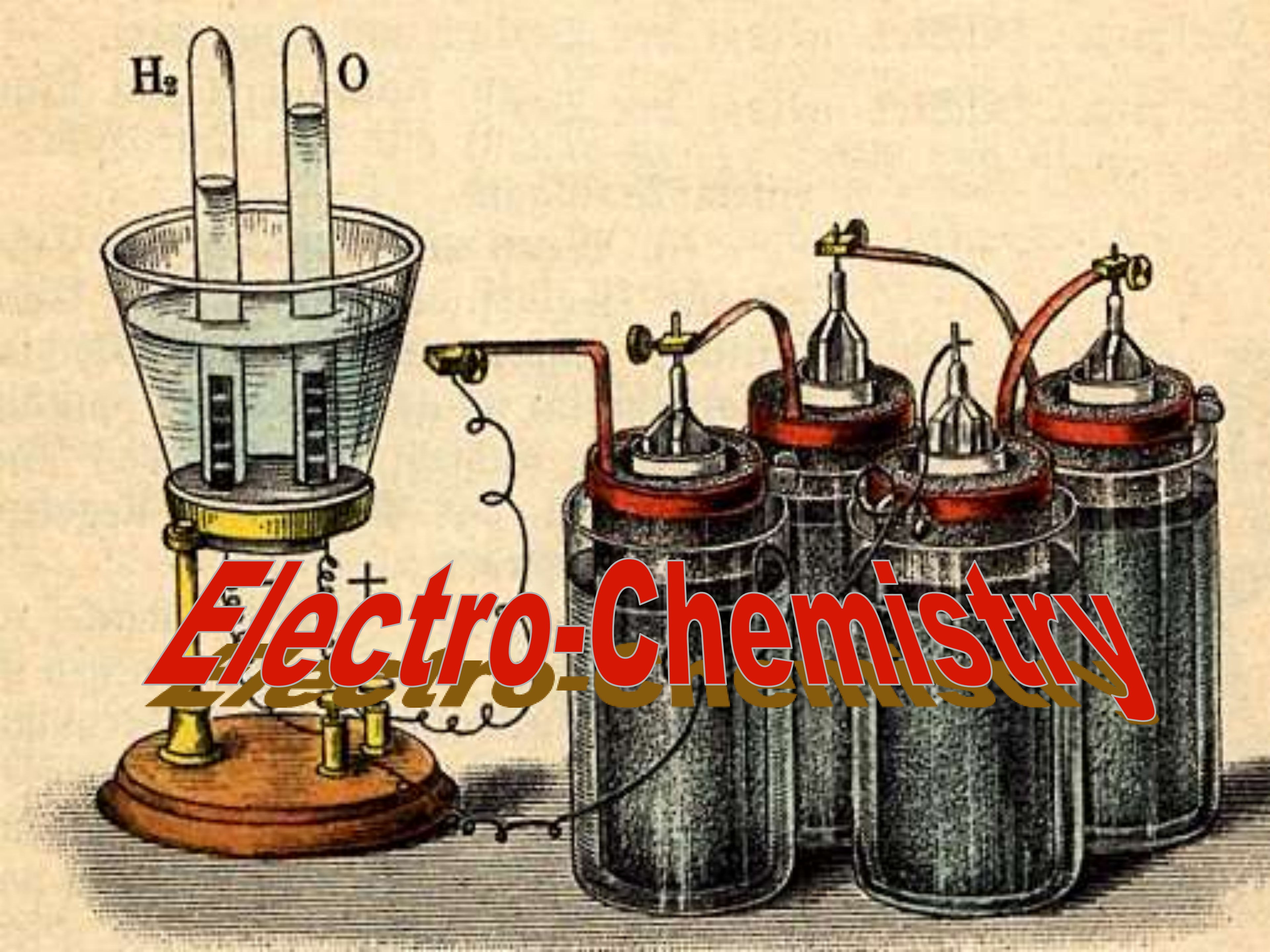
Electro-Chemistry



Agenda for the Week

Energy conservation, conversion, and transformation

- Potential energy, kinetic energy, work, and power
  - Variable force, chemical rearrangement energy (Enthalpy)
  - Examples
- Kinetic energy transfer,
  - Dissipation, randomization and spontaneous processes
  - Examples of thermal motion, Maxwell-Boltzmann distribution
- Transfer of thermal energy (heat)
  - Conduction, convection, radiation (cooling)
  - Internal energy, equivalence of work and heat
  - First Law & Second Law of Thermodynamics, Entropy
- Thermal engines
  - Ideal Carnot processes
  - Real gases/substances

- Electric Phenomena, Electricity and Electromagnetic Power
  - Electrolytic solutions, batteries, fuel cells
  - electromagnetic fields, induction, generators & motors

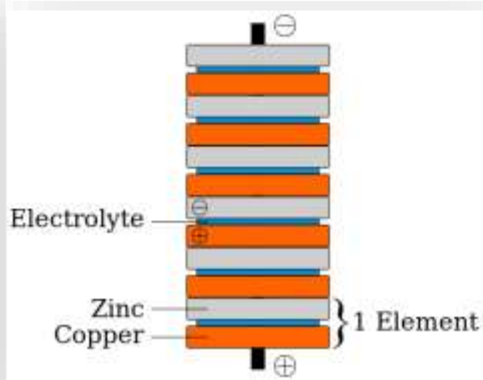
Electricity: Transformative Historical Power

Luigi Galvani (1737-1798)

Alessandro Volta (1745-1827)

Static electricity know since ancient times (Thales, 600 BCE). Created by rubbing of amber with animal fur, Galvani's physiological frog leg experiments. Volta assisted Galvani, disagreed on nature of electricity.
Volta discovered battery ("Voltaic Pile"), announced March 20, 1800 to Royal Society, London.

Replica of Volta's first battery ("Voltaic Pile") Museum Tempio Voltiano.



Schematics of Voltaic Pile

Stack of pairs of alternating copper (or silver) and zinc discs (electrodes) separated by cloth or cardboard soaked in brine (electrolyte). Electro-motive force (emf, unit=Volt) generated by chemical reaction between metals.

Top and bottom contact wires produce spark when touching.

Electric current is due to moving electrons: current increases with height of the stack (number of elements).

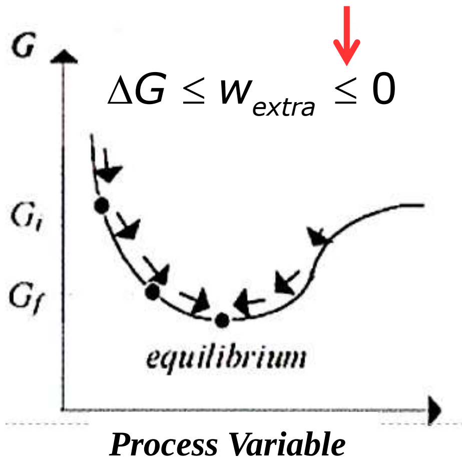
Electrons= constituents of atoms → how to ionize atoms
Electrostatic forces & energies

Thermodynamic Energies & Driving Potentials

Energy gain *per product mole* *in reaction* $\Delta H^0_{rxn} = H^0_{products} - H^0_{reagents}$

$\rightarrow$ *energetically allowed by structural energy difference.*

Does not imply spontaneous process will occur. $\rightarrow \Delta S > 0$?



Helmholtz free energy $A = U - T \cdot S$ *used @ const* V, T

System will do spontaneously : $w_{process} = \Delta A_{process} < 0$

Gibbs free energy $G = H - T \cdot S$ *used @ const* p, T

System will do spontaneously : $w_{process} = \Delta G_{process} < 0$

Maximum "extra" work a system can do, beyond pV : $w_{extra} = \Delta G$

Add additional (electric, solvation) potentials to A,G

Electrical potential Φ, *charge* e

$$A = U - T \cdot S \rightarrow A = (U + e \cdot \Phi) - T \cdot S \quad \text{or}$$

$$G = H - T \cdot S \rightarrow G = (H + e \cdot \Phi) - T \cdot S$$

Thermodynamic Energies & Driving Potentials

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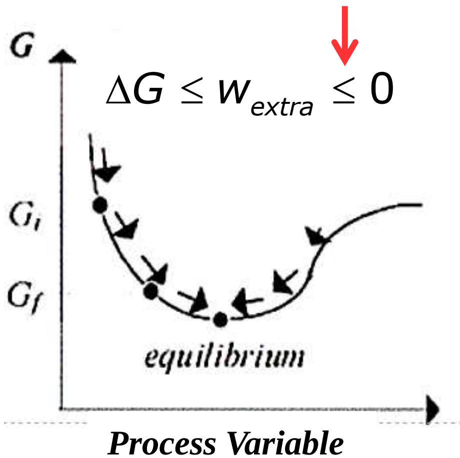

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Maximum "extra" work a system can do, beyond pV : $w_{extra} = \Delta G$

Electrical potential Φ, *charge* $e \rightarrow$ $work = e \cdot d\Phi$

$$dG = d\left(U + e \cdot \Phi + p \cdot V\right) - d\left(T \cdot S\right) \quad (p, T = const)$$

$$dG = dU + d\left(e \cdot \Phi\right) + \cancel{dp \cdot V} + \cancel{p \cdot dV} - \cancel{dT \cdot S} - \cancel{T \cdot dS}$$

$$dU = heat + work\ on\ system = \cancel{T \cdot dS} - \cancel{p \cdot dV}$$

Extra electrical work

$$dG = d\left(e \cdot \Phi\right) = w_{extra}$$

Spontaneous if <0 !

Thermodynamic Potentials: Gibbs Solvation Energy

$$1/2\,H_2(g) + 1/2\,Cl_2(g) \longrightarrow H^+(aq) + Cl^-(aq) \qquad \Delta G^\circ_R = -131.2\ \text{kJ mol}^{-1}$$

$$1/2\,H_2(g) \longrightarrow H(g) \qquad \Delta G^\circ_R = 203.3\ \text{kJ mol}^{-1}$$

$$1/2\,Cl_2(g) \longrightarrow Cl(g) \qquad \Delta G^\circ_R = 105.7\ \text{kJ mol}^{-1}$$

$$H(g) \longrightarrow H^+(g) + e^- \qquad \Delta G^\circ_R = 1312\ \text{kJ mol}^{-1}$$

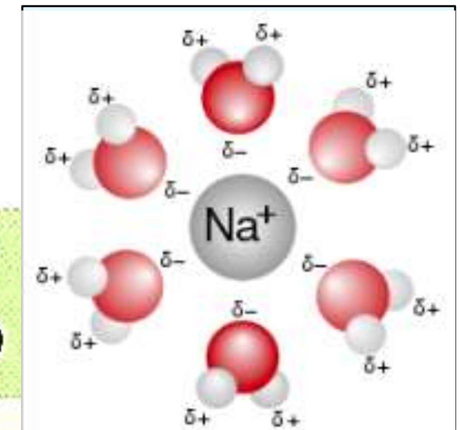
$$Cl(g) + e^- \longrightarrow Cl^-(g) \qquad \Delta G^\circ_R = -349\ \text{kJ mol}^{-1}$$

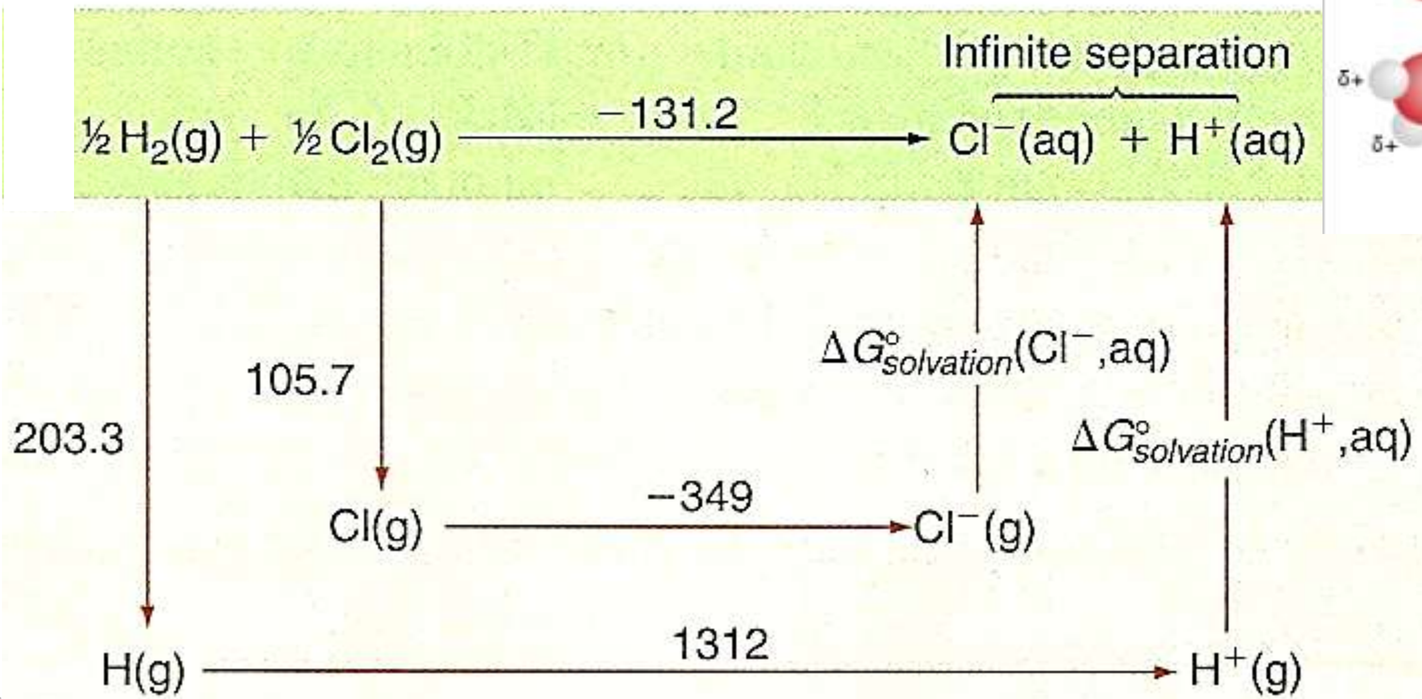
(sum of the four steps above) $= 1272\,kJ/mol$

$$Cl^-(g) \longrightarrow Cl^-(aq) \qquad \Delta G^\circ_R = \Delta G^\circ_{solvation}(Cl^-, aq) = -74.5\,kJ/mol$$

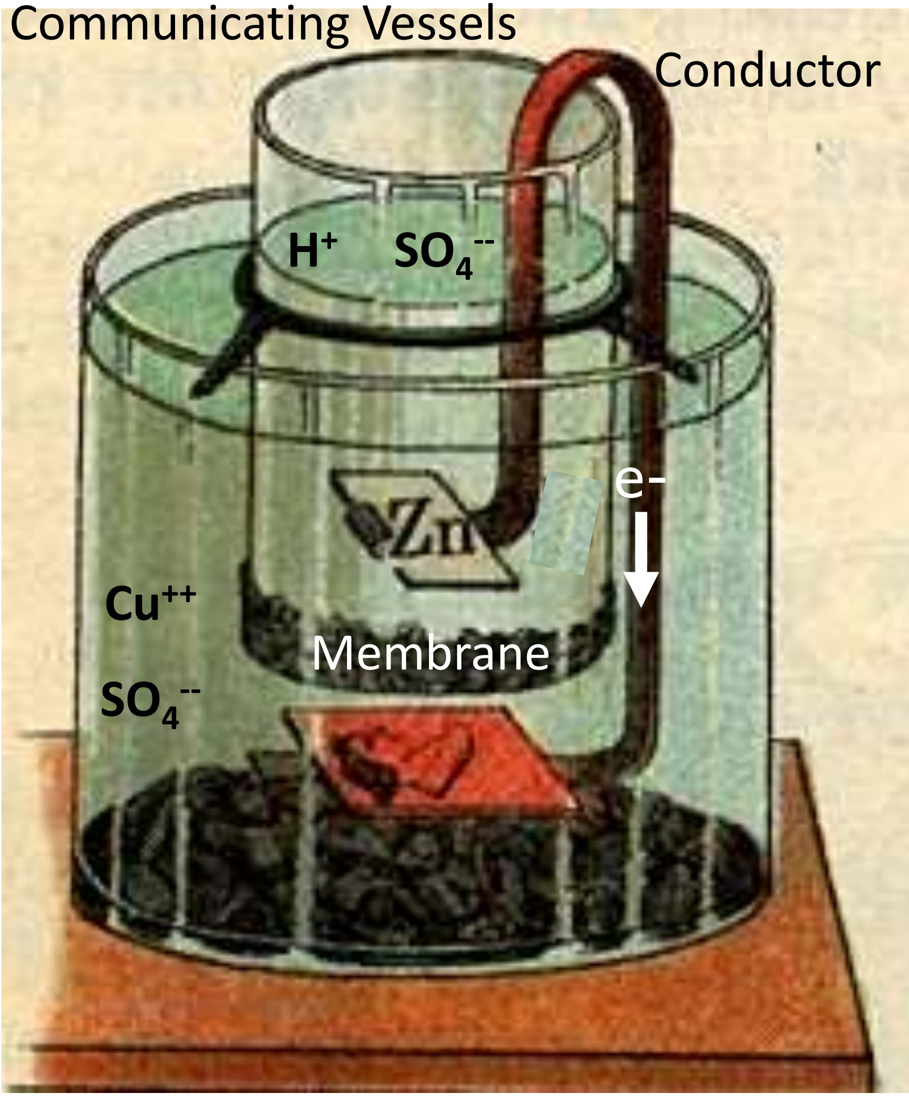
$$H^+(g) \longrightarrow H^+(aq) \qquad \Delta G^\circ_R = \Delta G^\circ_{solvation}(H^+, aq) = -1050\,kJ/mol$$

Chemical elements dissolve as ions in electrolytic solvents like H^+ & Cl^- in H_2O
→ Charged solution





Electrolyte Solutions: Electroplating



Daniell Cell: Zn(s)| Zn^{2+}(aq)| Cu^{2+}(aq)|Cu(s)

Communicating vessels separated by membrane with ion permeability. Electrons have small free path before capture. Electrodes immersed in dissociated electrolyte solute. External conductor guides electrons. → electrostatic potential $\Delta\Phi$

Cu in aqueous $CuSO_4$ solution is deposited on graphite image matrix,

Zn dissolves, Cu precipitates:

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

2 "half reactions"

1) *Oxidation of Zn:*

$$Zn(s) \rightarrow Zn^{2+}(aq)+2e^-$$

2) *Reduction of Cu:*

$$Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$$

$$\Delta G^0 = -213\, kJ/mol$$

Galvanic/Voltaic Cell

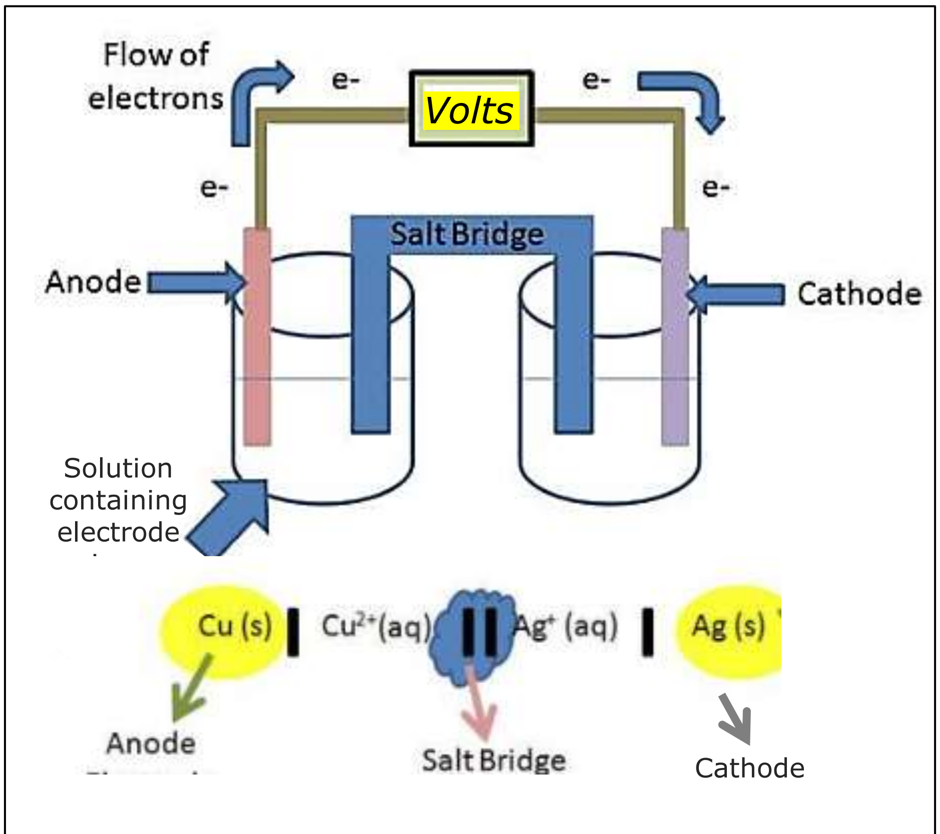
$$RedOx\ reaction:\ Cu(s) + 2Ag^{+} \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

anode cathode

Cu=anode is oxidized
Ag=cathode=reduced

$$\left[Ag^{+} + e^{-} \rightarrow Ag(s)\right]\ x2 \rightarrow\ E^{0}_{Red} = +0.800\ V$$

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-} \rightarrow E^{o}_{Ox} = -0.340\ V$$



$$E^{0}_{Cell} = E^{0}_{Red}(Cathode) - E^{0}_{Red}(Anode)$$
$$= E^{0}_{Red}(Cathode) + E^{0}_{Ox}(Anode)$$

$$\Delta G^{0} = Q \cdot \Delta\Phi_{cell} = n_{e} \cdot F \cdot E^{0}_{cell}$$
$$F = 96485\ Coulomb/mol\ \ Faraday$$

$$E_{cell} = E^{0}_{cell} - \frac{R \cdot T}{n_{e} \cdot F} LogQ$$

Nernst Equation

Reaction quotient
concentrations [ ]
$$= \frac{([\ ]\cdot[\ ])_{prod}}{([\ ]\cdot[\ ])_{reag}}$$

Standard Reduction Potentials

Half-reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^- \rightarrow Au$	1.50
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954

Standard Reduction Potentials

Half-reaction	$\mathscr{E}°$ (V)
$O_2 + 2H_2O + 4e^-$ n $4OH^-$	0.40
$Cu^{2+} + 2e^-$ n Cu	0.34
$Hg_2Cl_2 + 2e^-$ n $2Hg + 2Cl^-$	0.34
$AgCl + e^-$ n $Ag + Cl^-$	0.22
$SO_4^{2-} + 4H^+ + 2e^-$ n $H_2SO_3 + H_2O$	0.20
$Cu^{2+} + e^-$ n Cu^+	0.16
$2H^+ + 2e^-$ n H_2	0.00
$Fe^{3+} + 3e^-$ n Fe	−0.036
$Pb^{2+} + 2e^-$ n Pb	−0.13
$Sn^{2+} + 2e^-$ n Sn	−0.14
$Ni^{2+} + 2e^-$ n Ni	−0.23
$PbSO_4 + 2e^-$ n $Pb + SO_4^{2-}$	−0.35
$Cd^{2+} + 2e^-$ n Cd	−0.40
$Fe^{2+} + 2e^-$ n Fe	−0.44
$Cr^{3+} + e^-$ n Cr^{2+}	−0.50
$Cr^{3+} + 3e^-$ n Cr	−0.73
$Zn^{2+} + 2e^-$ n Zn	−0.76
$2H_2O + 2e^-$ n $H_2 + 2OH^-$	−0.83
$Mn^{2+} + 2e^-$ n Mn	−1.18
$Al^{3+} + 3e^-$ n Al	−1.66
$H_2 + 2e^-$ n $2H^-$	−2.23
$Mg^{2+} + 2e^-$ n Mg	−2.37
$La^{3+} + 3e^-$ n La	−2.37
$Na^+ + e^-$ n Na	−2.71
$Ca^{2+} + 2e^-$ n Ca	−2.76
$Ba^{2+} + 2e^-$ n Ba	−2.90
$K^+ + e^-$ n K	−2.92
$Li^+ + e^-$ n Li	−3.05

Cu-Zn Galvanic Element

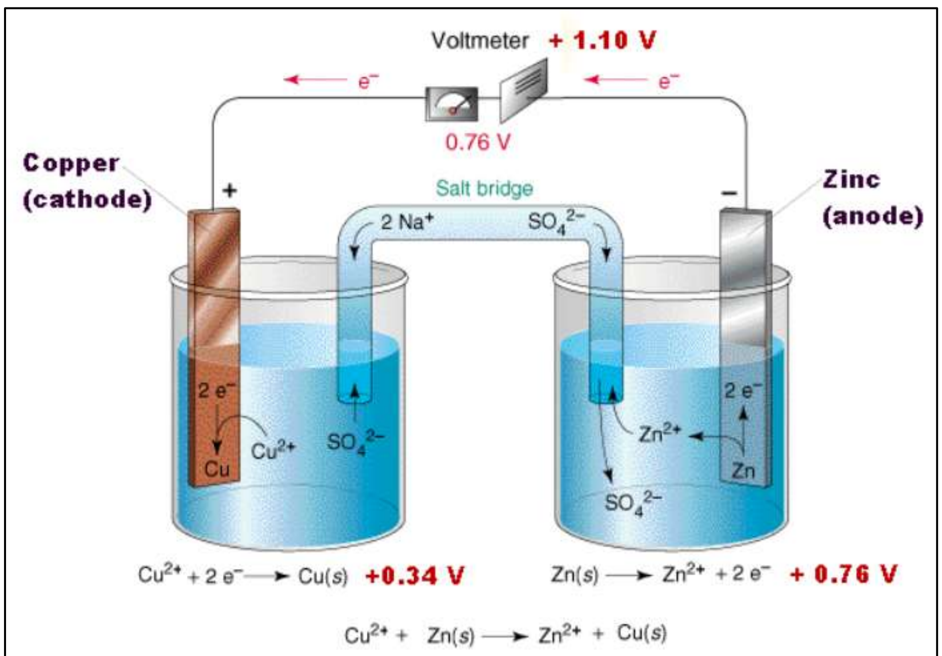
Redox: $Zn(s) + Cu^{2+}(a=1) \rightarrow Zn^{2+}(a=1) + Cu(s)$ $\mathcal{E}^0_{cell}$ = 1.100 V

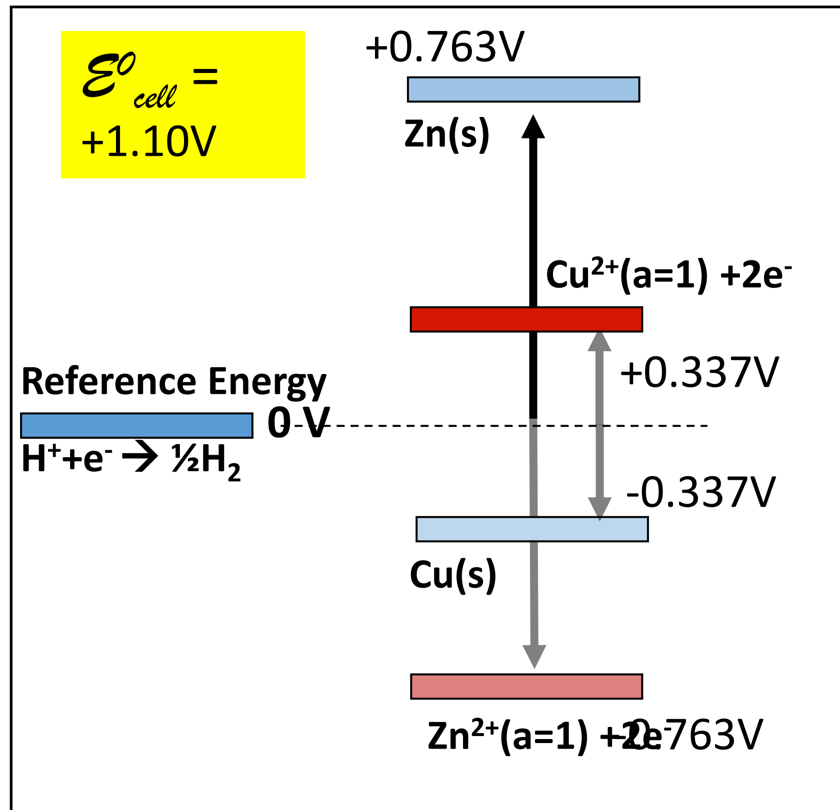
Oxidation: $Zn(s) \rightarrow Zn^{2+}(a=1) + 2e^-$ $\mathcal{E}^0$ =- (-0.763)V

Reduction: $Cu^{2+}(a=1) + 2e^- \rightarrow Cu(s)$ $\mathcal{E}^0$ = +0.337 V

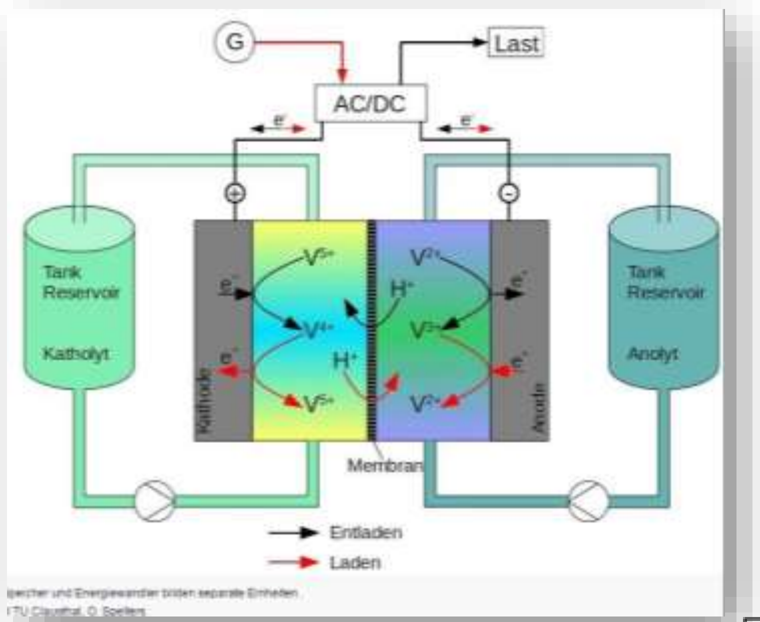
Look up in table the half-cell reduction potentials, subtract:

a=1 → solute standard





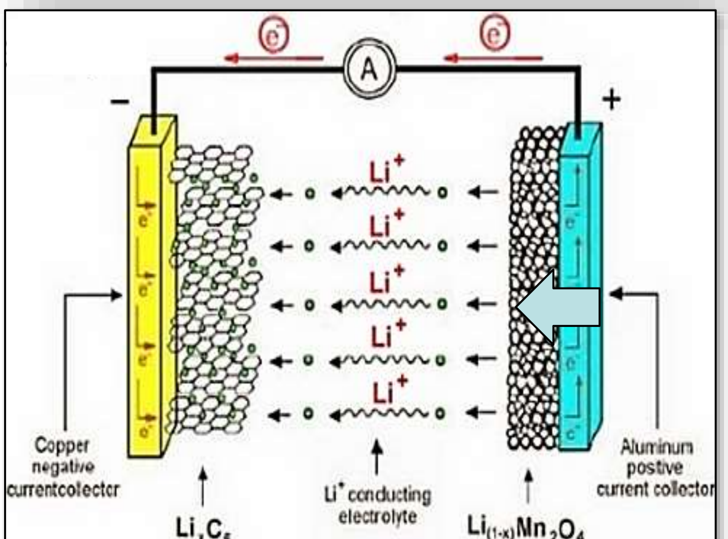
Electron and Ion Transfer Batteries



Redox-Flow Batteries: electrochemical cell, where the ionic solutions (electrolytes) are stored in external tanks and can be fed into the active cell to generate electricity.

Solid-State Batteries

Solid state batteries R&D: rapid diffusion of ions, both in the electrodes and through the electrolytes.



Li-Ion Batteries : Li ions from a transition metal oxide move to a carbon electrode, traverse a polymer electrolyte. No water!

Li – Ion Battery (Discharge)

$$\text{Negative}\quad Li_xC_6 \rightarrow C_6 + xLi^+ + xe^-$$

$$\text{Positive}\quad Li_{1-x}CoO_2 + xe^- + xLi^+ \rightarrow LiCoO_2$$

$$\text{Total}\quad Li_xC_6 + Li_{1-x}CoO_2 \rightarrow C_6 + LiCoO_2$$

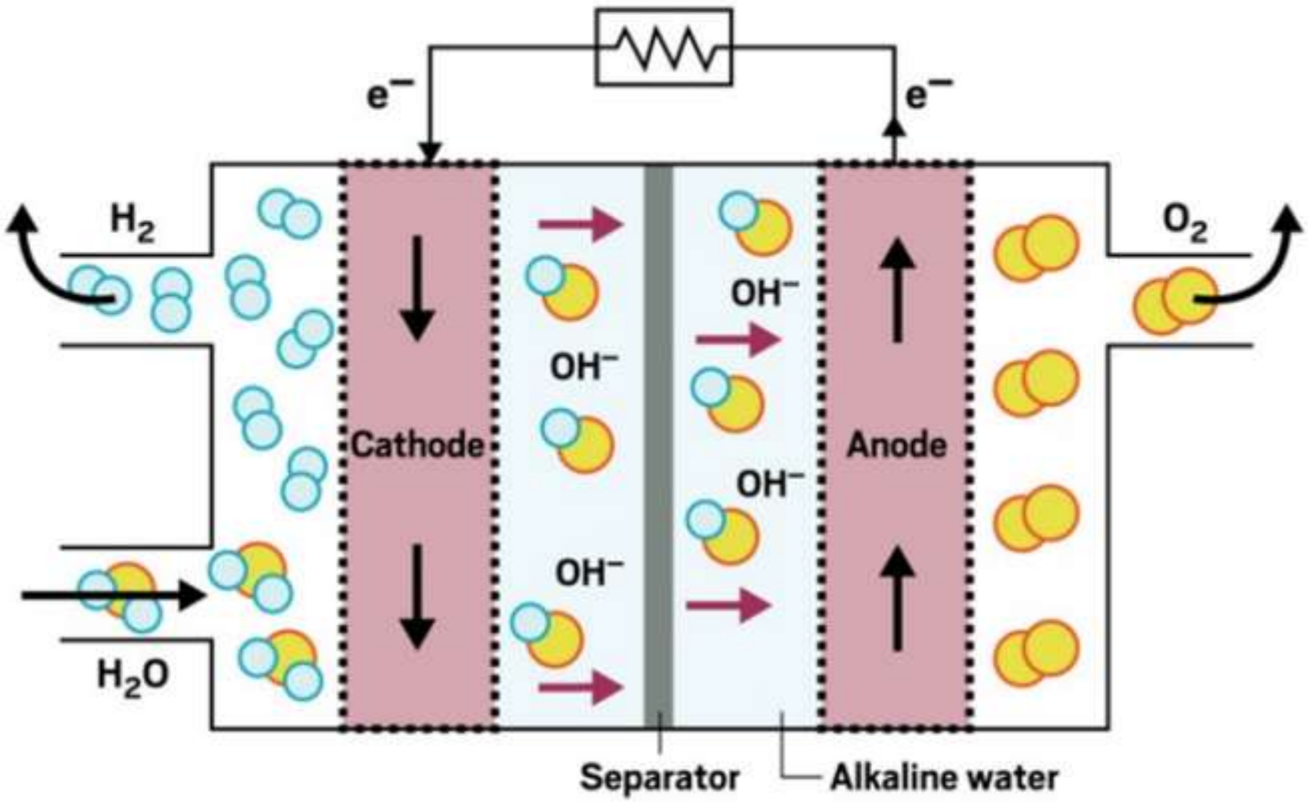
Porous membrane, organic electrolyte

No water!

12

Work-ower-Electricity

Electrolyzer: Alkaline Hydrolysis Cell



Cathode reaction

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode reaction

$2OH^- \rightarrow H_2O + ½O_2 + 2e^-$

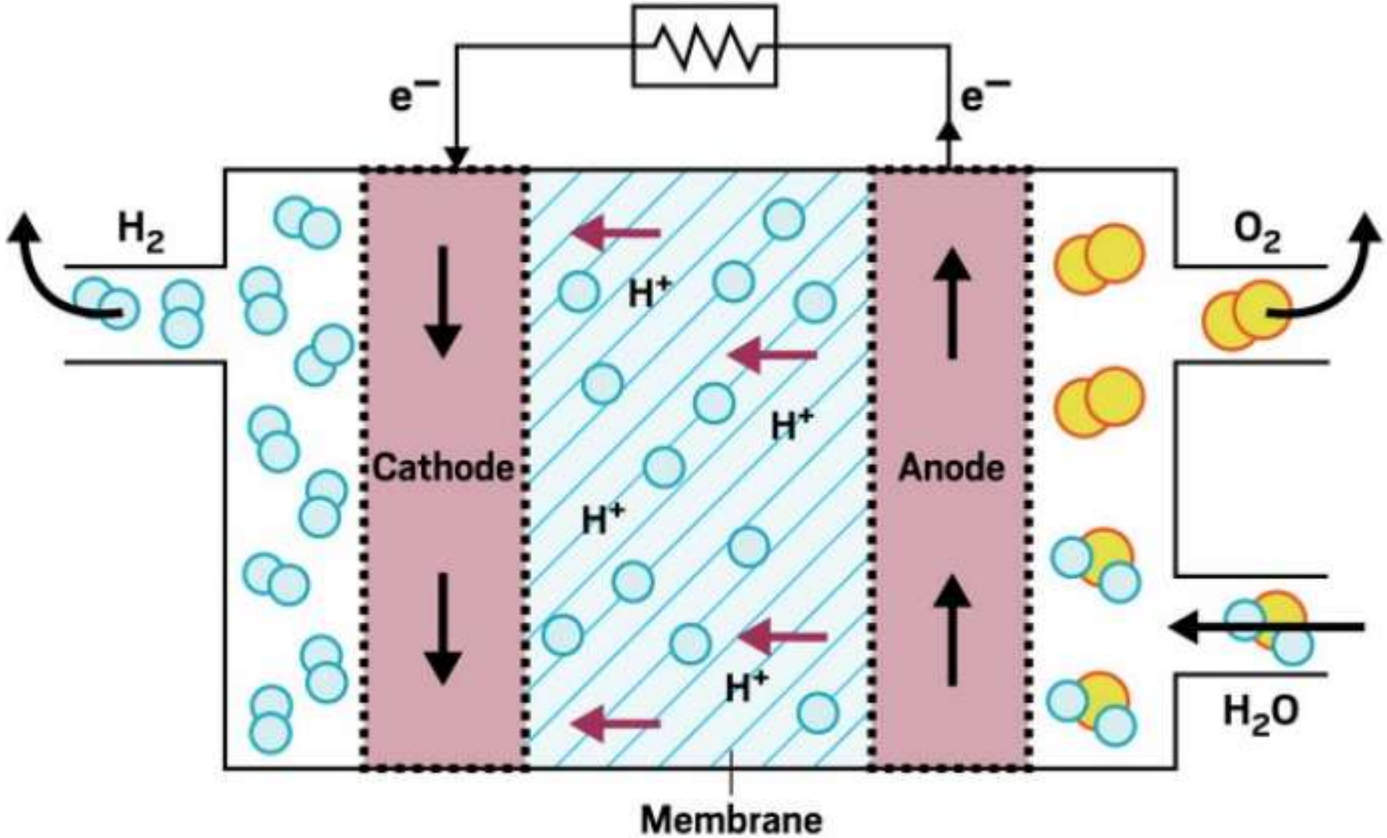
Pro: Strong track record

Con: Large, hazardous equipment

Research need: Increase of hydrogen output pressure

Best use case: Large hydrogen-demand centers with steady power

Proton Exchange Membrane (PEM) Hydrolysis Cell



Cathode reaction

$2H^+ + 2e^- \rightarrow H_2$

Anode reaction

$H_2O \rightarrow 2H^+ + ½O_2 + 2e^-$

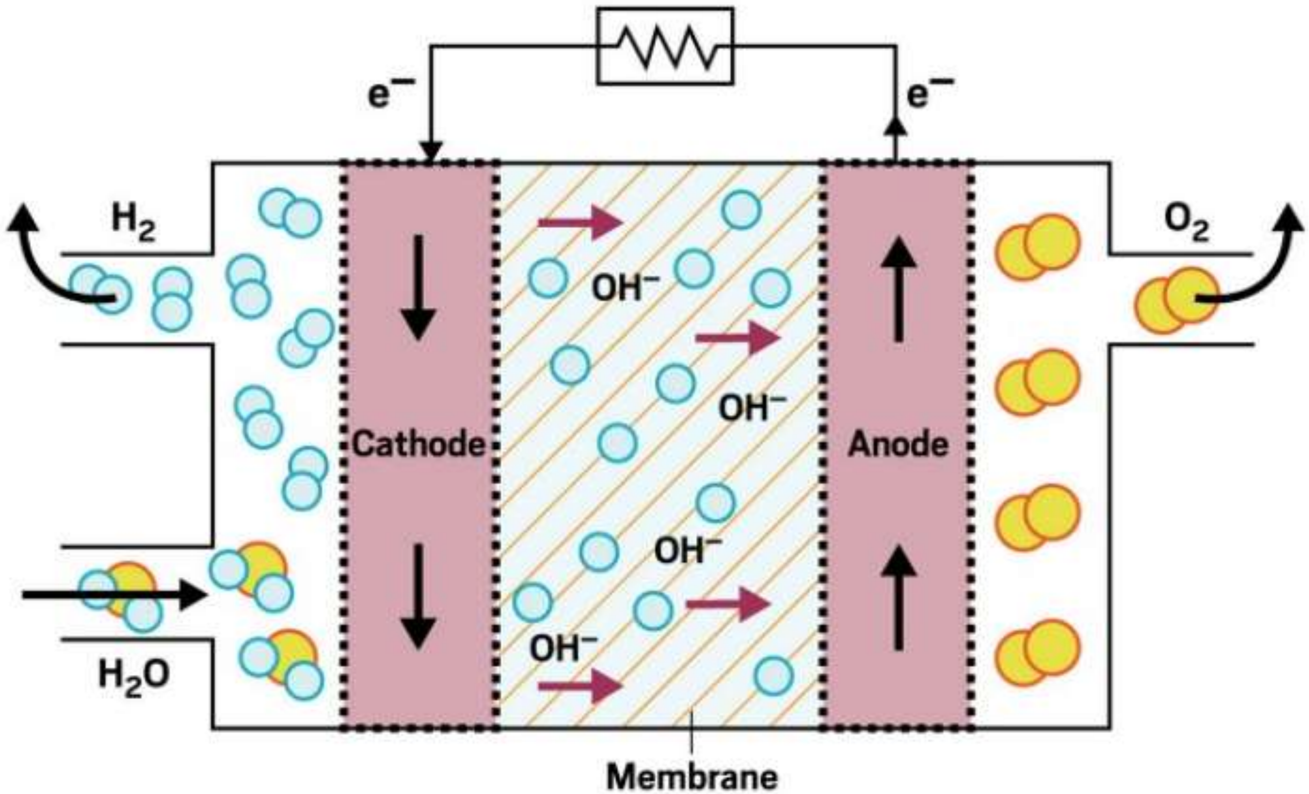
Pro: Flexible size and throughput

Con: Limited availability at large scale

Research need: Reduction or elimination of iridium and platinum in electrodes

Best use case: Tight quarters or facilities where it can be paired with renewables

Anion Exchange Membrane (PEM) Hydrolysis Cell



Cathode reaction

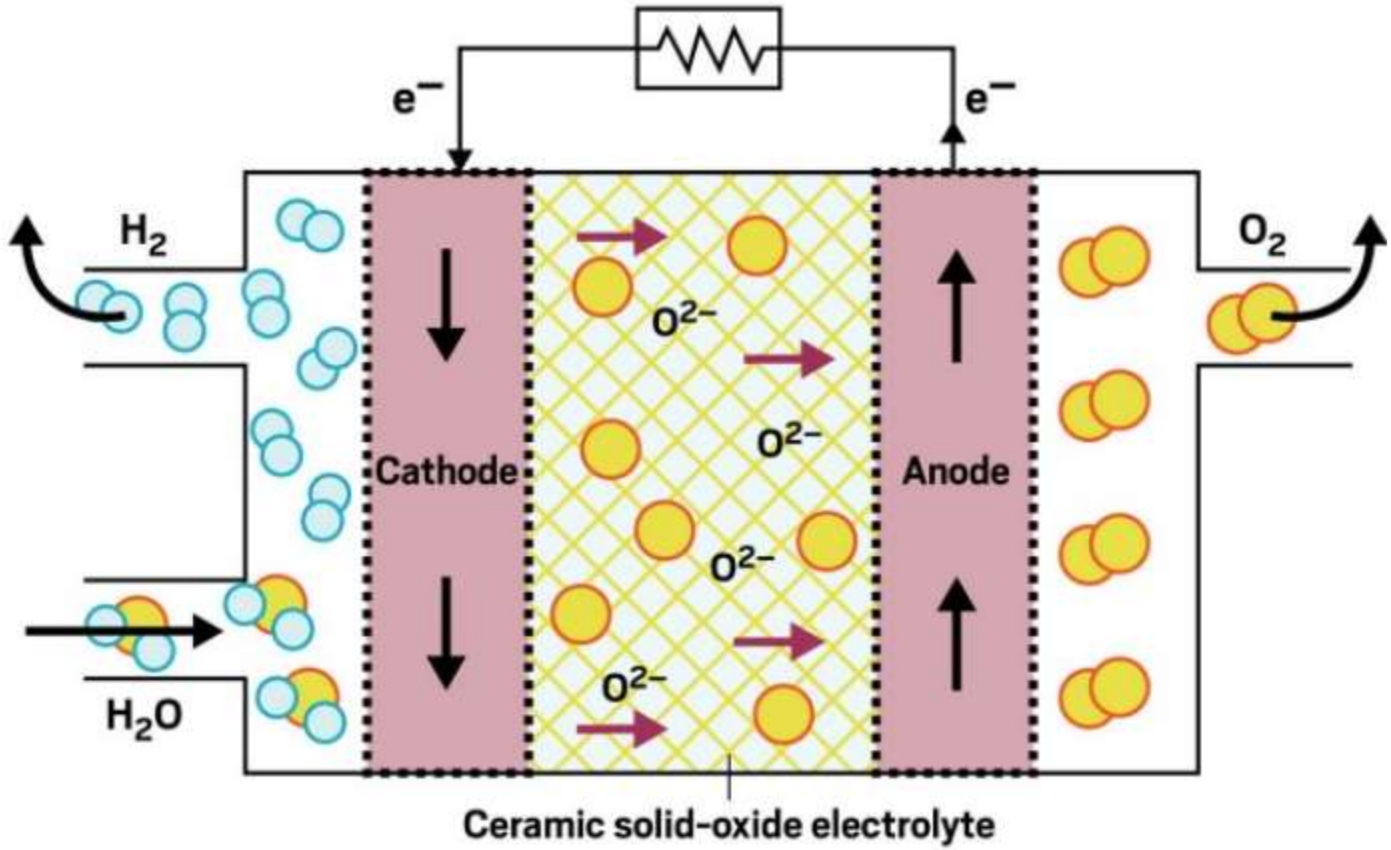
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode reaction

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

Pro: Flexibility without precious metals
Con: Short cell lifetime
Research need: Membrane materials that can withstand alkaline conditions
Best use case: Small, mobile fueling stations

Solid-Oxide Electrolysis Cell



Cathode reaction

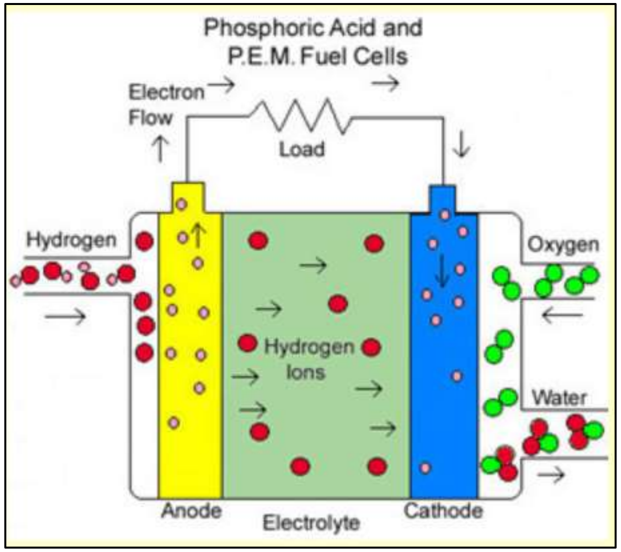
$2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-}$

Anode reaction

$2O^{2-} \rightarrow O_2 + 4e^-$

Pro: Electrical efficiencies of 90–100%
Con: Untested at commercial scale
Research need: Improvements to current density and cell lifetime
Best use case: Industrial or nuclear sites with waste heat

Hydrogen Fuel Cells



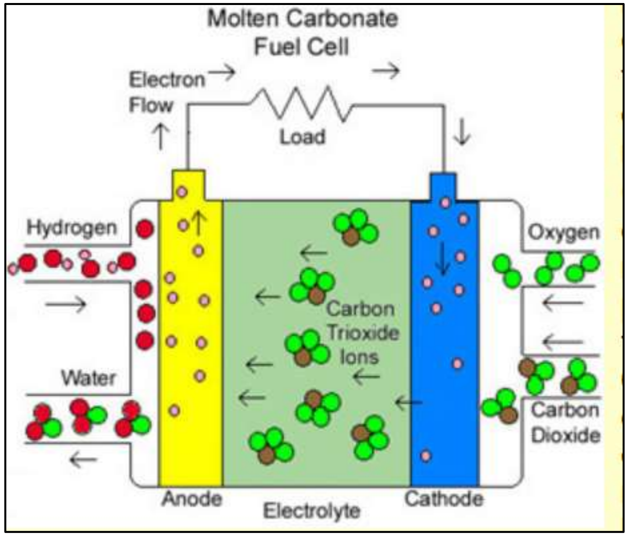
- Direct conversion of chemical fuels into electricity
- Clean & high efficiency energy production
- Quiet operation, compact size, scalable technology

  P=100W – MW, T= 200^0C-1000^0C, ε=30-80%

- Wide range of applications: stationary & mobile

But need catalyst (Pt, Ni,..)

PEM: flexible polymer electrolyte sheet, 80^0C, e=40-50%, 50-250kW
Alkali: electrolyte KOH_{aq}. ε= 70 %
@150 - 200 degrees C, output 300 W - 5 kW.
MCFC: XCO_3, 650^0C, ε= 60-80 %



- Polymer electrolyte membrane fuel cells
- Direct methanol fuel cells
- Alkaline fuel cells
- Phosphoric acid fuel cells
- Molten carbonate fuel cells
- Solid oxide fuel cells
- Reversible fuel cells, hydrolyzer

Fuel cells are classified by electrolyte type.

Fuel Cell type	PEMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Polymer electrolyte	$KOH_{(aq)}$	H_3PO_4 (conc)	Li & CO_3^{2-} salt	YSZ
Mobile ion	H^+	OH^-	O^{2-}	CO_3^{2-}	O^{2-}
Efficiency	34 - 45%	45-50%	34 - 45%	45 - 55%	45 - 55%
Operating temperature (° C)	50 - 120	80 - 100	175 - 220	600 - 650	800 - 1000

low to medium operating temp.	high operating temp.

PEMFC = Polymer Electrolyte Membrane Fuel Cell, AFC = Alkaline Fuel Cell, PAFC = Phosphoric Acid Fuel Cell, MCFC = Molten Carbonated Fuel Cell, SOFC = Solid Oxide Fuel Cell

Design of Automotive Fuel Cell

Specs

- mass: 1000 kg
- FC mass: < 300 kg
- peak power: 100 kW (134 hp)
- cruise power: 30 kW
- range per load: 400 km

Assumptions

- 9.0 g H_2 / km
- max current density: 1.2 A/cm^2
- max voltage (zero current): 1.0 V
- voltage at max power: 0.55 V
- 500 atm storage tank (7350 psi)

Determine:

- number of cells
- mass of FC stack
- size of storage tank (compressed H_2)
- heat to be removed at peak power

M. Anthamatten, UR CHE

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  Variable force, chemical rearrangement energy (Enthalpy)
  Examples
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  Dissipation, randomization and spontaneous processes
  Examples of thermal motion, Maxwell-Boltzmann distribution
- Transfer of thermal energy (heat)
  Conduction, convection, radiation (cooling)
  Internal energy, equivalence of work and heat
  First Law & Second Law of Thermodynamics, Entropy
- Thermal engines
  Ideal Carnot processes
  Real gases/substances

- Electric Phenomena, Electricity and Electromagnetic Power
  Electrolytic solutions, batteries, fuel cells
  electromagnetic fields, induction, generators & motors