

Materials, Electronics and Renewable Energy

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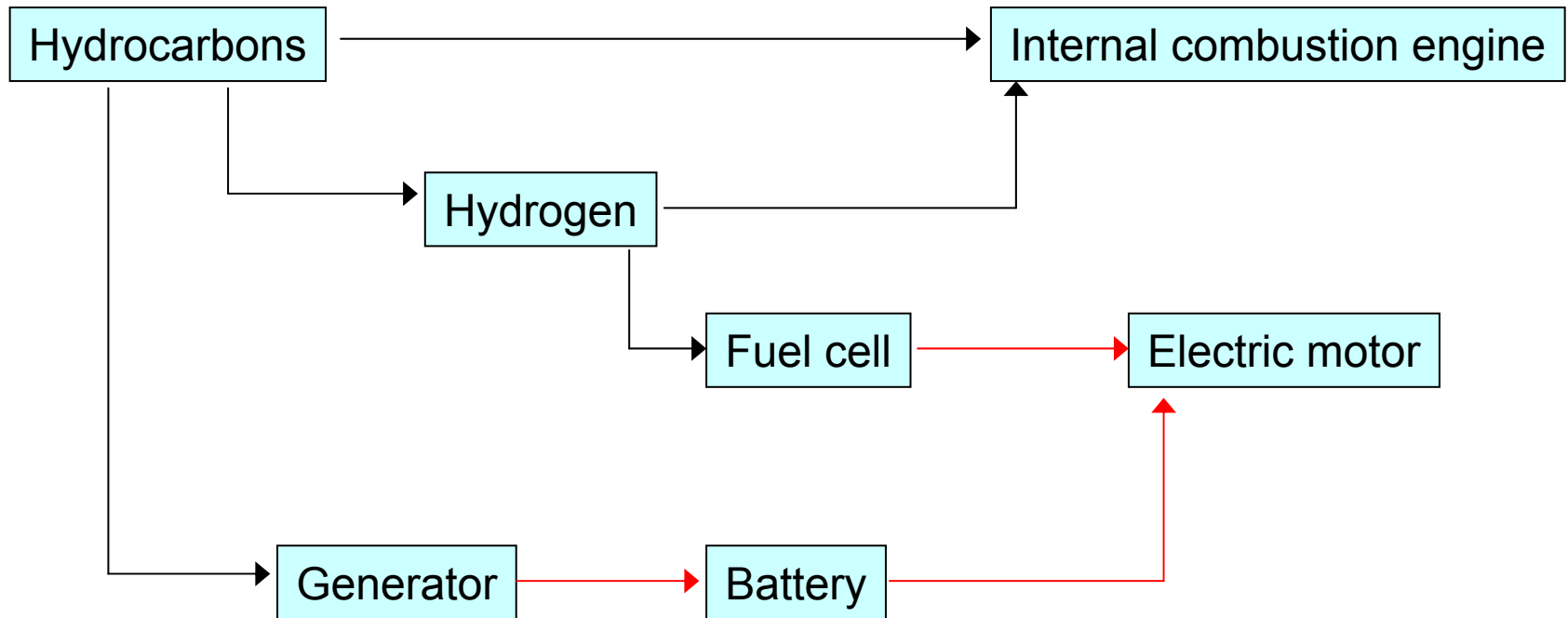
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The hydrogen economy

Electrochemistry

- batteries
- fuel cells

“Transport fuels”



We need to understand

- hydrogen generation
- batteries
- fuel cells

} electrochemistry



“Conventional” car
40-100 kWh per 100 km



Honda Clarity Fuel Cell vehicle
70 kWh per 100 km



BMW Hydrogen 7
254 kWh per 100 km



Tesla electric car
15 kWh per 100 km

Making hydrogen

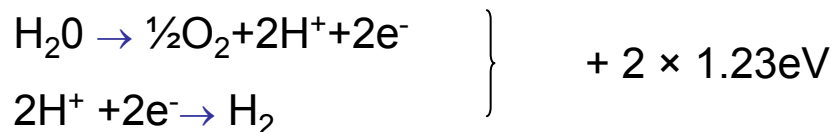
“There's a lot of hydrogen out there, but it's stuck to other stuff, and it's tough to break it off.” James May, Top Gear

Cheapest production is from methane:



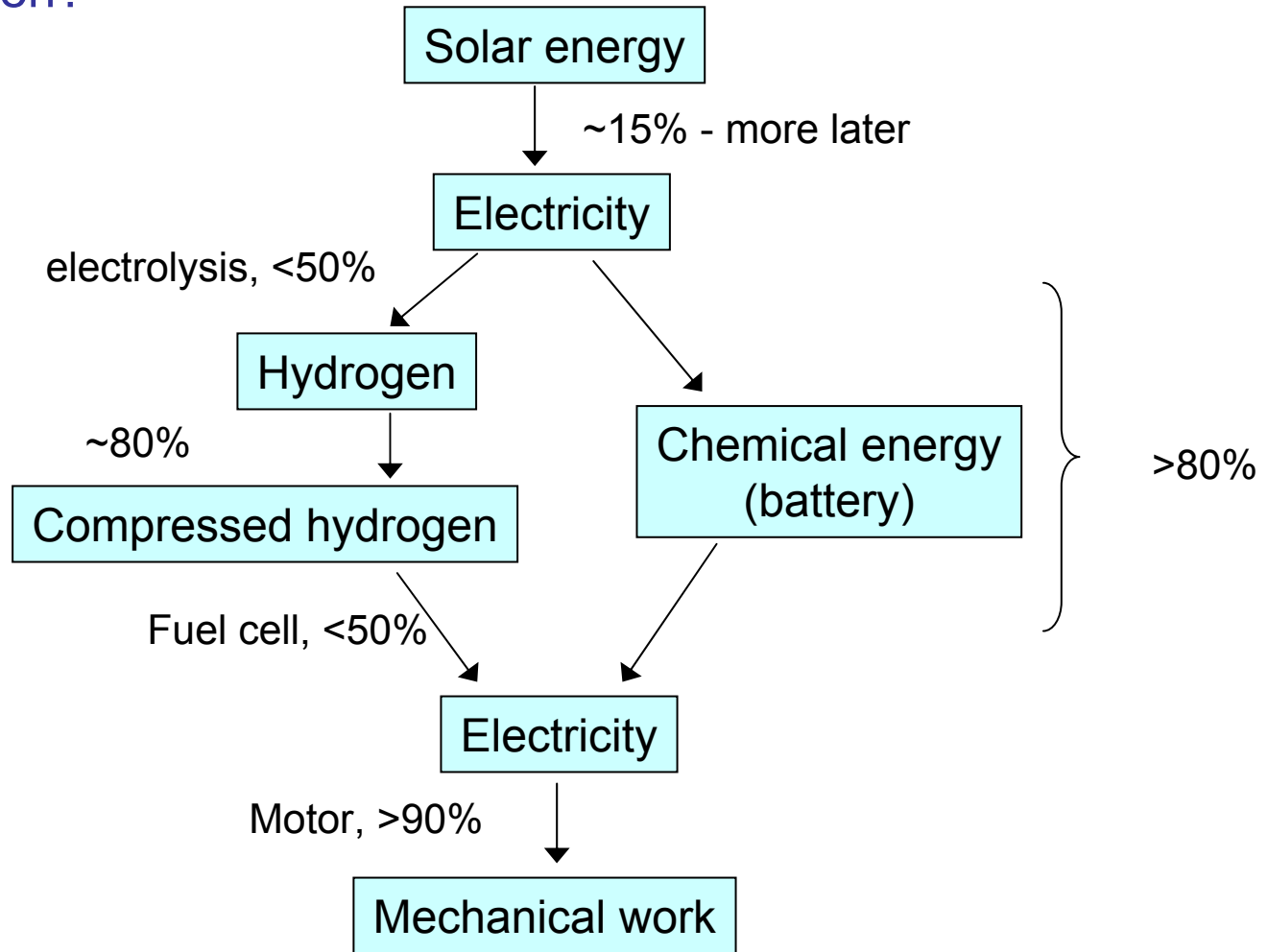
Note: substantial generation of CO_2 , problems also with contamination of H_2 (especially with CO) so not generally suitable for fuel cells

Hydrogen from electrolysis:

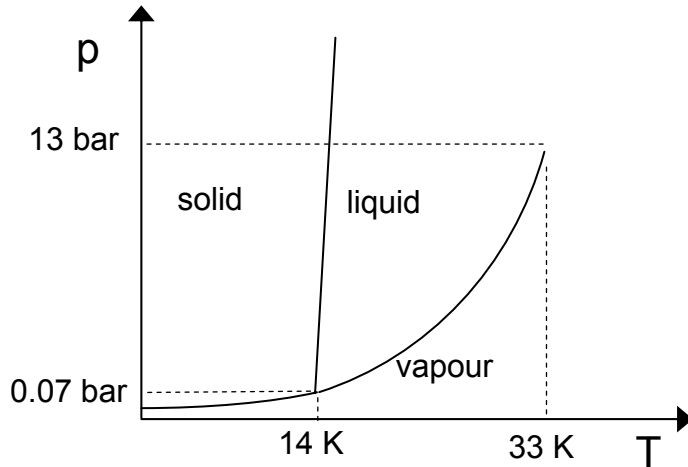


Direct photolysis of water? }
Biological sources? } more later

Solar Hydrogen?



Hydrogen Storage

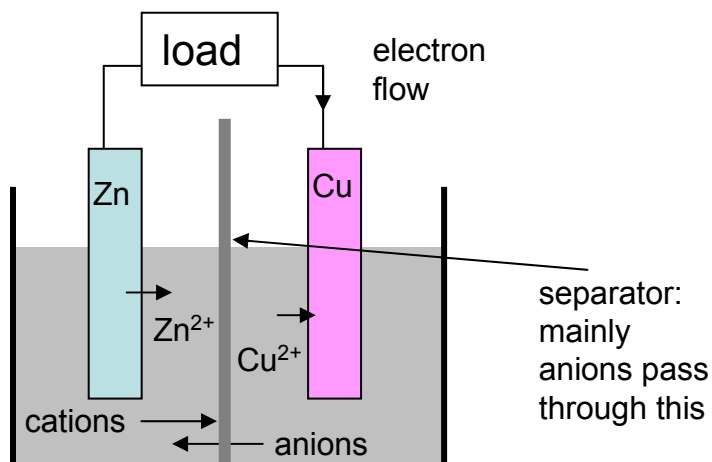


- High-pressure gas
- Low-temperature liquid

- Storing and transporting liquid hydrogen (20 K) is expensive (N.B. density only 0.07 g cm^{-3})
- High pressure equipment (steel cylinders) is also expensive and heavy
- Diffusion of hydrogen through container is a serious problem
- Solid “hosts” have been proposed – need $>10\%$ hydrogen by weight
 - Early reports of $>50\%$ H_2 storage in carbon nanotubes are wrong
 - Polymers?
 - Metal hydrides (e.g. LiAlH_4) – promising but highly reactive, and require high temperatures for hydrogen recovery
 - No practical solid-state storage exists yet

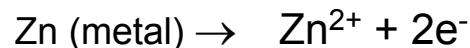
Electrochemistry:

The Daniell cell: Zn and Cu electrodes in an aqueous solution of zinc sulphate (near zinc electrode) and copper sulphate (near copper electrode)



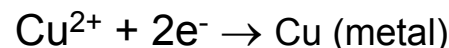
Discharge reactions:

at the zinc electrode (anode):



- electrons flow round external circuit
- Zn cations move into solution

at the copper electrode (cathode):



- electrons flow round external circuit
- Cu cations deposit on the Cu electrode

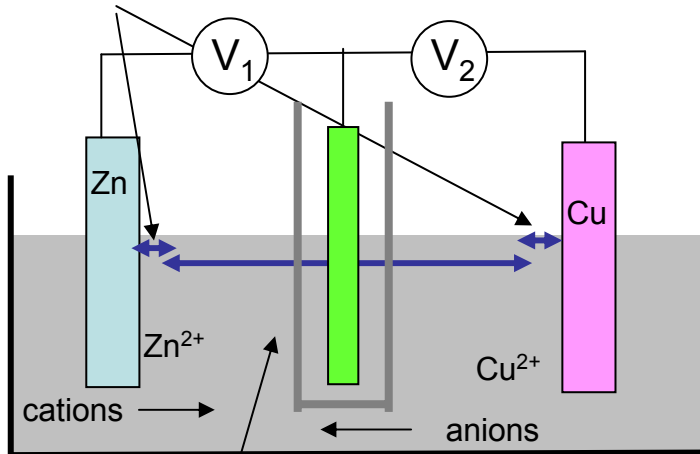
Replace 'load' with voltage source:

- zero current flows when voltage = cell 'emf'
- discharge reaction when voltage < emf
- charging reaction when voltage > emf

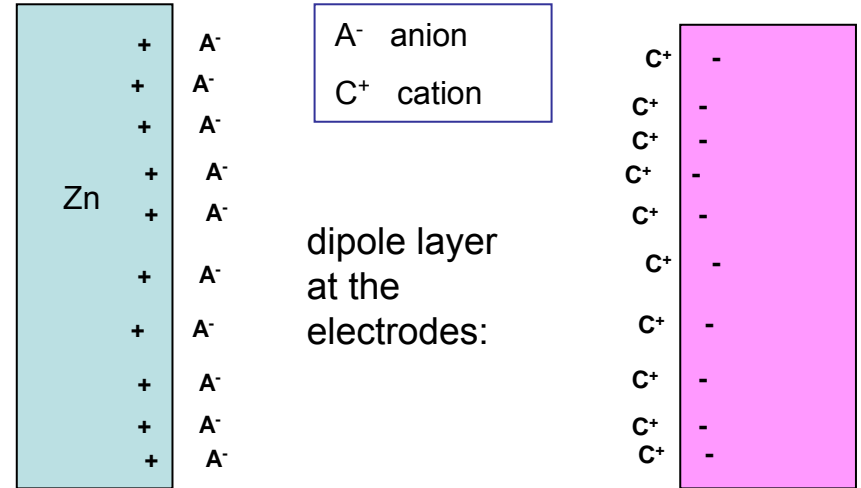
'Reversible' cell – reactions can run both ways – infinitesimal change in V away from cell emf switches reaction direction

components to the cell...

electric field only present close to the electrodes – dipole layer of ionic charge/electronic charge in electrode



zero electric field in the bulk of the electrolyte (certainly true when $V = \text{cell emf}$)



we can describe the cell as the sum of two 'half cells' provided by the two electrodes

- introduce a third electrode (the 'reference' electrode)
- measure potential at the other electrodes with respect to the reference electrode
- standard reference is the 'hydrogen electrode'

Standard hydrogen electrode:

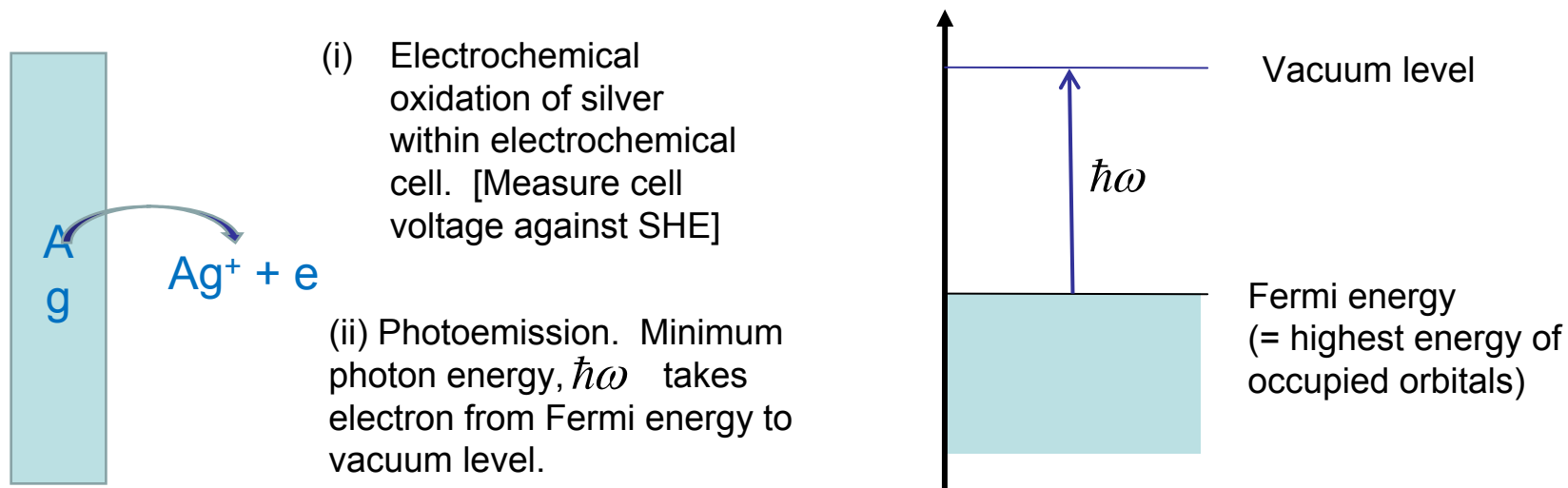
platinum metal electrode (with large surface area) dipped into a solution with hydrogen ions at unit 'activity' (1 Molar) and in the presence of hydrogen gas at 1 atmosphere.

cell reaction is $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$

the 'SHE' is taken as the base line for measurement of half-cell potentials – i.e. this sets the SHE to zero potential.

Match to a more familiar energy baseline? the SHE potential lies 4.5 ± 0.1 V below the **vacuum level**

Connection between SHE 'zero' and vacuum level?



(i) and (ii) are not exactly the same – the Ag ion in (i) ends up solvated by e.g. water, but is still on the surface of the Ag electrode in (ii)

Concentration dependences of cell voltages: Nernst Equation

Consider half-cell reaction $C \rightarrow C^+ + e^-$

Or more generally, just $A \rightarrow B$ (consider the electrons as part of work done)

Relevant potential is Gibbs free energy, ΔG

$$\Delta G = \Delta H - T\Delta S = \Delta U + \Delta(pV) - T\Delta S$$

Justification: at constant temperature and pressure, ΔG is the maximum non-expansion work w_{ne} which can be done.

$$dH = dU + d(pV) = dq + dw + d(pV)$$

$$dG = \cancel{TdS} - \cancel{pdV} + dw_{ne} + \underbrace{\cancel{pdV} + Vdp}_{\substack{= \\ 0 \text{ at const. } p}} - \cancel{TdS}$$

$$dG = dw_{ne}$$

For half-cell at half-cell voltage

Consider reaction of δn molecules $A \rightarrow B$

chemical potential $\mu = \left(\frac{\partial G}{\partial n} \right)_{p,T}$

$$\underbrace{-\delta n e V}_{\text{electrical work}} = \delta G = \delta n (\mu_B - \mu_A)$$

But, chemical potential depends on concentration

E.g. for ideal (i.e. non-interacting) gas

$$\mu = \mu^{\ominus} + kT \ln \left(\frac{p}{p^{\ominus}} \right)$$

standard conditions \uparrow \nwarrow configurational entropy term

Proof: from earlier, if $dw_{ne} = 0$

- $dG = V dp$
- write $V = n k T/p$ and integrate
- divide by n to get μ

More complicated for solutions: concentration \equiv pressure, but interactions between ions mean enthalpy also depends on concentration

$$\mu = \mu^{\ominus} + kT \ln \left(\gamma \frac{m}{m^{\ominus}} \right) = \mu^{\ominus} + kT \ln(a)$$

\swarrow molality \nwarrow "activity" $\gamma \rightarrow 1$ as $m \rightarrow 0$

For half-cell:

$$V = V^{\ominus} - \frac{kT}{e} \ln \left[\frac{a_B}{a_A} \right]$$

"Nernst equation"

Basic requirements for the electrochemical cell:

two electrodes capable of bringing/removing electrons to the reaction surface

species capable of redox reaction present at each electrode (e.g. Zn metal to Zn^{2+} ions)

electrolyte which provides for a flow of cations and/or anions

‘Primary’ cells – reaction runs once only – resultant products not arranged to allow the reaction to run in reverse (? electrode has disintegrated..)

Alkaline manganese cells (standard AA and AAA batteries):

- anode: metallic zinc (finely-divided powder stabilised in a polymer-based gel)
- cathode: manganese dioxide (an insulator) compressed with finely-divided graphite (an electrical conductor)
- electrolyte: concentrated KOH (stabilised in a cellulose gel/fabric separator)
- cell reaction: $\text{Zn} + \text{MnO}_2 \rightarrow \text{ZnO} + \text{MnO}$ (water also involved)
- cell voltage is 1.55V



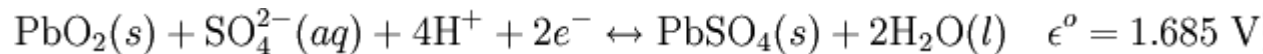
‘Secondary’ cells – reversible reactions allow multiple cycles

require electrodes which retain integrity of electrical conduction pathway?

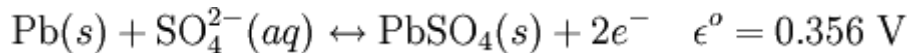
Lead-acid battery: electrodes are lead and lead dioxide, electrolyte is sulphuric acid

The chemical reactions are (charged to discharged):

Anode (oxidation):



Cathode(reduction):



reversible battery requires repeated
electrochemical etching and re-plating.....
durability perhaps 500 cycles

Nickel-Cadmium cells:

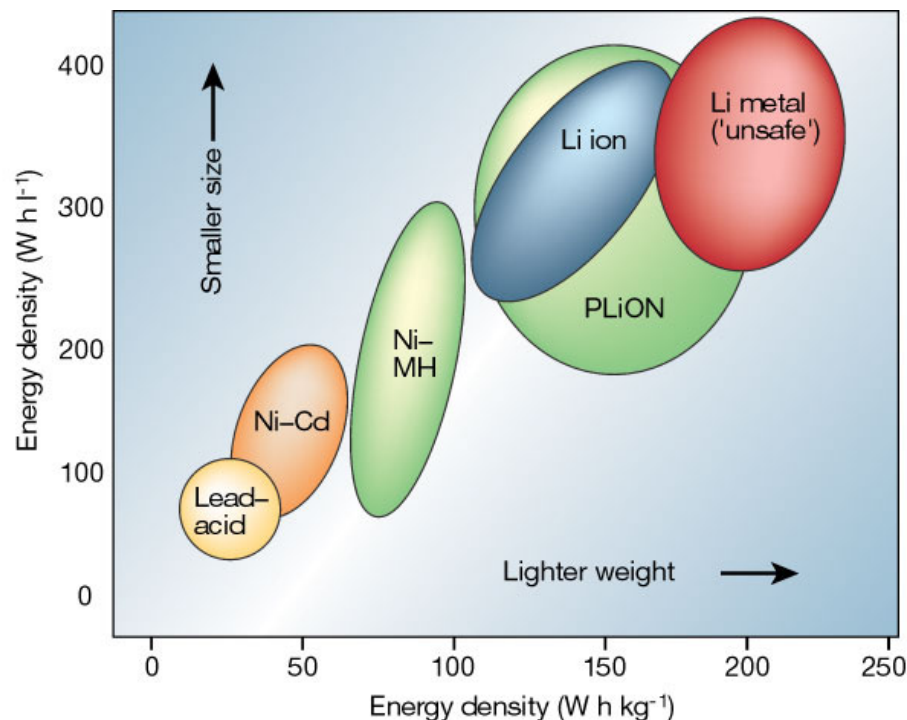
cell reaction is: $2 \text{NiO}(\text{OH}) + \text{Cd} + 2 \text{H}_2\text{O} \leftrightarrow 2 \text{Ni}(\text{OH})_2 + \text{Cd}(\text{OH})_2$
left side = ‘charged’, right side = ‘discharged’

Lithium-ion secondary batteries

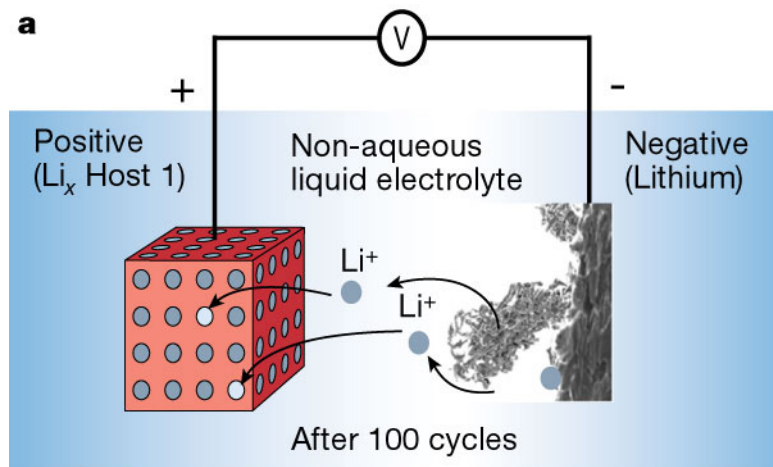
review: Tarascon and Armand, Nature **414**, 359 (2001)

Virtue of lithium-ion batteries is energy density – up to 200Whr/kg

- lithium is low density
- lithium is very reactive (low work function – 3 V away from the SHE potential), so high open-circuit voltages are possible
- lithium is small, and can be reasonably easily inserted and extracted from ‘host’ electrodes

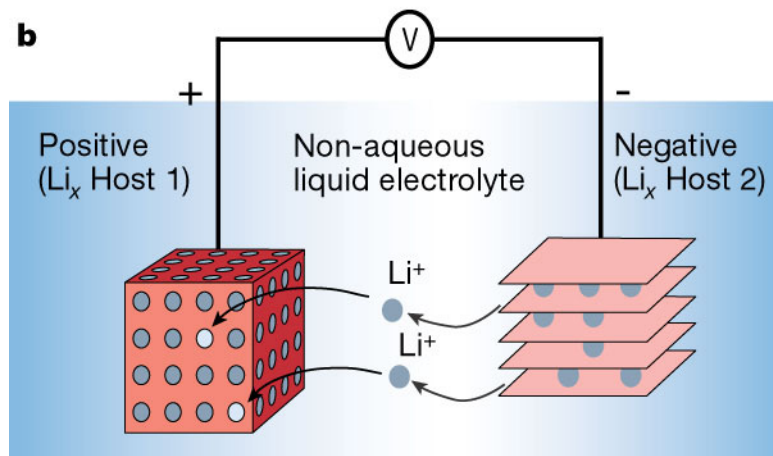


“The share of worldwide sales for Ni–Cd, Ni–MeH and Li-ion portable batteries in 2000 was 23, 14 and 63%, respectively. The use of Pb–acid batteries is restricted mainly to SLI (starting, lighting, ignition) in automobiles or standby applications, whereas Ni–Cd batteries remain the most suitable technologies for high-power applications (for example, power tools).”



Metallic lithium gives highest cell voltages but is not easy to cycle:

a, Rechargeable Li-metal battery (the picture of the dendrite growth at the Li surface was obtained directly from *in situ* scanning electron microscopy measurements). Positive electrode is usually LiCoO_2



b, Rechargeable Li-ion battery. Negative electrode is graphite. Lithium is easily 'intercalated' and 'de-intercalated' between the layers.

Electrode reaction:

$\text{Li}^+ + \text{graphite} + \text{electron} \rightarrow$

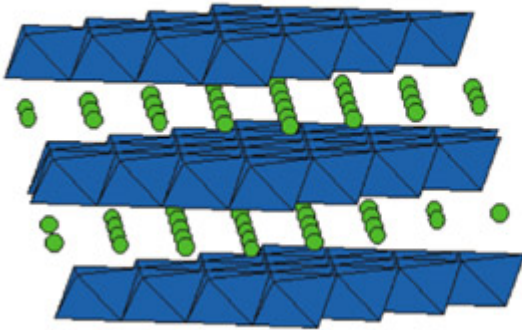
Li-graphite intercalation complex

Lithium remains substantially ionic in sites between graphite layers, and the transferred electron 'fills up' the graphite bandstructure – converting graphite from a semimetal to a very good metal (and for some intercalation complexes, e.g. with calcium, a good superconductor)

Positive electrodes: ‘insertion’ compounds which can reversibly accept/expel Li ions, and which remain electrically conducting – requires rigid sheets or cages, and easily-accessible energy bands with a high density of states (generally transition metal ‘d’ bands)

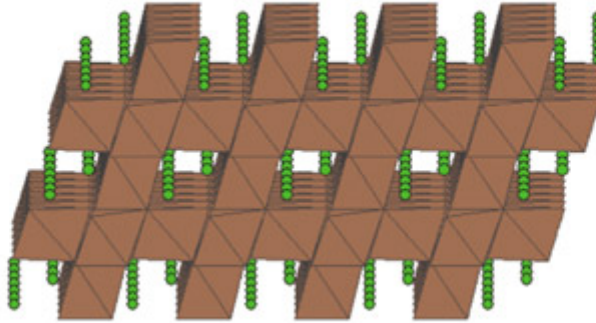
a

LiCoO_2 : layered structure



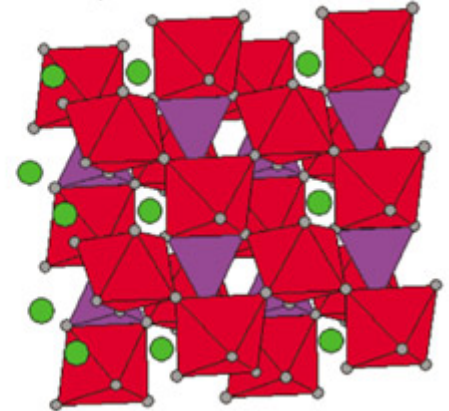
b

LiMn_2O_4 : spinel structure



c

LiFePO_4 : olivine structure



Layered, spinel and olivine structures of positive electrode materials for lithium batteries. These materials are required to be good conductors of both lithium ions (green circles) and electrons.

a, In the layered structure of LiCoO_2 , a face-centred cubic oxygen array provides a two-dimensional network of edge-shared CoO_6 octahedra (blue) for the lithium ions.

b, In the spinel structure of LiMn_2O_4 the face-centred cubic oxygen array provides a three-dimensional array of edge-shared MnO_6 octahedra (brown) for the lithium ions.

c, The olivine structure of LiFePO_4 has a hexagonally-close-packed oxygen array in which there are corner-shared FeO_6 octahedra (red) and PO_4 tetrahedra (purple). **This structure is a poor electron conductor.** Chiang and colleagues at MIT reported (Nature Materials, 2001) a greatly improved the electronic conductivity of LiFePO_4 by doping it with low levels of a multivalent cation. Others in the field don't agree – but with addition of ‘carbon black’ it seems to work..

Commercialisation of the lithium iron phosphate battery (2001 to 2006):

Powerstream,
<http://www.powerstream.com/LLLF.htm>

“The DEWALT 36V battery technology, which has a unique Nano-Phosphate lithium-ion design that offers a high level of power, run-time and durability when compared to other conventional lithium technologies. The DEWALT 36V battery delivers up to 2,000 recharges, over three times more than any other formula of lithium-ion tested.”

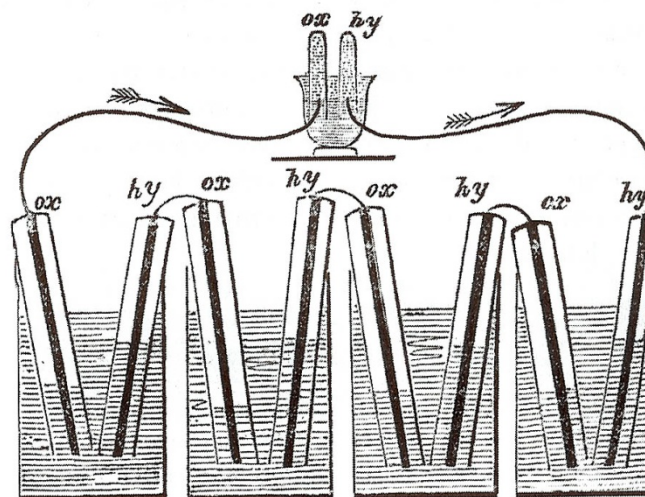


The hydrogen fuel cell:

William Grove – 1839

‘the gaseous voltaic battery’ (renamed ‘fuel cell’ in 1922)

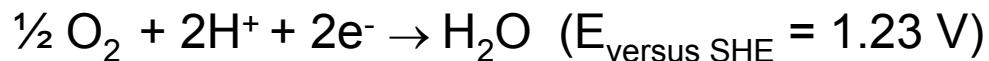
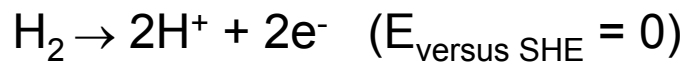
both electrodes made with platinum



electrolyte aqueous sulphuric acid

up-turned test-tubes with oxygen and hydrogen contained

electrode reactions (when the electrolyte allows transport of protons from the H electrode to the O electrode):

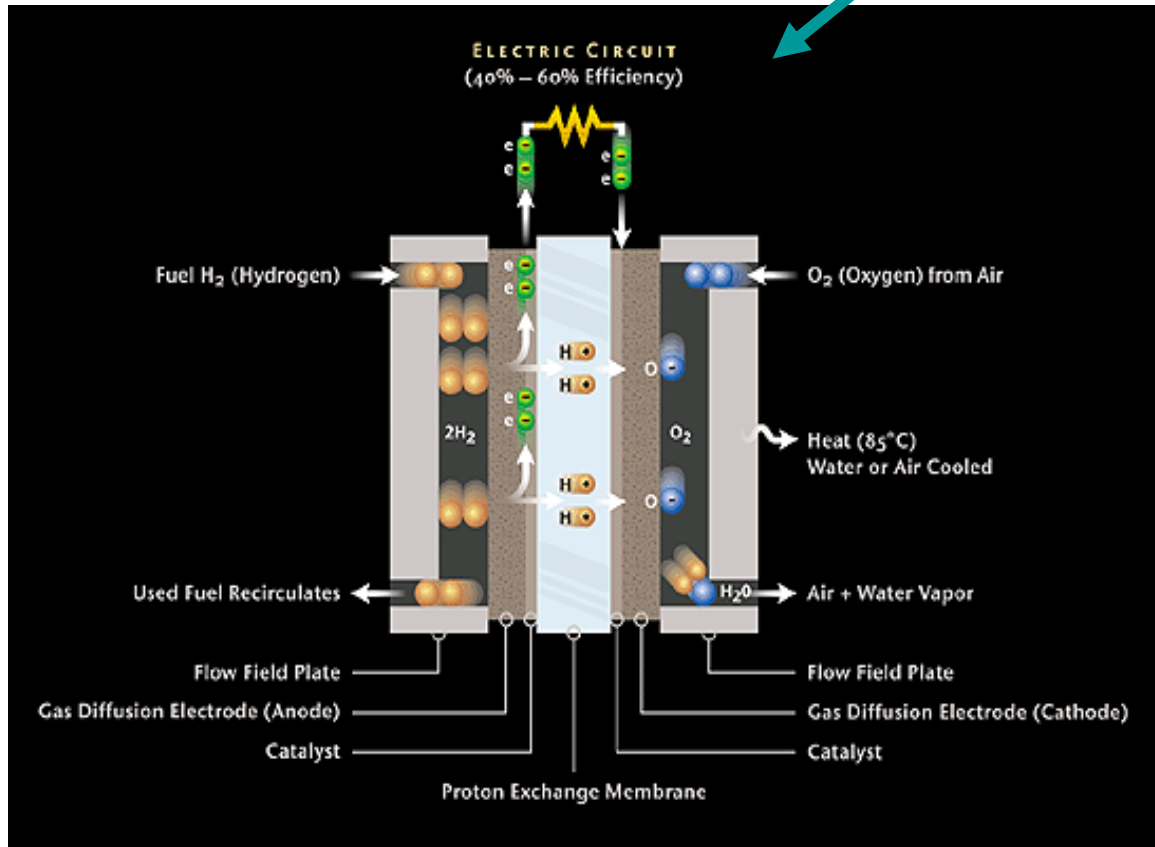


Note: H^+ ions are transported through the sulphuric acid (diffusion in concentration gradient)

The hydrogen fuel cell – progress since 1839...

Ballard – leading company
developing fuel cells for transport

Note: efficiency
< 50%....



Hydrogen electrode:

still platinum (but very small particles on graphite matrix)

Oxygen electrode:

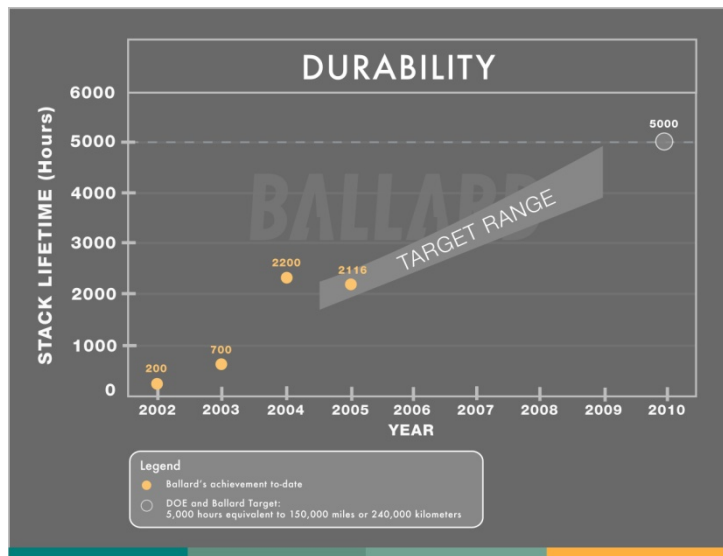
still platinum (but very small particles on graphite matrix)

electrolyte:

big improvement through use of 'proton exchange membrane' which allows only protons through – and avoids O_2/H_2 contamination

membrane = nafion – this is PTFE (teflon) with small ionic pores – usually sulphate side-groups. (Gortex...)

Can also choose **oxygen-permeable membranes** – various metal oxide ceramics can be used – generally requires high temperatures to get adequate ion mobility

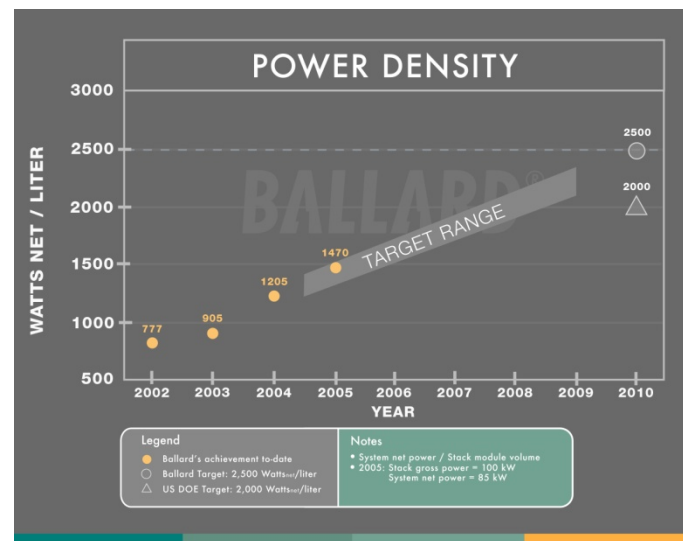
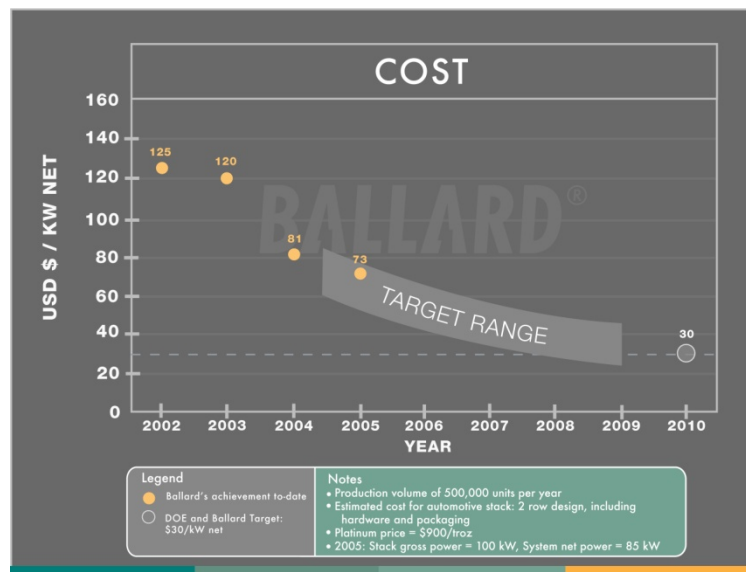


Ballard – 2005 performance:

durability – a few thousand hours

power density – 1.5 kW/litre. [target 100 kW for a car = 100 litres – so several hundred kg..?]

cost: \$70 per kW = \$7000 for 100 kW target



What holds back fuel cells?

- the starting components are molecular oxygen and molecular hydrogen
 - the useful electrode reactions only happen after the molecules have dissociated to atomic H and atomic O. At room temperature (and at quite high temperatures), this requires a very effective catalyst. However, the kinetics of this reaction are slow, especially for O₂ (1000 times slower than H₂)
 - slow kinetics cause reduced output voltage – at usable current densities – typically 0.7 V (c.f. reversible cell voltage of 1.23 V)
 - cf. batteries, designed to charge and discharge much closer to cell voltage
- [Note: a catalyst does not change the energy of the reaction, just the kinetics, by lowering the activation energy for the reaction]

The platinum group elements (e.g. palladium, nickel) are the only known ‘good’ catalysts for dissociation of gaseous molecules – surfaces and interstices of the lattice are able to absorb atomic species. (Platinum will absorb large quantities of hydrogen). Platinum group metals are used as catalysts in ‘cat converters’ on car exhausts, production of ammonia from N₂ and H₂.]

Not much progress since 1839....

Fuel cells

‘large’ fuel cells, as used for vehicle propulsion systems:

direct use of H₂ gas:

- problem with contamination with CO₂ and CO present (if produced from carbon sources)

on-demand ‘reforming’

- generate H₂ from local liquid hydrocarbon-based fuel.
- most realistic is methanol – relatively ‘low’ temperatures are needed (200-300°C)

direct use of hydrocarbon-based fuel?

- ‘direct methanol fuel cell’ much investigated.
- anode reaction: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ ($E = 0.046\text{V}$ wrt SHE)
- severe problems with the kinetics of this reaction (much slower than with H₂) and with poisoning of the catalyst.