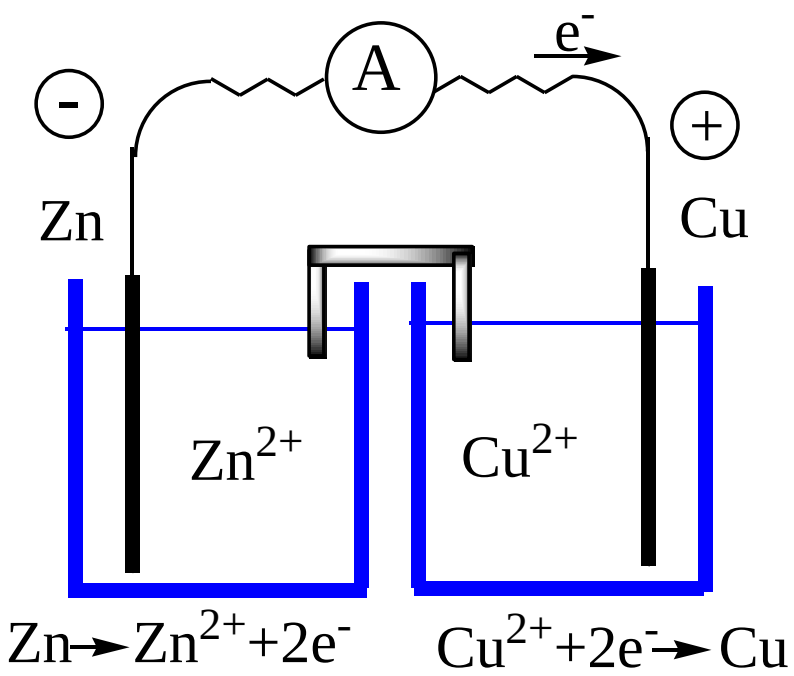
$Pt \mid MnO_4^-, Mn^{2+}, H^+$

$E_{MnO_4^-/Mn^{2+}} = E^0_{MnO_4^-/Mn^{2+}} + \frac{0{,}0592}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$



PILE

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}} = E^0 + \frac{0{,}0592}{n}\log\frac{a_{ox}}{a_{red}}$$



$$Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$$

$$E_{PILA} = E_+ - E_-$$

ox red

\+ $Cu^{2+} + 2\,e^- \rightarrow Cu^0$

$$E_+ = E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0{,}0592}{2}\log[Cu^{2+}]$$

red ox

\- $Zn^0 \rightarrow Zn^{2+} + 2\,e^-$

$$E_- = E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} + \frac{0{,}0592}{2}\log[Zn^{2+}]$$

t= 0 $[Cu^{2+=}]= [Zn^{2+}]=1M$ $E°_{Cu^{2+}/Cu} > E°_{Zn^{2+}/Zn}$

PILA → dispositivo che utilizza una REAZIONE REDOX SPONTANEA
per produrre LAVORO ELETTRICO Energia chimica → Energia elettrica

$\Delta G<0$

$\Delta G = -L_{ELETTRICO} = -Q\Delta V = -nFE_{PILA}$

F= 96500 C

$ox_1 + ne^- \rightarrow red_1$

$red_2 \rightarrow ox_2 + ne^-$

$ox_1 + red_2 \rightarrow red_1 + ox_2$

$\Delta G° = -nFE°_{PILA} = -nF(E°_+ - E°_-)$

$\Delta G° = -RT\ln K$

$nFE° = RT\ln K$

$K = e^{\frac{nFE°}{RT}}$

$E°_+ > E°_-$ $E°_{PILA} > 0$ $\Delta G° < 0$ $K>1$

PILA → dispositivo che utilizza una REAZIONE REDOX SPONTANEA ($\Delta G < 0$) per produrre ENERGIA ELETTRICA

Energia chimica → Energia elettrica

$G = H - TS \Rightarrow dG = dH - TdS - SdT$

$H = E + PV \Rightarrow dG = dE + PdV + VdP - TdS - SdT$

T= costante $SdT = 0$ P= costante $VdP = 0$

$dG = dE + PdV - TdS$

$dE = dQ - dW$ $dQ = TdS$ (reversibile)

$dG = dQ - dW + TdS - PdV = -dW + PdV$

$dW = PdV + dW_{elettr} \Rightarrow dG = -dW_{elettr}$ $\Delta G = -W_{elettr} = -nFE_{pila}$

$\Delta G° = -nFE°_{PILA} = -nF(E°_{+} - E°_{+})$ $-\frac{\Delta G^0}{nF} = E^0_{PILA} = E^0_{+} - E^0_{-}$

$\Delta G° = -RT\ln K = -nFE°$

$$E^0_{PILA} = -\frac{\Delta G^0}{nF} = \frac{RT}{nF}\ln K$$

$\Delta G = nFE_{pila}$ $E_{PILA} = E_+ - E_-$ $E_1 = E_+$ $E_2 = E_-$ $E_1 > E_2$

$Ox_1 + n_1e^- \leftrightarrows Red_1$ x n_2

$Red_2 \leftrightarrows Ox_2 + n_2e^-$ x n_1

$n = n_1n_2$

$n_2\,Ox_1 + n_1Red_2 \leftrightarrows n_2\,Red_1 + n_1Ox_2$

$\Delta G_{REAZ} = \Sigma_i\,\nu_i\,G_i - \Sigma_i\,\nu_iG_i = n_2\,G_{Red_1} + n_1G_{Ox_2} - n_2\,G_{Ox_1} - n_1G_{Red_2}$

$G = G° + RT \ln a$

Gas	a=P
Soluzione	a= M
Solido	a= 1

$\Delta G_{REAZ} = n_2\,(G°_{Red_1} + RT \ln a_{Red_1}) + n_1\,(G°_{Ox_2} + RT \ln a_{Ox_2})$

$- n_2\,(G°_{Ox_1} + RT \ln a_{Ox_1}) - n_1\,(G°_{Red_2} + RT \ln a_{Red_2}) =$

$n_2\,(G°_{Red_1} - G°_{Ox_1} + RT \ln \frac{a_{Red_1}}{a_{Ox_1}}) - n_1\,(G°_{Red_2} - G°_{Ox_2} + RT \ln \frac{a_{Red2}}{a_{Ox2}}) =$

$n_2\,(\Delta G°_1 - RT \ln \frac{a_{Ox_1}}{a_{Red_1}}) - n_1\,(\Delta G°_2 - RT \ln \frac{a_{Ox2}}{a_{ox2}}) = \Delta G$

$\Delta G°_1 = G°_{Red_1} - G°_{Ox_1}$ $\Delta G°_2 = G°_{Red_2} - G°_{Ox_2}$

$$n_2\,(\Delta G^\circ_1 - RT\ln\frac{a_{Ox1}}{a_{Red1}}) - n_1\,(\Delta G^\circ_2 - RT\ln\frac{a_{Ox2}}{a_{ox2}}) = \Delta G = -nFE_{pila} = -n_1n_2(E_1-E_2)$$

$$n = n_1n_2 \qquad E_{pila} = E_1 - E_2$$

$$E_{pila} = E_1 - E_2 = -\frac{\Delta G_1^0}{n_1F} + \frac{RT}{n_1F}\ln\left[\frac{a_{Ox1}}{a_{Red1}}\right] + \frac{\Delta G_2^0}{n_2F} + \frac{RT}{n_2F}\ln\left[\frac{a_{Ox2}}{a_{Red2}}\right]$$

$$E_1 = E_1^0 + \frac{RT}{n_1F}\ln\left[\frac{a_{Ox1}}{a_{Red1}}\right]$$

$$E_2 = E_2^0 + \frac{RT}{n_2F}\ln\left[\frac{a_{Ox2}}{a_{Red2}}\right]$$

$E_{PILA} = 0 \quad \rightarrow \quad \Delta G_{REAZ} = 0 \qquad\qquad \Delta G^\circ_{REAZ} = -RT\ln K$

$$-\frac{\Delta G^0}{nF} = E^0{}_{PILA} = E_+^0 - E_-^0 = \frac{RT\ln K}{nF}$$

PILE A CONCENTRAZIONE

- $Cu \,|\, [Cu^{2+}]_- \,||\, [Cu^{2+}]_+ \,|\, Cu$ +

$Cu^{2+} + 2\,e^- \rightarrow Cu^0$

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0{,}0592}{2}\log[Cu^{2+}]$$

$+ Cu^{2+} + 2\,e^- \rightarrow Cu^0$

$$E_+ = E^0_{Cu^{2+}/Cu} + \frac{0{,}0592}{2}\log[Cu^{2+}]_+$$

$- Cu^0 \rightarrow Cu^{2+} + 2\,e^-$

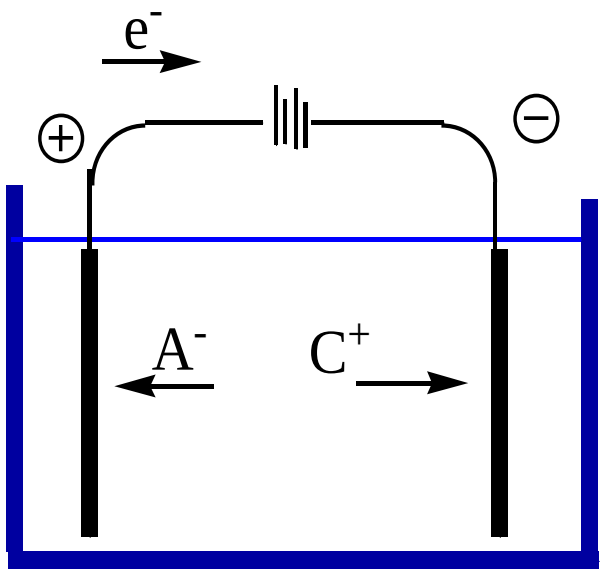
$$E_- = E^0_{Cu^{2+}/Cu} + \frac{0{,}0592}{2}\log[Cu^{2+}]_-$$

$$E_{PILA} = E_+ - E = \frac{0{,}0592}{2}(\log[Cu^{2+}]_+ - \log[Cu^{2+}]_-) = \frac{0{,}0592}{2}\log\frac{[Cu^{2+}]_+}{[Cu^{2+}]_-}$$

$[Cu^{2+}]_+ > [Cu^{2+}]_-$ $\quad E_{PILA} > 0$

Driving force: ΔG_{MIX}

ELETTROLISI



Energia elettrica → Energia chimica

Reazioni non spontanee (ΔG>0)

Elettrolisi di NaCl

Sale fuso

$C^+ = Na^+$ $A^- = Cl^-$

Polo - $Na^+ + e^- \rightarrow Na$

Polo + $Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$

$NaCl \rightarrow \frac{1}{2}Cl_2 + Na$

Soluzione acquosa

$C^+ = Na^+, H^+$ $A^- = Cl^-, OH^-$

Polo - ~~$Na^+ + e^- \rightarrow Na$~~

$H^+ + e^- \rightarrow \frac{1}{2} H_2$

Polo + $Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$

$2OH^- \rightarrow \frac{1}{2}O_2 + 2e^- + H_2O$

LEGGI DI FARADAY

-La quantità di sostanza che viene ossidata o ridotta ad un elettrodo è proporzionale alla quantità di elettricità passata

$w = w_e \cdot Q = w_e \cdot I \cdot t$ w_e = equivalente elettrochimico

-Uguali quantità di carica Q determinano la deposizione di un uguale numero di equivalenti di specie ossidate o ridotte.

$P_{EQ} = PM/z$ $P_{EQ} = PA/z$

1F = 96500 C ⇨ 1 equivalente $F = N_A \cdot e^-$

$$w = n_{EQ} P_{EQ} = \frac{Q}{F} P_{EQ} = \frac{It}{F} P_{EQ}$$

$H^+ + e^- \rightarrow 1/2\ H_2$ 1 eq = 1 mole → 1F = N_A e^-

$Fe^{2+} + 2e^- \rightarrow Fe$ 1 eq = 1/2 mole → 1F = N_A e^-

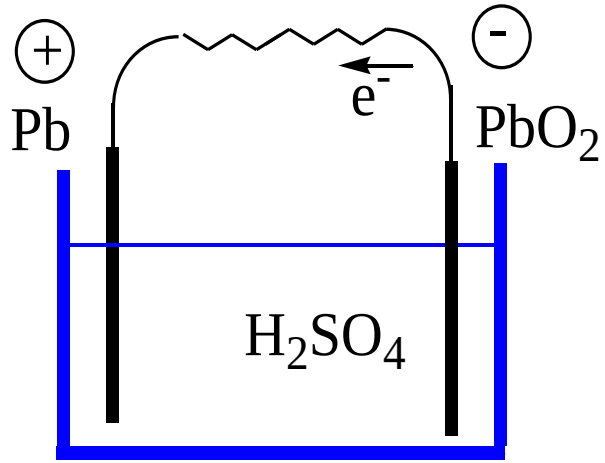
$Al^{3+} + 3e^- \rightarrow Al$ 1 eq = 1/3 mole → 1F = N_A e^-

ACCUMULATORI

$$Pb \mid PbSO_4, H_2SO_4 \mid PbO_2$$

$$E°_{PbO_2/Pb^{2+}} > E°_{Pb^{2+}/Pb}$$

Carica: elettrolisi

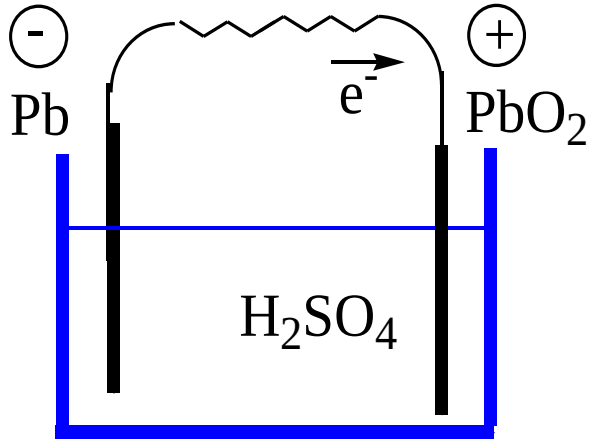


$$+ \quad Pb^{2+} + 2e^- \rightarrow Pb$$

$$- \quad Pb^{2+} + 2H_2O \rightarrow PbO_2 + 2e^- + 4H^+$$

$$2Pb^{2+} + 2H_2O \rightarrow PbO_2 + Pb + 4H^+$$

Scarica: pila



$$+ \quad PbO_2 + 2e^- + 4H^+ \rightarrow Pb^{2+} + 2H_2O$$

$$- \quad Pb \rightarrow Pb^{2+} + 2e^-$$

$$PbO_2 + Pb + 4H^+ \rightarrow 2Pb^{2+} + 2H_2O$$