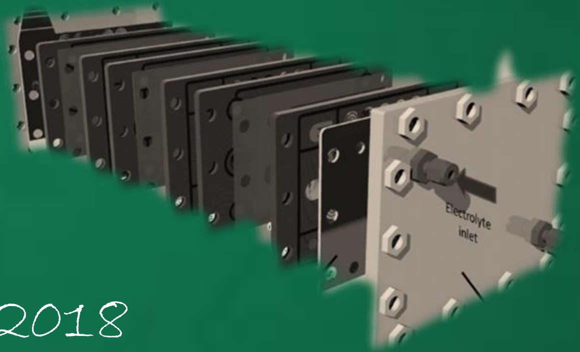
Autumn School Flow Battery



Barcelona – 12th-13th of November 2018

LEITAT managing technologies

IREC Institut de Recerca en Energia de Catalunya Catalonia Institute for Energy Research

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JENA BATTERIES

BATTERIES AS ELECTROCHEMICAL SYSTEMS

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Pere L. Cabot

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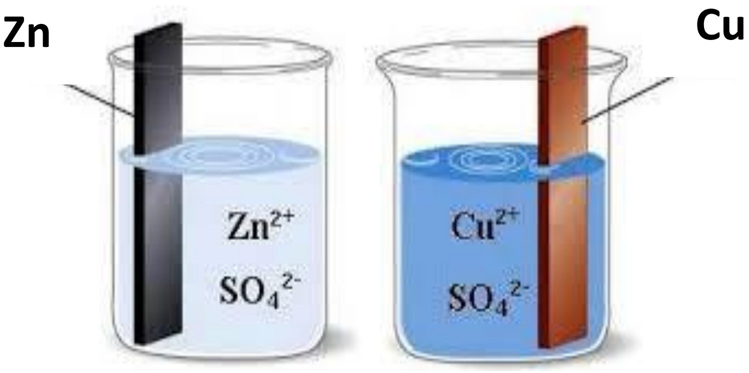
Electrochemistry
studies the properties and processes taking place in heterogeneous systems in which there is a potential difference between the constituent phases

REDOX reactions

$$\nu_O O + n\, e^- \rightleftarrows \nu_R R$$

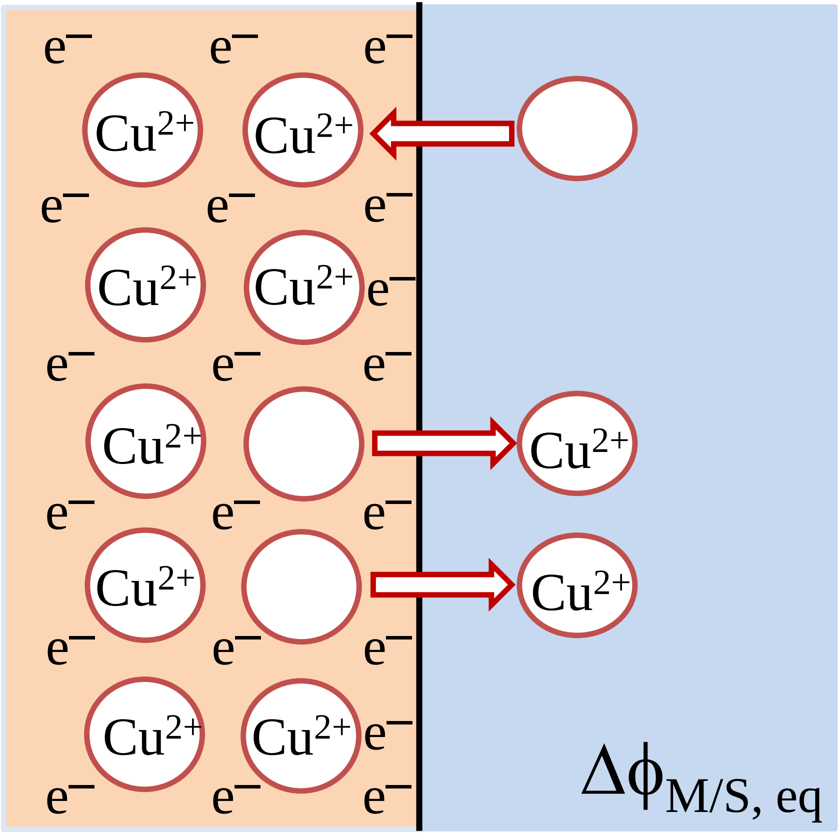
BATTERIES AS ELECTROCHEMICAL SYSTEMS



http://www.chimica-online.it/download/pila-daniell.htm

$$Zn^{2+} + 2\,e^{-} \rightleftharpoons Zn$$

$$Cu^{2+} + 2\,e^{-} \rightleftharpoons Cu$$



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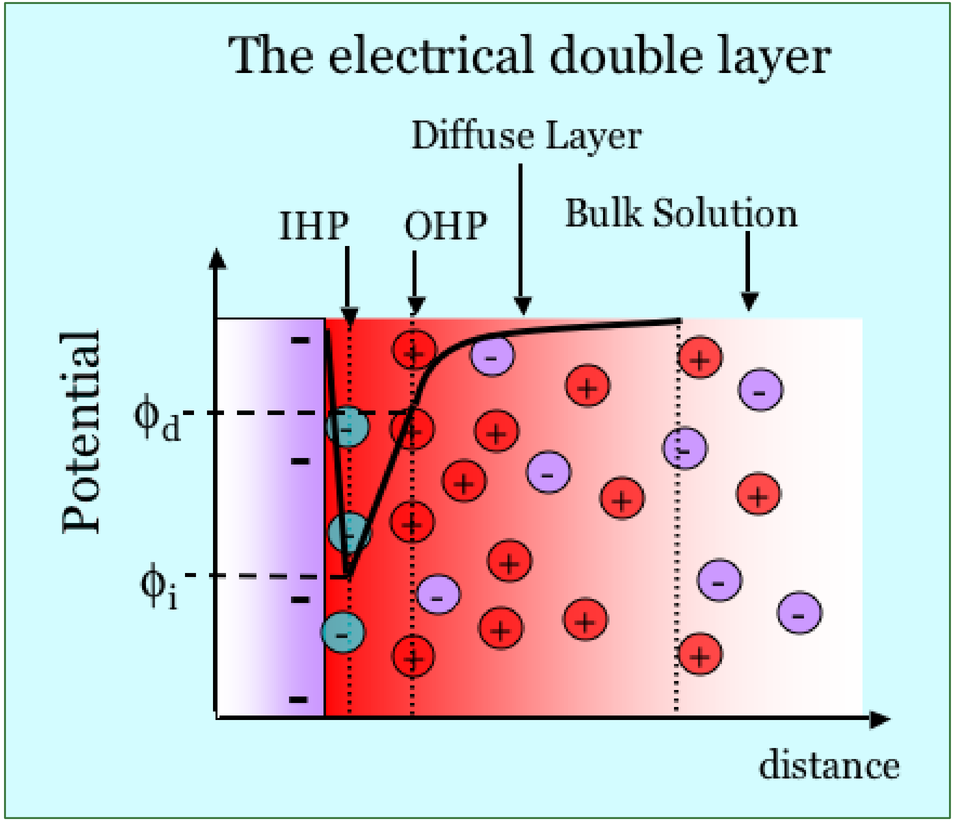

BATTERIES AS ELECTROCHEMICAL SYSTEMS

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OPEN CIRCUIT

$$(-)\ Zn \rightleftharpoons Zn^{2+} + 2\,e_{Zn}^{-}$$

$$(+)\ Cu^{2+} + 2\,e_{Cu}^{-} \rightleftharpoons Cu$$

$$Zn + Cu^{2+} + 2\,e_{Cu}^{-} \rightleftharpoons Cu + Zn^{2+} + 2\,e_{Zn}^{-}$$

NERNST EQUATION

$$E = E^{o} - \frac{RT}{nF}\ln\frac{a_{Cu}\,a_{Zn2+}}{a_{Zn}\,a_{Cu2+}}$$

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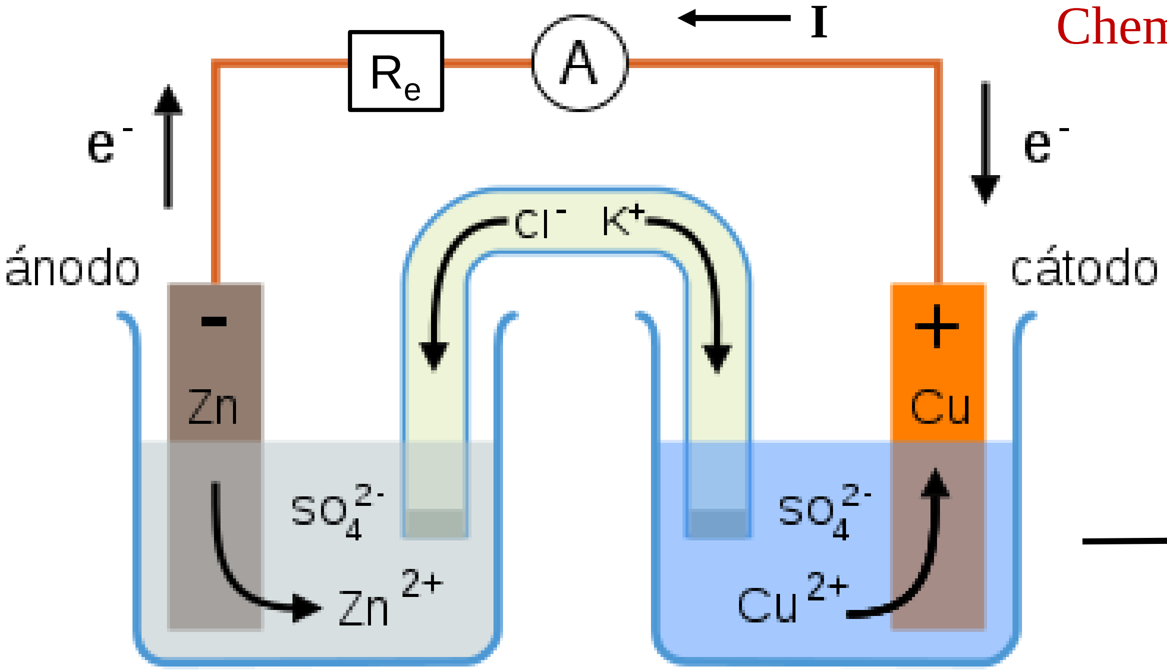

Chemical reaction related to the cell

Net current.

Spontaneous process

$$(-)\ Zn \longrightarrow Zn^{2+} + 2\,e^-$$

$$(+)\ Cu^{2+} + 2\,e^- \longrightarrow Cu$$

$$Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+}$$

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Galvanic cells

(direct conversion of chemical to electrical energy)

Batteries: anodic and cathodic reactants stored internally and cannot be replaced

- Primary: only one discharge (irreversible reactions)
- Secondary or accumulators: repetitive cycles of charge-discharge (reversible reactions)

Fuel Cells: anodic (fuel) and cathodic (oxidizing) reactants externally and continuously fed

(Redox) Flow Batteries: reversible cell with external storage of electrolyte (they may be used like fuel cells or like rechargeable batteries)

Hybrid Cells: one electrode operates as in a battery, the other as in a fuel cell

BATTERIES AS ELECTROCHEMICAL SYSTEMS

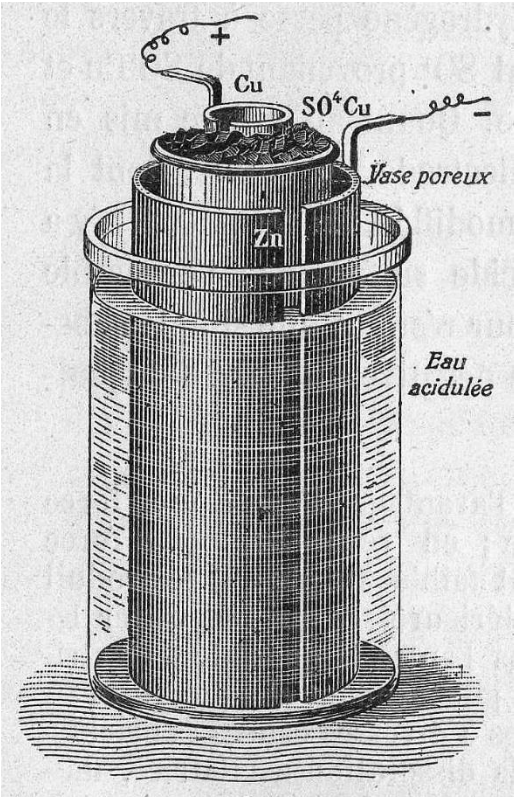


Fig. 284. — Élément Daniell.

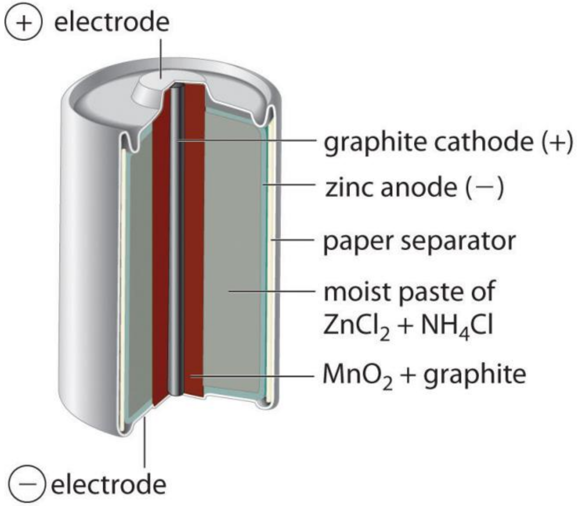
Primary cells

Daniell cell (1836)

https://ca.wikipedia.org/wiki/Pila_Daniell#/media/File:%C3%89l%C3%A9ment_Daniell.jpg

BATTERIES AS ELECTROCHEMICAL SYSTEMS

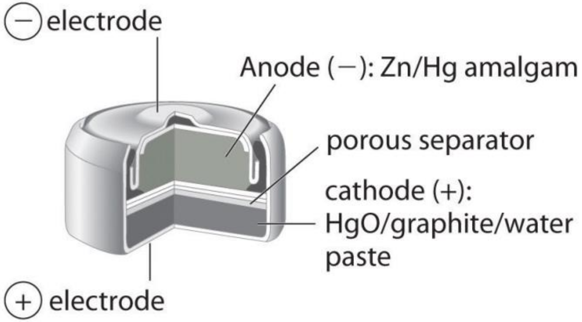
Primary cells



cell reaction:

$2MnO_2(s) + 2NH_4Cl(aq) + Zn(s) \rightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l)$

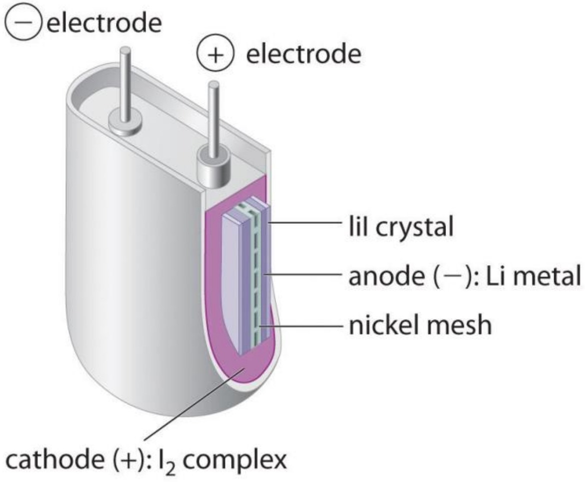
(a) Leclanché dry cell



cell reaction:

$Zn(s) + HgO(s) \rightarrow Hg(l) + ZnO(s)$

(b) Button battery



cell reaction:

$2Li(s) + I_2(s) \rightarrow 2LiI(s)$

(c) Lithium-iodine battery

http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Case_Studies/Commercial_Galvanic_Cells

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Secondary cells

Discharge (galvanic cell)

Charge (electrolytic cell)

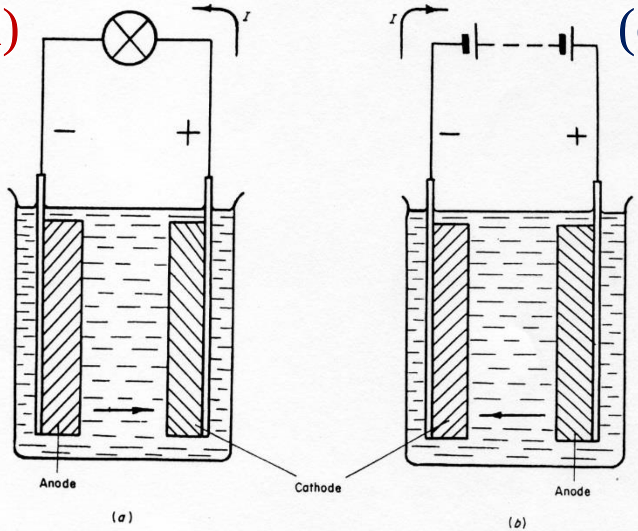


Fig. 2. Current direction (a) in a discharging cell, and (b) in a storage cell being charged or in an electrolyser.

Zn/Ag_2O cell

Discharge:

(-) $Zn + 2\,OH^- \rightarrow ZnO + H_2O + 2\,e^-$

(+) $Ag_2O + H_2O + 2\,e^- \rightarrow 2\,Ag + 2\,OH^-$

$Ag_2O + Zn \rightarrow 2\,Ag + ZnO$

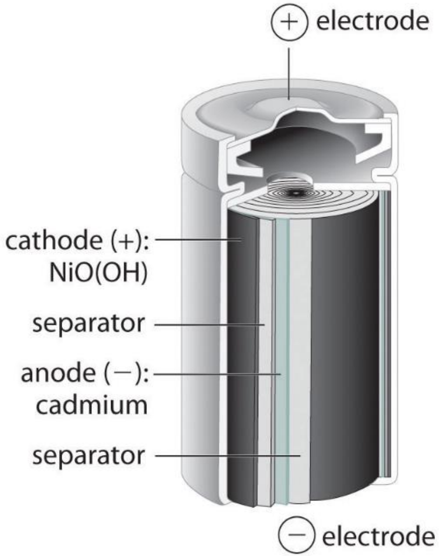
Charge:

(-) $ZnO + H_2O + 2\,e^- \rightarrow Zn + 2\,OH^-$

(+) $2\,Ag + 2\,OH^- \rightarrow Ag_2O + H_2O + 2\,e^-$

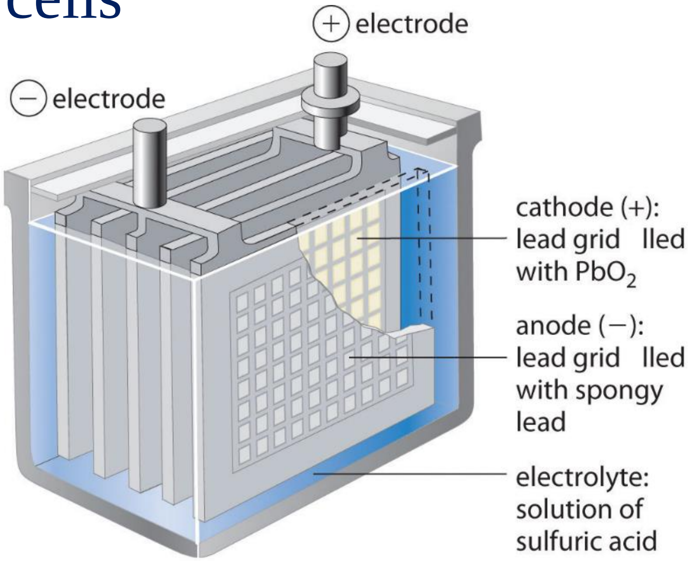
$Ag + ZnO \rightarrow Ag_2O + Zn$

Secondary cells



cell reaction:

$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow$
$Cd(OH)_2(s) + 2Ni(OH)_2(s)$



cell reaction:

$Pb(s) + PbO_2(s) + 2HSO_4^-(aq) + 2H^+(aq) \rightarrow$
$2PbSO_4(s) + 2H_2O(l)$

http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Case_Studies/Commercial_Galvanic_Cells

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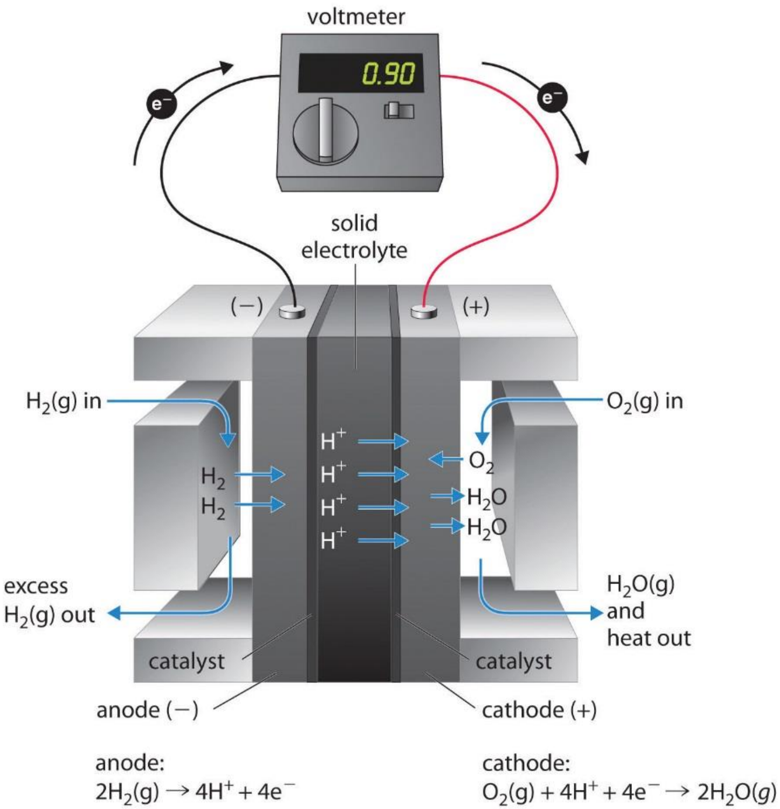
Fuel Cells



H_2/O_2 Fuel Cell

http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Case_Studies/Commercial_Galvanic_Cells

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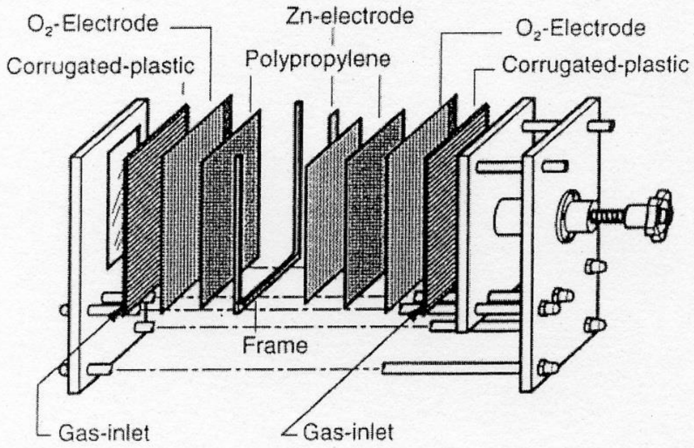

Fig. 13.45. Schematic view of the Zn-air battery consisting of a single cell with a central Zn anode facing two bifunctional air electrodes. (Reprinted from K. Müller, R. Holze, and O. Haas, "Progress Towards a 20 Ah/12V Electrically Rechargeable Zinc/Air Battery," in *Batteries for Portable Applications and Electric Vehicles*, C. F. Holmes and A. R. Landgrebe, eds., Electrochemical Society Proc. PV 97-18, pp. 859–868, Fig. 2, 1997. Reproduced by permission of The Electrochemical Society, Inc.)

Hybrid cell

Zn/air Semi-Fuel Cell

(-) $Zn + 4\,OH^- \rightarrow Zn(OH)_4^{2-} + 2\,e^-$

(+) $\frac{1}{2}\,O_2 + 4\,H^+ + 2\,e^- \rightarrow OH^-$

$Zn + \frac{1}{2}\,O_2 + H_2O + 2\,OH^- \rightarrow Zn(OH)_4^{2-}$

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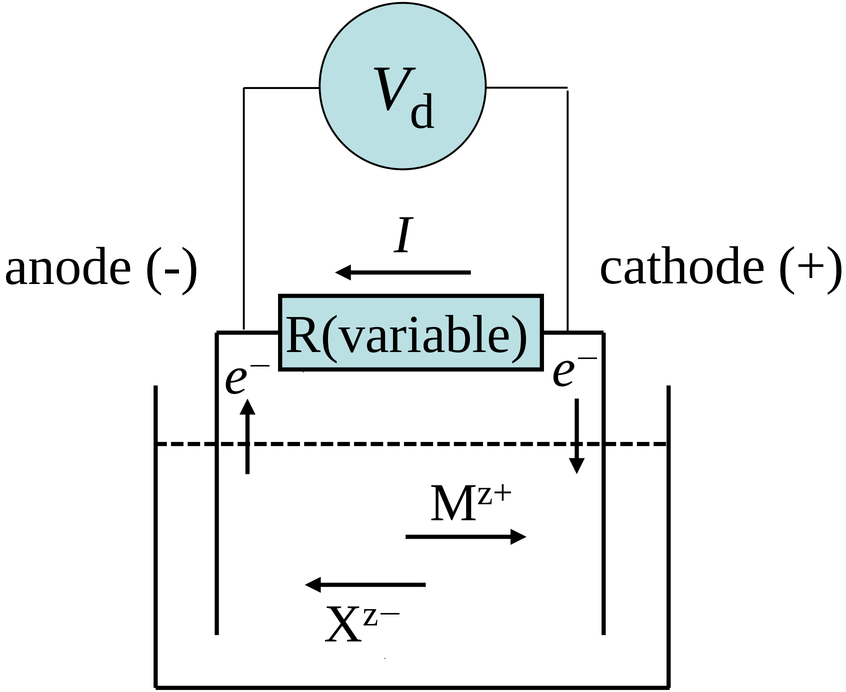
Production of electrical energy from fossil fuels by means of the conventional technology:

Chemical energy → thermal (heat) → mechanical → electrical

CARNOT'S CYCLE

Direct conversion in galvanic cells:

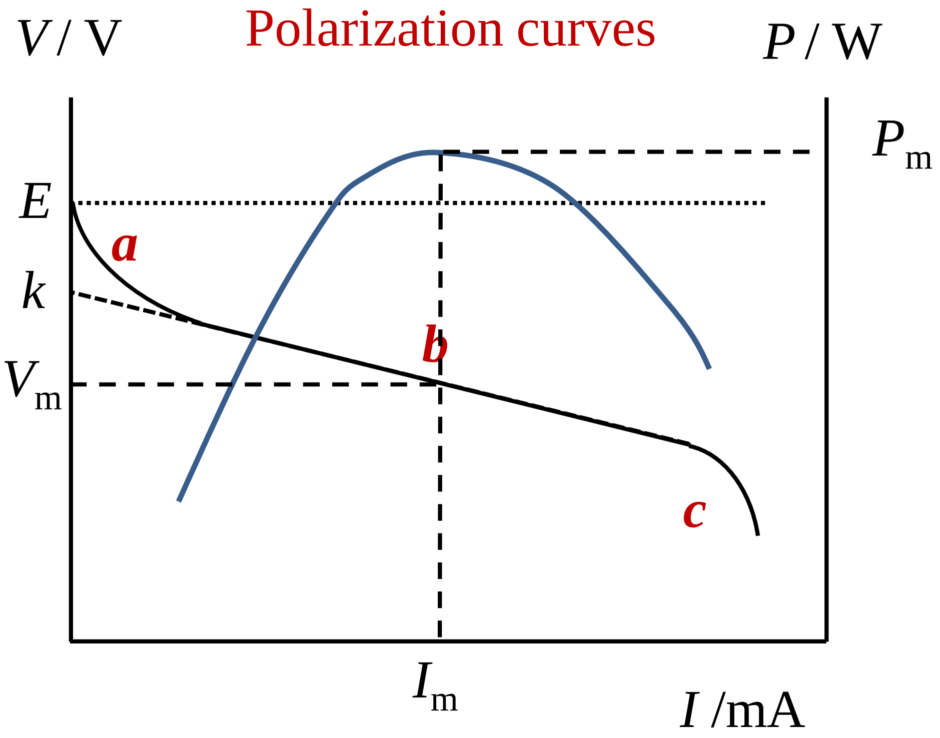
Chemical energy → electrical



Measuring the discharge voltage

$$V_d = I\,R_{ext}$$

$$P = I\,V_d$$



$$E = E_{eq(+)} - E_{eq(-)}$$

$$V_d = k - IR_{int}$$

$$P = I\,V_d = I\,(k - IR_{int})$$

$$P_m = I_m V_m$$
$$(\text{with } I_m = k / 2R_{int})$$

BATTERIES AS ELECTROCHEMICAL SYSTEMS

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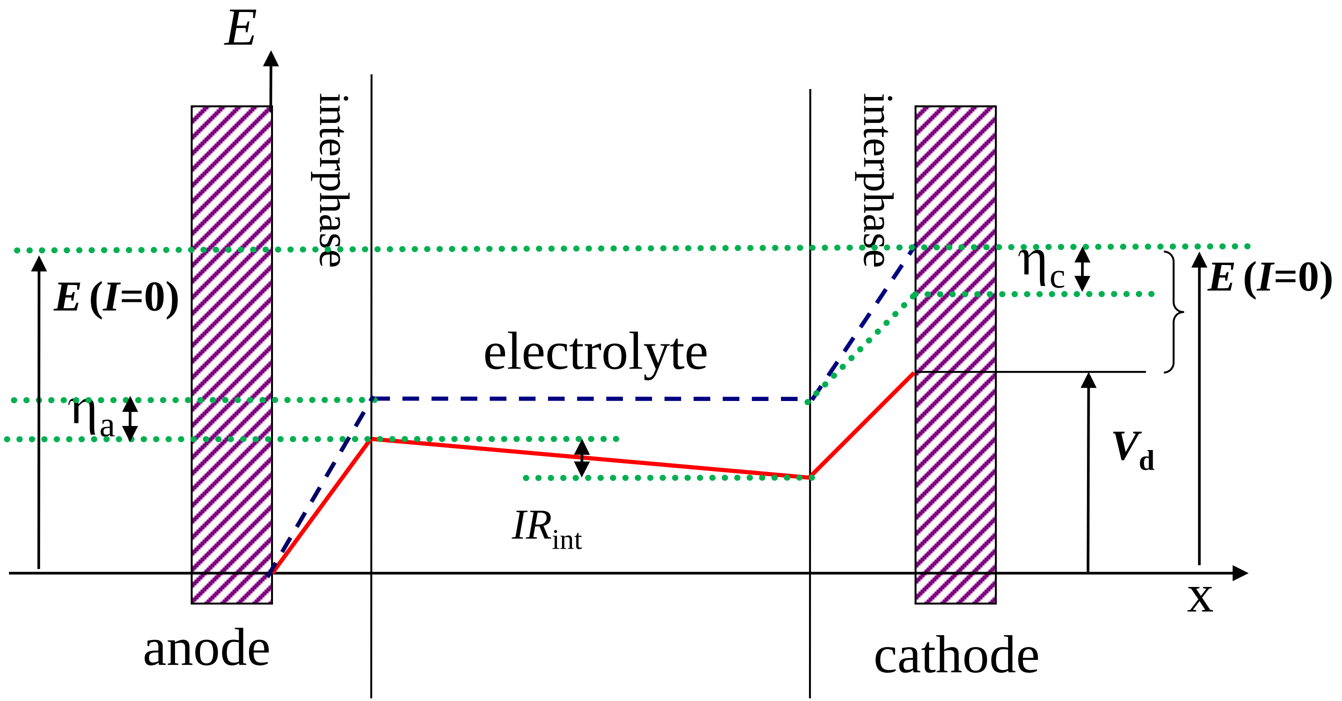

$$V = E_c - E_a - I\,R_{int} = E - |\eta_c| - \eta_a - I\,R_{int} < E$$

Major factors contributing to the cell performance:

- Activation control
- Diffusion control
- Ohmic control

BUTLER-VOLMER EQUATION

(activation or charge-transfer control)

$$j = j_o \, [\exp(\alpha_{ox} F\eta/RT) - \exp(-\alpha_{red} F\eta\,/RT)]$$

j_o is the exchange current density

α_{ox} and α_{red} are the charge transfer coefficients

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ACTIVATION OVERPOTENTIAL

High field for the anodic reaction (Tafel): $\eta_a >> 0$ ($\eta_a > 120$ mV)

$$j_a = j_{o,a} [\exp(\alpha_a F \eta_a / RT)]$$

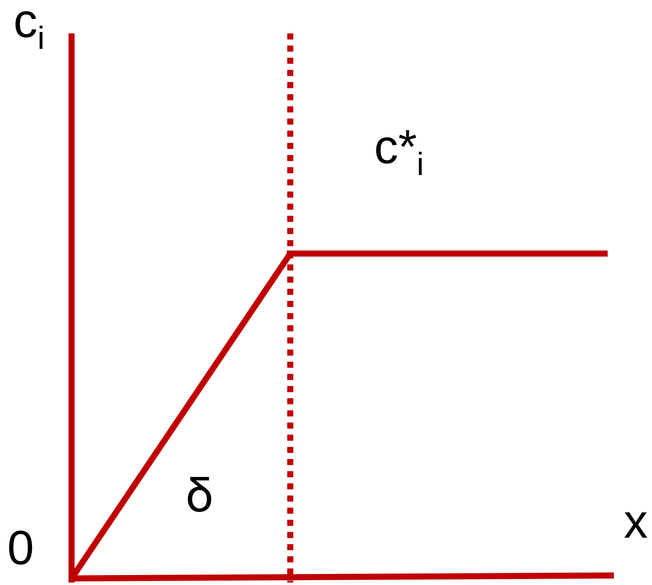
$$\eta_a = (RT/\alpha_a F) \ln (j_a / j_{o,a})$$

High field for the cathodic reaction (Tafel): $\eta << 0$ ($\eta < -120$ mV)

$$| j_c | = j_{o,c} [\exp(-\alpha_c F \eta_c / RT)]$$

$$\eta_c = - (RT/\alpha_a F) \ln | j_c / j_{o,c} |$$

DIFFUSION OVERPOTENTIAL



1st Fick's law: $J = -D\,(dc_i/dx)$

$$j = nFD\,(c^o - c^*)\,/\,\delta$$

D, diffusion coefficient

n, number of electrons transferred

c^o and c^*, concentration in the bulk and at the interface

$$j\,/\,j_L = (c^o - c^*)\,/\,c^o = 1 - (c^*/\,c^o)$$

$$j = j_o\,[(c_R^*/\,c_R^o)\exp(\alpha_a F\eta/RT) - (c_O^*/\,c_O^{\,o})\exp(-\alpha_c F\eta\,/RT)]$$

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$$j = j_o\,[(1 - j_{ox} / j_{L,ox})\exp(\alpha_{ox} F\eta/RT) - (1 - j_{red} / j_{L,red})\exp(-\alpha_{red} F\eta/RT)]$$

When $j_{L,red} << j_o >> j_{L,ox}$, the term into [ ] $\cong 0$

$$\eta_d = \frac{RT}{nF}\ln\frac{1-\frac{j_{red}}{j_{L,red}}}{1-\frac{j_{ox}}{j_{L,ox}}}$$

Anodic process in the cell ($j_{L,red} >> j_{red}$): $\eta_{d,a} = -\dfrac{RT}{n_a F}\ln\left(1-\dfrac{j_a}{j_{L,a}}\right)$

Cathodic process in the cell ($j_{L,ox} >> j_{ox}$): $\eta_{d,c} = \dfrac{RT}{n_c F}\ln\left(1-\dfrac{j_c}{j_{L,c}}\right)$

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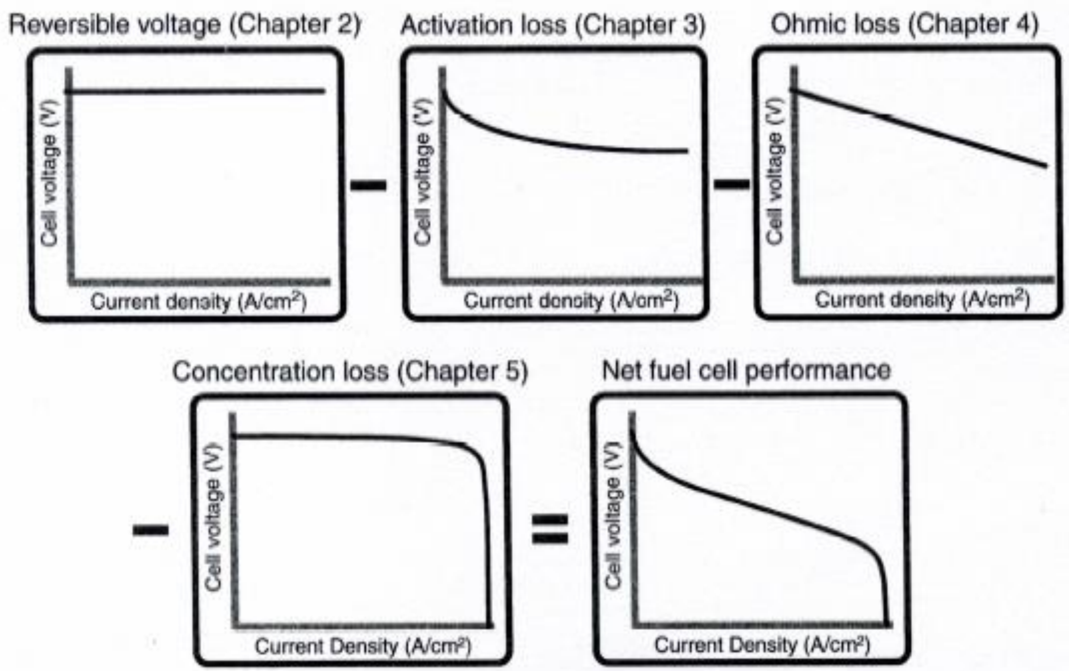

Major factors contributing to the cell performance

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Kinetic equations for plain electrodes

$$V = I\,R_{ext} = E - \{(RT/\alpha_a F)\ln(j_a/j_{o,a}) + (RT/nF)\ln(1-[j_a/j_{L,a}])\} -$$

$$- \{(RT/\alpha_c F)\ln|j_c/j_{o,c}| + (RT/nF)\ln(1-[j_c/j_{L,c}])\} - I\,R_{int}$$

Linear region:

$$V = E - k_1 - IR_{int}$$

Limiting current:

$$V = E - k_2 - (RT/nF)\ln(1-[j_a/j_{L,a}] - (RT/nF)\ln(1-[j_c/j_{L,c}]$$

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When $j_a = |j_c| = |j|$

$$V_d = I\,R_{ext} = E - \{a_a + b_a \ln|j|\} - \{a_c + b_c \ln|j|\} -$$

$$- c \ln(|j_L| / [|j_L| - |j|]) - I\,R_{int}$$

It is necessary to fix 7 parameters: a_a,b_a, a_c, b_c, c, R_{int} and j_L.

When the cathode is limiting, 4 are enough: α_c, j_{oc}, R_{int} and j_L.

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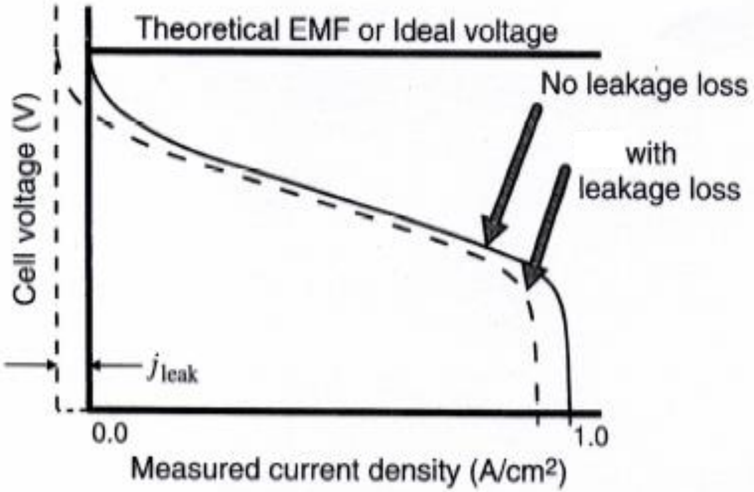

$$V_d = I\,R_{ext} = E - \{a_a + b_a \ln[|j| + |j_{leak}|]\} - \{a_c + b_c \ln[|j| + |j_{leak}|]\} -$$

$$- c \ln\{|j_L| / [|j_L| - (|j| + |j_{leak}|)]\} - I\,R_{int}$$

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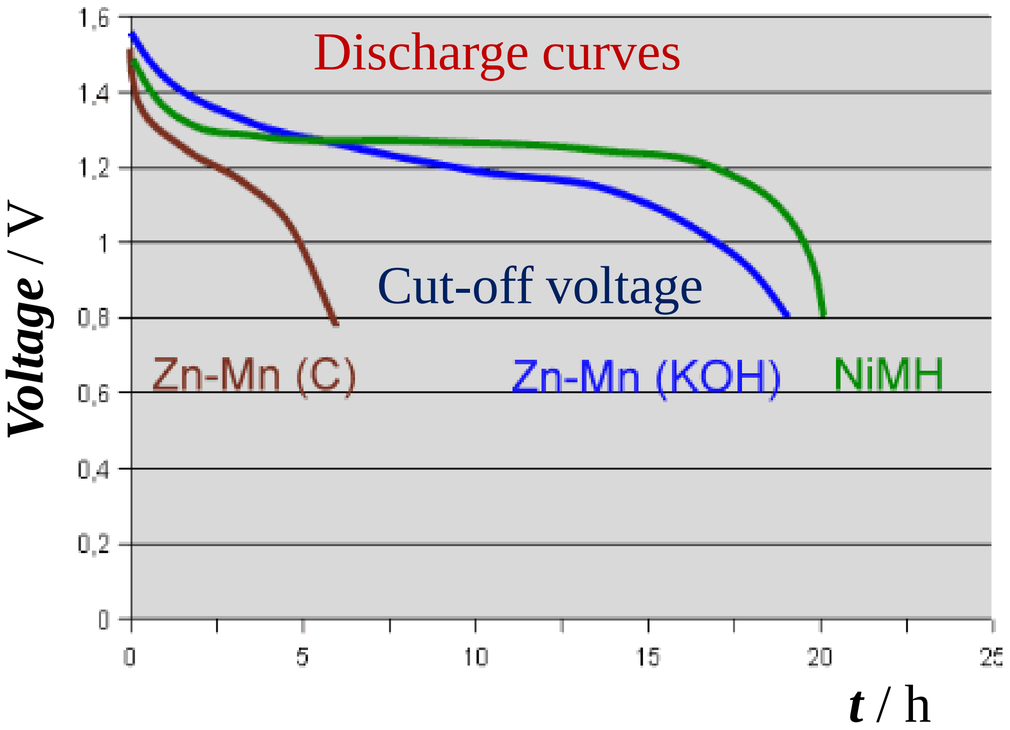

http://commons.wikimedia.org/wiki/File:Nimhcharakteristikrp.png

Cell properties:

Capacity (Ah): $Q = It$

Power (W): $P = IV$

Power density (W kg^{-1})

Energy (Wh): $U = QV$

Energy density (Wh kg^{-1})

BATTERIES AS ELECTROCHEMICAL SYSTEMS

$$(\partial G/\partial \xi)_{P,T} = \Sigma \nu_i \mu_i = - nFE \quad \text{(sometimes called } \Delta G\text{)}$$

$$dG_{P,T} \leq \delta w_{useful} = \delta w_{\ electric} \Rightarrow \Delta G = \text{maximum useful work}$$

$$\Delta S = -(d\Delta G/dT) = nF\,(dE/dT)$$

$$\Delta H = \Delta G + T\,\Delta S = -\ Q_t \qquad (Q_t = \text{heat delivered})$$

Thermoneutral voltage $E_t = -\Delta H\,/\,nF = E - T\,(dE/dT) = Q_t\,/\,nF$

$$E_t > 0 \text{ if } \Delta H < 0$$

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$$-\Delta H = nFE - nFT\,(\mathrm{d}E/\mathrm{d}T) = nFE + Q_S$$

(Q_S = entropy term, energy not useful as electric energy)

$$Q_S = nF\,(E_t - E)$$

In discharge, $V_d < E$ and the excess energy delivered as heat is done by

$$Q_U = nFE - nFV_d \qquad (E \text{ y } V_d > 0)$$

Then, the overall heat delivered by the cell is

$$Q_P = Q_S + Q_U = nF\,(E_t - V_d)$$

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Theoretical specific consumption of the reactant per unit of energy (g_W^T)

$$Ag_2O + Zn \rightarrow 2\,Ag + ZnO \qquad E_{ocv} = 1{,}60\ V$$

$$W_{max} = nFE_{ocv}$$

$$g_W^T(Ag_2O) = 231{,}74\ g\ /\ 53{,}6\ Ah * 1{,}60\ V = 2{,}70\ g/Wh$$

$$g_W^T(Zn) = 63{,}37\ g\ /\ 53{,}6\ Ah * 1{,}60\ V = 0{,}76\ g/Wh$$

Usage coefficient of the reactant (λ):

$\lambda = g_W^T / g_W^P$ (normally between 0.2 and 0.98).

Where g_W^P is the practical specific consumption of the reactant

Theoretical specific consumption of reactants per unit charge (g_Q^T)

$$Ag_2O + Zn \rightarrow 2\ Ag + ZnO$$

$$F = 96486\ C = 26{,}8\ Ah$$

$$g_Q^T(Ag_2O) = 231{,}74\ g\ /\ 53{,}6\ Ah = 4{,}32\ g/Ah$$

$$g_Q^T(Zn) = 63{,}37\ g\ /\ 53{,}6\ Ah = 1{,}22\ g/Ah$$

Usage coefficient of the reactant (λ):

$\lambda = g_Q^T / g_Q^P$ (normally between 0.2 and 0.98).

where g_Q^P is the practical specific consumption of the reactant

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Thermodynamic efficiency

(maximum)

$$\eta_{(T)} = E/E_t$$

Voltage efficiency

$$\eta_{(V)} = V_d/E$$

Net efficiency

$$\eta_n = \lambda\ V_d/E_t = \lambda\ \eta_{(V)}\ \eta_{(T)}$$

$$(\eta_n = 60 – 80\%)$$

Autumn School Flow Battery

Barcelona – 12th-13th of November 2018

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