

Energy Generation, Storage, and Transformation

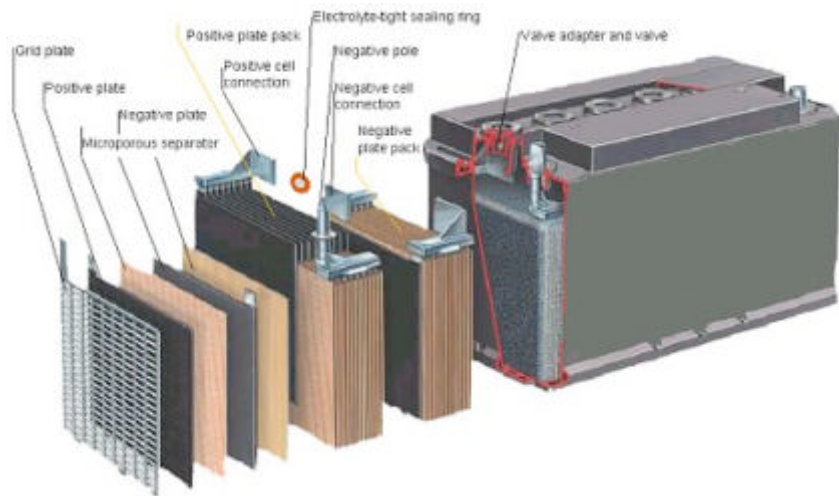
Roderick M. Macrae

IGSS'09

The Institute for Green and Sustainable Science

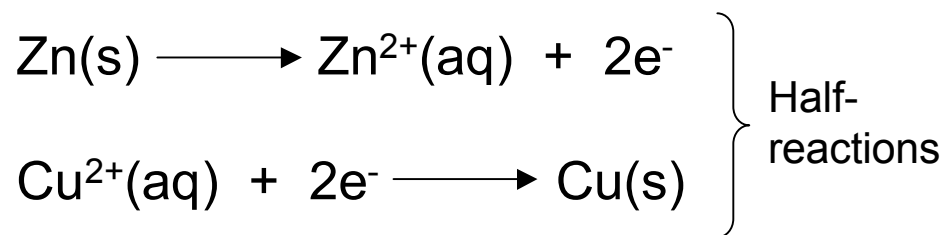
MARIAN UNIVERSITY
— Indianapolis —

Storage of Electrical Energy - Batteries

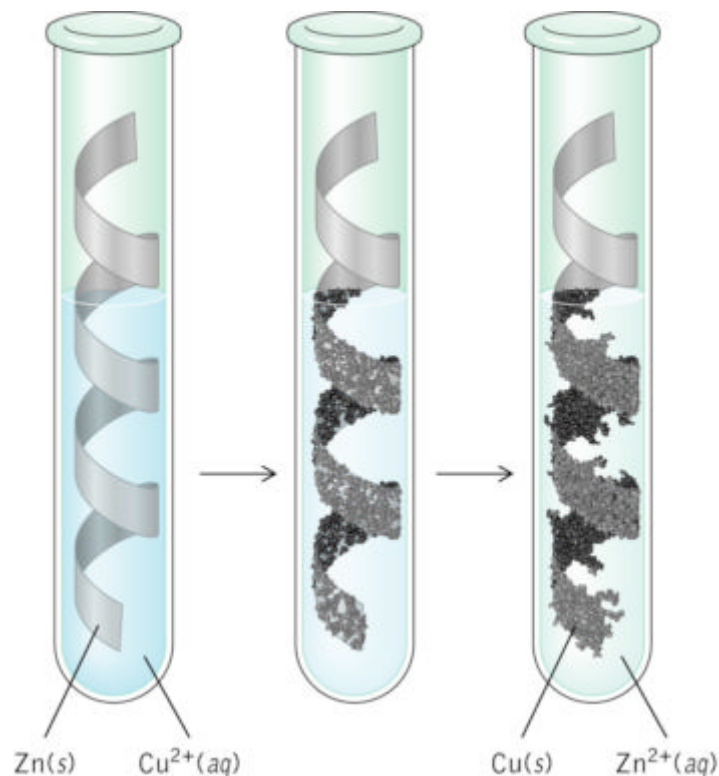
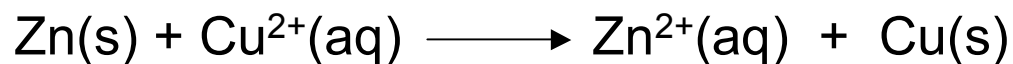


Electrochemistry

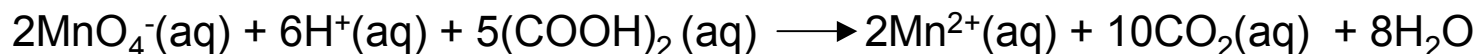
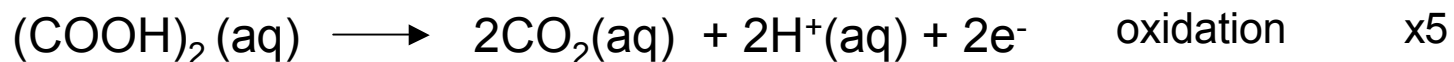
Redox reactions:



overall

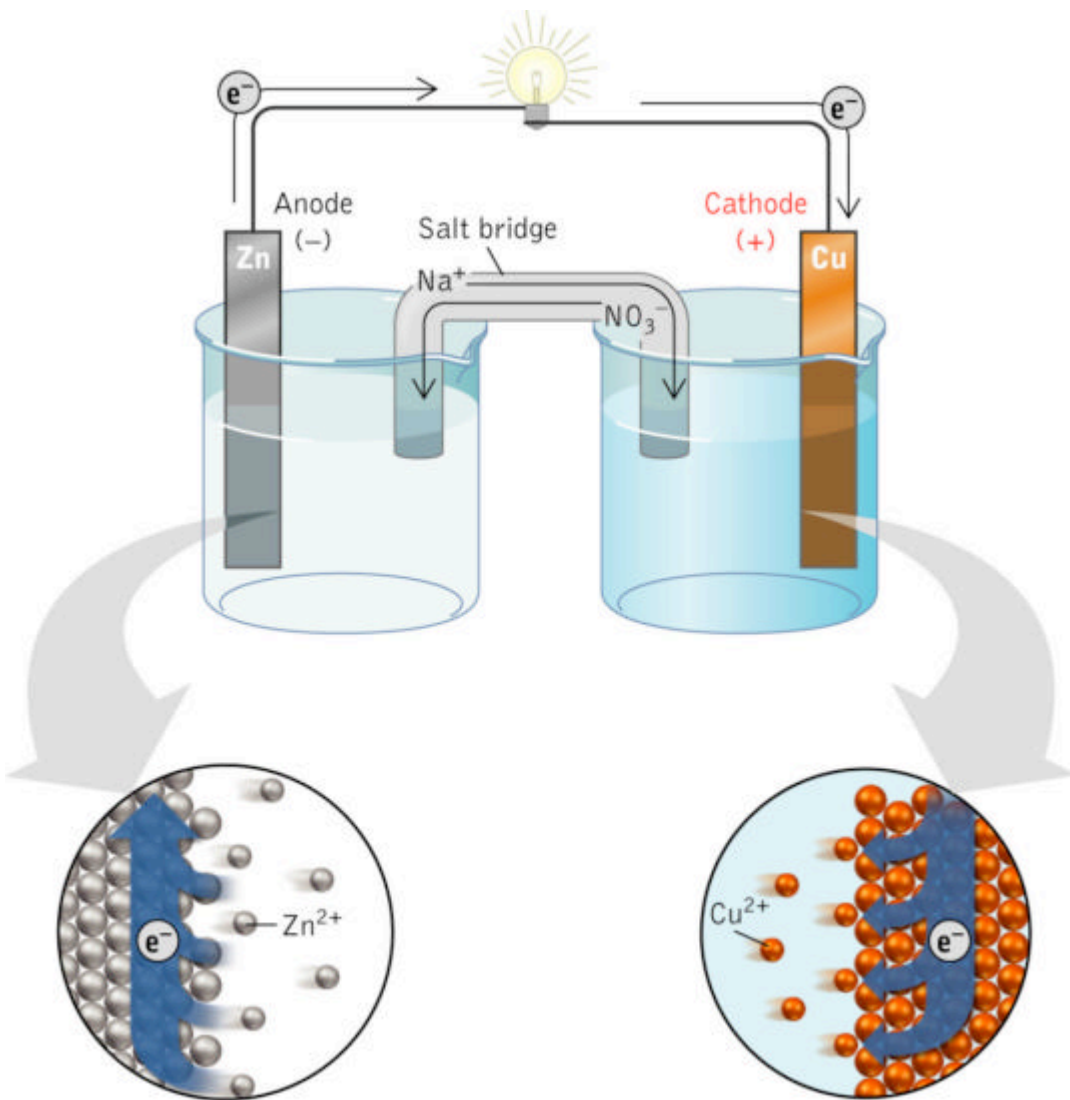


Method: Balance electron numbers and add half-reactions. E.g. Oxalic acid + KMnO_4

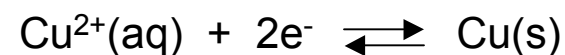


10 (moles of) electrons transferred

Voltaic Cell - physical separation of half-reactions



Equilibria:



Reduction at **cathode**

Oxidation at **anode**

Electrons flow through wire;
ions flow through salt bridge.

Notation:



Cell Potentials (E)

Voltage (EMF) - difference in electrical potential energy between electrodes - can be used to do (electrical) work.

$$w = Q \times E$$

work charge potential difference

$$Q = I \times t$$

current,A time,s

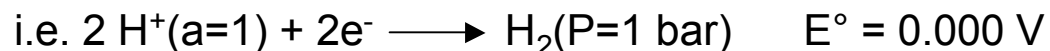
$$e = 1.602 \times 10^{-19} \text{ C}$$
$$1 \text{ C} = 1 \text{ A} \times 1 \text{ s}$$
$$1 \text{ V} = 1 \text{ J / C}$$

volt joule coulomb

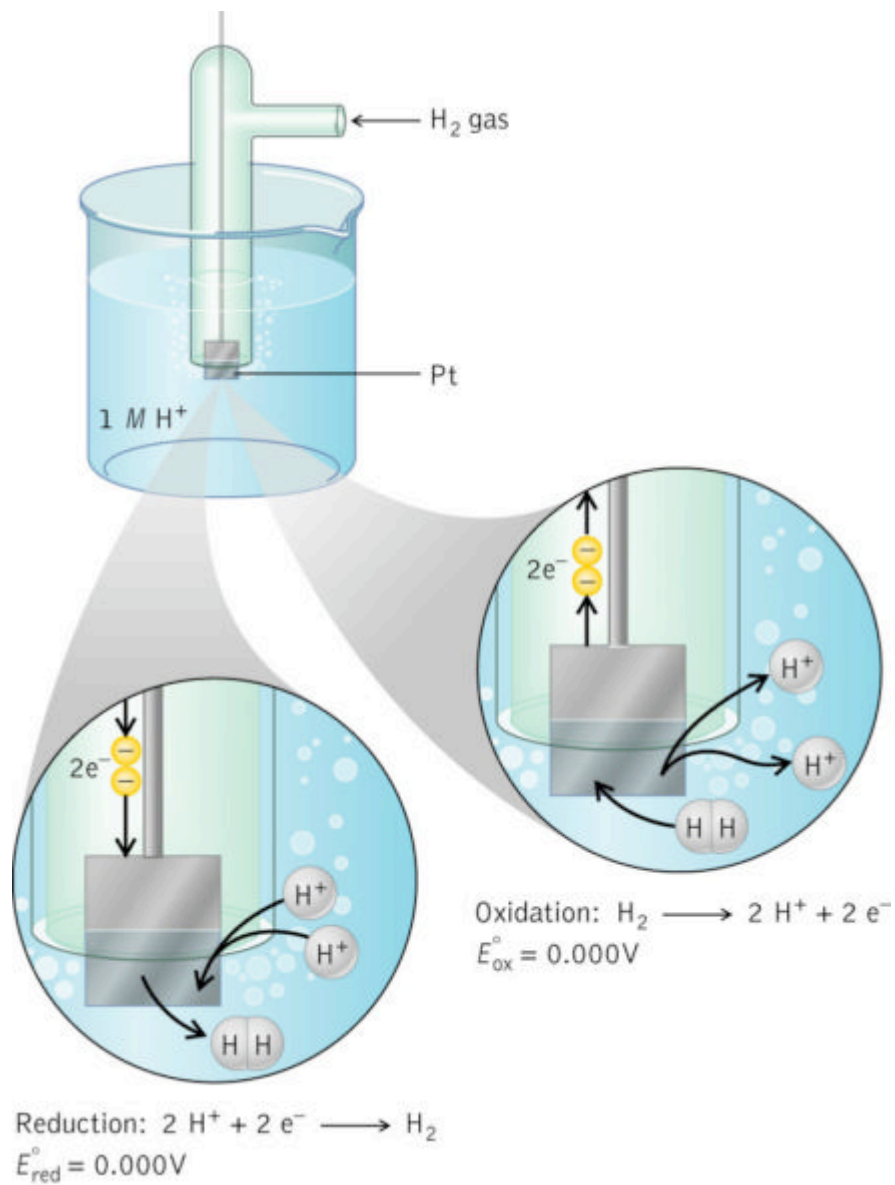
Potential for a given half-reaction is defined with respect to a **standard potential**:

1 M solutions

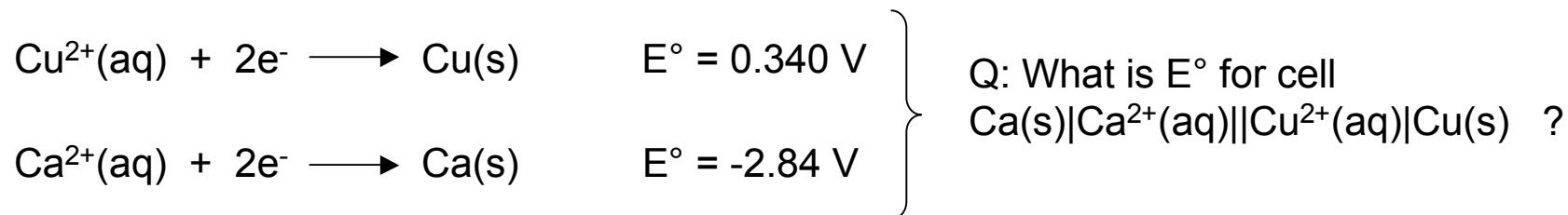
one electrode is a **standard hydrogen electrode (SHE)**



Standard Hydrogen Electrode



Other half-reactions are tabulated as **reduction** potentials:



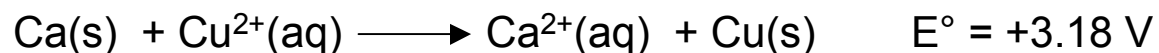
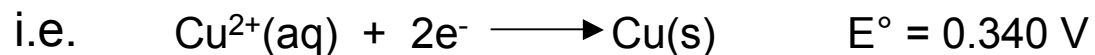
Rule: The more negative the reduction potential, the more likely the reaction will reverse and go as an oxidation (reversing sign of E°). (Convention: Oxidation on left.)

Using this convention:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}}$$

(where E°_{R} and E°_{L} are the reduction values)

$$= 0.340 \text{ V} - (-2.84 \text{ V}) = \mathbf{3.18 \text{ V}}$$



Note: In cases where multiplication e.g. by 2 is necessary, this does not change E . What changes is the **current** - see below.

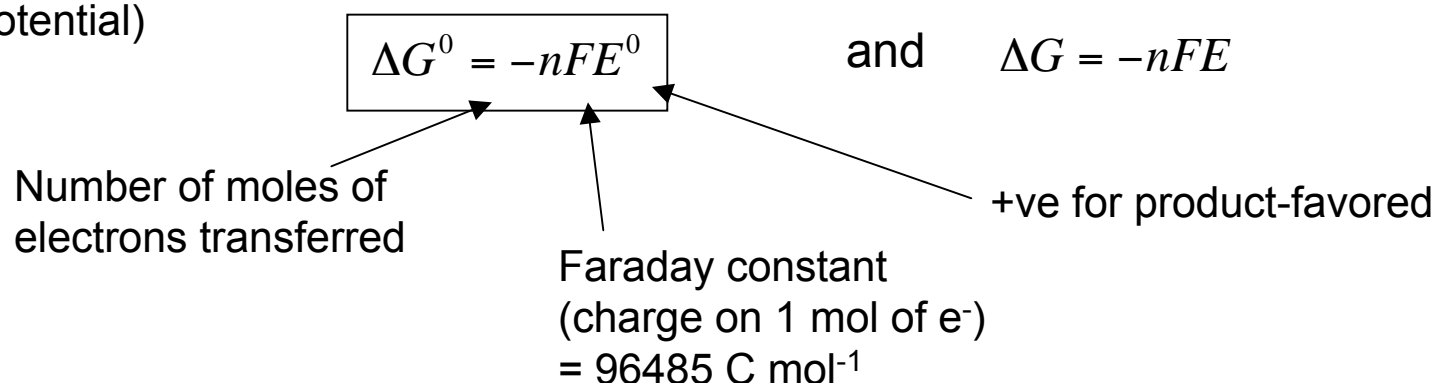
E° and ΔG

ΔG = Maximum (electrical) work done (by cell). *Exergy* = ΔG

Proportional to:

Number of moles of electrons transferred (charge = current x time)

E° of cell (potential)



e.g. $\text{Ca(s)}|\text{Ca}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ $E^{\circ} = 3.18 \text{ V}$, 2 mol e⁻ transferred per mol Ca/Cu

$\Rightarrow \Delta G^{\circ} = -2 \text{ mol} \times 96485 \text{ C mol}^{-1} \times 3.18 \text{ V} = -613,6 \text{ kJ mol}^{-1} \text{ (Cu/Ca)}$

Also, $\Delta G^{\circ} = -RT \ln K \Rightarrow -nFE^{\circ} = -RT \ln K \Rightarrow E^{\circ} = \frac{RT}{nF} \ln K$

For $T = 298 \text{ K}$, $RT/F = 0.0257 \text{ V}$.

E and Concentration

$$\Delta G = \Delta G^0 + RT \ln Q \quad \text{i.e.} \quad -nFE^0 = \Delta G^0 + RT \ln Q$$

$$\text{i.e.} \quad E = E^0 - \frac{RT}{nF} \ln Q$$

Nernst equation

As Ca/Cu cell continues to generate electricity

$\left\{ \begin{array}{l} \text{Ca} \rightarrow \text{Ca}^{2+} \text{ i.e. } [\text{Ca}^{2+}] \text{ increases} \\ \text{Cu}^{2+} \rightarrow \text{Cu} \text{ i.e. } [\text{Cu}^{2+}] \text{ decreases} \end{array} \right.$

Consider 2 cases:

In principle, all expressions should use *activities* rather than concentrations.

(1) $[\text{Ca}^{2+}] = [\text{Ca}^{2+}] = 1 \text{ M}$

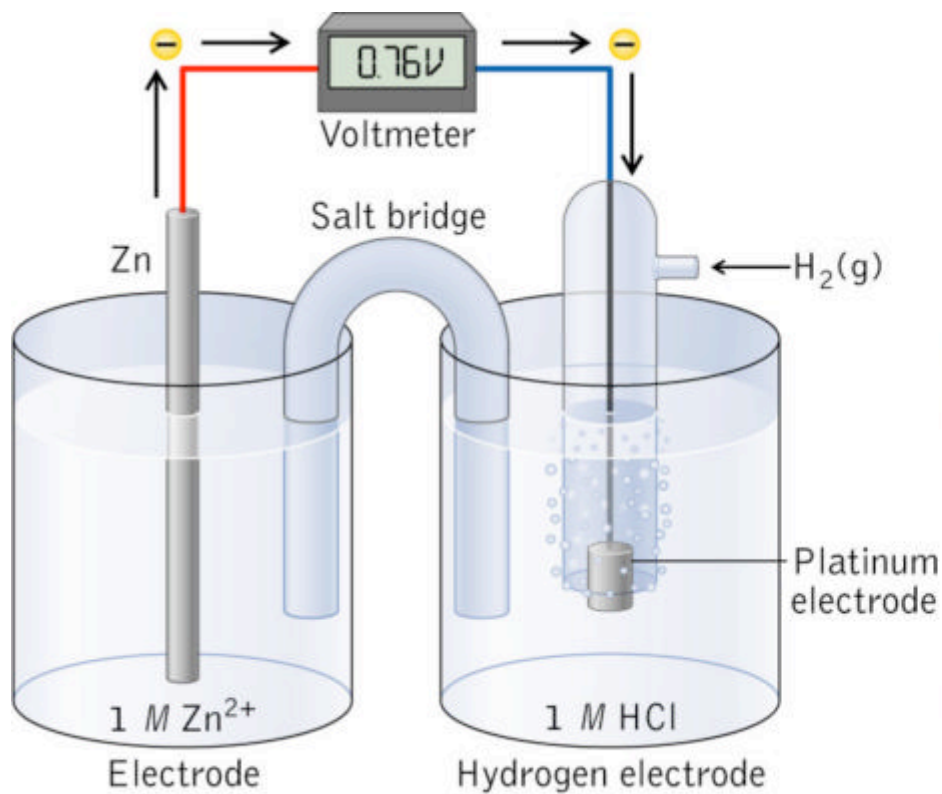
$$E = E^0 \quad \Delta G = \Delta G^0$$

(2) Equilibrium

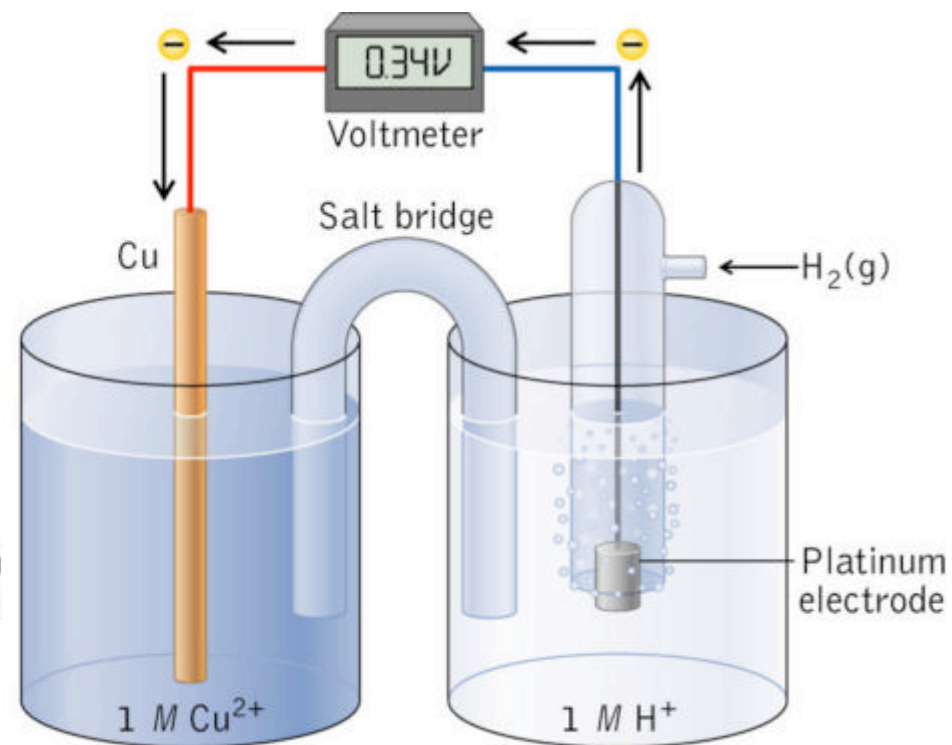
$$\Delta G = 0 \text{ i.e. } nFE^0 = RT \ln Q$$

$$\text{i.e.} \quad \ln Q = \frac{nFE^0}{RT} = \frac{2 \text{ mol} \times 96485 \text{ C mol}^{-1} \times 3.18 \text{ V}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 247.7$$

$$\text{i.e.} \quad Q = e^{247.7} = 3.76 \times 10^{107} (!) \quad \text{i.e. Reaction goes to completion.}$$



A



B

Electrochemical Cells as Energy Sources

Principle: electrochemical reaction occurring in a galvanic cell.

Earliest case: alternate Cu and Zn sheets separated by wet cloth (origin of Daniell cell).

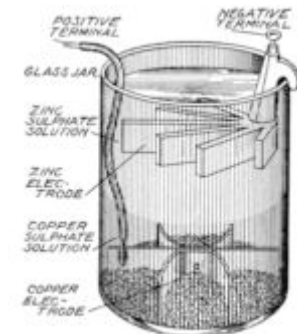
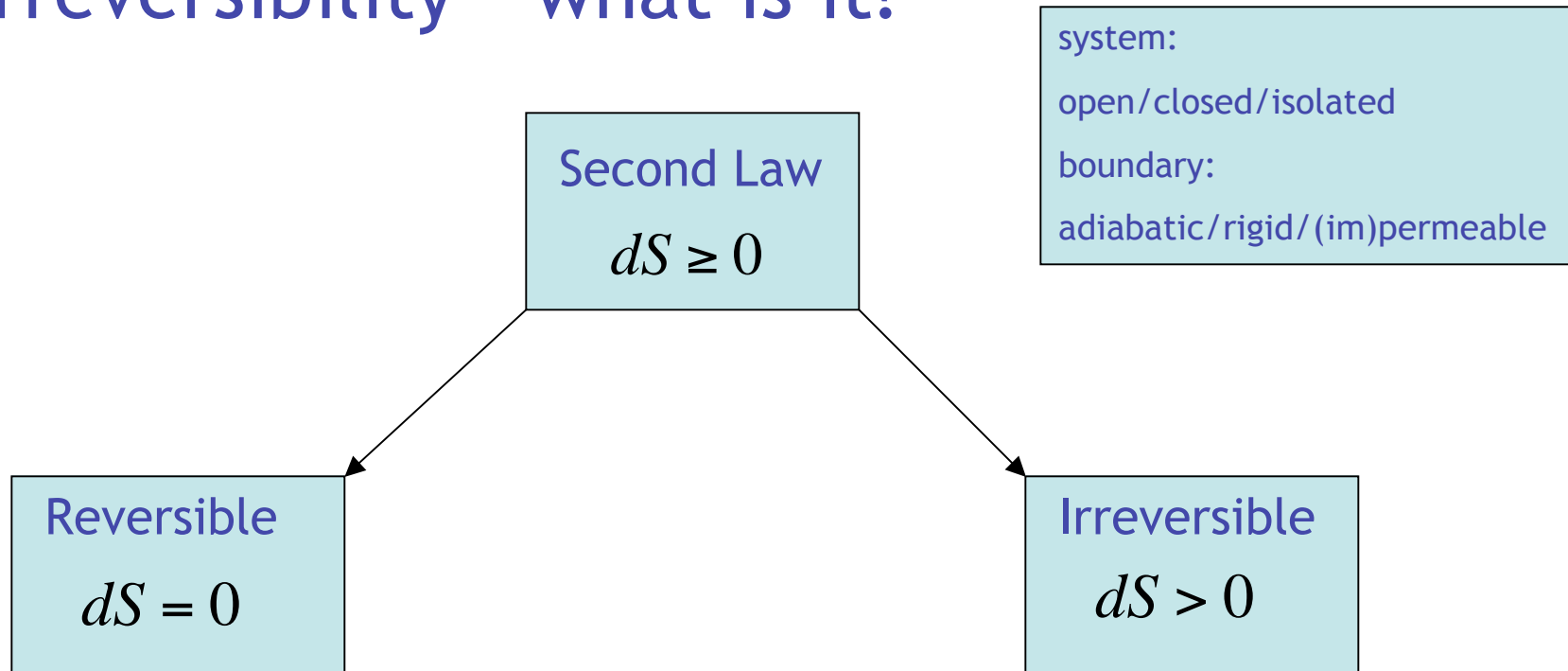


Fig. 64. Gravity Cell

Three basic types:

- 1) Primary cells - based on irreversible reactions (no recharging possible)
- 2) Accumulators (storage batteries) - based on “almost reversible” electrode processes. Efficiency of recharging reduced by side reactions.
- 3) Fuel cells - direct conversion of energy from chemical processes into electricity (to obtain maximum useful fraction of reaction ΔG).

Irreversibility - what is it?



System has well-defined *state* (P,V,T)

Infinitesimal changes (e.g. $P = P_{\text{ext}}$)

No T gradients

No turbulent flows

Rapid changes

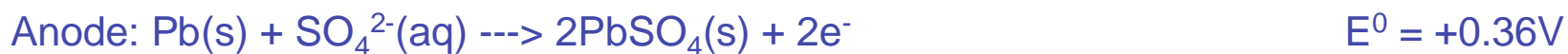
Gradients in T, concentration, etc.

Disorder

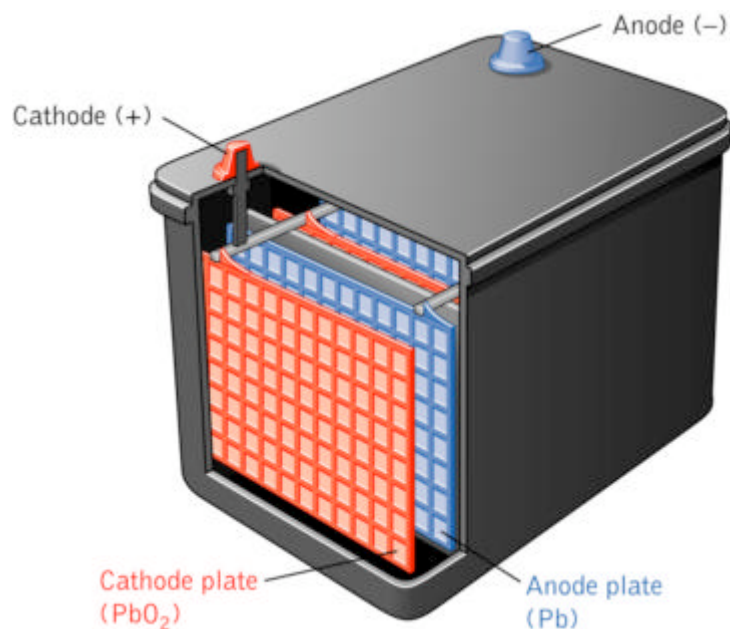
Convection, turbulence

Lead-acid Batteries

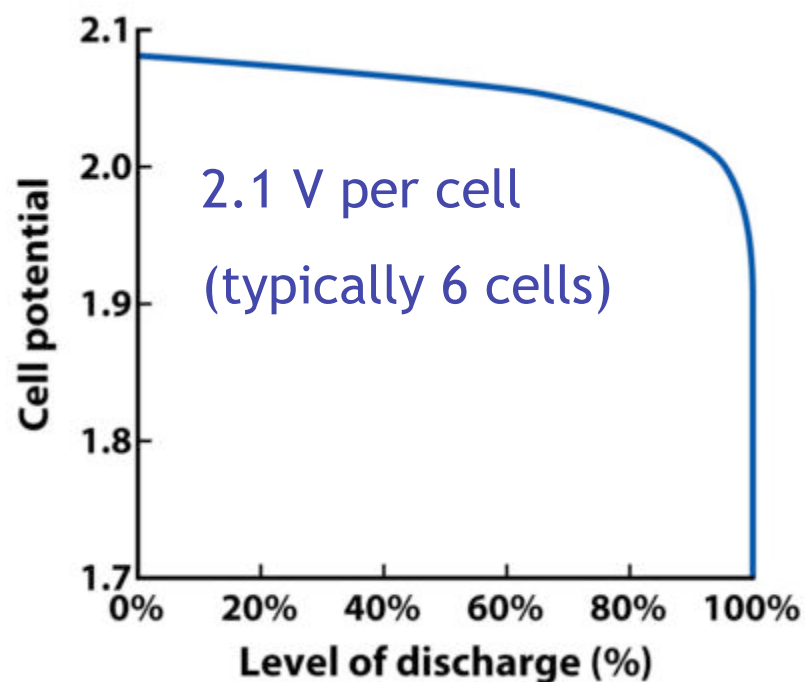
Half-reactions:



Net reaction (discharging):



electrodes are *porous*



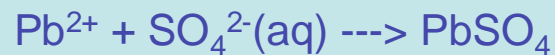
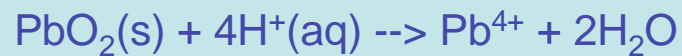
Lead-acid Batteries

In more detail (discharging):

Lead electrode:



Lead oxide electrode:



Not completely reversible due to:

Lead electrode:



Lead oxide electrode:



Potential at electrodes:

PbO₂:

$$E_{\text{PbO}_2} = E_{\text{Pb}^{4+}/\text{Pb}^{2+}}^0 + \frac{RT}{2F} \ln \frac{a_{\text{Pb}^{4+}}}{a_{\text{Pb}^{2+}}}$$

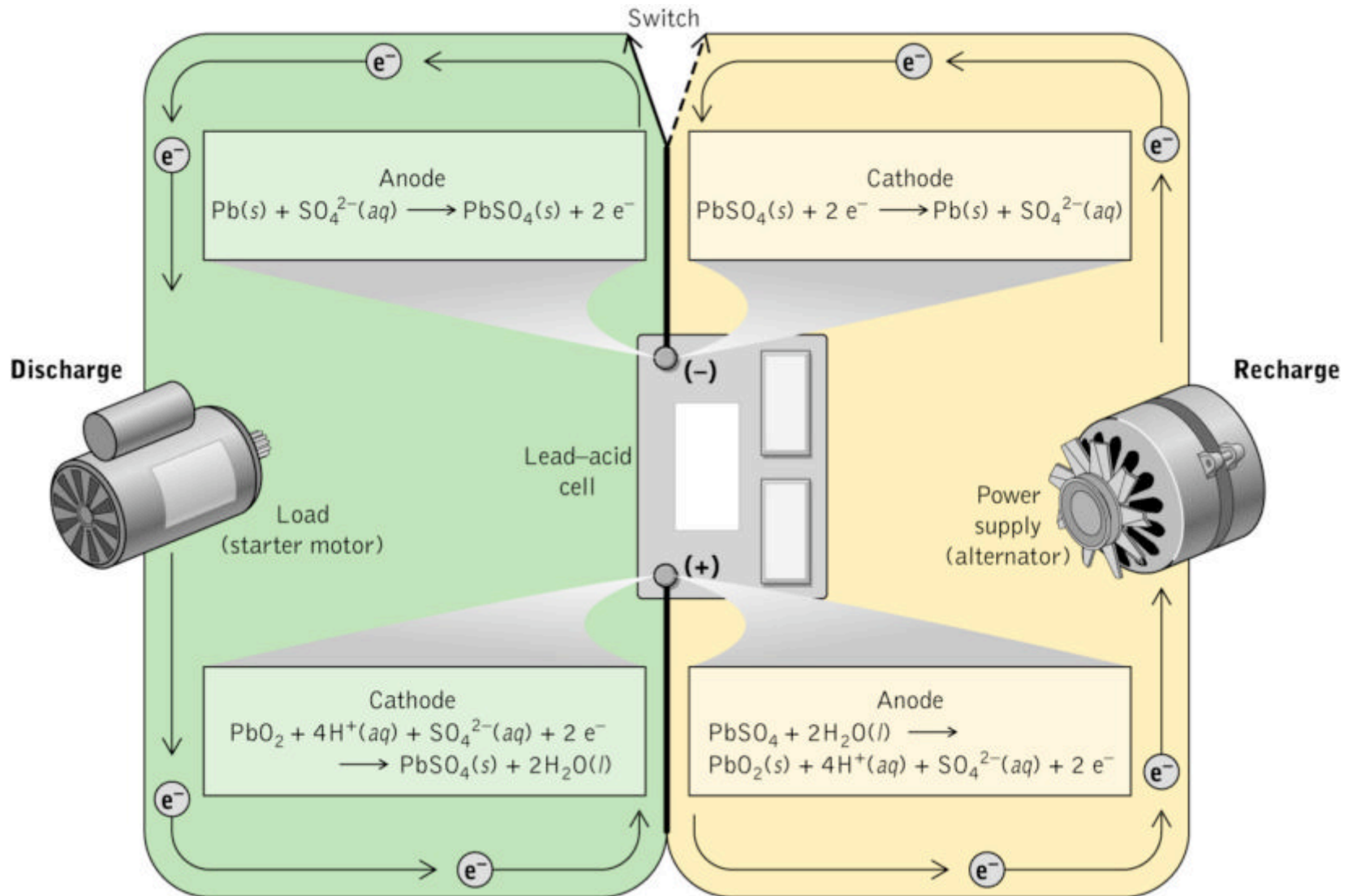
$$\approx E_{\text{Pb}^{4+}/\text{Pb}^{2+}}^0 \approx 1.70\text{V}$$

Pb:

$$E_{\text{Pb}} = E_{\text{Pb}^{2+}/\text{Pb}}^0 + \frac{RT}{2F} \ln a_{\text{Pb}^{2+}} \approx -0.28\text{V}$$

Lead-acid Batteries

Discharging and recharging cycles



Lead-acid Batteries

Types:

Shallow cycle - no more than 20% should be discharged per cycle (not useful for power applications).

Deep cycle - up to 80% can be discharged, but lifetime is enhanced by limiting discharge. Irreversibility reduced by the use of thicker plates or immobilized electrolyte.

All lead-acid batteries should be recharged fully after each cycle - leaving battery in partially charged state leads to sulfation of positive plate and diminution in capacity.

Presence of (dense) lead in cells results in low energy per unit mass (30-40 Wh/kg)

500-800 recharge cycles

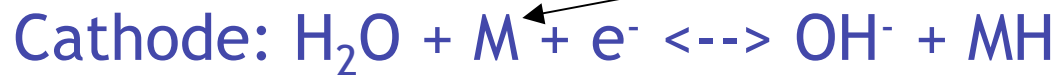
Nickel-Metal Hydride Batteries

Used in: Toyota Prius, Honda Civic Hybrid



Reactions:

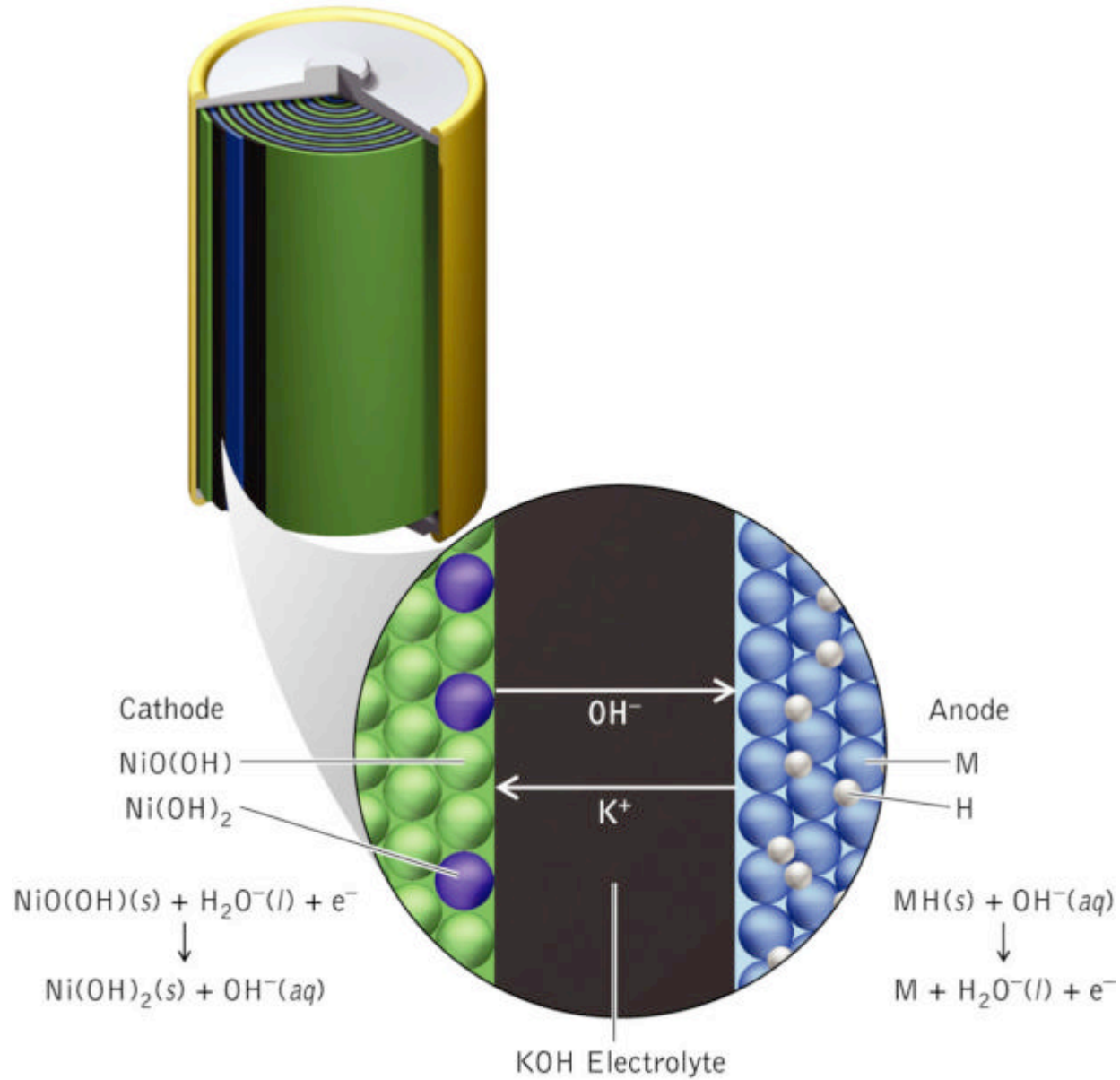
M: typically AB₅ intermetallic (A: rare earth such as La; B: Ni or Co)



Energy density higher than lead-acid (30-80 Wh/kg)

500-1000 charge/discharge cycles

Nickel-Metal Hydride Batteries



Lithium-ion Batteries

Several types: Lithium cobalt oxide, lithium manganese oxide, lithium iron phosphate

High energy density 100-160 Wh/kg

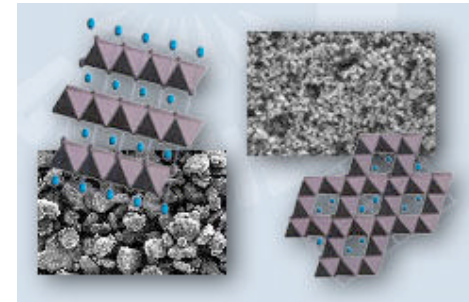
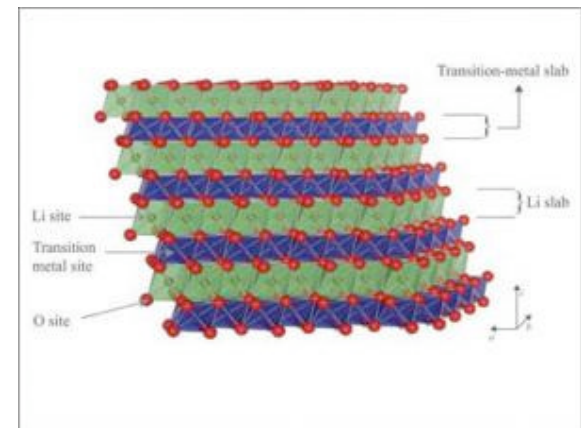
>1000 charge/discharge cycles

Explosion hazard with lithium cobalt oxide

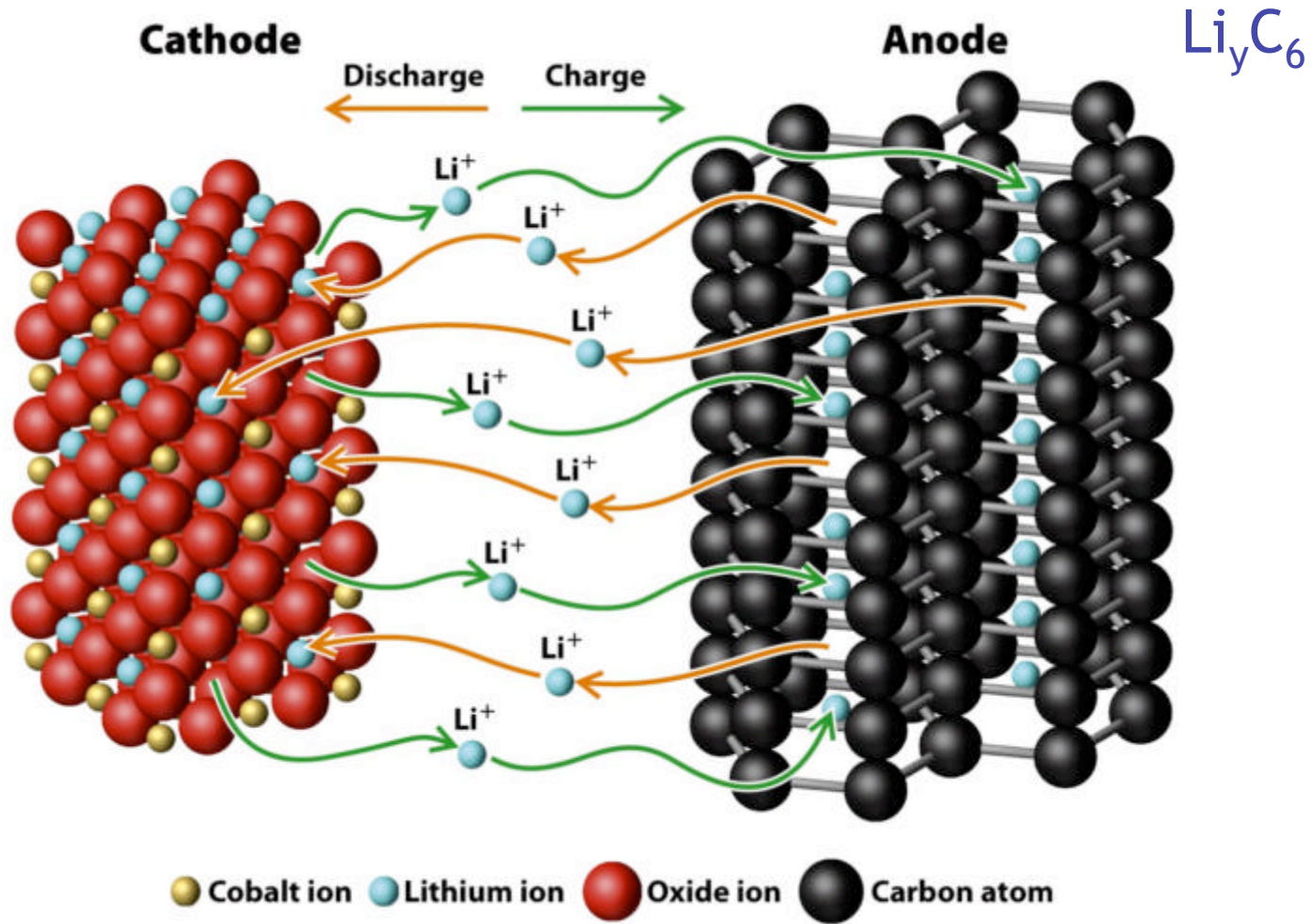
Relatively slow power delivery - rapid Li^+ diffusion requires accessible surface channels

Good reversibility because of reversible intercalation of Li in graphite anode (without expansion)

“Nanostructured architectures” of electrodes (3D thin films, interdigitated electrodes) improve performance



Lithium-ion Batteries



Fuel Cells

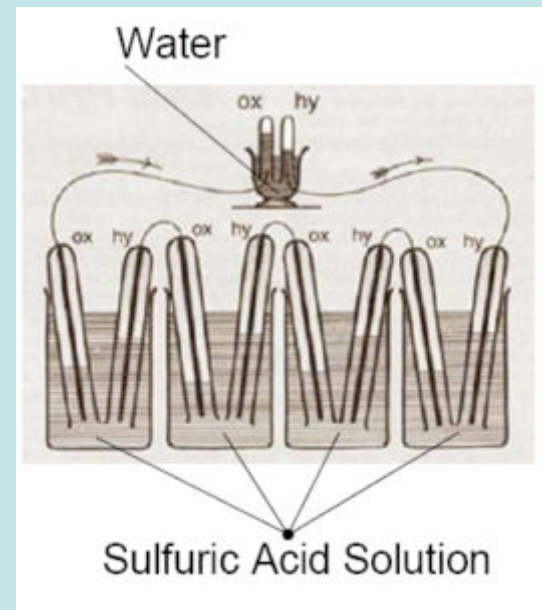
Electrochemical devices which transform chemical energy into electrical energy.

Differ from batteries in that the reactants are continuously replenished (thermodynamically, they are open systems).

Fuel cells have been around for a while...

Early design

W. R. Grove Phil. Mag. XIV (1839) 127



Fuel Cells

Various types exist:

Metal hydride fuel cell

Electro-galvanic fuel cell

Microbial fuel cell

Direct methanol fuel cell

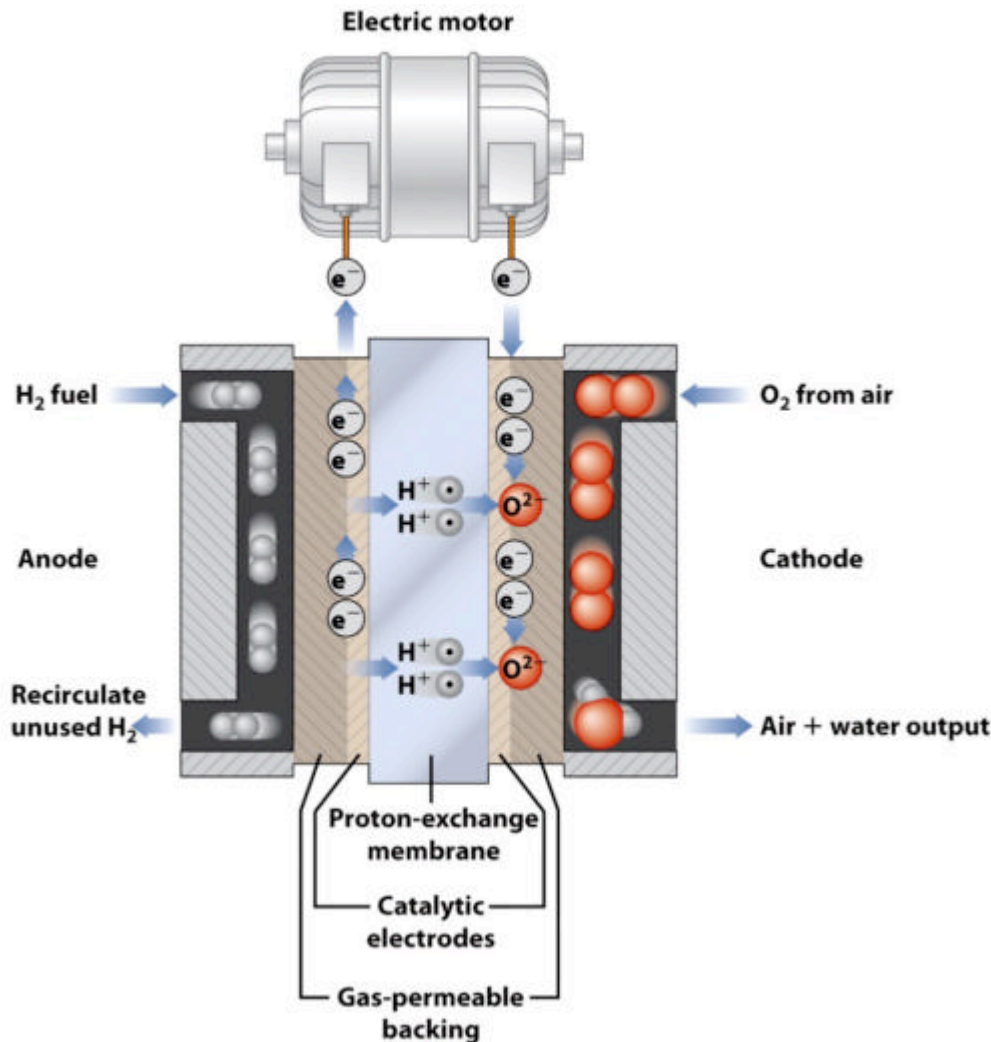
Proton Exchange Membrane Fuel Cell

Molten Carbonate Fuel Cell

Etc...



Fuel Cells



Proton Exchange Membrane (PEM) Fuel Cell

Anode - catalytic splitting of H_2 into protons and electrons (Pt or similar catalyst).

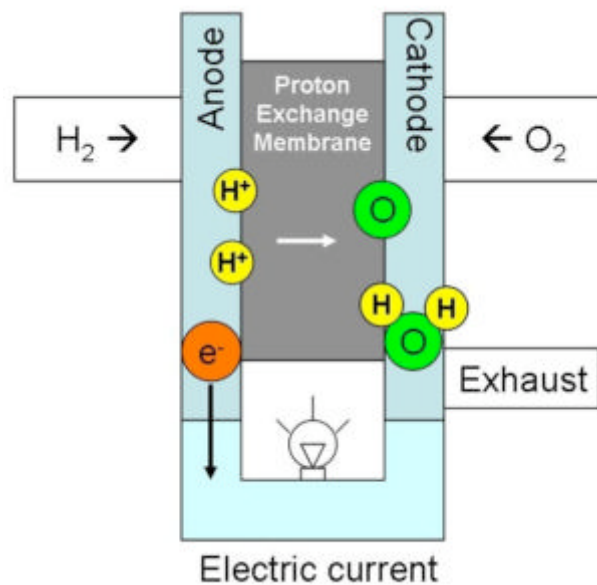
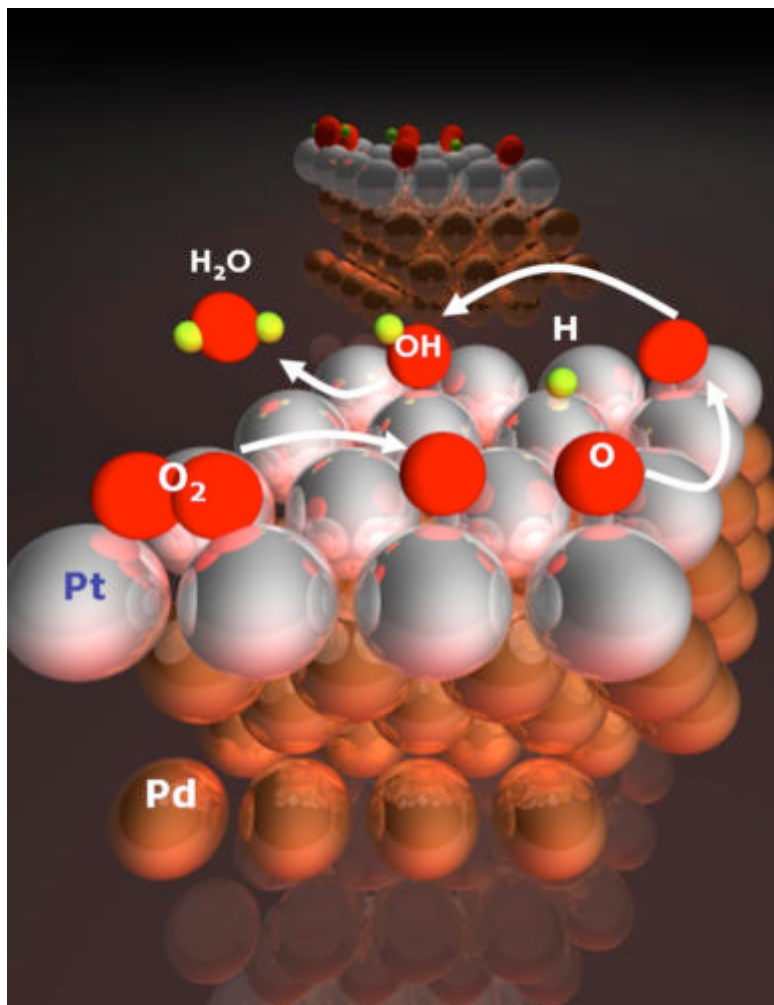
Polymer electrolyte membrane allows passage of positive ions only. Electrons travel through external circuit, producing current.

Cathode - “Oxygen reduction” - splitting of O_2 into atoms and subsequent reaction with H^+ and e^- to produce water (which flows out of the cell).

Maximum theoretical efficiency is 83% at $25^\circ C$. Cathode step is present efficiency limit on fuel cells.

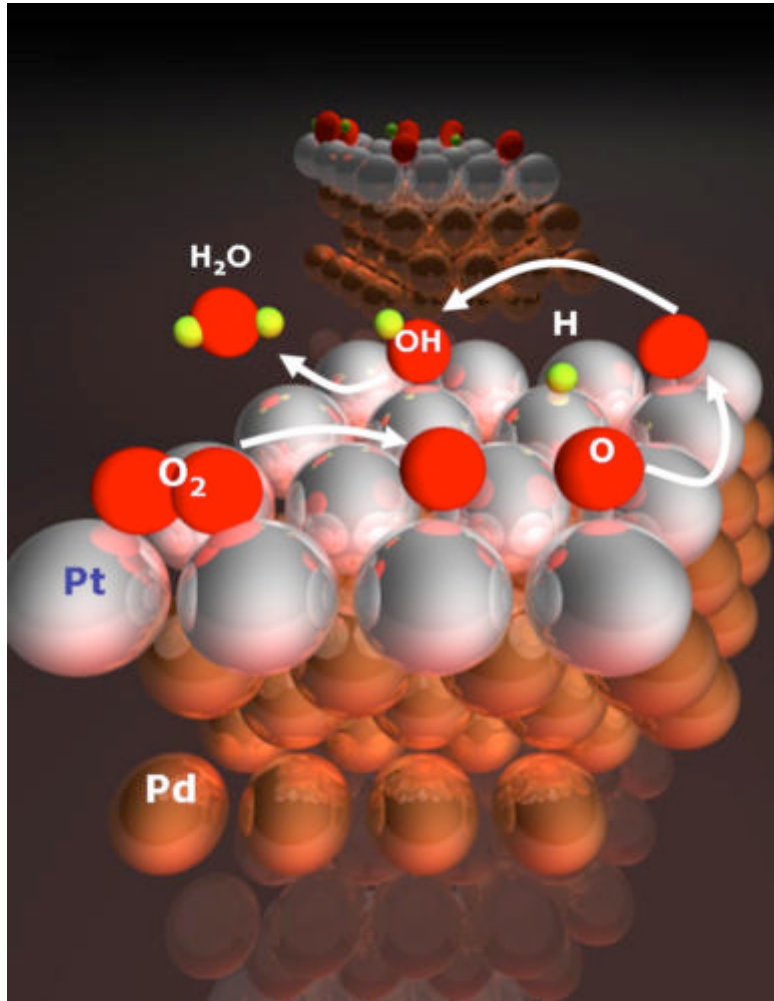
Fuel Cells

Computational study (using “Tungsten” cluster at NCSA):



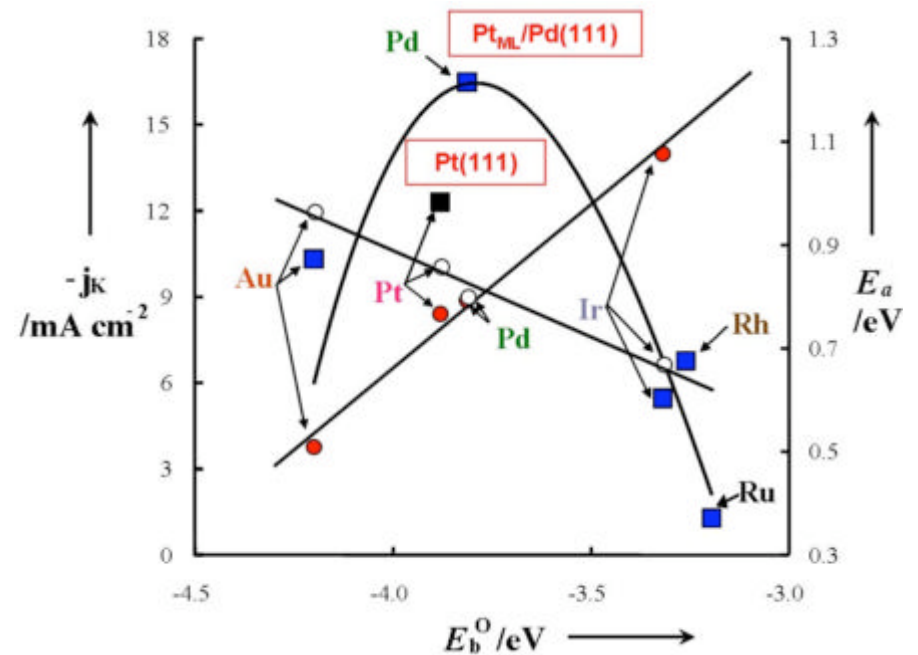
<http://access.ncsa.uiuc.edu/Stories/pt-monolayer/>

Fuel Cells



Experiment: Kinetic current vs binding energy of atomic O on various catalytic surfaces. Optimum current implies balance between efficient oxygen dissociation and efficient proton addition.

Theory calculations: Activation energies for oxygen dissociation (red circles) and proton addition (white circles).

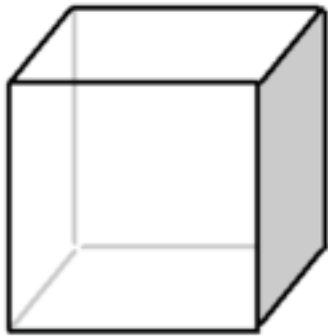


Surfaces - what do the numbers mean?

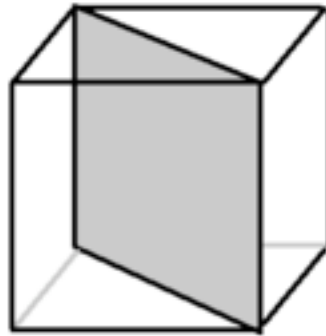
e.g. (100), (110), (111)

Miller Indices - (hkl) describes a plane orthogonal to the reciprocal lattice vectors, i.e. intersecting the ordinary lattice vectors at $(a/h, b/k, c/l)$

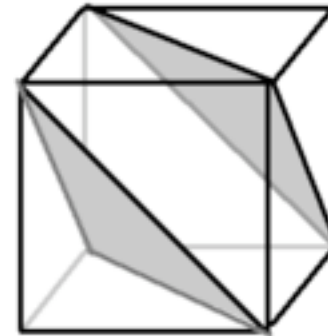
In the cubic systems:



(100)



(110)

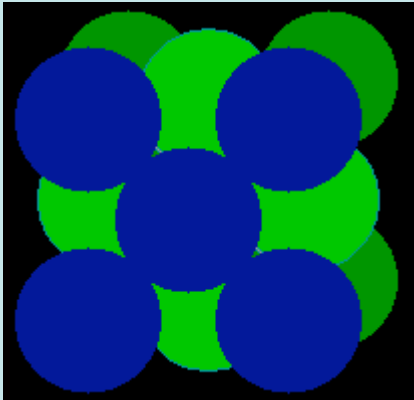


(111)

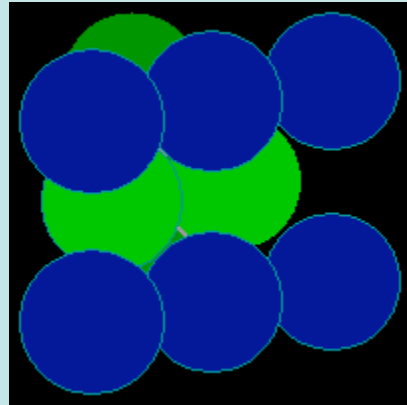
Sets of equivalent vectors exist, e.g. (100), (010), (001),...

Surfaces - what do the numbers mean?

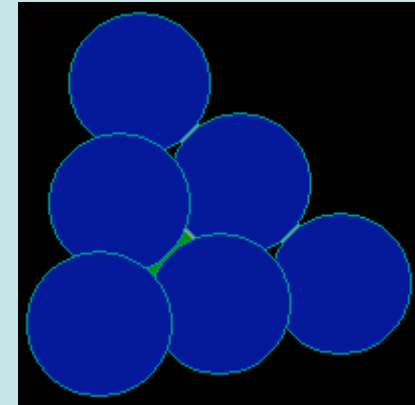
fcc lattice



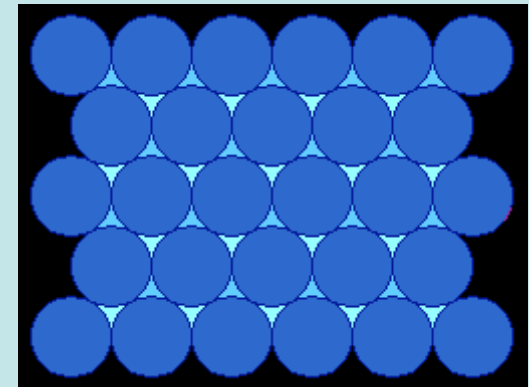
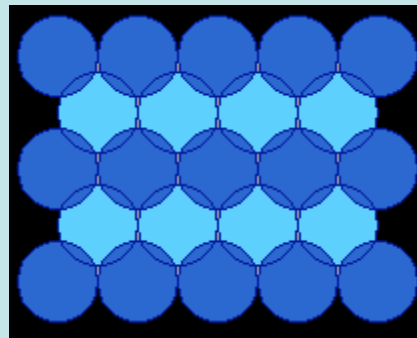
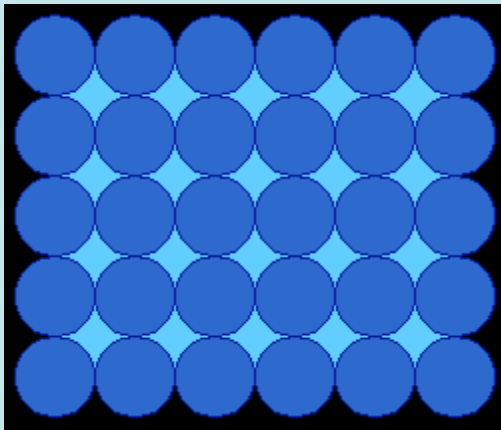
(100) face



(110) face



(111) face

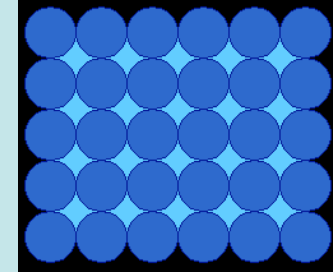


Surfaces - what do the numbers mean?

(100) face

Fourfold symmetry

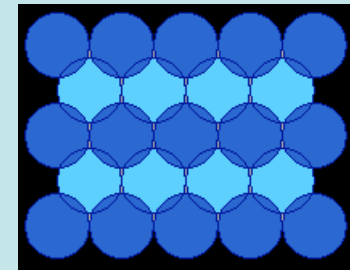
Surface is smooth.



(110) face

Twofold symmetry

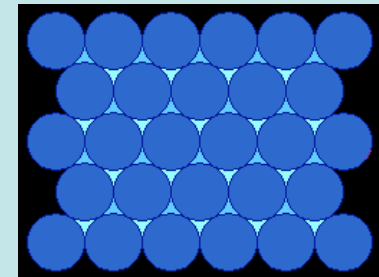
Surface is "rough" and anisotropic.



(111) face

Threefold symmetry

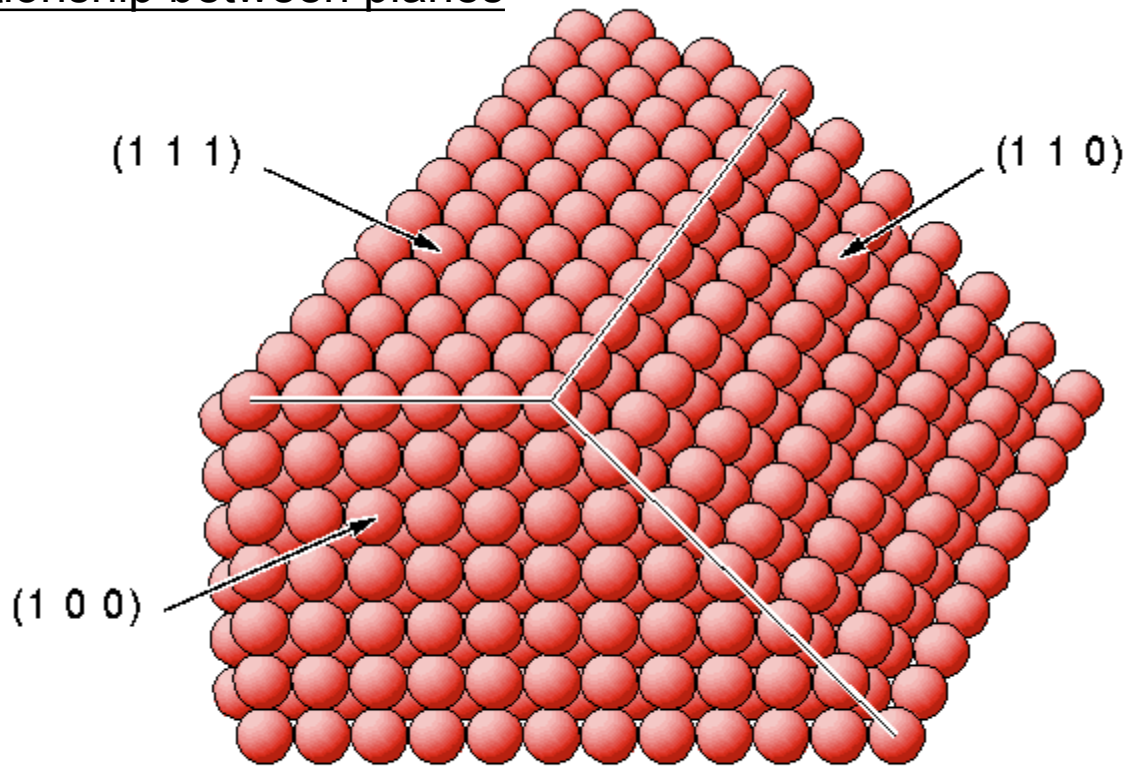
Surface is smooth.



All spacings can be determined from atomic radii (e.g. 139 pm for Pt)

Surfaces - what do the numbers mean?

Relationship between planes

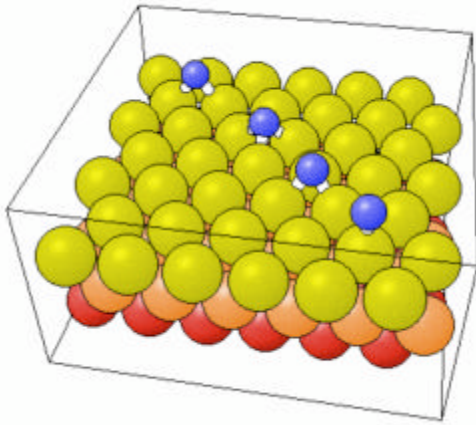


fcc lattice : different net planes

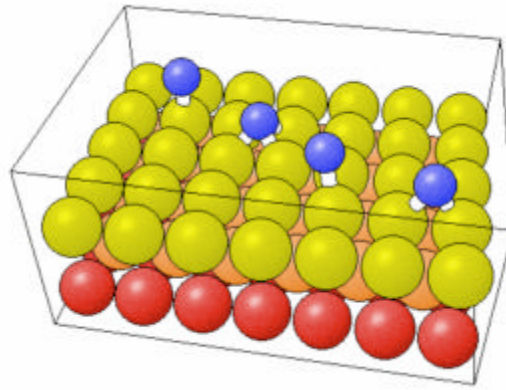
BSE65C.ppt

Surfaces - what do the numbers mean?

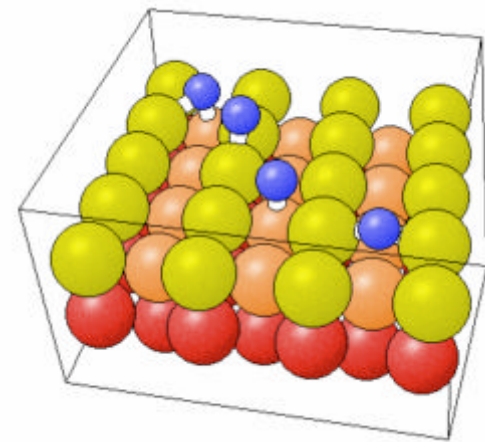
With adsorbates



(111)



(100)



(110)

Images from NIST surface database via <http://w3.rz-berlin.mpg.de/~hermann/hermann/SSDpictures.html>

Generate your own surfaces at: http://w3.rz-berlin.mpg.de/~rammer/surfexp_prod/SXinput.html

Fuel Cells

The Direct Carbon Fuel Cell



converts fuel (coal, waste wood, biomass) and air directly to electricity and CO₂, without water or steam turbines.

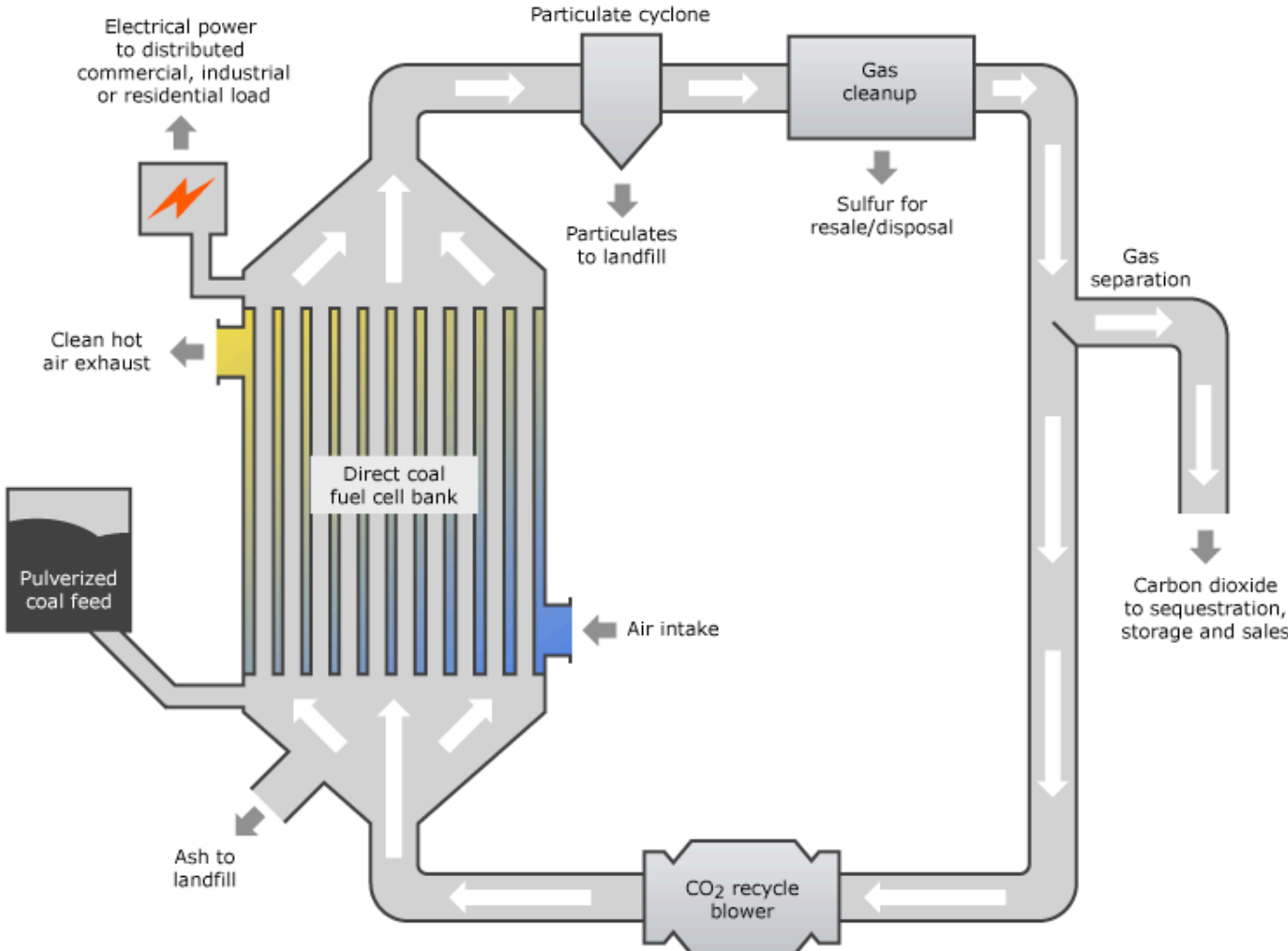
Process:

- 1) Carbon content of coal or biomass is gasified into CO via recirculating CO₂ according to $C + CO_2 \rightarrow 2CO$
- 2) O₂ in air is reduced to O²⁻ and crosses barrier to bind with CO producing CO₂ via $2CO + 2O^{2-} \rightarrow 2CO_2 + 4e^-$

greater current density
than H₂ cells

Fuel Cells

Direct Carbon

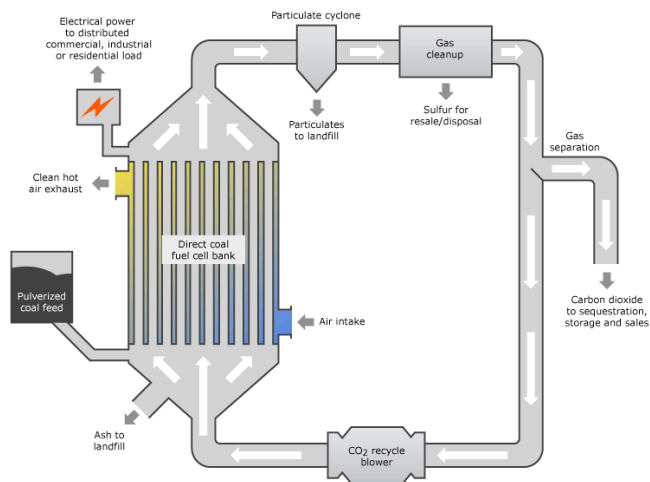


Fuel Cells

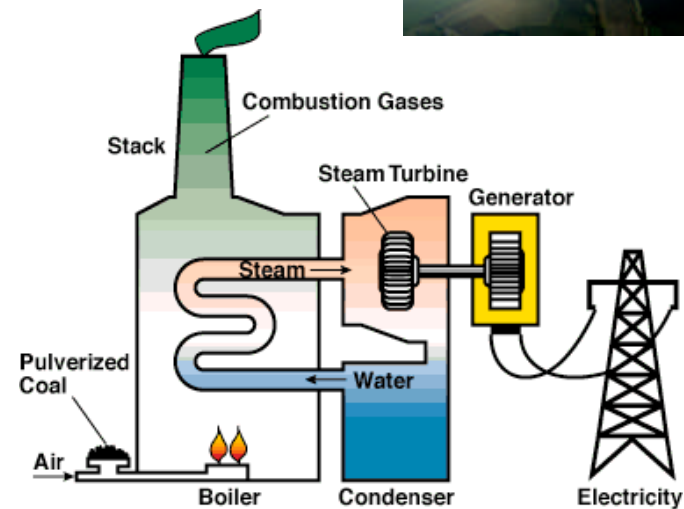
Direct Carbon

Billed as a cleaner use of coal (which is, of course, still a fossil fuel)

More thermodynamically efficient (makes fuller use of “exergetic content” of fuels) than: combustion --> heat --> turbine --> electricity (by a factor of about 2)



VS



Fuel Cells

Thermodynamic considerations:

Starting from: $\Delta G = -nFE$

and (Gibbs-Helmholtz): $\Delta H = \Delta G - T \left[\frac{\partial(\Delta G)}{\partial T} \right]_P = -nFE + nFT \left(\frac{\partial E}{\partial T} \right)_P$

by the use of $\Delta G = \Delta H - T\Delta S$

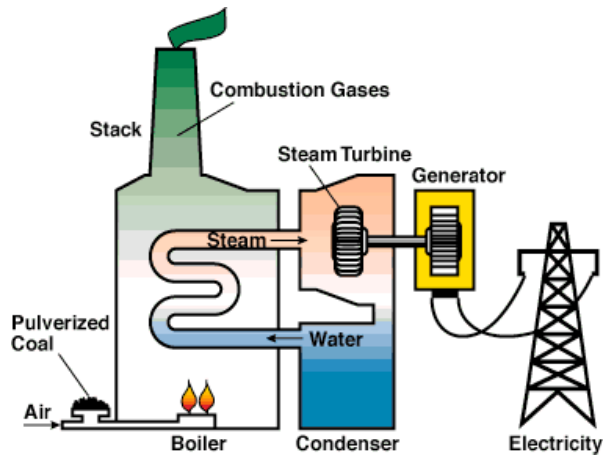
we obtain

(1) Ideal efficiency $\varepsilon = \frac{\Delta G}{\Delta H}$ i.e. $\varepsilon = \frac{E}{E - T \left(\frac{\partial E}{\partial T} \right)_P}$

(2) Entropy $\Delta S = \frac{\Delta H - \Delta G}{T}$ i.e. $\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_P$

Fuel Cells

Comparison with conventional power plants:



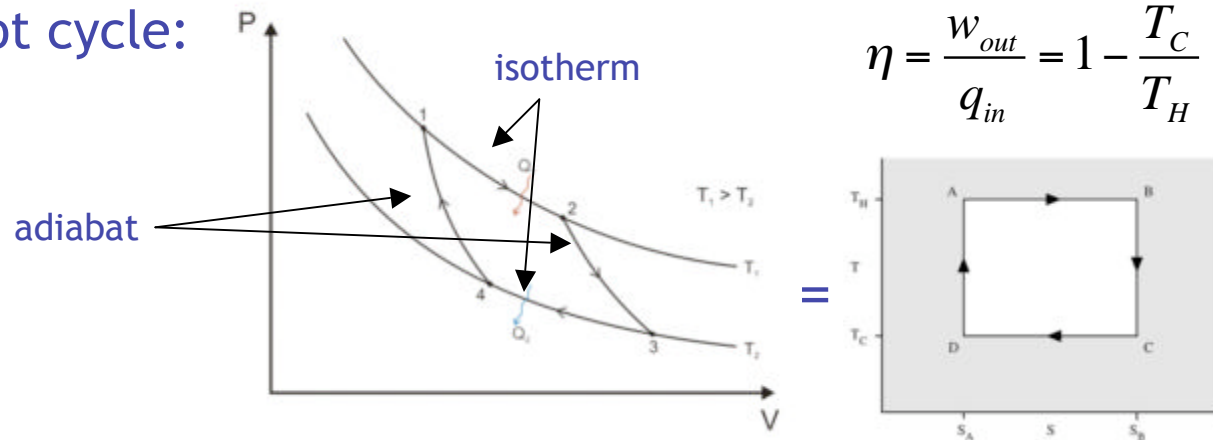
Thermodynamic description: “heat engine”
 - a device which transforms heat into mechanical work by exploiting the temperature difference between a *hot reservoir* and a *cold reservoir*.

Reverse cycle = “heat pump”

Ideal case - Carnot cycle:

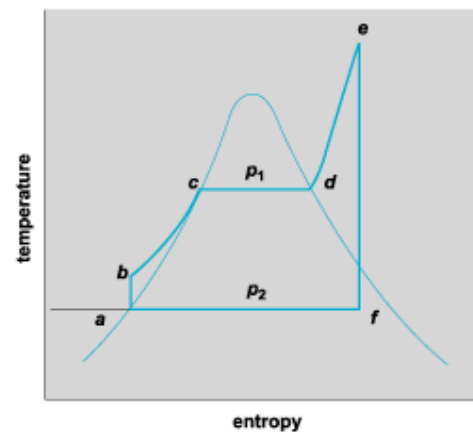
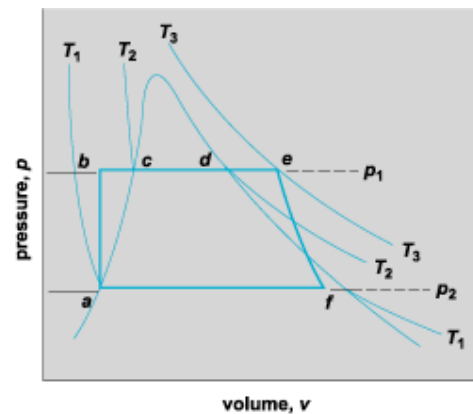


Sadi Carnot, 1796-1832



Fuel Cells

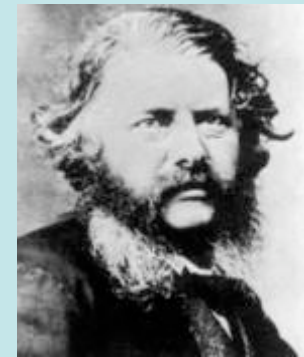
Comparison with conventional power plants:



Rankine cycle

(William John MacQuorn Rankine, 1820-1872)

- thermodynamic cycle describing a heat engine in which the working fluid is a condensable vapor (e.g. water)



b-e Isobaric heat supply (boiler)

e-f Isentropic expansion (steam turbine)

f-a Isobaric heat rejection (condenser)

a-b Isentropic compression (pump)

Unless supercritical fluids are used, operating temperature restrictions limit efficiency to around 42%.

Fuel Cells

Further information:

General

<http://www.fuelcells.org/info/links.html>

Direct Carbon (DOE Workshop)

<http://tinyurl.com/directcarbonworkshop>