

Hydrogen and Electrical Energy Storage



28 February 2013

F.M. Mulder & M. Wagemaker

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Radiation, Radionuclides and Reactors

Who am I?

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Fundamental Aspects of Materials and Energy
Radiation, Radionuclides and Reactors
Faculty Applied Physics

Background: Physics
Research: Li-ion/Na-ion battery material properties
Experimental: Neutron diffraction (see Li), NMR (see Li), XAFS, Electrochemistry,
Neutron depth profiling, X-ray diffraction and absorption
Calculational: Density Functional Theory, Molecular Dynamics, and Statistical
Thermodynamics



Learning goals Batteries

Learning Goals

At the end of the 5 battery lectures you should be able to:

Knowledge:

List the major types of Li batteries and their characteristics

Reproduce the major challenges in batteries

Understand:

Explain how a battery works and the functioning of each component

List and explain the different reaction types in batteries

Explain the different charge transfer processes in batteries

Explain the working of super capacitors

List and explain the different mechanisms that limit the cycle life of batteries.

Apply:

Apply Nernst Law describing redox reactions

Apply the Tafel equation describing the charge transfer between electrode and electrolyte

Calculate energy densities and power densities from observed properties

Derive from a phase diagram the different phases that will occur upon lithiation.

Apply the Gibbs Phase rule to predict constant of variable output voltage

Derive the voltage curve from the shape of the Gibbs Free energy

Analyse:

Predict the basic redox reaction of two electrodes given the formation energy or the standard potentials

Compare different battery systems and differentiate.

Synthesize:

Discuss scientific results observed battery performance and to relate this to material properties.

Program Batteries

- Lecture 1: History, Applications, basic Electrochemistry and thermodynamics of batteries: Redox reactions, Gibbs free energy, chemical potential, Nernst.
Feb 27
- Lecture 2: Solid state electrode reaction mechanisms, phase diagrams, phase rule, Gibbs Free energy, voltage profiles, capacities and energy densities. Li-ion batteries
March 6
- Lecture 3: Continue topics Lecture 2. Electrolyte stability: Pourbaix diagram, band structure solids, Cycle life.
March 13
- Lecture 4: Kinetics, Buttlar-Volmer, diffusion, solid state diffusion Discussion on Science paper 6 seconds discharge.
March 20
- Lecture 5: Super capacitors Future systems: Li-air, Li-sulphur Flow-cells Costs and Performance comparison batteries/systems Material Abundance
March 27

Practical Issues

Book chapters, scientific literature and sheets will be available on BB

- Lecture 1: Electrochemistry 2.3-2.5
- Lecture 2: Advanced Batteries: Chapter 1, 2 and 3.1-3.3
- Lecture 3: Advanced Batteries Chapter 14.1,14.2,14.B1-4, 16.1-2,16B,
Review Goodenough et al. Chemistry of Materials and lecture sheets
- Lecture 4: Electrochemistry 3.1-3.3, Lecture sheets
- Lecture 5: Lecture sheets, Review Bruce et al. Li-air/Li-sulphur

Practical Issues

Basic electrochemistry:

http://www.saskschools.ca/curr_content/chem30_05/6_redox/practice/practice.htm

Relevant Literature (from scientific journals):

Available via blackboard

Prof. Fokko Mulder: f.m.mulder@tudelft.nl

Dr. Marnix Wagemaker: m.wagemaker@tudelft.nl

Online survey test

I have a smart phone to participate

a) Yes



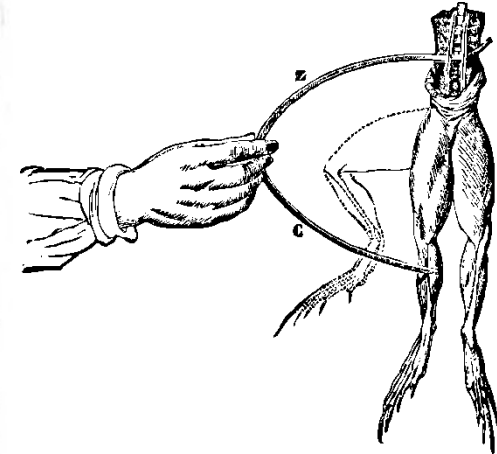
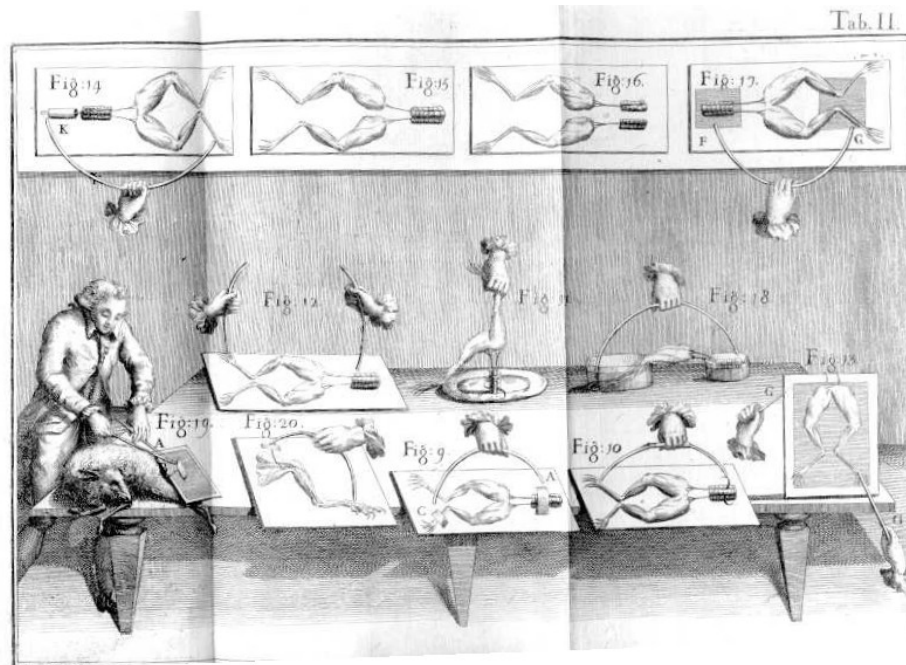
<http://www.edupinion.nl/c264>

Result

Short History of Batteries



Short history electrochemical cells

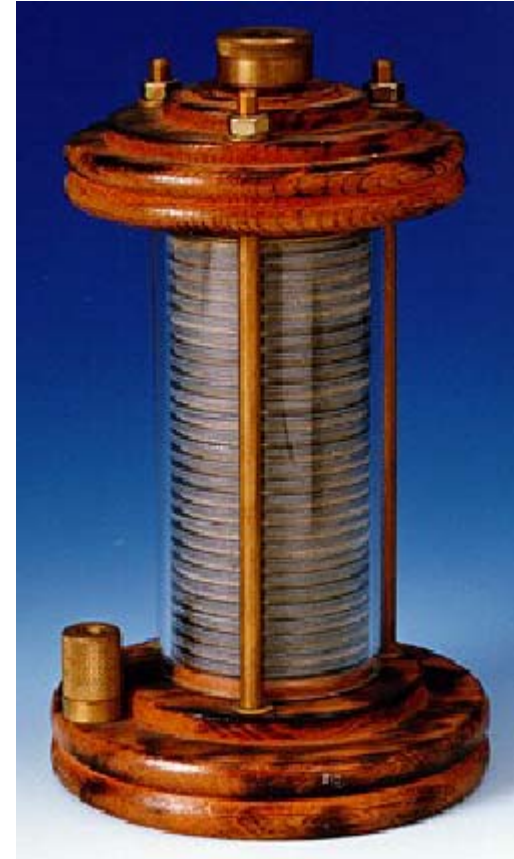


Shown here is an illustration of Luigi Galvani's famous frog experiments taken from his work, *De Viribus - Electricitatis in Motu Musculari*. 1792. A chance observation led Luigi Galvani (1737-98) to discover animal electricity in 1781. When the nerve of a frog that Galvani's wife was preparing for soup was accidentally touched with a knife a muscle contraction occurred despite the frog not being connected to an electrical machine.

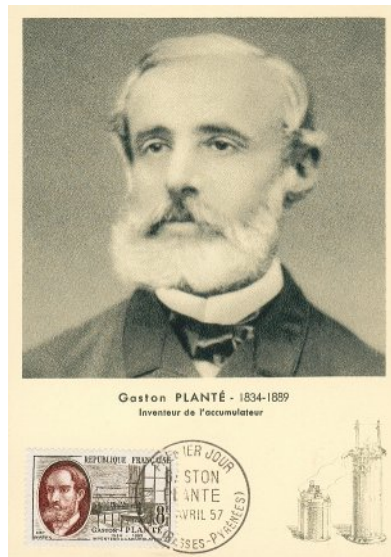
Short history electrochemical cells



Alessandro Conte di Volta (1745 to 1827): Stacked copper and zinc plates alternately and placed a piece of paper soaked in salt solution between each plate. This "voltaic pile", or the "artificial electrical organ" as Volta named it, provided electricity when the plates were connected with a wire. In further research the connection between chemical reactions and electrical energy was quickly recognized.



Short history electrochemical cells



The lead/sulfuric acid/lead dioxide system was discovered by Gaston Planté (1834 to 1889) in 1859: the lead-acid battery was born. This system was used for storing electricity for telegraphy, e.g. he used lead plates as electrodes. These batteries were not yet suitable for industrial production.



Electrical Car is not new

First car with combustion engine 1885 (Karl Benz)

First electrical car 1881

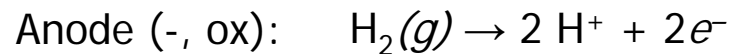
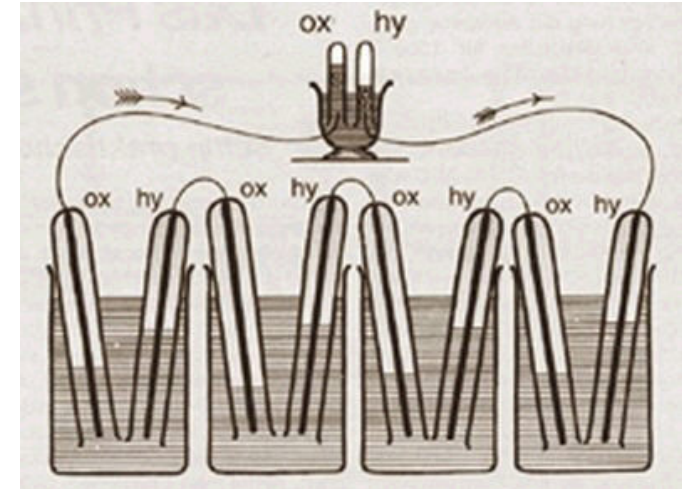
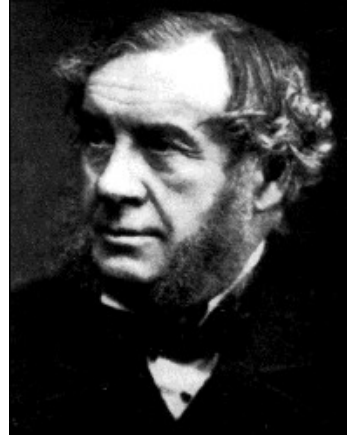
Around 1900, competing options electric versus combustion.



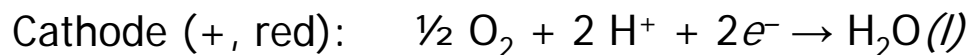
Speed record 1899-1901 Camille Jenatton

Short history electrochemical cells

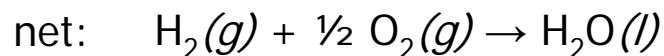
The Fuel Cell was first demonstrated in 1839 by Sir William Grove, a lawyer and amateur chemist. At the time, it was already known that water could be decomposed into hydrogen and oxygen by electrolysis; Grove tried recombining the two gases in a simple apparatus, and discovered what he called "reverse electrolysis"— that is, the recombination of H_2 and O_2 into water— causing a potential difference to be generated between the two electrodes:



$$\varepsilon^\circ = 0 \text{ v}$$

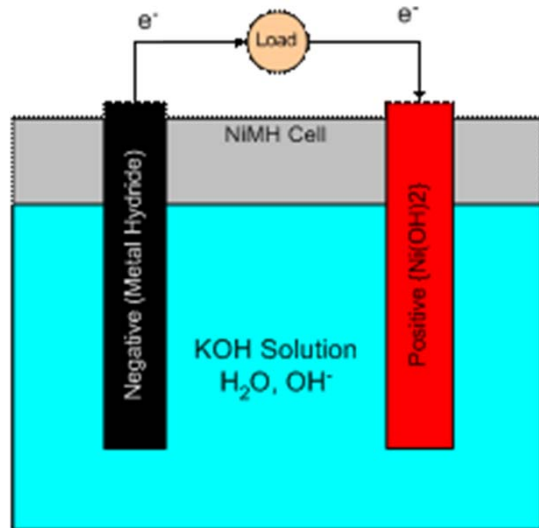


$$\varepsilon^\circ = +1.23 \text{ v}$$



$$\varepsilon^\circ = +1.23 \text{ v}$$

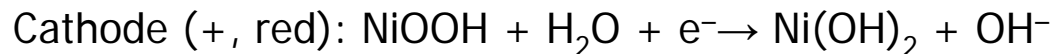
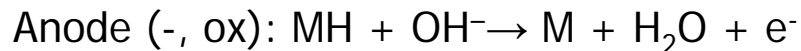
Short history electrochemical cells



Nickel-metal hydride cells (1960's)

The discovery that certain compounds such as LaNi₅ can act as "hydrogen sponges" (LaNi₅H₆) made it practical to employ metal hydrides as a cathode material. These reversible (secondary) batteries are widely used in cell phones, computers, and portable power tools:

Discharge:



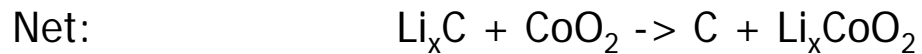
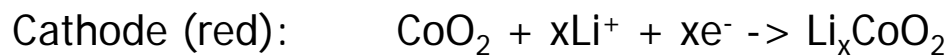
$$V_{\text{Cell}} = \sim 1.2 \text{ V}$$

H-storage is already used for 40 years

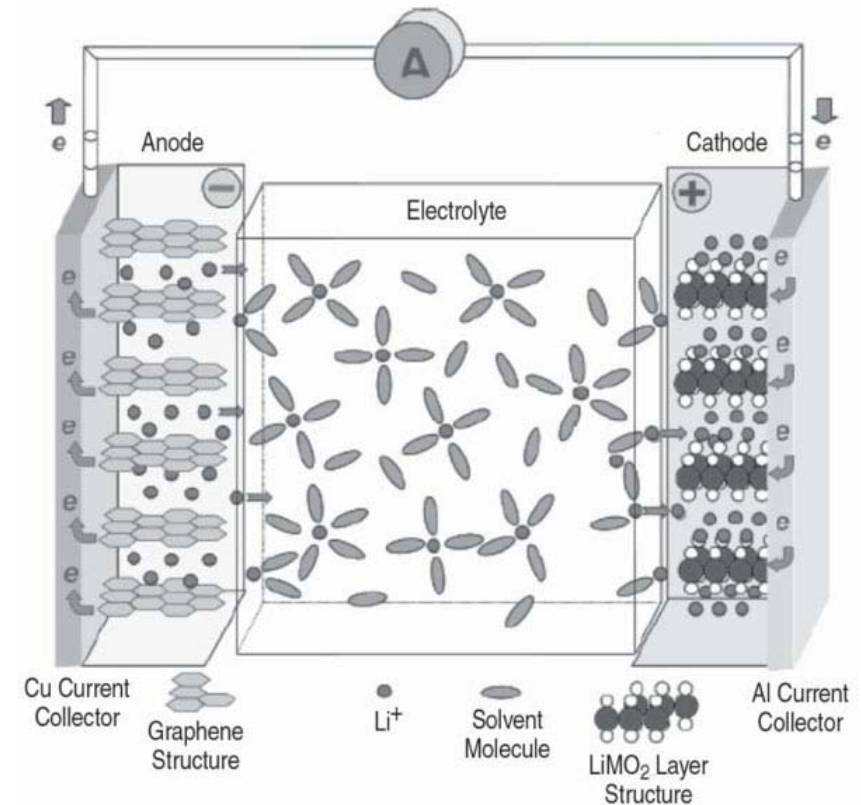
Short history electrochemical cells

Lithium cells (1990's Sony Corp.)
Lithium is an ideal anode material owing to its low density and high reduction potential, making Li-based cells the most compact ways of storing electrical energy. Lithium cells are used in wristwatches, cardiac pacemakers, digital cameras, laptops etc.

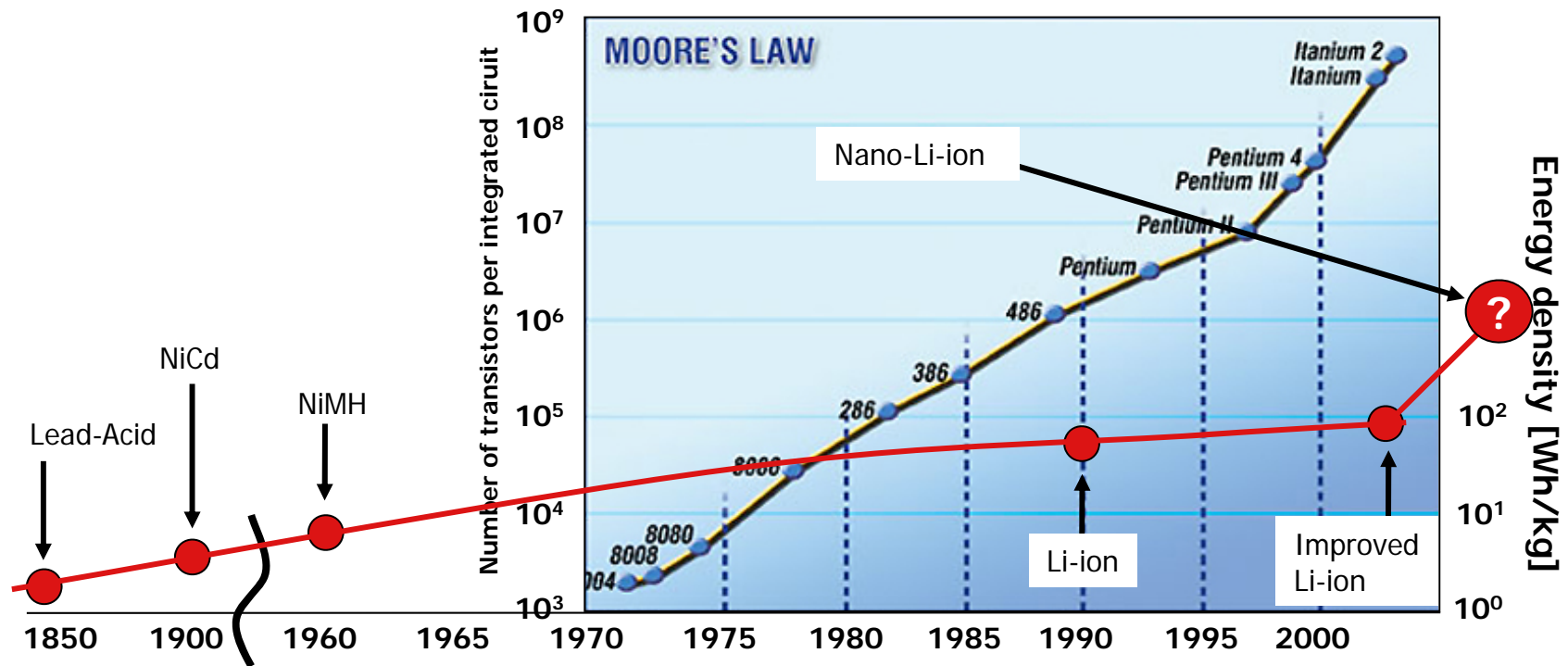
Example



$$V_{\text{Cell}} = \sim 3.6 \text{ V}$$



Moore's law for Li-ion batteries?



Energy

1 Wh = 3.6 kJ

1 cal = 4.2 J

1 MJ=0.28 kWh

36 MJ= 10 kWh

Energy to lift 100 kg 3.7 meters

Energy to raise the temperature of
1 g water with 1 degree

Energy to accelerate a car of 1000
kg to 161 km/h (no air resistance)

Energy contents of 1 liter gasoline

Questions Energy

1. The energy required for a pacemaker battery is:

- a) <0.01 Wh
- b) <0.01 Wh and <100 Wh
- c) >100 Wh
- d) no clue

2. Energy required to drive a light electrical car for 150 km

- a) 50-100 kWh
- b) 100-200 kWh
- c) 200-500 kWh
- d) no clue

Questions Energy

- 1 Wh = 3.6 kJ Energy to lift 100 kg 3.7 meters
1 cal = 4.2 J Energy to raise the temperature of
1 g water with 1 degree
- 1 MJ=0.28 kWh Energy to accelerate a car of 1000
kg to 161 km/h (no air resistance)
- 36 MJ= 10 kWh Energy contents of 1 liter gasoline

<http://www.edupinion.nl/c468>

Result



Questions Energy

1. The energy required for a pacemaker battery is:

Guess from size: AAA battery: 0.4 – 1.1 Wh

=> b) $0.01 <$ and < 100 Wh

2. Energy required to drive a light electrical car for 150 km

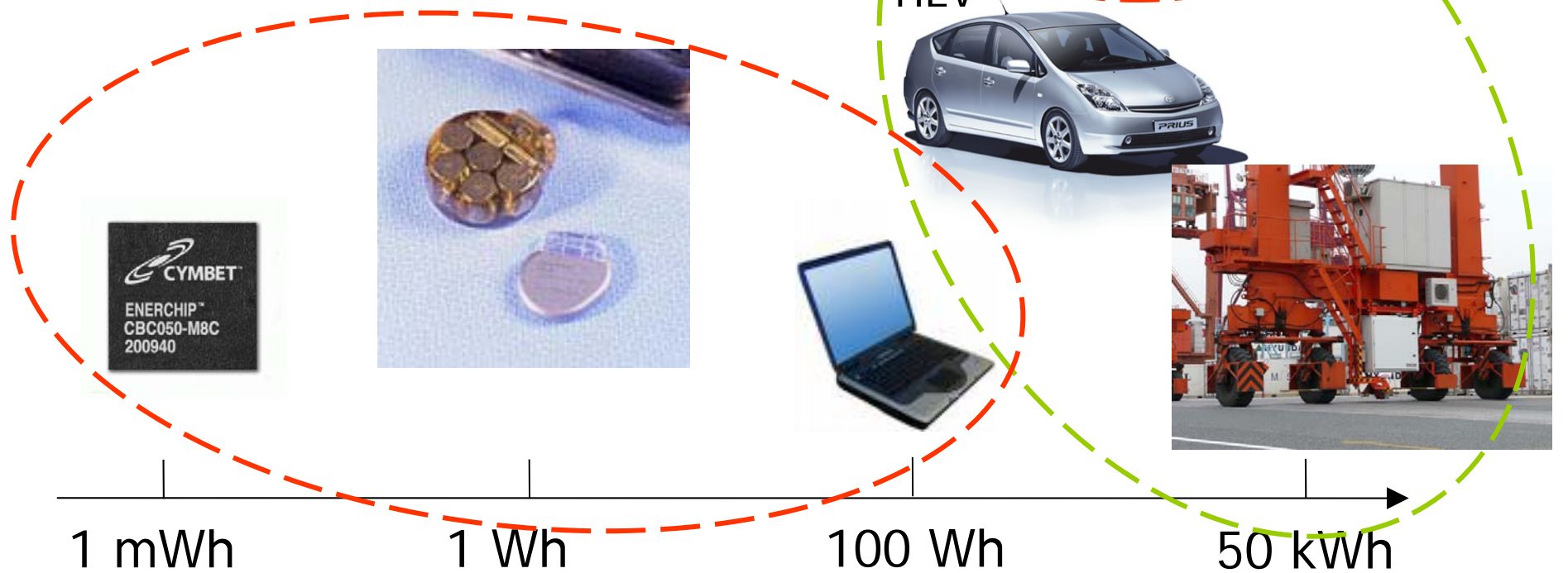
=> 10 liters of gasoline ~ 100 kWh, high efficiency battery

=> a) 50-100 kWh

mWh-kWh Storage applications

Efficient use of Energy

Mobile Energy Storage



MWh – GWh Storage Applications

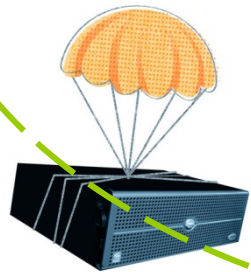
Efficient use of Energy

Energy: Enable Solar and Wind, store energy on a scale of hours/days

Not for batteries



Power: Backup, Grid stabilisation, Efficiency, timescale minutes/seconds



100 kWh

10 MWh

10000 MWh

Electrical Cars

Nissan Leaf:



Range: 175 km (120)
Capacity: 24kWh
Power: 90 kW
Weight: 300 kg
Full Charge time: 8 hours
Lifetime: 160000 km
Battery: Li-ion, (+) LiMn_2O_4 based, (-) Carbon?

Tesla:

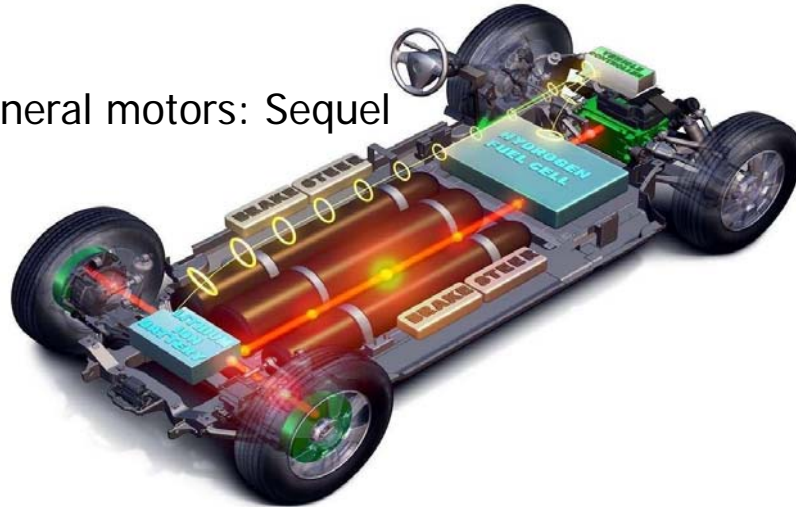


Range: 350 km (250)
Capacity: 56 kWh
Power: 215 kW
Weight: 450 kg
Full Charge time: 3.5 hours
Lifetime: 80000 km
Battery: Li-ion, (+)?, (-) Carbon?

Applications in cars, battery vs H-storage

Versus

General motors: Sequel



Hydrogen as fuel: $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + 286 \text{ kJ/mol}$

Starting with solar energy, Total energy efficiency:

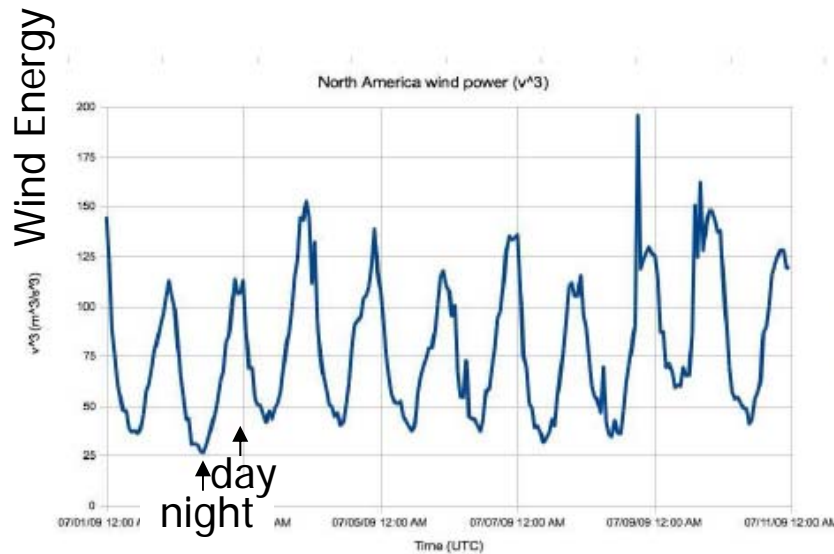
H_2 production, storage, conversion (fuel-cell): ~ **17%**



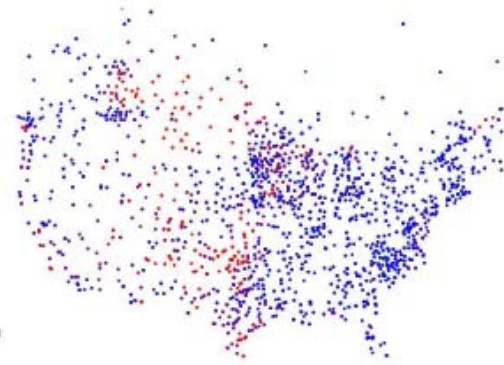
Starting with solar energy, Total energy efficiency:

Electricity transport, battery storage, electrical motor: ~ **70%**

Enable wind and solar



Available wind energy US:

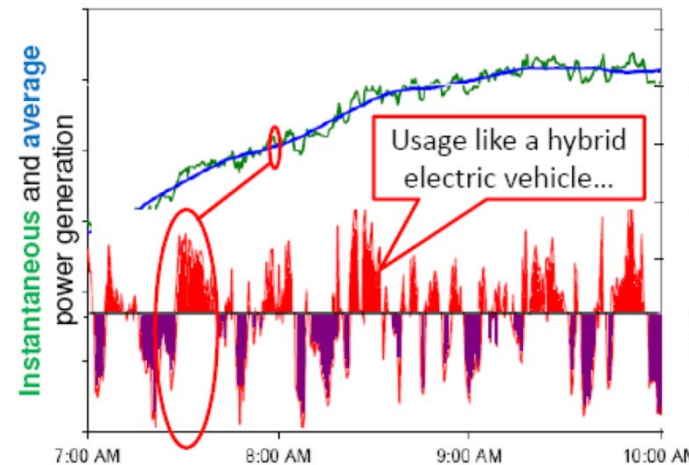


Difference in supply and demand is not lifted by integrating over a large area!
Storage will reduce the amount of installed power required

More efficient use of fossile fuels

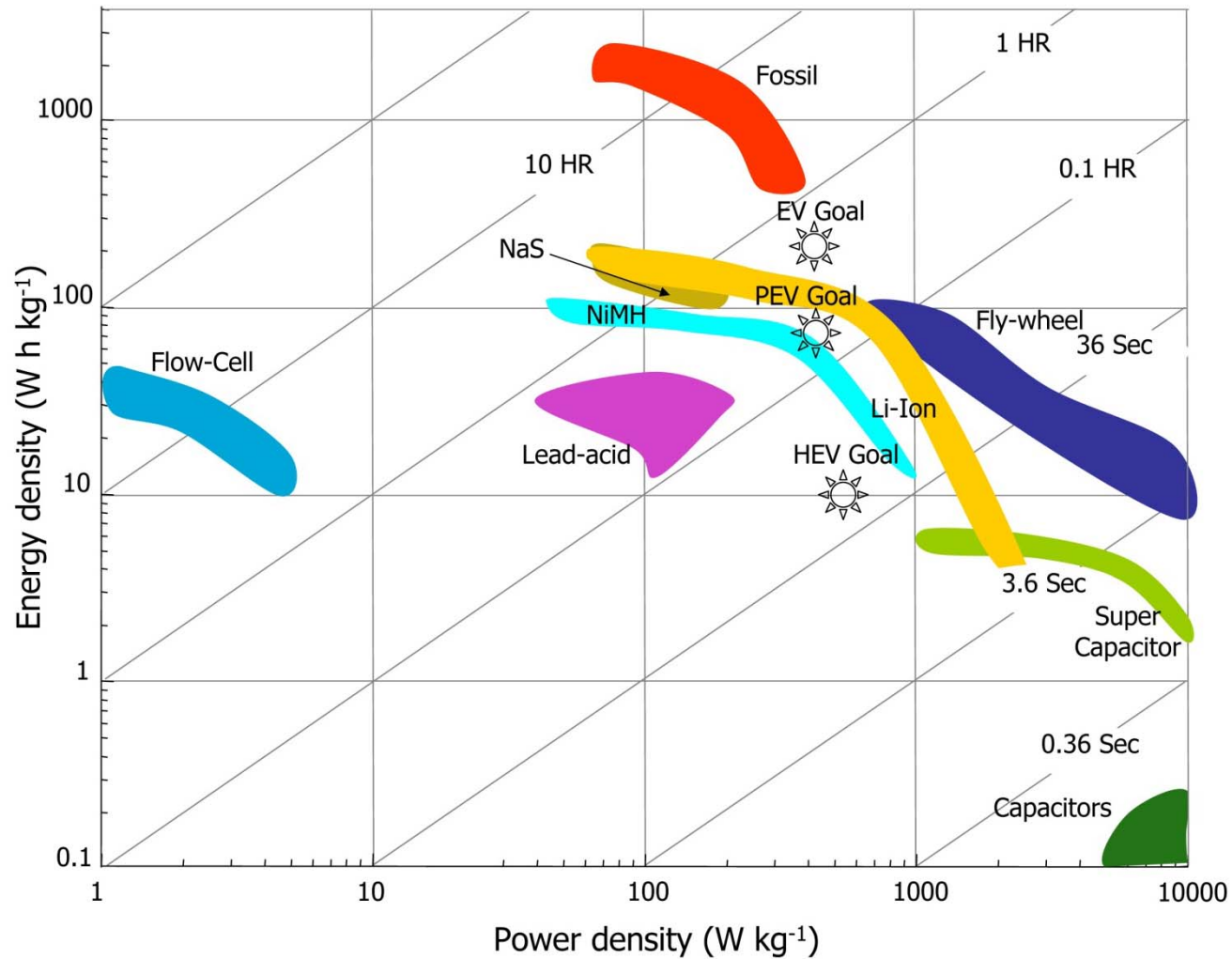


+



Large energy power plants cant respond to the fast changes in energy demand
This leads to an efficiency loss up to 10-20% due to over and under shoot.
Battery can solve this problem, ms responds time

Ragone Plot Energy vs Power density



Power: energy per unit time

1 W=1 J/s	Power to burn a 1 Watt light (bike)
1 pk=0.746 W	Power of a small horse English mines around 1800
100 pk=74.6 kW	Power average gasoline car
2 MW	Research nuclear reactor Delft
3 MW	Large wind turbine
1000 MW	Large power plant

Questions Ragone Plot

3. If an electrical car requires 75 kWh what is the approximate Li-ion battery weight?

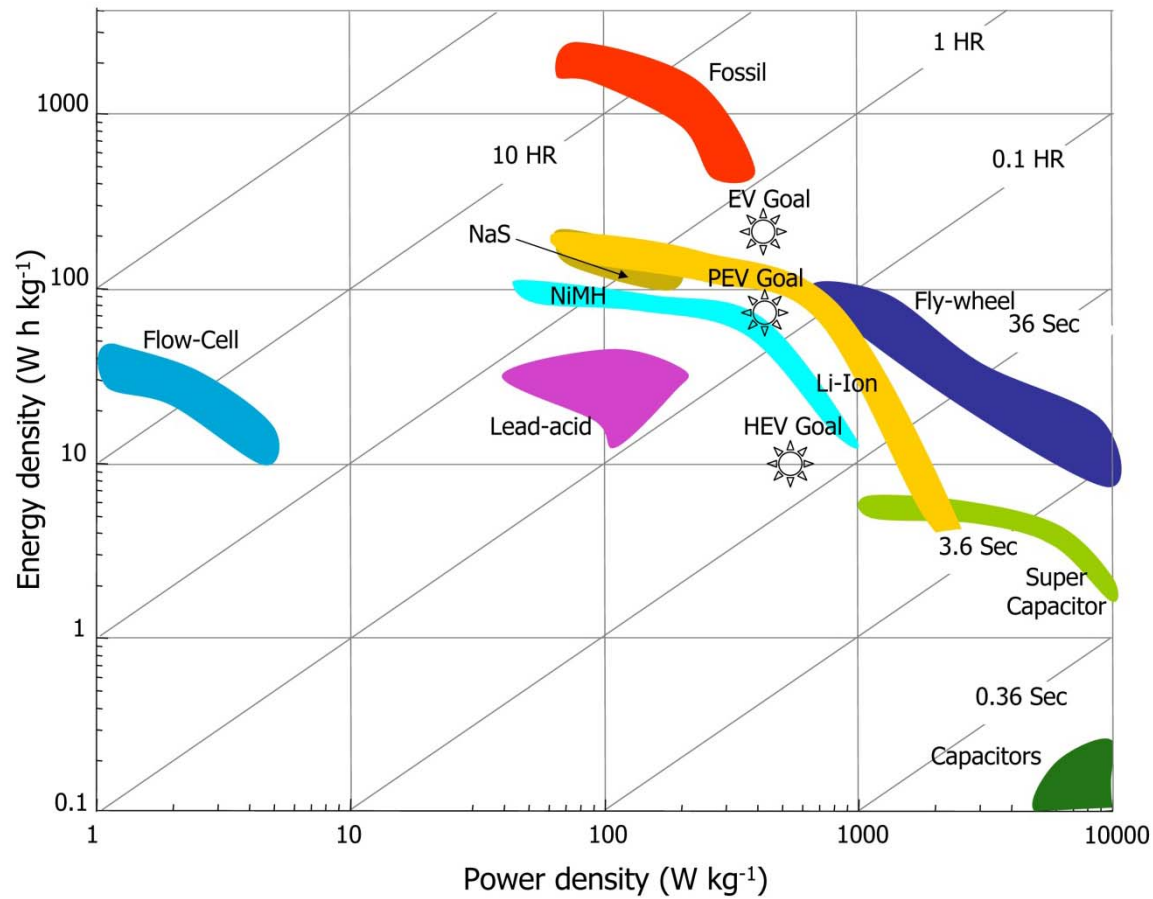
- a) 50 kg
- b) 150 kg,
- c) 600 kg,
- d) 1000 kg
- e) No clue

4. If an electrical car requires 50 kW what is the approximate Li-ion battery weight?

- a) 75 kg
- b) 300 kg
- c) 800 kg
- d) 1200 kg
- e) No clue



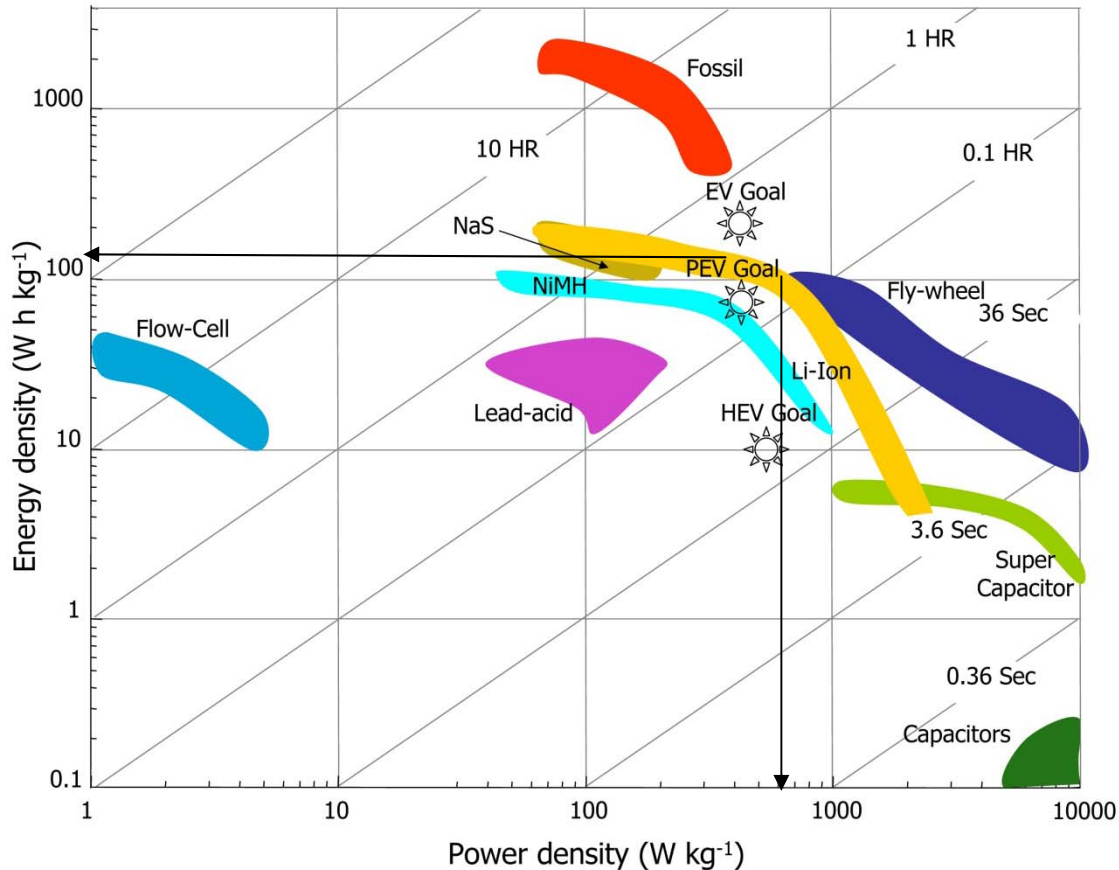
Questions Ragone Plot



Result

<http://www.edupinion.nl/c042>

Questions Ragone Plot



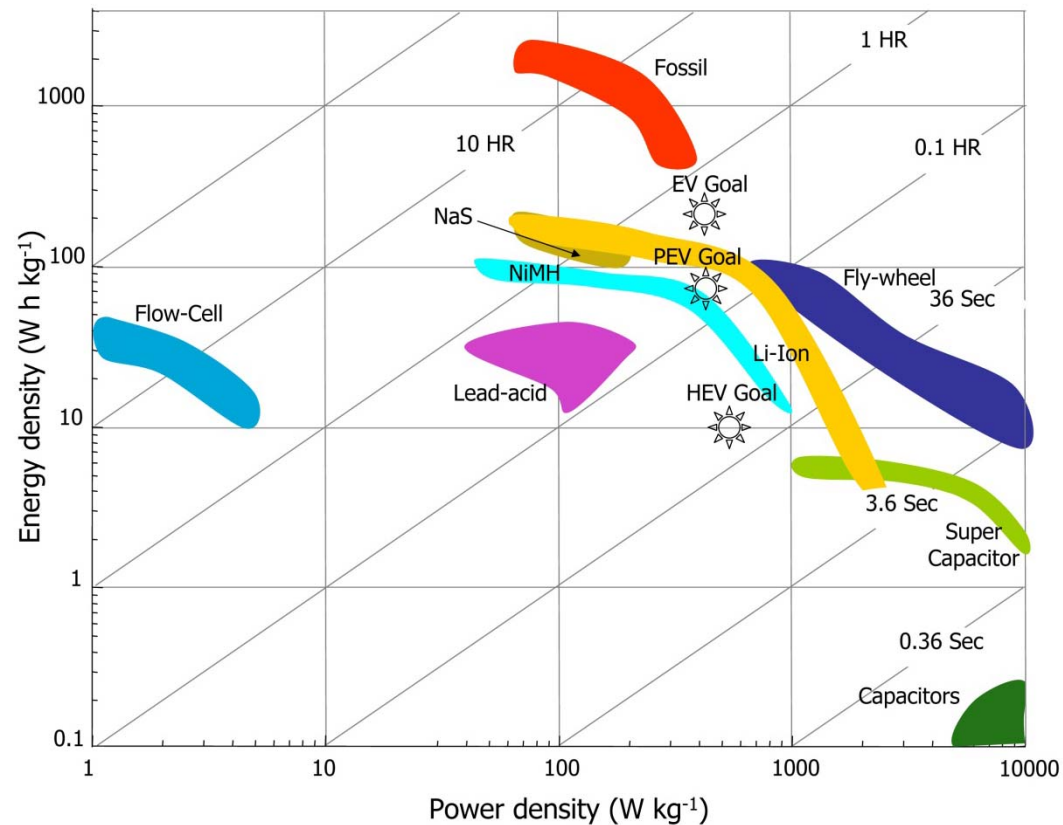
3. If an electrical car requires 75 kW what is the approximate Li-ion battery weight?

=> 150 Wh/kg
 $75000/150 = 500 \text{ kg}$
 => c)

4. If an electrical car requires 50 kWh what is the approximate Li-ion battery weight?

=> 50 Wh/kg
 $50000/600 = 83 \text{ kg}$
 => a)

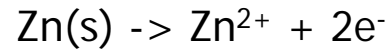
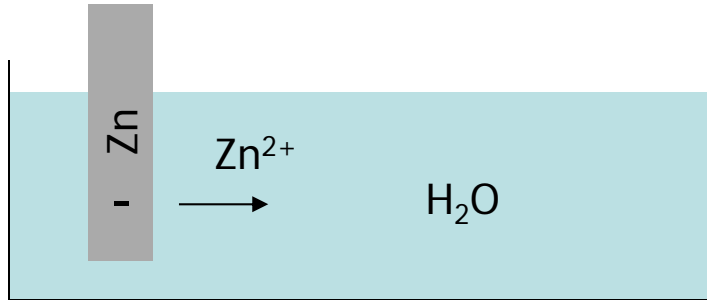
Questions Ragone Plot



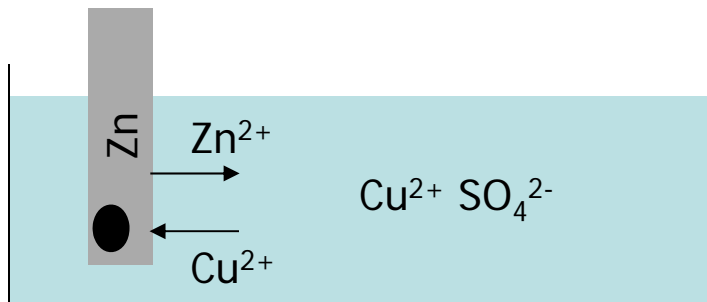
5. Why does the energy density always decrease with increasing power?

Introduction to Redox Reactions

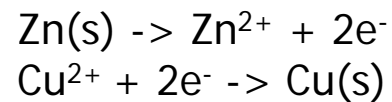
Electrochemical cells, Introduction



Charge neutrality, stops the Zn²⁺ going into solution, basically a potential is build up over the electrode interface



Add copper sulfate



No charge build up, reaction proceeds!

Electrochemical cells, Introduction

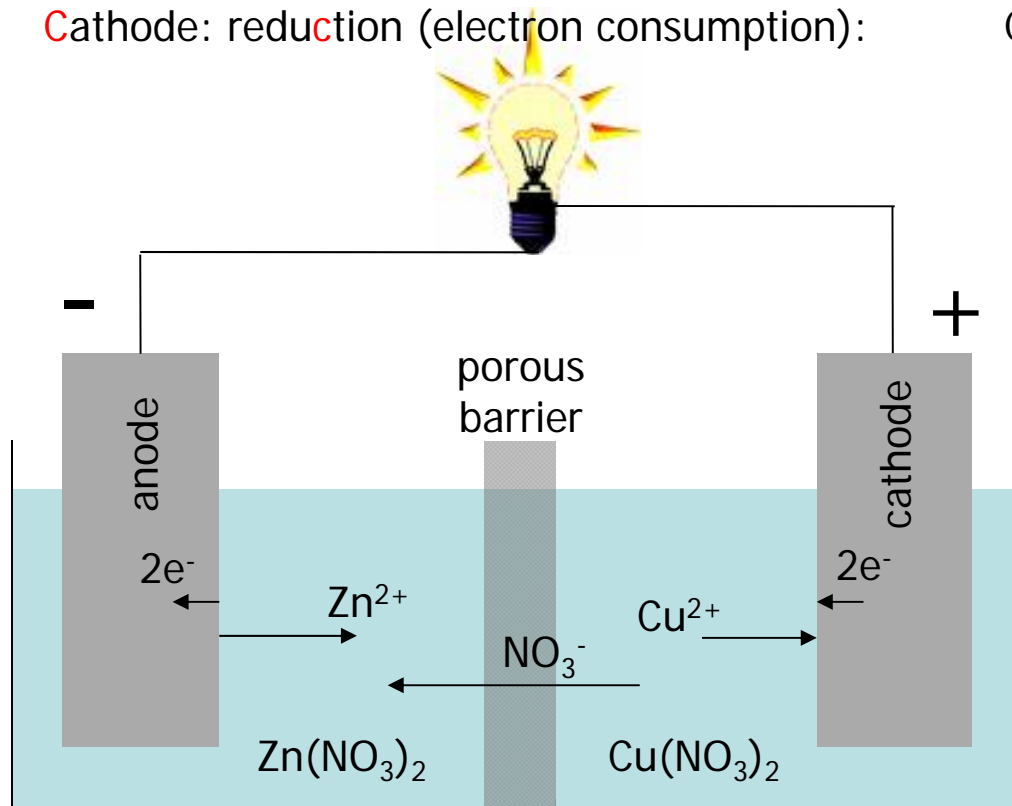
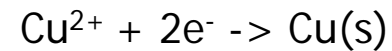
The previous reaction made useful, the Daniel element, example of a electrochemical cell

Redox (Reduction-Oxidation) reactions:

Anode: oxidation (electron production):

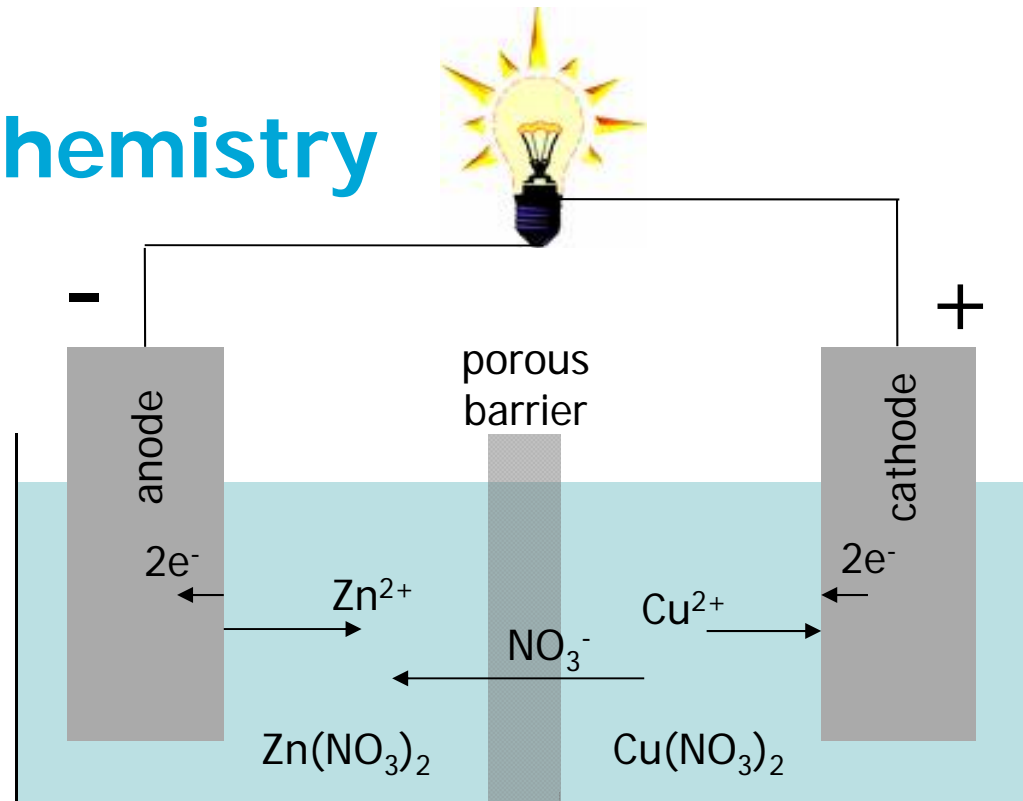


Cathode: reduction (electron consumption):



Ionic charge transport is compensated by electron transport in the external circuit

Question Electrochemistry

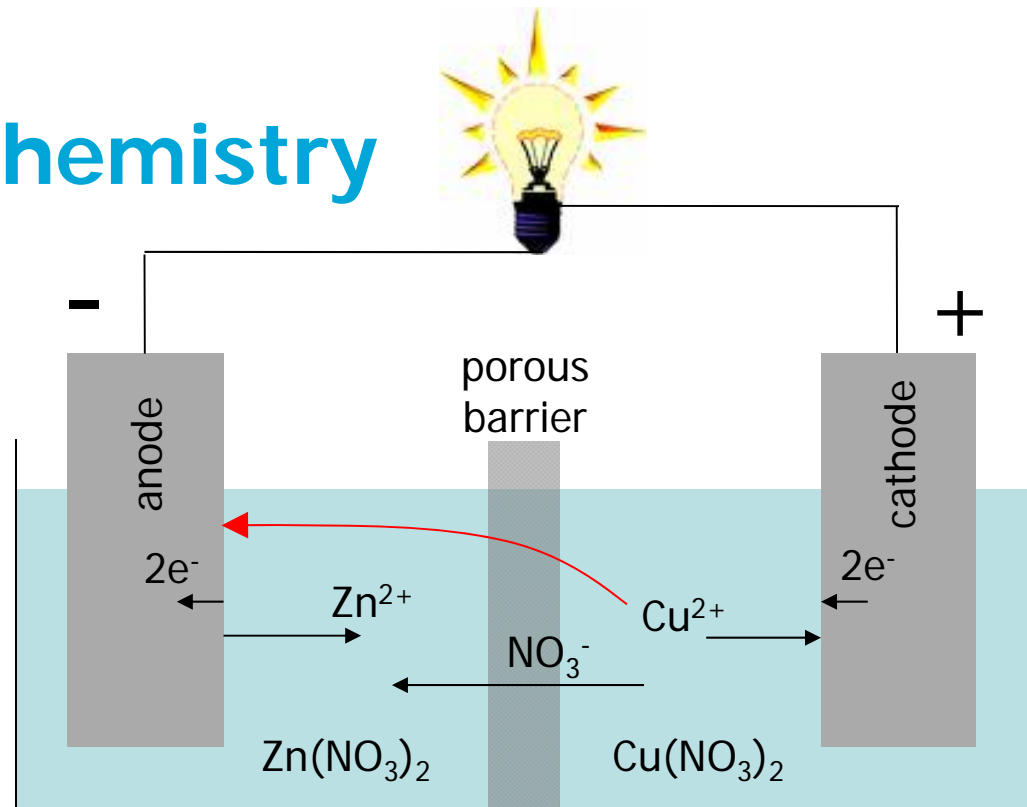


6. Why the porous barrier?
- a) to conduct NO_3^- ions
 - b) to prevent short circuit
 - c) to prevent mixing of the Zn^{2+} and Cu^{2+} ions
 - d) No clue

<http://www.edupinion.nl/c275>

Results

Question Electrochemistry

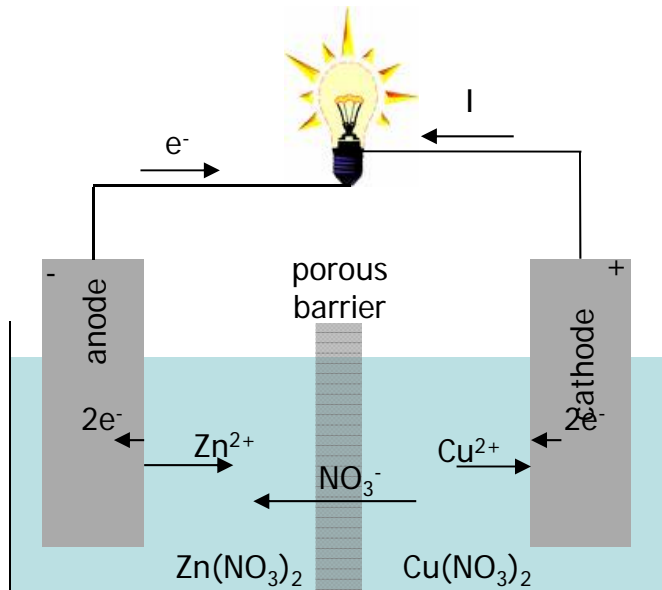


6. Why the porous barrier?
=> c), and actually also b)

Electrochemical cells, Definitions

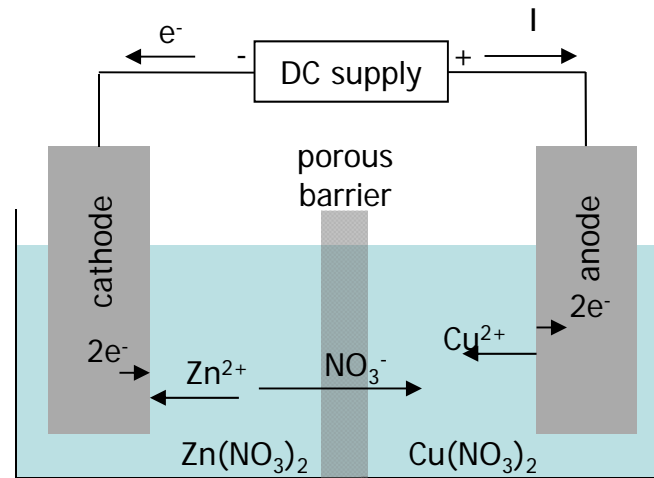
Galvanic cell (Discharge)

Chemical \rightarrow Electrical energy
Spontaneous redox reaction $\Delta G < 0$
+ Cathode (red) / - Anode (ox)



Electrolytic cell (Charge)

Electrical \rightarrow Chemical Energy
Forced redox reaction $\Delta G > 0$
+ Anode (ox) / - Cathode (red)



Note: oxidation always occurs at the anode, reduction at the cathode (not related to the sign of the electrode!)

Electrochemical cells, Introduction

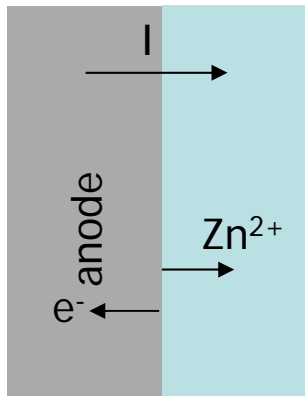
Anodic (Oxidation) Reaction:

Reductant \rightarrow Oxidant + ze^-



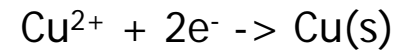
Zn is oxidized under the loss of electrons

Definition $I > 0$



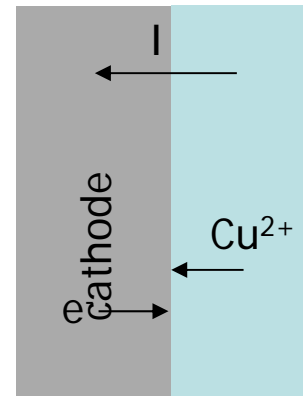
Cathodic (Reduction) Reaction:

Oxidant + $ze^- \rightarrow$ Reductant



Cu^{2+} is reduced by the gain of electrons

Definition $I < 0$



Why thermodynamics of redox reactions

What is the direction of a redox reaction?

What is the voltage that a redox reaction can deliver?

What is the energy density of a battery?

What is the power density of a battery? -> kinetics

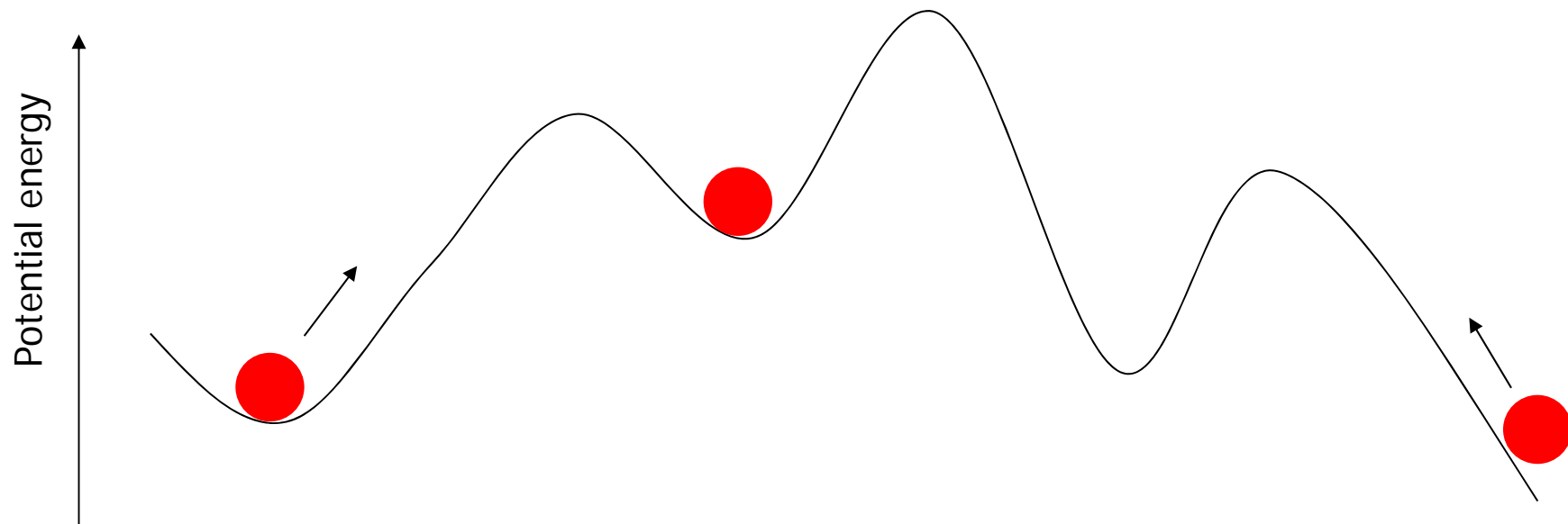
What determines the cycle life of a battery -> side reactions/structural changes

Thermodynamics and electrochemistry

Basic thermodynamics

Thermodynamics deals with *Equilibrium States* and these equilibrium states can be uniquely defined specified by *State Variables*

State Variables have values that are independent of the path by which the equilibrium state is reached



Basic thermodynamics

State Variables (that characterize equilibrium states) are determined as follows:

A) Laws of Thermodynamics introduce three state variables:

0th law: Introduces T , Temperature

1st law: Introduces U , the internal energy by conservation of energy. The increase in the internal energy equals the net energy added to the system due to heat transfer (δQ) plus the mechanical and/or electrical work (δW) done on the system:

$$dU = \delta Q + \delta W$$

The first law tells us that energy can be transformed (work \rightarrow heat etc) and is not lost

Basic thermodynamics

A) Laws of Thermodynamics introduce three state variables:

2nd law: Introduces S , Entropy. The entropy of an isolated system which is not in equilibrium will tend to increase over time, approaching a maximum value at equilibrium. Hence, where the first law tells us how energy is transformed, the second law tells us in what direction this will happen in a specific case. The change in entropy is:

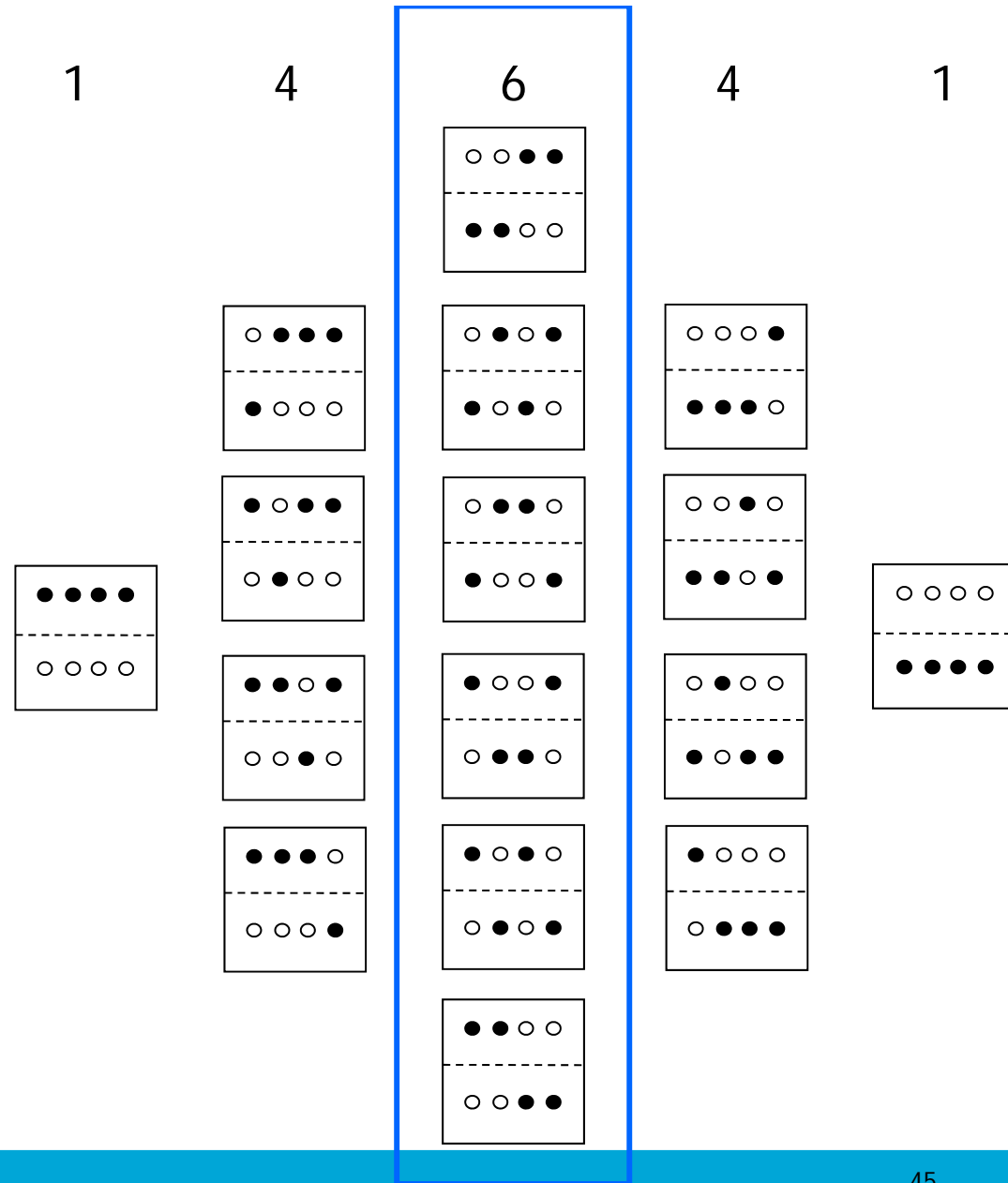
$$dS \geq \frac{\delta Q}{T}$$

Statistical Mechanics defines the entropy as the number of accessible arrangements, lets do an experiment:



Marbles Defy Entropy!.flv

Number of ways to arrange the marbles in the two halves of the box:



More possible ways, therefore more likely that the marbles mix, more disorder, higher entropy

Basic thermodynamics

- B) State variable introduced by different forms of work δW . Depends on constraints imposed on the system (example: constant pressure). The reversible work introduce “mechanical” state variables in the form of:

$$\delta W = \sum_i Y_i dX_i$$

where Y_i *intensive* “forces” and X_i are *extensive* “displacements”.

Examples: Mechanical pressure work: $\delta W = -pdV$

Electrical work: $\delta W = EdQ$ (E Electrical field, Q charge)

Adding mass work: $\delta W = \mu dn$ (μ chemical potential, n number of moles added)

Final underlying principle of thermodynamics for macroscopic systems is the property of *extensivity* (breaks down for nano particles). Extensive variables such as V, U, S etc scale with the size of the system. That is, if the number of particles is doubled, i.e. $N \rightarrow 2N$, then all extensive variables of the system will also double, i.e. $V \rightarrow 2V$, $U \rightarrow 2U$, $S \rightarrow 2S$. In contrast to *intensive* variables like p , T , μ etc

Question thermodynamics 1

7. The kinetic energy of a particle or subject is
- a) Is an intensive non-state variable
 - b) Is an intensive state variable
 - c) Is an extensive non-state variable
 - d) Is an extensive state variable
 - e) No clue



<http://www.edupinion.nl/c523>

result

Question thermodynamics 1

7. The kinetic energy of a particle or subject is:

The kinetic energy ($\frac{1}{2} Mv^2$) scales with the size of the system
=> extensive

The kinetic energy is independent on the way it was build up
=> state variable

=> d) Is an extensive state variable

Basic thermodynamics

Fundamental equation of reversible thermodynamics (combination of the previous):

$$dU = \delta Q + \delta W = TdS + \sum_i Y_i dX_i$$

Note: we set $Q = TdS$, which means we work in equilibrium, infinitely small steps

Most common form (pressure volume work):

$$dU = TdS - pdV$$

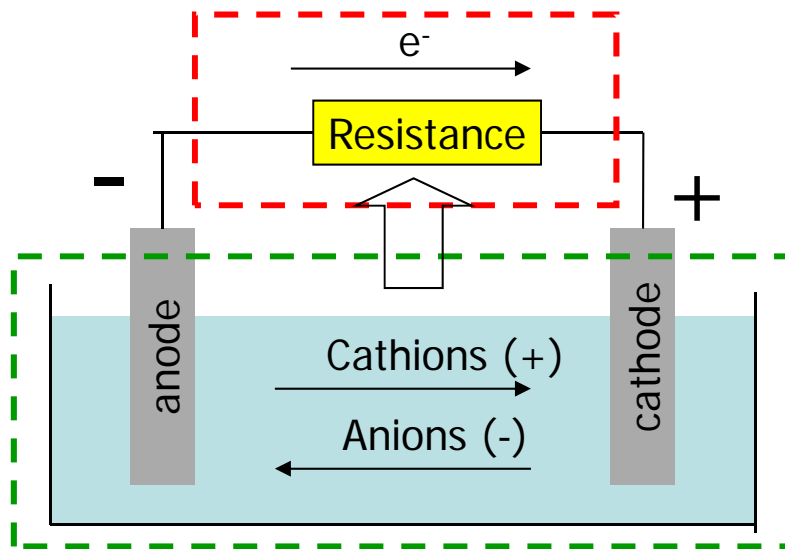
Note: determining U by integration is not easy because the natural variables of U are S and V , which are not easy to control!

Change natural (dependent) variables to p and T (easy to control and constant during battery operation) by Legendre transformation (define new state variable $G = U - TS + pV$)

$$dG = Vdp - SdT + \sum_i Y_i dX_i$$

Equilibrium electrochemistry

Think of Battery: we have mass flow in the battery (ions) that cause the charge flow. The mass flow represents chemical work (moving ions) which is converted to electrical work outside the battery.



During discharge

In the Resistance outside the battery:

$$W_{Elec} = -E_{cell} dQ$$

In the battery:

$$W_{chem} = \sum_i \mu_j dn_j$$

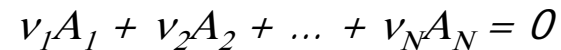
The battery does chemical work which is converted to useable electrical work outside:

$$\delta W_{Chem} = \delta W_{Elec}$$

Equilibrium electrochemistry

$$\sum_j \mu_j dn_j = -E_{cell} dQ$$

In general chemical reactions can be written as:



Where A_j the chemical species and ν_j the coefficient. This implies that $\nu_1 dn$ of species 1 leads to $\nu_2 dn$ conversion of species 2, Example the reaction $H_2 + Cl_2 \rightarrow 2HCl$:

$A_1 = H_2$, $A_2 = Cl_2$, $A_3 = HCl$, $\nu_1 = -1$, $\nu_2 = -1$, $\nu_3 = 2$ (product has positive sign)

So if we convert $dn H_2$ we will also convert $dn Cl$ and produce $2dn HCL$, in other words:

$$\left(\sum_j \nu_j \mu_j \right) dn = -E_{cell} dQ$$

Next express charge (Coulomb) in dn amount of moles reacted charge z species:

$$dQ = zF dn$$

Where F is Faraday's constant 96458 C/mol. This then results in:

$$E_{Cell} = - \frac{\sum_j \nu_j \mu_j}{zF}$$

Equilibrium electrochemistry

Application on Daniel element:

Anode (-): oxidation $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

Cathode (+): reduction $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$

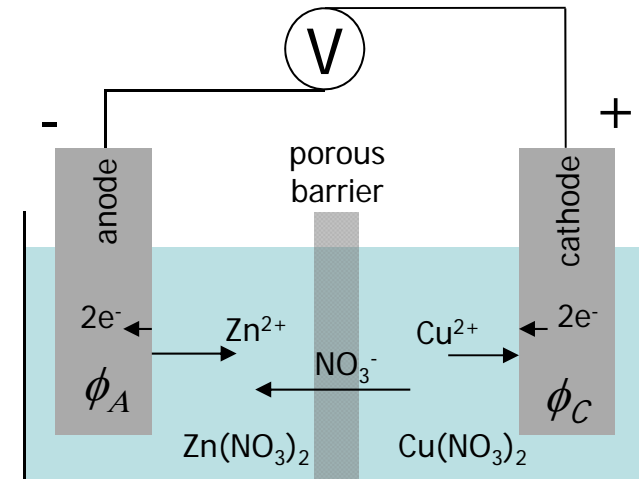
Total: $\text{Cu}^{2+} + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}$

$$E_{\text{Cell}} = (\phi_C - \phi_A) = -\frac{\sum_j \nu_j \mu_j}{zF} = -\frac{(\mu_{\text{Cu}} + \mu_{\text{Zn}^{2+}} - \mu_{\text{Cu}^{2+}} - \mu_{\text{Zn}})}{2F}$$

$$E_{\text{Cell}} = \frac{(\mu_{\text{Cu}^{2+}} - \mu_{\text{Cu}})}{2F} - \frac{(\mu_{\text{Zn}^{2+}} - \mu_{\text{Zn}})}{2F}$$

$$E_{\text{Cell}} = \varepsilon_{\text{Cu/Cu}^{2+}} - \varepsilon_{\text{Zn/Zn}^{2+}}$$

The potential of an electrochemical cell is equal to the difference of the potential of the half cells, which is determined by the chemical potential difference of the redox couple.



Electrochemical cells, driving force

Standard reduction potentials are commonly denoted by the symbol ε° . (means under standard conditions 293 K and 1 bar, 1 molair concentrations) ε° values for hundreds of electrodes have been determined and are usually tabulated in order of increasing tendency to accept electrons (increasing oxidizing power.)

The more positive the half-cell EMF, the smaller the tendency of the reductant to donate electrons, and the larger the tendency of the oxidant to accept electrons

oxidant (electron acceptor)	reductant (electron donor)	E° , volts
$\text{Na}^+ + e^- \rightarrow$	$\text{Na}(s)$	-2.71
$\text{Zn}^{2+} + 2e^- \rightarrow$	$\text{Zn}(s)$	-0.76
$\text{Fe}^{2+} + 2e^- \rightarrow$	$\text{Fe}(s)$	-0.44
$\text{Cd}^{2+} + 2e^- \rightarrow$	$\text{Cd}(s)$	-0.40
$\text{Pb}^{2+} + 2e^- \rightarrow$	$\text{Pb}(s)$	-0.126
$2\text{H}^+ + 2e^- \rightarrow$	$\text{H}_2(g)$	0.000
$\text{AgCl}(s) + e^- \rightarrow$	$\text{Ag}(s) + \text{Cl}^-(aq)$	+0.222
$\text{Hg}_2\text{Cl}_2(s) + 2e^- \rightarrow$	$2\text{Cl}^-(aq) + 2\text{Hg}(l)$	+0.268
$\text{Cu}^{2+} + 2e^- \rightarrow$	$\text{Cu}(s)$	+0.337
$\text{I}_2(s) + 2e^- \rightarrow$	$2\text{I}^-(s)$	+0.535
$\text{Fe}^{3+} + e^- \rightarrow$	$\text{Fe}^{2+}(aq)$	+0.771
$\text{Ag}^+ + e^- \rightarrow$	$\text{Ag}(s)$	+0.799
$\text{O}_2(g) + 4\text{H}^+ + 4e^- \rightarrow$	$2\text{H}_2\text{O}(l)$	+1.23
$\text{Cl}_2(g) + 2e^- \rightarrow$	$2\text{Cl}^-(g)$	+1.36

More noble
More likely to run to the right

What is the potential difference ε (Volt, $V=J/C$) build up?

$$\text{Zn}(s) + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}(s), \quad E^\circ_{\text{cell}} = \varepsilon^\circ_{\text{Cu}/\text{Cu}^{2+}} - \varepsilon^\circ_{\text{Zn}/\text{Zn}^{2+}} = 0.337 - (-0.76) = 1.097 \text{ V}$$

Equilibrium electrochemistry: Relation cell voltage and Gibbs Free energy

$$dG = Vdp - SdT + \sum_j \mu_j dn_j \quad \text{Constant p and T} = \sum_j \mu_j dn_j$$
$$dG = \delta W_{chem} = \sum_j \mu_j dn_j = -EdQ = \delta W_{elec}$$

$$\Delta G = -E\Delta Q$$

$$\Delta G^0 = -zFE^0$$

Application on Daniel element (standard conditions):



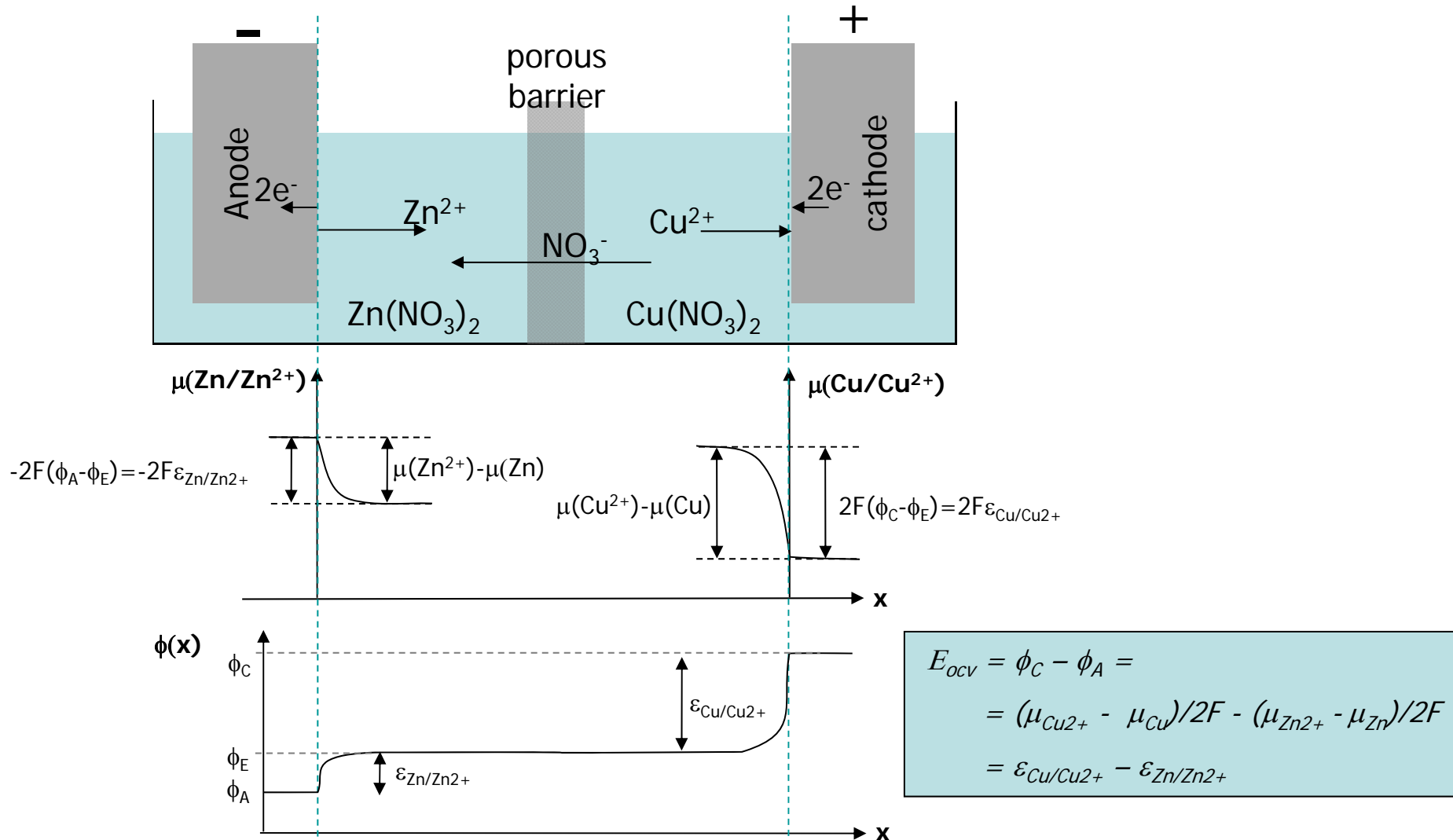
$$\Delta G^0 = -zFE^0 = -2 \cdot 96500 \cdot 1.1 = -212.3 \text{ kJ/mol}$$

$\Delta G < 0$ Reaction occurs spontaneous (battery discharge)

General: $\Delta G < 0$: $E > 0$: discharge exothermic

$\Delta G > 0$: $E < 0$: charge, endothermic

Balancing field and chemical potential



Electrochemical potential

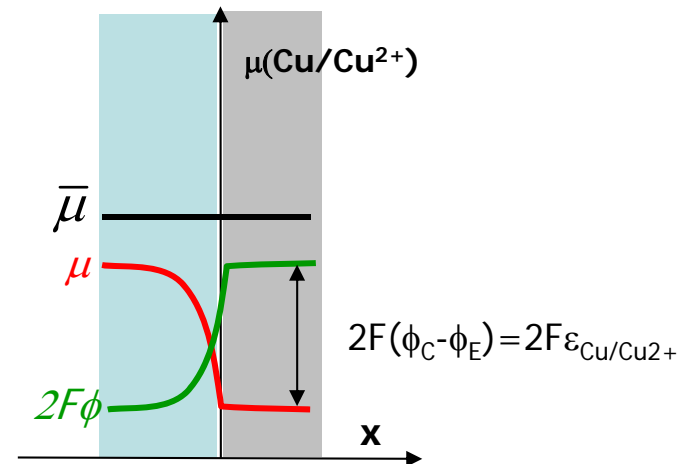
In equilibrium the chemical potential is not equal in electrode and electrolyte!

Define the electrochemical potential, the difference in energy to move add mass with charge from vacuum (adds a electrical field term)

$$(\phi_C - \phi_E) = -\frac{(\mu_{Cu} - \mu_{Cu^{2+}})}{2F}$$

$$\mu_{Cu} + 2F\phi_C = \mu_{Cu^{2+}} + 2F\phi_E$$

$$\bar{\mu}_{Cu} = \bar{\mu}_{Cu^{2+}}$$



In an electrochemical cell in equilibrium the electrochemical potential of each species is constant

The Electrochemical double layer

When we immerse an electrode in a solution a potential difference develops due to a difference in chemical potential:

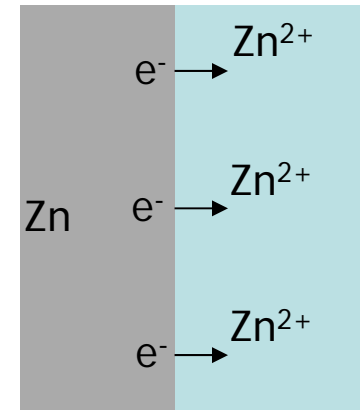
For example for the reaction $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

$$\phi_A - \phi_E = \varepsilon_{\text{Zn}/\text{Zn}^{2+}} = (\mu_{\text{Zn}^{2+}} - \mu_{\text{Zn}}) / 2F$$

or

$$\bar{\mu}_{\text{Zn}} = \mu_{\text{Zn}} + 2F\phi_A = \mu_{\text{Zn}^{2+}} + 2F\phi_{El} = \bar{\mu}_{\text{Zn}^{2+}}$$

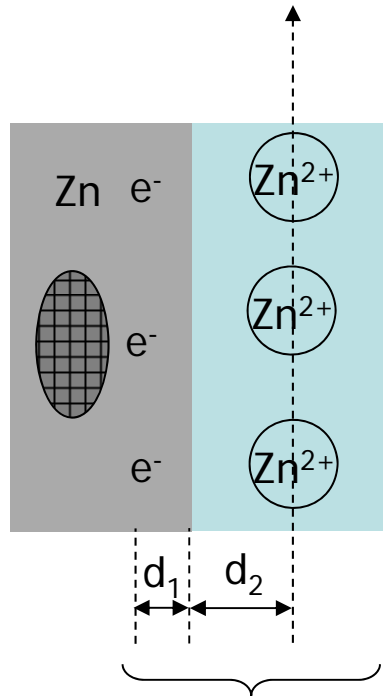
$$\bar{\mu}_{\text{Zn}} = \bar{\mu}_{\text{Zn}^{2+}} \quad \text{Electrochemical equilibrium}$$



How does the charge distribute?
This determines the electrical potential drop!

The Electrochemical double layer

Outer Helmholtz plain (OHP)



Electrochemical
Double Layer
(EDL)

In equilibrium no net charge current

⇒ No net force on charge hence no electric flux E

$$\vec{E} = \frac{\vec{F}}{q} = 0$$

$$\oint_S \vec{E}_n dA = \frac{q_{in}}{\epsilon_0} \text{ (Gauss)}$$

$$\Rightarrow q_{in} = 0$$

No charge in bulk!

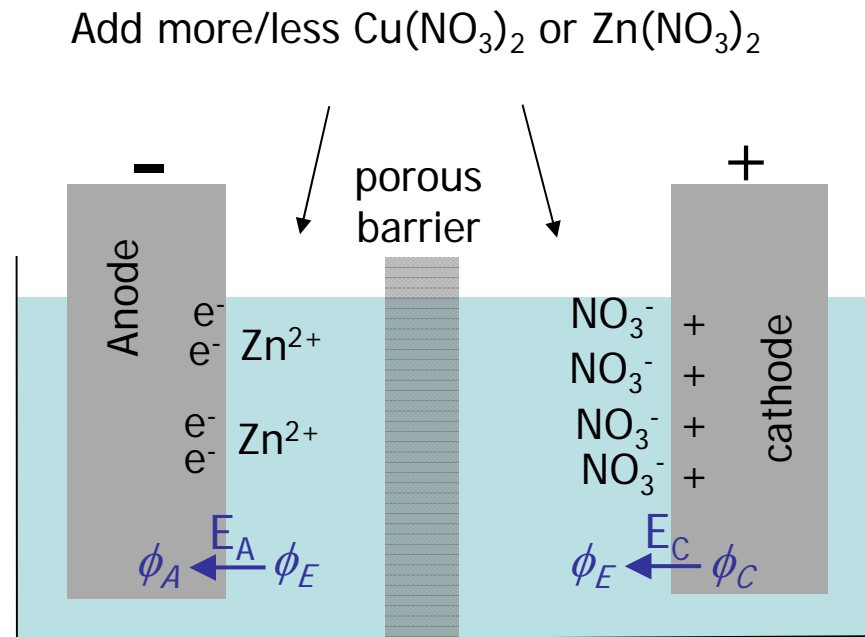
Charge has to be at the interface!

And therefore the potential drop is over the interface

Double layer thickness depends on ionic/electronic conductivity
Conductor: $d \sim 0.1 \text{ nm}$, in semiconductor and
electrolyte $\sim 1\text{-}100 \text{ nm}$

Equilibrium electrochemistry

Up till now standard conditions (1 molair, 1 bar and RT), what if the concentrations change?



What is the influence of concentrations (activities) on the electrode potential?

Equilibrium electrochemistry

What is the influence of concentrations (activities) on the electrode potential?

We already found for the potential of a redox reaction:

$$E_{Cell} = -\frac{\sum_j \nu_j \mu_j}{zF}$$

Using $\mu = \mu^o + RT \ln c$ (derived for ideal gas, dilute solutions) this leads to the Nernst equation:

$$E_{Cell} = E^o - \frac{RT}{zF} \ln \prod c_j^{\nu_j} = E^o - \frac{RT}{zF} \ln(K)$$

Where K is the equilibrium constant of the redox reaction

Equilibrium electrochemistry

Examples of using $\varepsilon = (\phi_C - \phi_A) = \varepsilon^0 - RT/zF [\ln \Pi c_j^{\nu_j}] = \varepsilon^0 - RT/zF \ln(K)$

Example 1: How does the electrode potential of the reaction $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$ depends on the concentration

For $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$ we find: $c_{\text{Cu}^{2+}}$, $\nu = -1$, $c_{\text{Cu(s)}}$, $\nu = 1$

So: $K = c_{\text{Cu(s)}} / c_{\text{Cu}^{2+}}$

Hence: $\varepsilon = \varepsilon_{\text{Cu/Cu}^{2+}}^0 - RT/2F [\ln (c_{\text{Cu(s)}}/c_{\text{Cu}^{2+}})] = 0.337 - 0.013 [\ln (c_{\text{Cu(s)}}/c_{\text{Cu}^{2+}})]$

where we used $R=8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $F=9.65 \cdot 10^4 \text{ C}\cdot\text{mol}^{-1}$

Similar for $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn(s)}$:

$\varepsilon = \varepsilon_{\text{Zn/Zn}^{2+}}^0 - RT/2F [\ln (c_{\text{Zn(s)}}/c_{\text{Zn}^{2+}})] = -0.76 - 0.013 [\ln (c_{\text{Zn(s)}}/c_{\text{Zn}^{2+}})]$

Daniel cell: $\text{Cu}^{2+} + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}$

Question Electrochemistry 2

<http://www.edupinion.nl/c404>

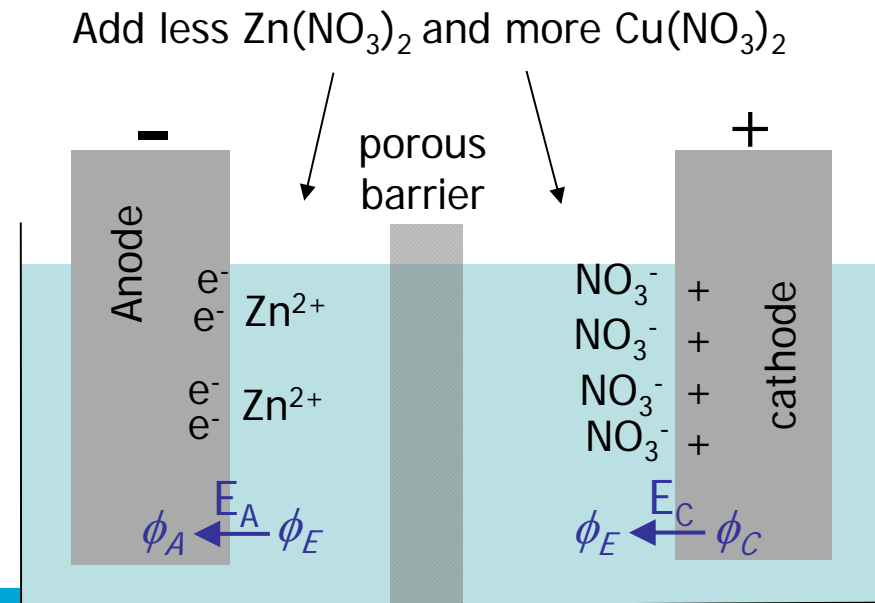
Result

$$E^{\circ}_{cell} = \varepsilon^{\circ}_{Cu/Cu^{2+}} - \varepsilon^{\circ}_{Zn/Zn^{2+}} = 0.337 - (-0.76) = 1.097 \text{ V}$$

$$\varepsilon_{Cu/Cu^{2+}} = -\frac{(\mu_{Cu} - \mu_{Cu^{2+}})}{2F} \quad \varepsilon_{Zn/Zn^{2+}} = -\frac{(\mu_{Zn} - \mu_{Zn^{2+}})}{2F}$$

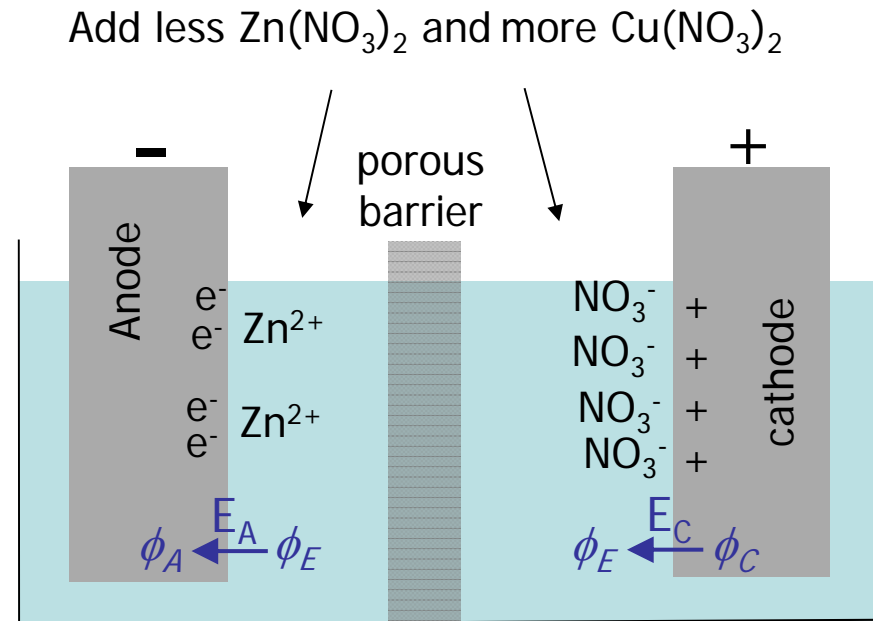


10. Does the open cell voltage go
- a) up or
 - b) down?
 - c) no clue



Question Electrochemistry 2

10. Does the open cell voltage go
 a) up or
 b) down?
 c) no clue



$$\varepsilon = \varepsilon^{\circ}_{\text{Cu}/\text{Cu}^{2+}} - \frac{RT}{2F} [\ln (c_{\text{Cu}(s)}/c_{\text{Cu}^{2+}})] = 0.337 - 0.013 [\ln (c_{\text{Cu}(s)}/c_{\text{Cu}^{2+}})] > 0.337$$

$$\varepsilon = \varepsilon^{\circ}_{\text{Zn}/\text{Zn}^{2+}} - \frac{RT}{2F} [\ln (c_{\text{Zn}(s)}/c_{\text{Zn}^{2+}})] = -0.76 - 0.013 [\ln (c_{\text{Zn}(s)}/c_{\text{Zn}^{2+}})] < -0.76$$

$$E_{\text{cell}} = \varepsilon_{\text{Cu}/\text{Cu}^{2+}} - \varepsilon_{\text{Zn}/\text{Zn}^{2+}} = (0.337+x) - (-0.76-y) = 1.097+x+y \text{ V} \Rightarrow \text{a) up}$$

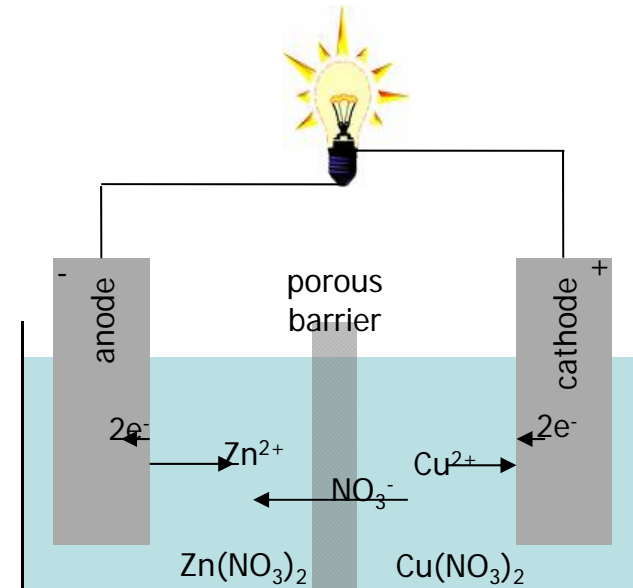
Equilibrium electrochemistry

Example 2: When does the Daniel reaction stop?

Daniel cell: $\text{Cu}^{2+} + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}$

Cathode: $\varepsilon_{\text{Cu}/\text{Cu}^{2+}} = 0.337 - 0.013 [\ln (c_{\text{Cu(s)}}/c_{\text{Cu}^{2+}})]$

Anode: $\varepsilon_{\text{Zn}/\text{Zn}^{2+}} = -0.76 - 0.013 [\ln (c_{\text{Zn(s)}}/c_{\text{Zn}^{2+}})]$



The condition to stop: $\phi_C = \phi_A \Rightarrow (\phi_C - \phi_{El}) = (\phi_A - \phi_{El}) \Rightarrow \varepsilon_{\text{Cu}/\text{Cu}^{2+}} = \varepsilon_{\text{Zn}/\text{Zn}^{2+}}$

$-0.76 - 0.013 [\ln (c_{\text{Zn(s)}}/c_{\text{Zn}^{2+}})] = 0.337 - 0.013 [\ln (c_{\text{Cu(s)}}/c_{\text{Cu}^{2+}})]$

$c_{\text{Zn}^{2+}}/c_{\text{Cu}^{2+}} = 4.4 \cdot 10^{37}$

(here we actually calculated the equilibrium constant $K = \ln(c_{\text{Zn}^{2+}}/c_{\text{Cu}^{2+}})$ of the Daniel cell reaction)

Practical questions



What is the direction of a redox reaction?



What is the voltage that a redox reaction can deliver?

What is the energy density of a battery?

What is the power density of a battery?

What determines the cycle life of a battery?

Energy density



$$\Delta G^0 = -zFE^0 = -2 \cdot 96500 \cdot 1.097 = -212.3 \text{ kJ/mol}$$

1 mol Cu corresponds to 63.5 g

1 mol Zn corresponds to 65.4 g

Just considering the metals the energy density would be: $212.3 \text{ kJ} / 0.1289 \text{ kg} = 1650 \text{ kJ/kg}$

However, we need to account for the electrolyte, the current collectors, and packing!

Practical questions



What is the direction of a redox reaction?



What is the voltage that a redox reaction can deliver?



What is the energy density of a battery?

What is the power density of a battery?

What determines the cycle life of a battery?

Question cell voltage 2

11. Does the cell voltage of the Daniel element remain constant during discharge?

- a) Yes
- b) No
- c) No clue



<http://www.edupinion.nl/c738>

Result

Question cell voltage

11. Does the cell voltage remain constant during discharge?

- a) Yes
- b) No
- c) No clue

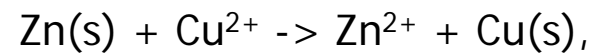
No!

$$\Delta G^0 = -zFE^0 = -2 \cdot 96500 \cdot 1.097 = -212.3 \text{ kJ/mol}$$

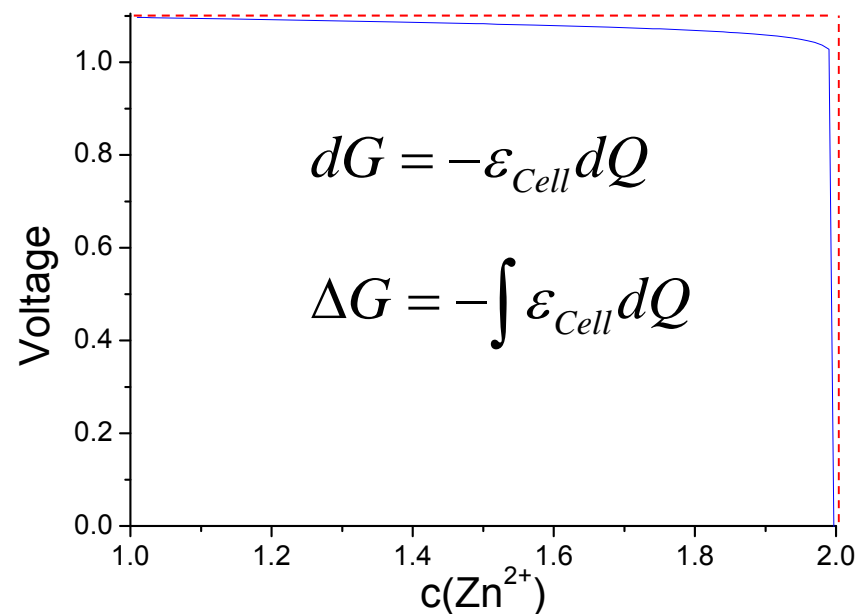
Assumes standard conditions, $c_{\text{Cu}^+} = c_{\text{Zn}^+} = 1 \text{ mol/liter}$

When reaction proceeds c_{Cu^+} reduces and c_{Zn^+} increases, Nernst

Energy density



$$E_{\text{cell}} = \varepsilon_{\text{Zn/Zn}^{2+}}^o - \frac{RT}{2F} \ln \left(\frac{c_{\text{Cu(s)}}}{c_{\text{Cu}^{2+}}} \right) - \varepsilon_{\text{Zn/Zn}^{2+}}^o + \frac{RT}{2F} \ln \left(\frac{c_{\text{Zn(s)}}}{c_{\text{Zn}^{2+}}} \right)$$



Home assignments

Read Chapters 1 and 2 Advanced Batteries

Practice Electrochemistry:

Plot the voltage of the daniel element as a function of $[Zn^{2+}]$ concentration
Assuming starting concentration $c_{Zn^{2+}} = 0.1 \text{ mol/l}$ and $c_{Cu^{2+}} = 1.0 \text{ mol/l}$ (assume $c_{Zn(s)} = c_{Cu(s)} = 1$, and the cell volume 0.01 l).

How much chemical energy was converted to electrical energy?

Consider the following redox reaction: $Cu_{(s)} + Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Ag_{(s)}$
What is the Gibbs free energy change under standard conditions? (Use standard reduction potentials)