17

CHAPTER

ELECTROCHEMISTRY

→ Interconversion of chemical and electrical energy through oxidation–reduction reactions.

*The exam will not include these contents s.

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→ Perhaps the most powerful characteristic of electrochemistry is its ability to control reversible chemical reactions by supplying or extracting electrical energy

17.1 ELECTROCHEMICAL CELLS

◆ Electrochemical reactions interconvert chemical and electrical energy through the oxidation (anode) and reduction (cathode) half reactions occurring on the surfaces of electrodes.

- **Galvanic cell** (or Voltaic cell):

  ~ Spontaneous chemical reaction ($\Delta G < 0$) → producing electricity

- **Electrolytic cell**

  ~ External input of electricity

  → driving nonspontaneous chemical reactions ($\Delta G > 0$)

◆ Galvanic Cells

Redox reaction in the above cell:

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

cathode (+) reduction half reaction: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$

anode (–) oxidation half reaction: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^{-}$

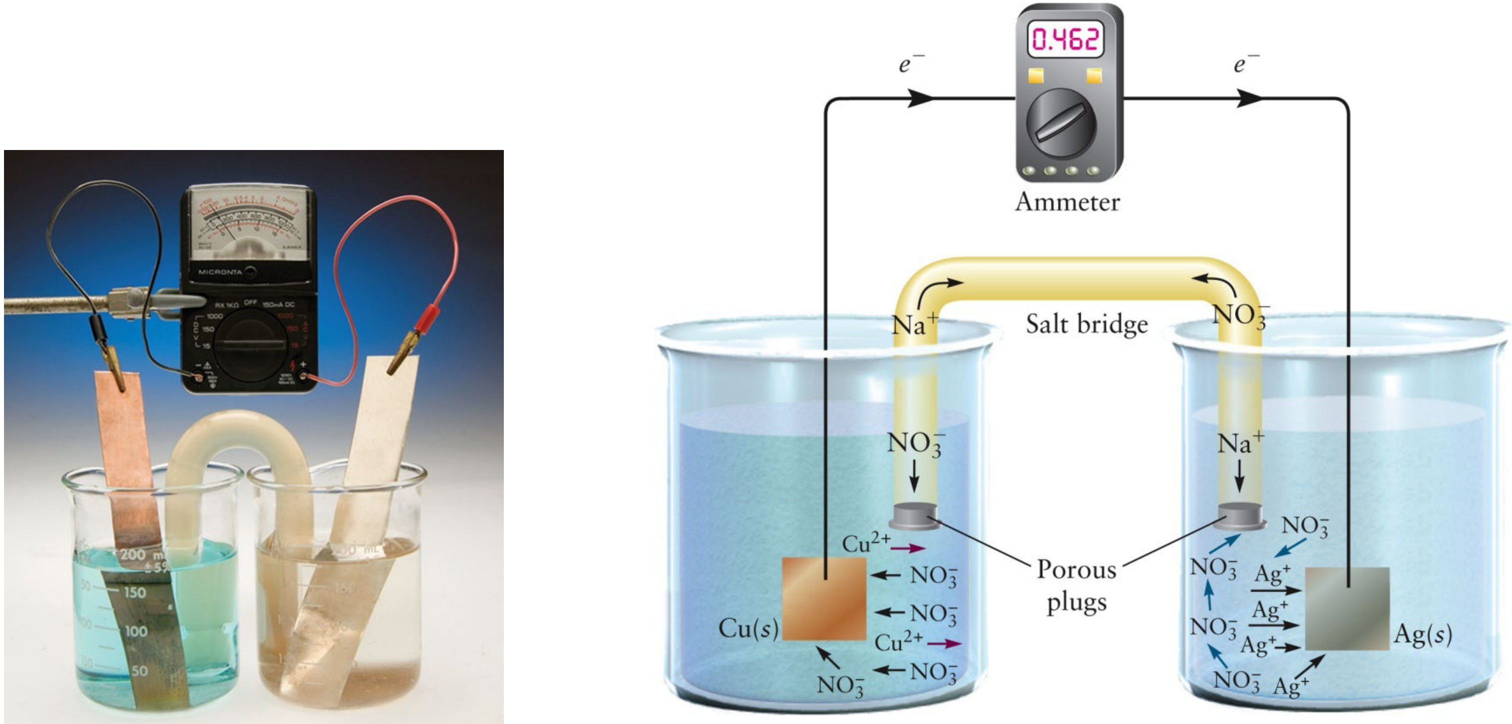
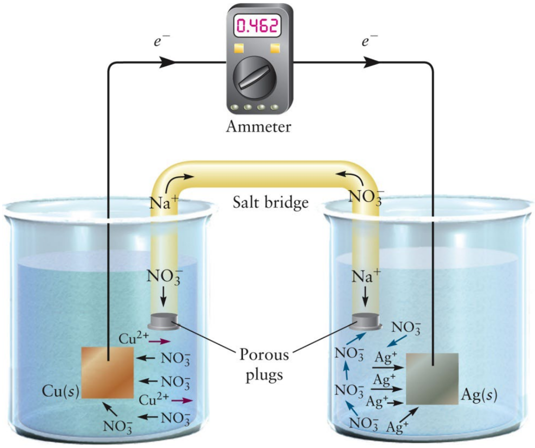


Fig. 17.1 & 2 Cu (anode) – Ag (cathode) in a Galvanic cell.

→ Electrons being transferred in a galvanic cell reaction spontaneously move from a region of higher electrostatic potential energy on the anode to a region of lower electrostatic potential energy on the cathode, in the same way that water flows downhill.

➢ Line Notation:



$\mathrm{Cu}(s)\,|\,\mathrm{Cu(NO_3)_2}(aq)\,||\,\mathrm{AgNO_3}(aq)\,|\,\mathrm{Ag}(s)$

or $\mathrm{Cu}\,|\,\mathrm{Cu^{2+}}\,||\,\mathrm{Ag^{+}}\,|\,\mathrm{Ag}$

| phase boundary, || salt bridge

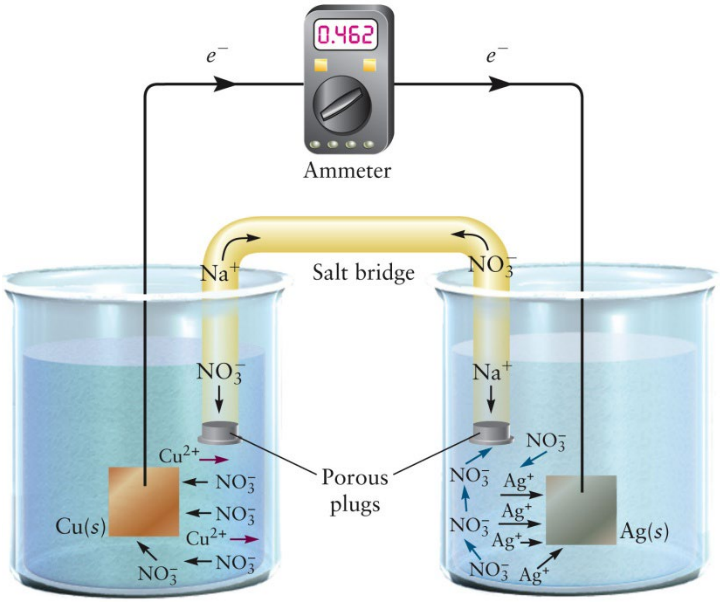
left: **anode** (negative), right: **cathode** (positive)

Commas are used to indicate the presence of different components in the same phase: $|\,\mathrm{H^+,Cl^-}\,|$

Half cells are physically separated but connected by a **salt bridge**.

~ Allows ion migration in solution but prevents extensive mixing of electrolytes

◆ Electrolytic Cells



Galvanic cell

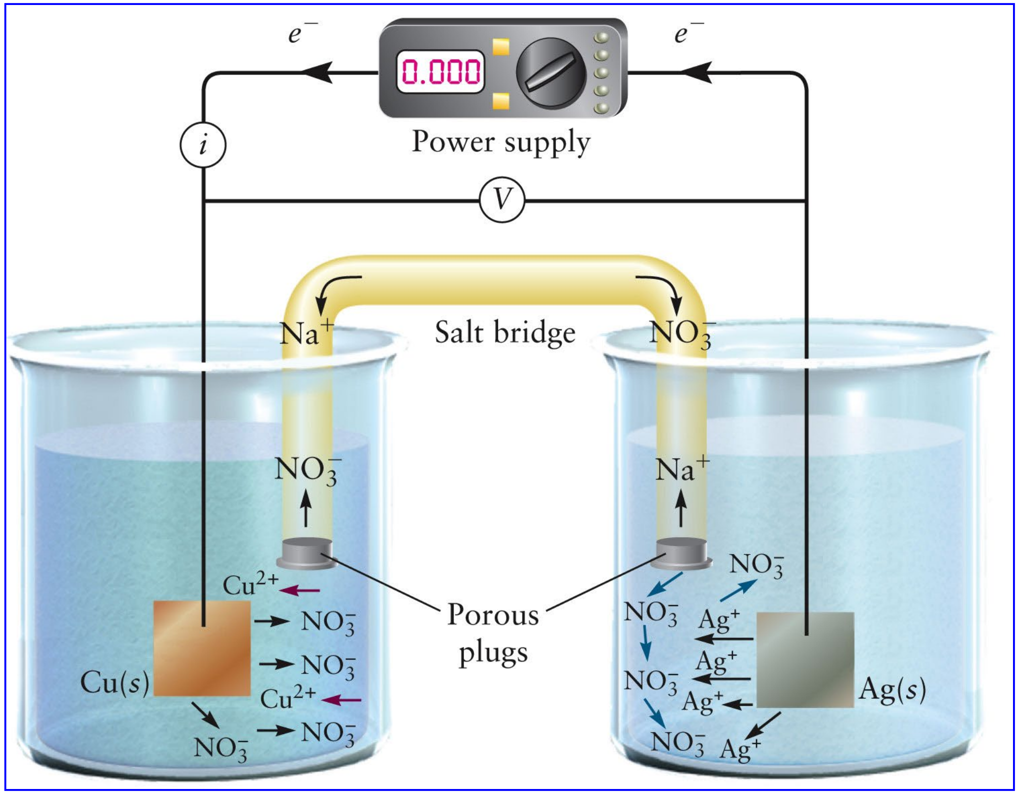


Fig. 17.3 A copper-silver **electrolytic cell**.

➢ Electrolytic cell:

Reversing the direction of a spontaneous process requires the application of an external potential (a power supply or a battery).

- The Coulomb (C) is defined as the total charge transferred by 1 A of current flowing for 1 s: 1 C = (1 A)(1 s)

- Total charge transferred by *i* A of current in *t* seconds

  = Total charge carried by *n* moles of electrons

$$Q = it = nF$$

n: number of moles of electrons

- Equivalent mass in a redox reaction: $W_{eq} = M / n'$

  M: molar mass

  n': number of moles of electrons transferred per mole of substance in the corresponding redox reaction

Ex. Zinc-silver Galvanic cell

(cathode) $Ag^+(aq) + 1e^- \rightarrow Ag(s)$ $W_{eq}(Ag) = (107.8)/1 = 107.8\ \mathrm{g\ mol^{-1}}$

(anode) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $W_{eq}(Zn) = (65.38)/2 = 32.69\ \mathrm{g\ mol^{-1}}$

→ summarize the stoichiometry of electrochemical processes

◆ Faraday's Law (1833)

1. The mass (W) of a substance that is produced or consumed in an electrochemical reaction is proportional to the quantity of electric charge passed. $W \propto Q \propto n$

2. Equivalent masses (W_{eq}) of different substances are produced or consumed in electrochemical reactions by a given amount of electric charge passed. $W \propto W_{eq} \propto (n')^{-1}$

1+ 2 $\boldsymbol{W = nW_{eq}}$

Let's express Faraday's laws in modern terms and relate the changes in masses observed to the charge that flows in electrochemical experiments. The charge e on a single electron (expressed in coulombs) has been very accurately determined to be

$$e = 1.60217646 \times 10^{-19} \text{ C}$$

so the charge of one mole of electrons is equal to

$$\begin{aligned} Q &= (6.0221420 \times 10^{23} \text{ mol}^{-1})(1.60217646 \times 10^{-19} \text{ C}) \\ &= 96{,}485.34 \text{ C} \end{aligned}$$

which is an enormously large quantity of charge, as shown in the chapter opening photograph on page 763. The charge of one mole of electrons has been given a special name and symbol, the **Faraday constant,**

$$F = 96{,}485.34 \text{ C mol}^{-1}$$

EXAMPLE 17.2 Cu-(AgCl/Ag) Electrolytic cell. 0.500 A current for 101 min. Mass of Cu dissolved and the mass of Ag deposited?

$$n = \frac{it}{F} = \frac{\left(0.500\ \mathrm{C\ s^{-1}}\right)\left(6.06\times10^{3}\ \mathrm{s}\right)}{96,485\ \mathrm{C\ mol^{-1}}} = 3.14\times10^{-2}\ \mathrm{mol}\ e^{-}$$

Half-reactions:

(cathode) $\mathrm{AgCl}(s) + 1e^{-} \rightarrow \mathrm{Ag}(s) + \mathrm{Cl}^{-}(aq)$ $(n' = 1)$

$W_{eq}(\mathrm{Ag}) = (107.8)/1 = 107.8\ \mathrm{g\ mol^{-1}}$

(anode) $\mathrm{Cu}(s) \rightarrow \mathrm{Cu}^{2+}(aq) + 2e^{-}$ $(n' = 2)$

$W_{eq}(\mathrm{Cu}) = (63.55)/2 = 31.78\ \mathrm{g\ mol^{-1}}$

$W(\mathrm{Ag}) = nW_{eq}(\mathrm{Ag}) = (3.14 \times 10^{-2}\ \mathrm{mol})(107.8\ \mathrm{g\ mol^{-1}}) = 3.38\ \mathrm{g}$

$W(\mathrm{Cu}) = nW_{eq}(\mathrm{Cu}) = (3.14 \times 10^{-2}\ \mathrm{mol})(31.78\ \mathrm{g\ mol^{-1}}) = 0.998\ \mathrm{g}$

→ The change in the potential energy of the electrons is defined as the electrical work

17.2 CELL POTENTIALS AND THE GIBBS FREE ENERGY

➢ Electrical work, w_{elec}

~ Change in the potential energy, ΔE_P (in joules), associated with the transfer of Q coulombs of negative charge through a potential difference ΔE (in volts) given by

$$w_{elec} = \Delta E_P = -Q\,\Delta E \equiv -QE_{cell} \qquad 1\text{ C}\times 1\text{ V} = 1\text{ J}$$

$$= -Q\,(E_{cathode} - E_{anode}) = -itE_{cell}$$

$E_{cell} > 0$ for a galvanic cell

(electrons from more negative E(anode) to positive E(cathode))

~ work done **by** the cell producing electrical work

$E_{cell} < 0$ for an electrolytic cell

~ work done **on** the cell by an external power supply

EXAMPLE 17.3

A 6.00 V battery delivers a steady current of 1.25 A for a period of 1.50 hours. Calculate the total charge Q, in coulombs, that passes through the circuit and the electrical work done *by* the battery.

Solution

Recalling that $1\ \mathrm{A} = 1\ \mathrm{C\ s^{-1}}$ and $1\ \mathrm{V} = 1\ \mathrm{J\ C^{-1}}$ we calculate the total charge as

$$Q = it = (1.25\ \mathrm{C\ s^{-1}})(1.50\ \mathrm{hr})(3600\ \mathrm{s\ hr^{-1}}) = 6750\ \mathrm{C}$$

and the electrical work as

$$w_{\mathrm{elec}} = -QE_{\mathrm{cell}} = -(6750\ \mathrm{C})(6.00\ \mathrm{J\ C^{-1}}) = -4.05 \times 10^4\ \mathrm{J}$$

This is the work done *on* the battery, so the work done *by* the battery is the negative of this quantity, or +40.5 kJ.

➢ Maximum electrical work utilizing a spontaneous reaction

$$\boxed{w_{\text{elec,rev}} = w_{\text{elec,max}} = \Delta G \quad (\text{at constant } T \text{ and } P)}$$

(Derivation)

$$G = H - TS = E + PV - TS$$

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad (\text{const } T \text{ and } P)$$

$$= q + w_{\text{elec}} - P_{\text{ext}}\,\Delta V + P\Delta V - T\Delta S$$

$$(E = q + w, \quad w = w_{\text{elec}} - P_{\text{ext}}\,\Delta V)$$

For a **reversible** process, $P_{\text{ext}} = P$ and $q_{\text{rev}} = T\Delta S$.

$$w_{\text{elec,rev}} = \Delta G$$

If *n moles of electrons* pass through the external circuit

of a **reversible** galvanic cell,

$$\boxed{w_{\text{elec,rev}} = \Delta G = -QE_{\text{cell}} = -nFE_{\text{cell}} \qquad (\text{reversible})}$$

EXAMPLE 17.4

A $Zn^{2+}|Zn$ half-cell is connected to a $Cu^{2+}|Cu$ half-cell to make a galvanic cell, in which $[Zn^{2+}] = [Cu^{2+}] = 1.00$ M. The cell potential at 25°C is measured to be $E^{o}_{cell} = 1.10$ V, which corresponds to the overall cell reaction

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

Calculate ΔG^{o} for this reaction under the given conditions.

Solution

$$\begin{aligned}\Delta G^{o} &= -nFE^{o}_{cell} = -(2.00 \text{ mol})(96{,}485 \text{ C mol}^{-1})(1.10 \text{ V}) \\ &= -2.12 \times 10^{5} \text{ J} = -212 \text{ kJ}\end{aligned}$$

◆ Standard Reduction Potentials

➢ Standard hydrogen electrode (SHE)

~ Primary reference electrode

$2\ H_3O^+(aq) + 2\ e^-$

$\rightarrow\ H_2(g) + 2\ H_2O(l)$, $E^o(\text{SHE}) = 0.00\text{ V}$

$$\left[H_3O^+\right] = 1\text{ M}\ \ (\text{or } a_{H_3O^+} = 1)$$

$$p_{H_2} = 1\text{ atm}\ \ (\text{or } a_{H_2} = 1)$$

➢ Standard cell potentials of half reactions are measured with reference to the SHE.

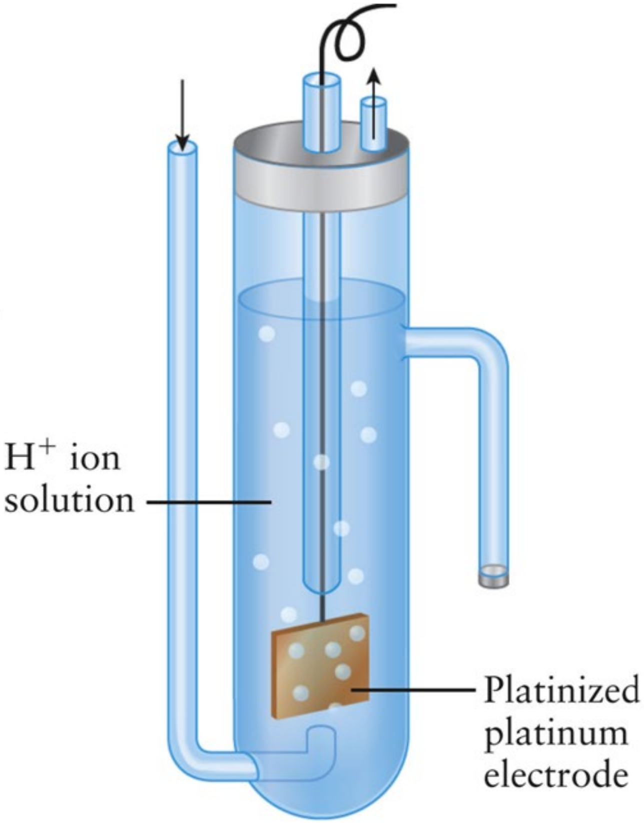


Fig. 17.4 Schematic of a standard hydrogen electrode

❖ Standard cell potential of a Galvanic cell

$$\boxed{E^o_{\text{cell}} = E^o_{\text{cathode}} - E^o_{\text{anode}}}$$

→ Half-reactions with positive potentials, with respect to SHE, proceed as reductions

→ The cell potential is simply the difference in the potentials of the two half-reactions (intensive property)

Ex. 2 Calculate the standard cell potential for the $Cu|Cu^{2+}||Ag^{+}|Ag$ cell.

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s), \qquad E^{o} = 0.799\ V$$

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

Cathode: $2\,Ag^{+}(aq) + 2\,e^{-} \rightarrow 2\,Ag(s)$

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

**Overall: $2\,Ag^{+}(aq) + Cu(s) \rightarrow 2\,Ag(s) + Cu^{2+}(aq)$

- Cell potential: $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = 0.799\ V - (0.34\ V) = 0.459\ V$

*The standard cell potential is an intensive property.

- Gibbs free energy change (or work done on the system)

$$\Delta G^{o} = -nFE^{o}_{cell} = (-2\ mol)(96,500\ C\ mol^{-1})(0.459\ V) = -0.886\ kJ$$

A work of -0.886 kJ was done on the system.

A work of +0.886 kJ was done by the system.

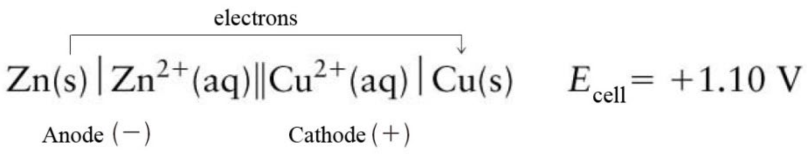
**Corrected from the typo in the textbook (p774)

TABLE 13.1 Standard Potentials at 25°C*

Species	Reduction half-reaction	*E*° (V)
Oxidized form is strongly oxidizing		
F_2/F^-	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.87
Au^+/Au	$Au^+(aq) + e^- \longrightarrow Au(s)$	+1.69
Ce^{4+}/Ce^{3+}	$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-,H^+/Mn^{2+},H_2O$	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
Cl_2/Cl^-	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.36
$Cr_2O_7^{2-},H^+/Cr^{3+},H_2O$	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33
$O_2,H^+/H_2O$	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.23; +0.82 at pH = 7
Br_2/Br^-	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.09
$NO_3^-,H^+/NO,H_2O$	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$	+0.96
Ag^+/Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Fe^{3+}/Fe^{2+}	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
I_2/I^-	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.54
$O_2,H_2O/OH^-$	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$	+0.40; +0.82 at pH = 7
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.34
$AgCl/Ag,Cl^-$	$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
H^+/H_2	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0, by definition
Fe^{3+}/Fe	$Fe^{3+}(aq) + 3\,e^- \longrightarrow Fe(s)$	−0.04
$O_2,H_2O/HO_2^-,OH^-$	$O_2(g) + H_2O(l) + 2\,e^- \longrightarrow HO_2^-(aq) + OH^-(aq)$	−0.08
Pb^{2+}/Pb	$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.13
Sn^{2+}/Sn	$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.14
Fe^{2+}/Fe	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.44
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.76
$H_2O/H_2,OH^-$	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83; −0.42 at pH = 7
Al^{3+}/Al	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.66
Mg^{2+}/Mg	$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.36
Na^+/Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
K^+/K	$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
Li^+/Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05
Reduced form is strongly reducing		

*For a more extensive table, see Appendix 2B.

- **Positive cell potential**



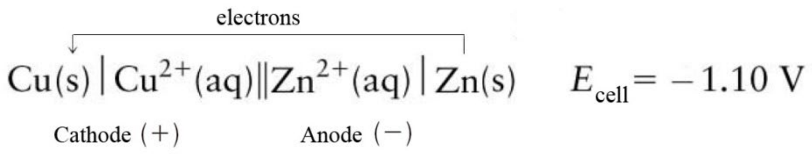
$\mathrm{Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)}$ $E_{cell} = +1.10\ \mathrm{V}$

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

Left (L)	Right (R)
$\mathrm{Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-}$	$\mathrm{Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)}$
(oxidation)	(reduction)

Overall (R + L): $\mathrm{Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)}$ $E_{cell} = +1.10\ \mathrm{V}$

- **Negative cell potential**



$\mathrm{Cu(s)\,|\,Cu^{2+}(aq)\,||\,Zn^{2+}(aq)\,|\,Zn(s)}$ $E_{cell} = -1.10\ \mathrm{V}$

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

Left (L)	Right (R)
$\mathrm{Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-}$	$\mathrm{Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)}$
(oxidation)	(reduction)

Overall (L + R): $\mathrm{Zn^{2+}(aq) + Cu(s) \longrightarrow Zn(s) + Cu^{2+}(aq)}$ $E_{cell} = -1.10\ \mathrm{V}$

◆ Adding and subtracting half-cell reactions

Ex. 3 Find E^o for a half-reaction from E^o's of other two half-reactions.

$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$, $E_1^o = E^o\,(Cu^{2+}|Cu) = 0.340\text{ V}$

$Cu^{+}(aq) + e^- \rightarrow Cu(s)$, $E_2^o = E^o\,(Cu^{+}|Cu) = 0.522\text{ V}$

$Cu^{2+}(aq) + e^- \rightarrow Cu^{+}(aq)$, $E_3^o = E^o\,(Cu^{2+}|Cu^{+}) = ?$

ΔG (not E^o) is an extensive property.

$$\Delta G_{hc}^o = -n_{hc}\,FE^o$$

$$\Delta G_3^o = \Delta G_1^o - \Delta G_2^o = -n_1FE_1^o + n_2FE_2^o = -n_3FE_3^o$$

$$E_3^o = (n_1\,E_1^o - n_2\,E_2^o)\,/\,n_3 = (2 \times 0.340 - 1 \times 0.522)\,/\,1 = 0.158\text{ V}$$

EXAMPLE 17.5

An aqueous solution of potassium permanganate ($KMnO_4$) appears deep purple. The permanganate ion can be reduced to the pale-pink manganese(II) ion (Mn^{2+}) in aqueous acidic solutions. The standard reduction potential of an MnO_4^-, Mn^{2+} half-cell is $E^\circ_{cell} = 1.49$ V. Suppose this half-cell is combined with a $Zn^{2+}|Zn$ half-cell in a galvanic cell, with $[Zn^{2+}] = [MnO_4^-] = [Mn^{2+}] = [H_3O^+] = 1$ M.

(a) Write equations for the reactions at the anode and the cathode.

(b) Write a balanced equation for the overall cell reaction.

(c) Calculate the standard cell potential difference, E°_{cell}.

Solution

(a) Permanganate ions will be reduced at the cathode because $E°(MnO_4^-, Mn^{2+}) = 1.49$ V is more positive than $E°(Zn^{2+}|Zn) = -0.76$ V. The balanced half-cell reaction requires the presence of H_3O^+ ions and water, giving

$$MnO_4^- + 8\,H_3O^+ + 5\,e^- \longrightarrow Mn^{2+} + 12\,H_2O$$

The anode half-reaction for the oxidation of Zn is

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

(b) The number of electrons delivered to the cathode must equal the number of electrons released by the anode, so the first equation must be multiplied by 2 and the second equation by 5 before adding them together to give the overall reaction:

$$2\,\mathrm{MnO_4^-} + 16\,\mathrm{H_3O^+} + 5\,\mathrm{Zn} \longrightarrow 2\,\mathrm{Mn^{2+}} + 24\,\mathrm{H_2O} + 5\,\mathrm{Zn^{2+}}$$

(c) The galvanic cell potential is the difference between the standard reduction potential for permanganate (at the cathode) and that for zinc (at the anode):

$$E° = E°(\mathrm{MnO_4^-}, \mathrm{Mn^{2+}}) - E°(\mathrm{Zn^{2+}}|\mathrm{Zn}) = 1.49 - (-0.76) = 2.25\ \mathrm{V}$$

Note that the half-cell potentials are not multiplied by their coefficients (2 and 5) before subtraction. Half-cell potentials are *intensive* properties of a galvanic cell and are therefore independent of the amount of the reacting species.

Oxidizing and Reducing Agents

- Oxidizing agent: easily reduced, large positive E^o (F_2, H_2O_2, MnO_4^-)
- Reducing agent: easily oxidized, large negative E^o,
  (alkali & alkaline earth metals)

Oxidizing powers of O_2 and O_3

~ Effective oxidizing agents in acidic solution at pH 0:

$$O_2 + 4\ H_3O^+ + 4\ e^- \rightarrow 6\ H_2O \qquad E^o = 1.229\ V$$

$$O_3 + 2\ H_3O^+ + 2\ e^- \rightarrow O_2 + 3\ H_2O \qquad E^o = 2.07\ V$$

O_3 is a stronger oxidizing agent than O_2 because $\Delta G_f^o(O_3) > 0$.

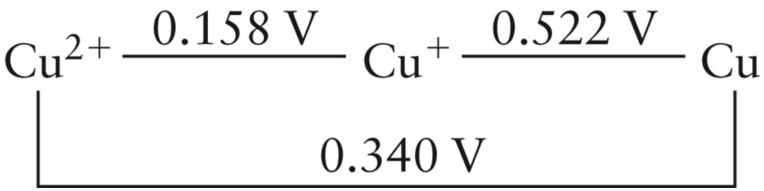
→ ΔG for the reduction of $H_3O^+(aq)$ by O_3 is more negative than ΔG for its reduction by O_2.

$$O_2 + 2\ H_2O + 4\ e^- \longrightarrow 4\ OH^- \qquad E^o = 0.401\ V$$

$$O_3 + H_2O + 2\ e^- \longrightarrow O_2 + 2\ OH^- \qquad E^o = 1.24\ V$$

◆ Reduction Potential Diagram

➢ Latimer diagram:



A species can disproportionate if and only if

E° (left; **reverse**) < *E*° (right; **forward**).

Then, thermodynamically feasible disproportionation of Cu^+ is

$$2\,Cu^+ \rightarrow Cu^{2+} + Cu$$

E^o = 0.522 V (right) – 0.158 V (left) = + 0.364 V > 0

$E^o > 0 \rightarrow \Delta G^o < 0$, spontaneous process !

◆ Adding and subtracting half-cell reactions

Ex. 3 Find E^o for a half-reaction from E^o's of other two half-reactions.

$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$, $E_1^o = E^o(Cu^{2+}|Cu) = 0.340\text{ V}$

$Cu^+(aq) + e^- \rightarrow Cu(s)$, $E_2^o = E^o(Cu^+|Cu) = 0.522\text{ V}$

$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$, $E_3^o = E^o(Cu^{2+}|Cu^+) = ?$

ΔG (not E^o) is an extensive property.

$$\Delta G_{hc}^o = -n_{hc} F E^o$$

$$\Delta G_3^o = \Delta G_1^o - \Delta G_2^o = -n_1 F E_1^o + n_2 F E_2^o = -n_3 F E_3^o$$

$$E_3^o = (n_1\, E_1^o - n_2\, E_2^o) / n_3 = (2 \times 0.340 - 1 \times 0.522) / 1 = 0.158\text{ V}$$

EXAMPLE 17.6

Hydrogen peroxide, H_2O_2, is a possible product of the reduction of oxygen in acidic solution:

$$O_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow H_2O_2 + 2\,H_2O \qquad E_3^\circ = ?$$

It can then be further reduced to water:

$$H_2O_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow 4\,H_2O \qquad E_2^\circ = 1.77\text{ V}$$

(a) Use the half-cell potential just given for the reduction of H_2O_2, together with that given earlier,

$$O_2 + 4\,H_3O^+ + 4\,e^- \longrightarrow 6\,H_2O \qquad E_1^\circ = 1.229\text{ V}$$

to calculate the standard half-cell potential for the reduction of O_2 to H_2O_2 in acidic solution.

(b) Write a reduction potential diagram for O_2, H_2O_2, and H_2O.

(c) Is H_2O_2 stable with respect to disproportionation in acidic solution?

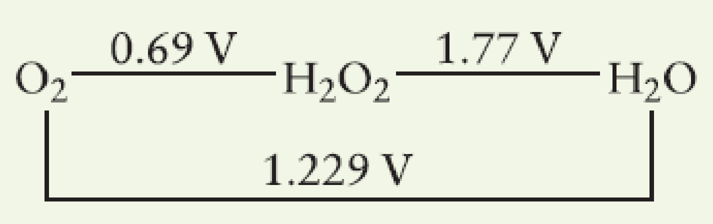
Solution

(a) The desired half-cell reaction is obtained by *subtracting* the reaction with potential E_2° from that with potential E_1°. The half-cell reduction potentials are not subtracted, however, but rather combined as described earlier in this section. Taking $n_1 = 4$, $n_2 = 2$, and $n_3 = 2$ gives

$$E_3^\circ = \frac{n_1 E_1^\circ - n_2 E_2^\circ}{n_3}$$

$$= \frac{(4 \text{ mol})(1.229 \text{ V}) - (2 \text{ mol})(1.77 \text{ V})}{2 \text{ mol}} = 0.69 \text{ V}$$

(b) The reduction potential diagram is obtained by omitting the electrons, water, and H_3O^+ from the corresponding half-equations:



(c) H_2O_2 is thermodynamically unstable to disproportionation in acidic solution because the half-cell potential to its right (1.77 V) is higher than that to its left (0.69 V). The disproportionation of H_2O_2 is also spontaneous in neutral solution, but it is slow enough that aqueous solutions of hydrogen peroxide can be stored for a long time without deteriorating, as long as they are kept out of the light.

→ Concentrations and pressures are rarely fixed at their standard state values in real world applications

17.3 CONCENTRATION EFFECTS AND THE NERNST EQUATION

Using $\Delta G = -nFE_{\text{cell}}$ and , $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$

$\Delta G = \Delta G^{\circ} + RT \ln Q$ (p. 647) → $-nFE_{\text{cell}} = -nFE^{\circ}_{\text{cell}} + RT \ln Q$

◆ Nernst Equation

$$\boxed{E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q}$$

or

$$\boxed{E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log_{10} Q \quad (\text{at } 25^{\circ}\text{C})}$$

n : number of moles of electrons transferred in the overall reaction as written.

- Nernst equation for **half-cell** reactions (*written as reductions*)

$$\boxed{E_{\text{hc}} = E^{\circ}_{\text{hc}} - \frac{0.0592\ V}{n_{\text{hc}}} \log_{10} Q_{\text{hc}}}$$

Ex. $Zn^{2+} + 2e^{-} \rightarrow Zn$ $n_{\text{hc}} = 2$, $Q_{\text{hc}} = 1/[Zn^{2+}]$

EXAMPLE 17.7

Suppose the $Zn|Zn^{2+}||\ MnO_4^-|Mn^{2+}$ cell from Example 17.5 is operated at pH 2.00 with $[MnO_4^-] = 0.12$ M, $[Mn^{2+}] = 0.0010$ M, and $[Zn^{2+}] = 0.015$ M. Calculate the cell potential E_{cell} at 25°C.

EXAMPLE 17.5

An aqueous solution of potassium permanganate ($KMnO_4$) appears deep purple. The permanganate ion can be reduced to the pale-pink manganese(II) ion (Mn^{2+}) in aqueous acidic solutions. The standard reduction potential of an MnO_4^-, Mn^{2+} half-cell is $E^\circ_{cell} = 1.49$ V. Suppose this half-cell is combined with a $Zn^{2+}|Zn$ half-cell in a galvanic cell, with $[Zn^{2+}] = [MnO_4^-] = [Mn^{2+}] = [H_3O^+] = 1$ M.

(a) Write equations for the reactions at the anode and the cathode.

(b) Write a balanced equation for the overall cell reaction.

(c) Calculate the standard cell potential difference, E°_{cell}.

Solution

(a) Permanganate ions will be reduced at the cathode because $E°(MnO_4^-, Mn^{2+}) = 1.49$ V is more positive than $E°(Zn^{2+}|Zn) = -0.76$ V. The balanced half-cell reaction requires the presence of H_3O^+ ions and water, giving

$$MnO_4^- + 8\ H_3O^+ + 5\ e^- \longrightarrow Mn^{2+} + 12\ H_2O$$

The anode half-reaction for the oxidation of Zn is

$$Zn \longrightarrow Zn^{2+} + 2\ e^-$$

EXAMPLE 17.7

Suppose the $Zn|Zn^{2+}||\ MnO_4^-|Mn^{2+}$ cell from Example 17.5 is operated at pH 2.00 with $[MnO_4^-] = 0.12$ M, $[Mn^{2+}] = 0.0010$ M, and $[Zn^{2+}] = 0.015$ M. Calculate the cell potential E_{cell} at 25°C.

Solution

Recall that the overall reaction is

$$2\ MnO_4^-(aq) + 5\ Zn(s) + 16\ H_3O^+(aq) \longrightarrow 2\ Mn^{2+}(aq) + 5\ Zn^{2+}(aq) + 24\ H_2O(\ell)$$

$$E_{hc} = E^{o}_{hc} - \frac{0.0592\ V}{n_{hc}} \log_{10} Q_{hc}$$

$$MnO_4^- + 8\ H_3O^+ + 5\ e^- \longrightarrow Mn^{2+} + 12\ H_2O$$

$$Zn \longrightarrow Zn^{2+} + 2\ e^-$$

$$E(MnO_4^-Mn^{2+}) = 1.49\ V - \frac{0.0592\ V}{10} \log_{10} \frac{(10^{-3})^2}{(0.12)^2(10^{-2})^{16}} = 1.33\ V$$

$$E(Zn|Zn^{2+}) = -0.76\ V - \frac{0.0592\ V}{2} \log_{10} \frac{1}{\cancel{(0.15)^2}} = \cancel{-0.808\ V}$$

$$E_{cell} = E_{cathode} - E_{anode} = 1.33 - \cancel{(-0.808)} = 2.14\ V$$

◆ Measuring Equilibrium Constants

From $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ and $\Delta G^\circ = -RT\ln K$

$$\boxed{\ln K = \frac{nF}{RT}E^\circ_{\text{cell}}}$$

or

$$\boxed{\log_{10} K = \frac{n}{0.0592\ \text{V}}E^\circ_{\text{cell}} \qquad \text{(at } 25^\circ\text{C)}}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{V}}{n}\log_{10} Q$$

$$E^\circ_{\text{cell}} = \frac{0.0592\ \text{V}}{n}\log_{10} K$$

EXAMPLE 17.8

Calculate the equilibrium constant for the redox reaction

$$2\ \mathrm{MnO_4^-}(aq) + 5\ \mathrm{Zn}(s) + 16\ \mathrm{H_3O^+}(aq) \longrightarrow 2\ \mathrm{Mn^{2+}}(aq) + 5\ \mathrm{Zn^{2+}}(aq) + 24\ \mathrm{H_2O}(\ell)$$

at 25°C using the cell potential calculated in Example 17.5.

Solution

$E^\circ = 2.25$ V and $n = 10$ for this reaction as shown in Examples 17.5 and 17.7. Therefore,

$$\log_{10} K = \frac{n}{0.0592\ \mathrm{V}} E^\circ_{\mathrm{cell}} = \frac{10}{0.0592\ \mathrm{V}}(2.25\ \mathrm{V}) = 380$$

$$K = 10^{380}$$

This overwhelmingly large equilibrium constant reflects the strength of permanganate ion as an oxidizing agent and that of zinc as a reducing agent. No $\mathrm{MnO_4^-}$ ions are present at equilibrium, for all practical purposes.

◆ Measuring Equilibrium Constants

From $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$ and $G^{\circ} = -RT\ln K$

$$\boxed{\ln K = \frac{nF}{RT}E^{\circ}_{\text{cell}}}$$

or

$$\boxed{\log_{10} K = \frac{n}{0.0592\ \text{V}}E^{\circ}_{\text{cell}} \qquad \text{(at } 25^{\circ}\text{C)}}$$

◆ pH Meters

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592\ \text{V}}{n}\log_{10} Q$$

(1) Simple pH meter using SHE

Pt | H_2(1 atm) | **H_3O^+(var)** || H_3O^+(1 M) | H_2(1 atm) | **Pt**

(anode) H_2(1 atm) + 2 H_2O(*l*) → **2 H_3O^+(var)** + 2 e^-

(cathode) 2 H_3O^+(1 M) + 2 e^- → H_2(1 atm) + 2 H_2O(*l*) SHE

n = 2, *Q* = $[H_3O^+(\text{var})]^2$, and E^0_{cell} = 0. (E^0_{hc}'s are the same)

$$\boxed{E_{\text{cell}} = -(0.0592\ \text{V}/2)\log_{10}[H_3O^+]^2 = (0.0592\ \text{V})\ \text{pH}}$$

We have just described a simple **pH meter.** It is not convenient to bubble hydrogen gas through both the unknown and reference half-cells, however, so a smaller and more portable pair of electrodes is used to replace the hydrogen half-cells. The early commercial pH meters used two electrodes that were dipped into a solution of unknown pH. One of these, called the **indicator electrode** (because it indicates the unknown pH of the analyte), was made of an AgCl-coated silver electrode in contact with an HCl solution of known concentration (i.e., 1.0 M) contained in a glass tube terminated by a thin-walled, bulb-shaped, glass membrane. A pH-dependent potential develops across this thin glass membrane when the glass electrode is immersed in a solution of different, and unknown, $[H_3O^+]$ concentration. The reference electrode used was often the saturated calomel electrode discussed above. The overall cell (Fig. 17.10) can be represented as

$$\mathrm{Ag}|\mathrm{AgCl}|\mathrm{Cl^-}(1.0\ \mathrm{M}), \mathrm{H_3O^+}(1.0\ \mathrm{M})|\mathrm{glass}|\mathrm{H_3O^+}(\mathrm{var})||\mathrm{Cl^-}(\mathrm{sat})|\mathrm{Hg_2Cl_2}(s)|\mathrm{Hg}|\mathrm{Pt}$$

(2) Smaller and more potable pH meter using two reference electrodes

$\mathbf{Ag|AgCl}|\mathrm{Cl^-(1.0\ M) + H_3O^+(1.0\ M)|glass}|\mathbf{H_3O^+(var)}||\mathrm{Cl^-(sat)|Hg_2Cl_2}(s)\mathrm{|Hg}|\mathbf{Pt}$

Glass indicator electrode **||** Saturated Calomel electrode (SCE)

Cathode: $\mathrm{Hg_2Cl_2}(s) + 2\,e^- \rightarrow 2\,\mathrm{Hg}(l) + 2\,\mathrm{Cl^-(sat)}$ $E_1^o = +0.2682\ \mathrm{V}$

Anode: $2\,\mathrm{Ag}(s) + 2\,\mathrm{Cl^-(1.0\ M)} \rightarrow 2\,\mathrm{AgCl(s)} + 2\,e^-$ $-E_2^o = -0.2223\ \mathrm{V}$

Dilution: $\mathrm{H_3O^+(1.0\ M)} \rightarrow \mathrm{H_3O^+(var)}$ $E_{dil} = (0.0592\ \mathrm{V})\ \mathrm{pH}$

Overall: $\mathrm{Hg_2Cl_2}(s) + 2\,\mathrm{Ag(s)} + 2\,\mathrm{Cl^-(1.0\ M)} + \mathrm{H_3O^+(1.0\ M)}$

$\rightarrow 2\,\mathrm{Hg}(l) + 2\,\mathrm{AgCl}(s) + 2\,\mathrm{Cl^-(sat)} + \mathrm{H_3O^+(var)}$ $E^o = E_1^o - E_2^o$

→ E_{dil}: the free energy of dilution of H_3O^+ from a concentration of 1.0 M to an unknown concentration.

→ That potential appears as a junction potential across the thin glass membrane of the indicator electrode.

Cathode: $Hg_2Cl_2(s) + 2\ e^- \rightarrow 2\ Hg(l) + 2\ Cl^-(\text{sat})$ $E_1^o = +0.2682$ V

Anode: $2\ Ag(s) + 2\ Cl^-(1.0\ M) \rightarrow 2\ AgCl(s) + 2\ e^-$ $-E_2^o = -0.2223$ V

Dilution: $H_3O^+(1.0\ M) \rightarrow H_3O^+(\text{var})$ $E_{dil} = (0.0592\ V)\ pH$

Overall: $Hg_2Cl_2(s) + 2\ Ag(s) + 2\ Cl^-(1.0\ M) + H_3O^+(1.0\ M)$

$\rightarrow 2\ Hg(l) + 2\ AgCl(s) + 2\ Cl^-(\text{sat}) + H_3O^+(\text{var})$ $E^o = E_1^o - E_2^o$

$$E = E^o - (0.0592\ V/2) \log [Cl^-(\text{sat})]^2 + E_{dil} = E_{ref} + (0.0592\ V)\ pH$$

$$\boxed{pH = \frac{E - E_{ref}}{0.0592\ V}}$$

where $E_{ref} = E^o - (0.0592\ V) \log [Cl^-(\text{sat})]$

❖ Potential for the saturated calomel electrode:

$$E(\text{SCE}) = E_1^{\circ} - (0.0592\ \text{V}) \log [\text{Cl}^-(\text{sat})] = +\ 0.241\ \text{V}$$

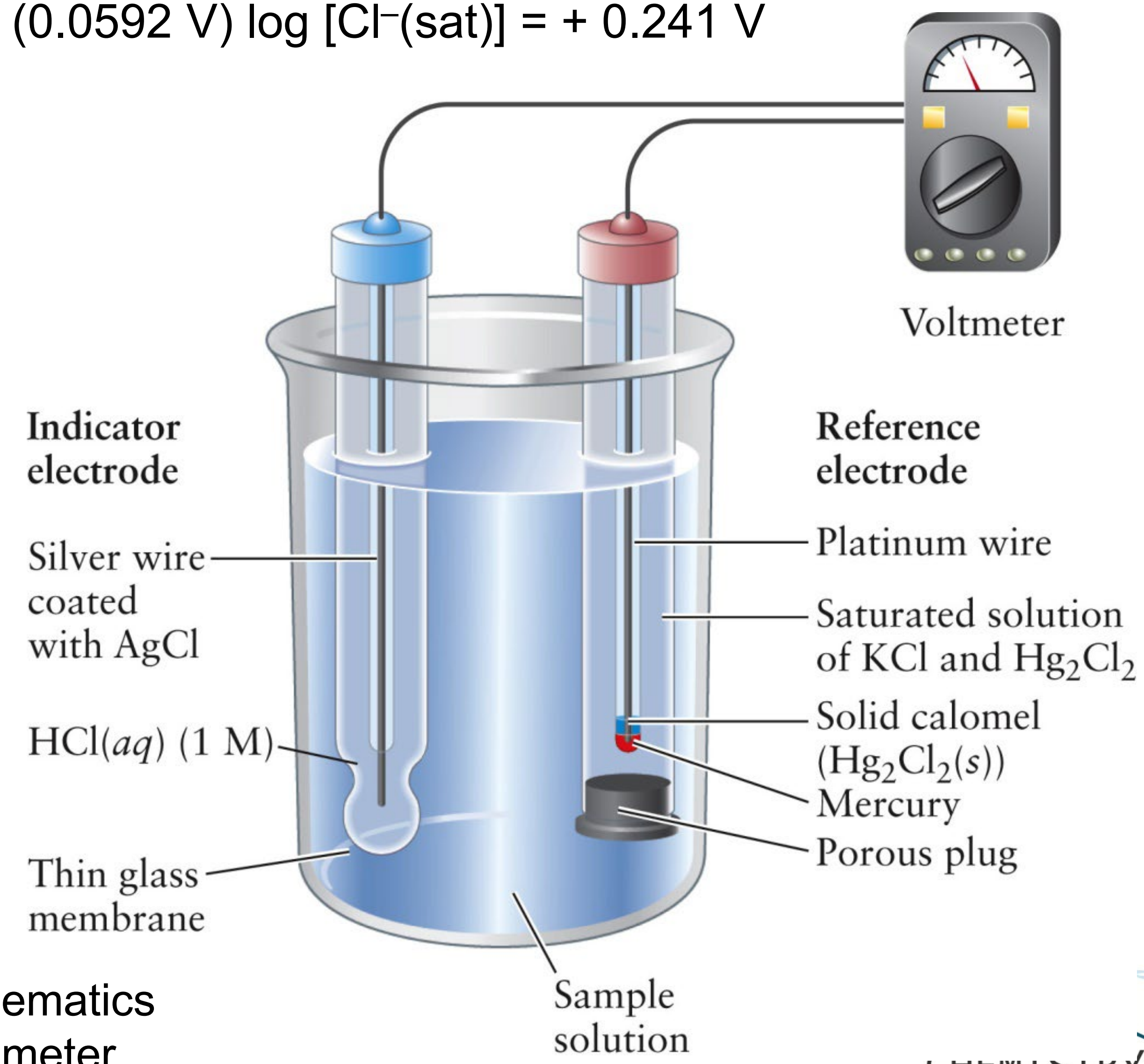
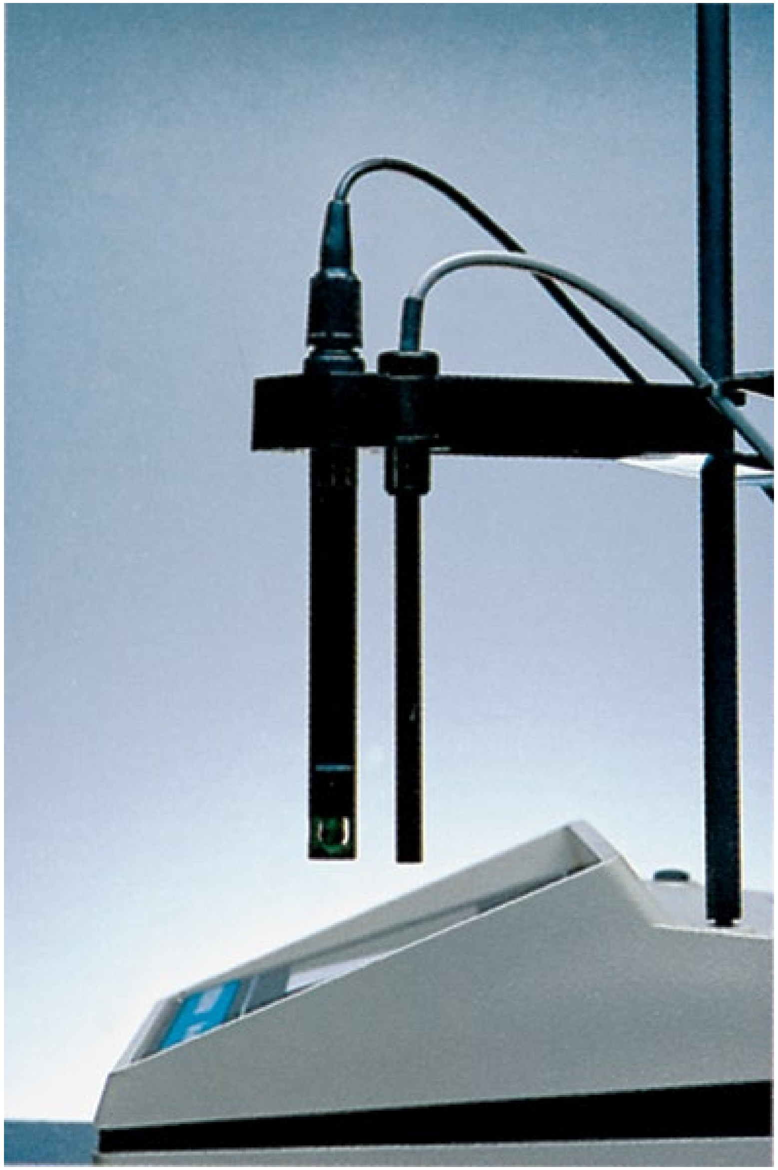


Fig. 17.10 Schematics of an early pH-meter.

Commercialized
pH
Sensor



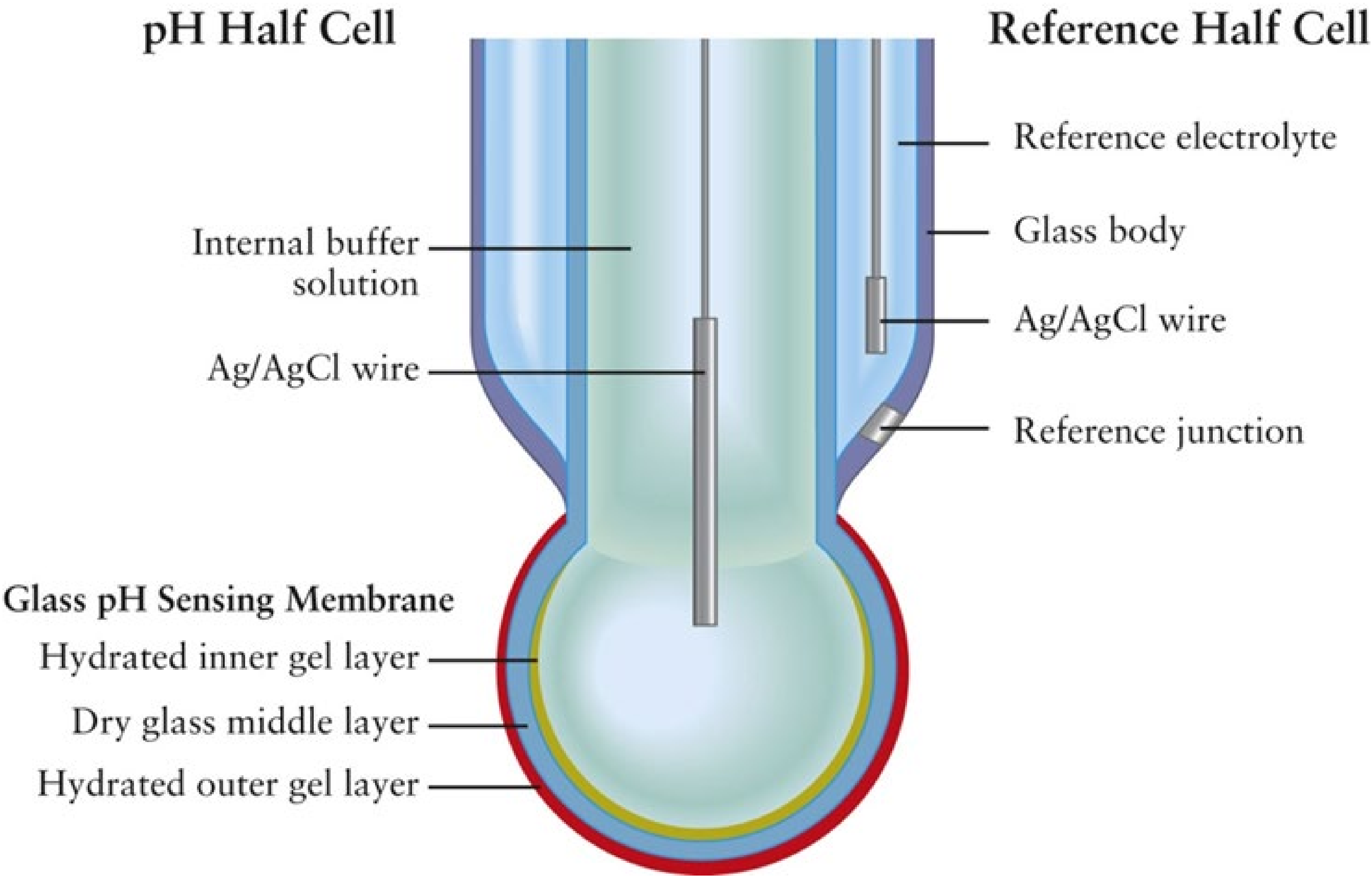


Fig. 17.11 A combination pH probe

17.4 MOLECULAR ELECTROCHEMISTRY

◆ Electrochemical Organic Synthesis

- **Monsanto process** for the production of adiponitrile

$CH_2{=}CHCN + 2\,e^- \rightarrow 2(CH_2{=}CHCN)^- + 2\,H^+ \rightarrow NC(CH_2)_4CN$

Adiponitrile → hexamethylenediamine → nylon

Electrochemical reactors with steel electrodes coated with Cd film

No need to use powerful but toxic redox agents

Suitable for synthesis of pharmaceuticals (speed, selectivity)

❖ **Glucose sensor test strip** contains…

① A capillary drawing in the blood sample

② A thin film carbon working electrode

③ A thin film Ag/AgCl electrode

(counter-reference electrodes)

④ Two planar auxiliary electrodes

(fill-detection electrodes)

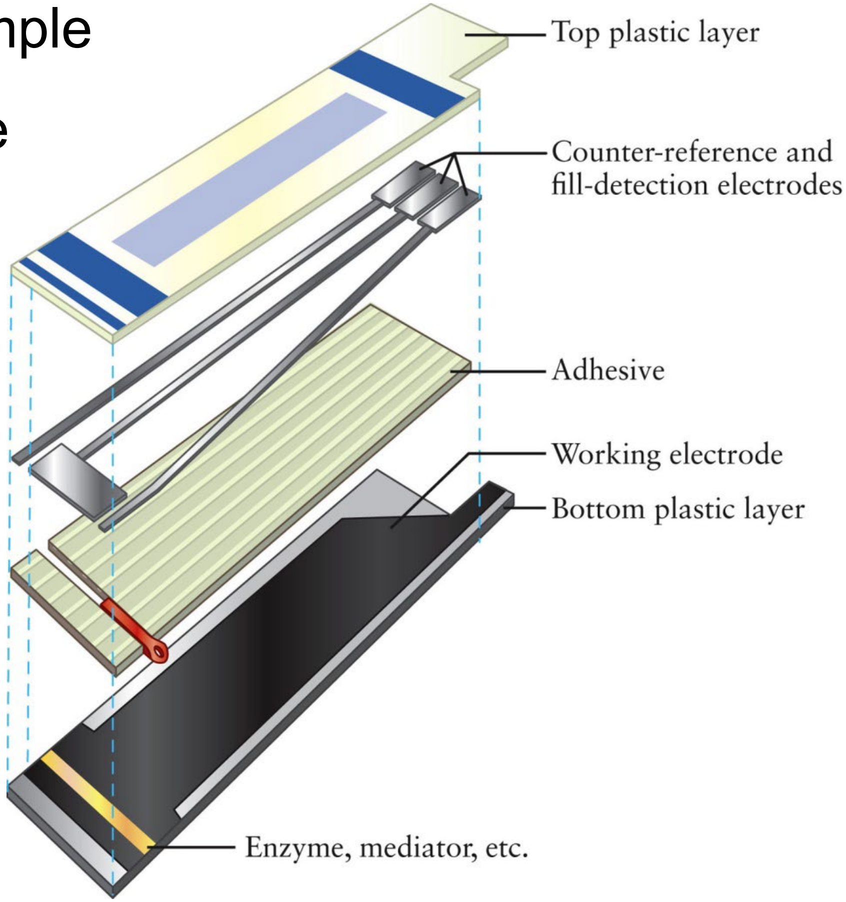


Fig. 17.7 Glucose sensor test strip

(1) Glucose sensor test strip monitors the concentration of glucose by measuring the total charge transferred to the carbon electrode that results from the oxidation of glucose by GDH, which converts an alcohol group into a ketone:

② $\text{glucose} \xrightarrow{\text{GDH}} \text{glucon(nonlactone)}$ → written as: $\text{glucose} \xrightarrow{\text{GDH}} \text{glucononlactone} + 2\,H^+ + 2\,e^-$

(2) Reduction half-reaction occurs at the Ag/AgCl reference electrode:

③ $2\,Ag^+ + 2\,e^- \longrightarrow 2\,Ag$

(3) Overall set of reaction:

$\text{glucose} + 2\,Ag^+ \xrightarrow{\text{GDH}} \text{glucononlactone} + 2\,Ag + 2\,H^+$

❖ Mediators:

~ Molecules facilitating electron transfer over large distances by a series of efficient electron transfer reactions

~ Mediators used in this particular sensor are coordination complexes of osmium (Os^{2+}/Os^{3+})

~ Redox potential is adjusted so that its oxidized form could be reduced by the enzyme, but not at the Ag/AgCl electrode.

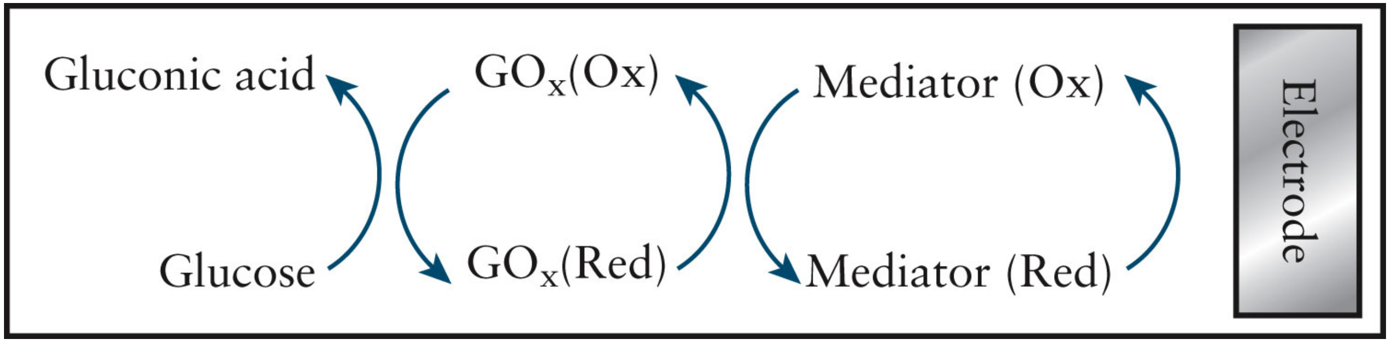


Fig. 17.13 Coupled redox reactions in the glucose test strip.

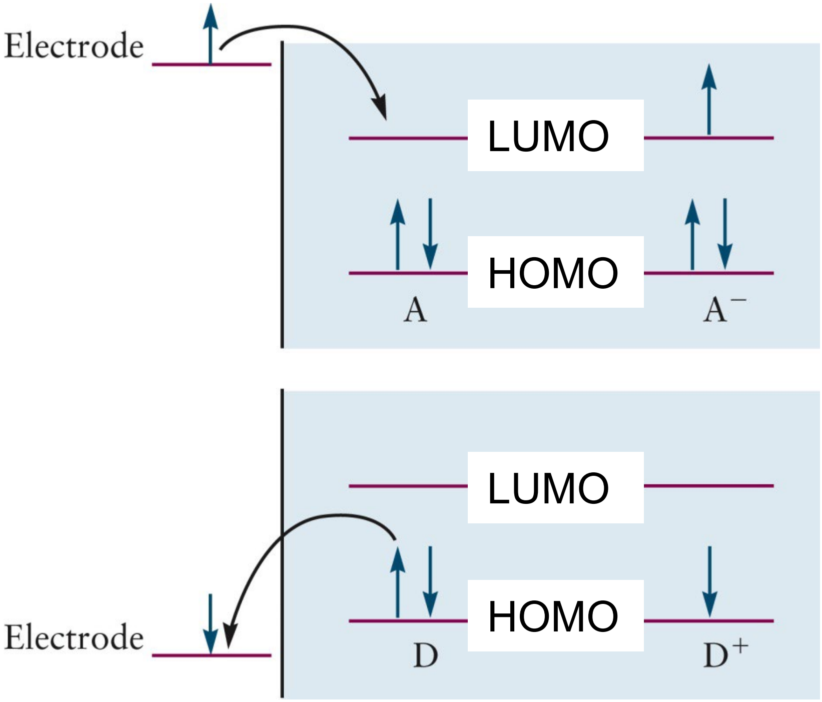
❖ Implantable glucose sensors

- Continuous measurement of glucose
- Transmitting signals of concentration change to a monitor
- 'Wired' enzyme:

  Fe^{2+}/Fe^{3+} (or Os-based) redox couple covalently attached to the polypeptide chain of glucose oxidase (GOx)
- GOx is incorporated into the mediator-bearing polymer

◆ Electrogenerated Chemiluminescence (ECL)

- Analytical technique for detecting biologically important molecules
- Emission from excited states molecular electronic states produced by charge transfer reactions between radical anions and radical HOMO cations:



$$A + e^- \longrightarrow A^{-\bullet}$$

$$D \longrightarrow D^{+\bullet} + e^-$$

$$A^{-\bullet} + D^{+\bullet} \longrightarrow A^* + D$$

$$A^* \longrightarrow A + h\nu$$

Fig. 17.8 Generation of a radical cation and a radical anion in an ECL experiment. $A^{-\bullet}$(or $D^{+\bullet}$) is formed when the electrode potential is made more negative (or positive) than the LUMO (or HOMO) of A (or D).

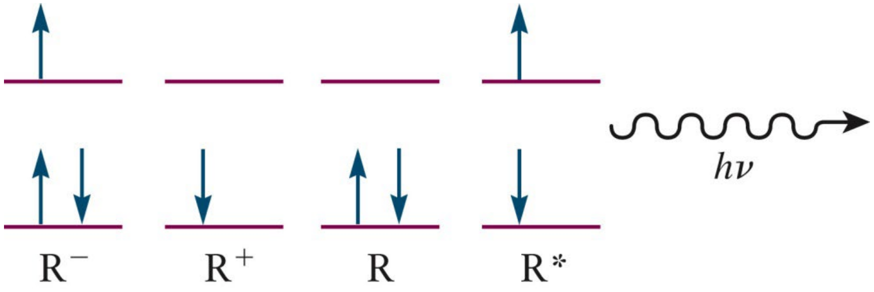
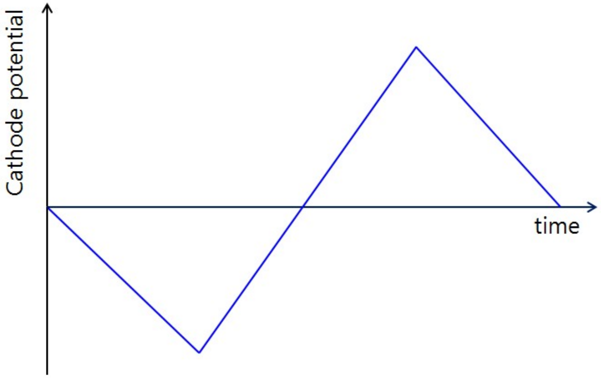
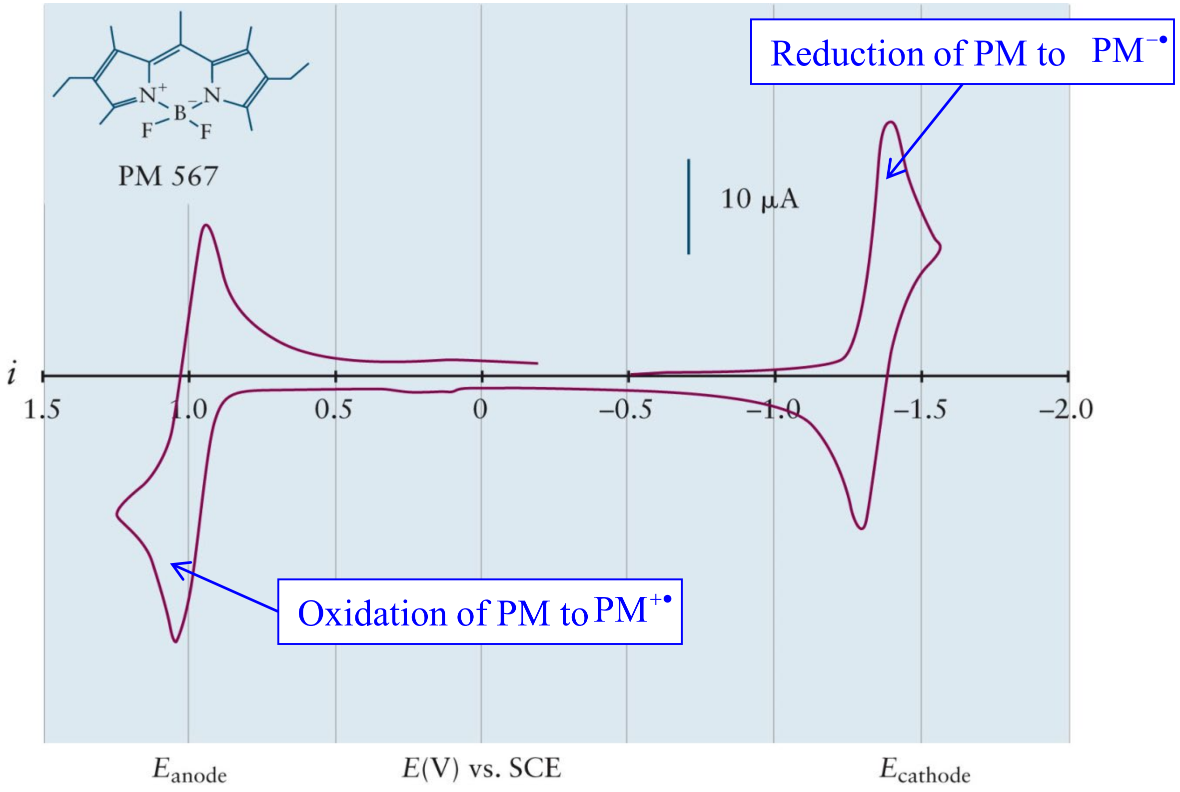


Fig. 17.9 Reaction of R$^-$ and R$^+$ to form R*, which emits light, in an ECL experiment.

◆ Cyclic voltammetry (CV)

- ~ Measures the current that flows as the electrode potential is scanned back and forth
- ~ Identify redox active materials
- ~ Locate the potentials at which various oxidations and reduction reactions occur
- ~ Information about the kinetics of electrochemical reactions





Reduction of PM to $PM^{-\bullet}$

Oxidation of PM to $PM^{+\bullet}$

Fig. 17.16 Cyclic voltammogram for an ECL dye, PM 567.

Cathode: Redox potential for the PM| couple: –1.4 V LUMO

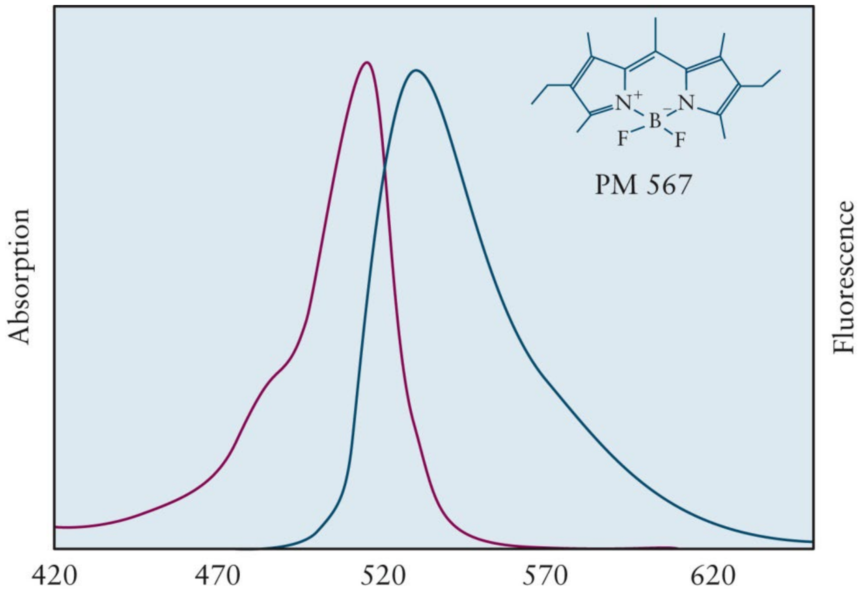
Anode: Redox potential for the |PM couple: 1.0 V HOMO

- Calculating the maximum amount of energy available to create an excited state, and the energy of the emitted photon from the reaction

$$\mathrm{PM}^{-\bullet} + \mathrm{PM}^{+\bullet} \longrightarrow \mathrm{PM} + \mathrm{PM}^{*} \longrightarrow \mathrm{PM} + h\nu$$

~ Energy available between two redox couples:

$$\varepsilon = -e\Delta E = -e\left(E_{\text{cathode}} - E_{\text{anode}}\right) = -e(-1.4 - 1.0) = 2.4\ \text{eV}$$



- Absorption peak at 514 nm → 2.4 eV

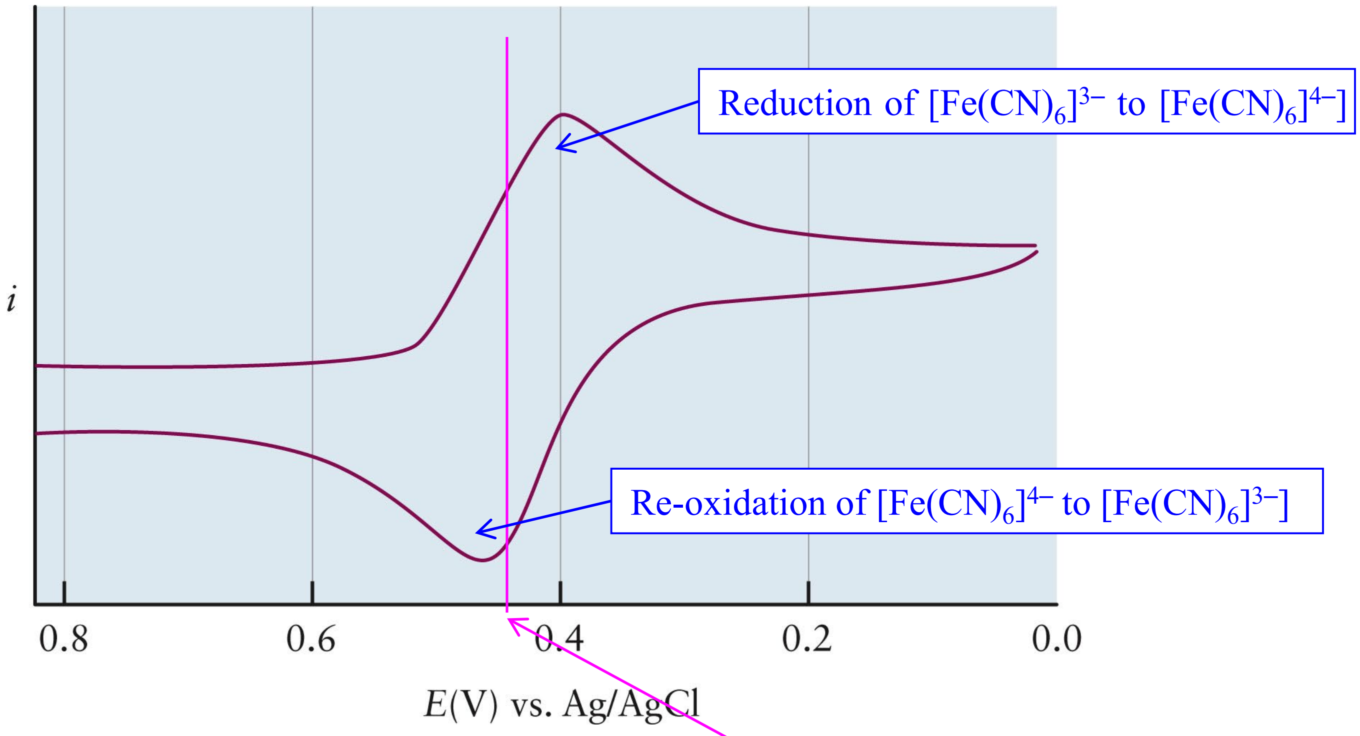
  ~ Energy available from the recombination reaction is sufficient to create the excited state

- Fluorescence peak at 567 nm

  ~ Typical shift to longer wavelength in aqueous solution

Fig. 17.17. Absorption and fluorescence spectra of PM 567.

Ex. 17.10 Cyclic voltammogram for $[Fe(CN)_6]^{3-}$ /$[Fe(CN)_6]^{4-}$] redox couple measure with respect to a Ag/AgCl reference electrode. The standard reduction potential for this system at pH=7 is 0.43 V.

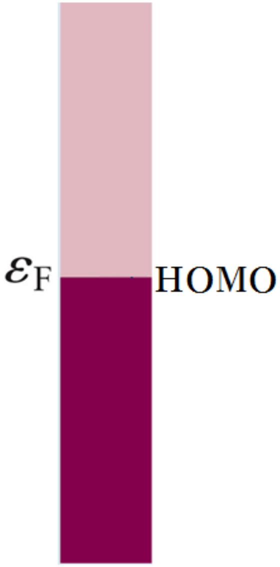


The redox potential is determined graphically by locating the midpoint between the two peaks, in this case 0.43 V.

- Energy levels of metals
  - ~ Continuous band of levels
  - ~ Only half of the orbitals are occupied for univalent metals that contribute one electron per atom
- Energy of the **Fermi level,** ε_F
  - ~ Highest Occupied Molecular Orbital **(HOMO)**

    $\varepsilon_F = -\Phi$, Φ: work function of the metal

    cf. Lowest Unoccupied Molecular Orbital **(LUMO)**
- Potential scale: $\varepsilon_\alpha = -eE_\alpha$



❖ **Chromophore** A molecule (or a semiconductor) that absorbs light

~ Lower energy level: HOMO (Valence Band, VB)

~ Higher energy band: LUMO (Conduction Band, CB)

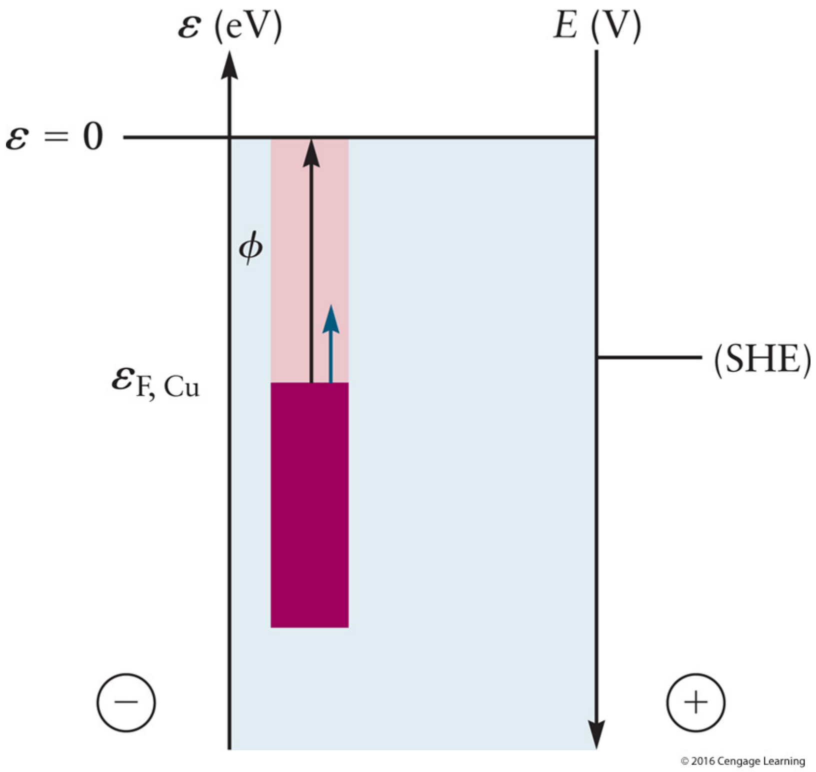


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Fig. 17.12 Electrons from the highest occupied metal orbital may be promoted to higher energy levels in the conduction band (light pink region) or given enough energy (black arrow), to be released from the metal (as in the photoelectric effect)

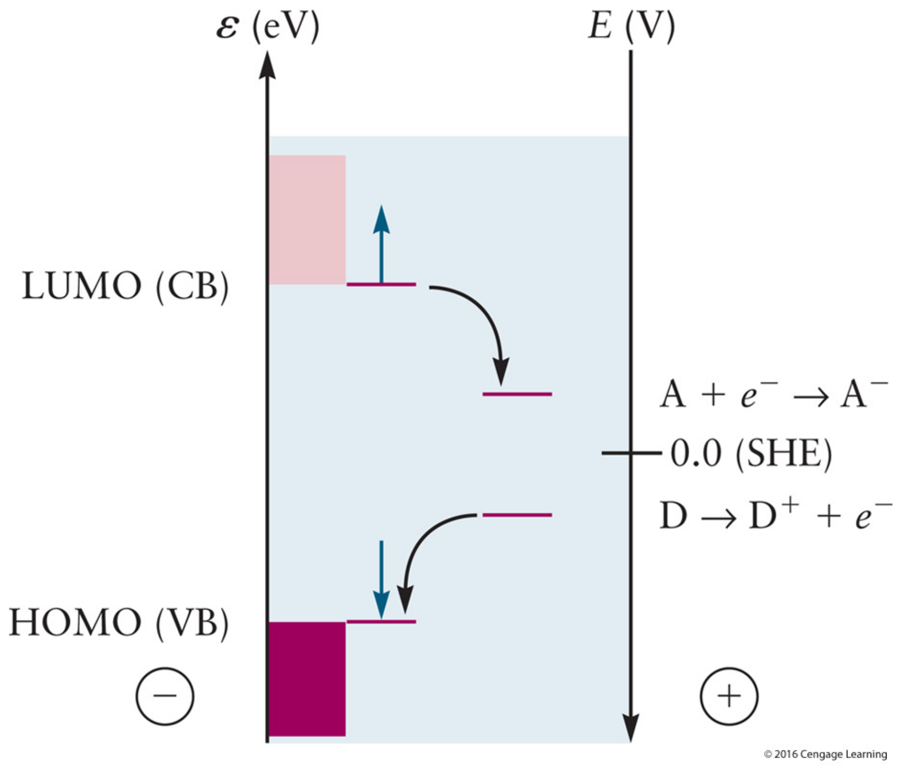

Fig. 17.13 Photoexcitation promotes electrons to higher energies, which make them stronger reducing agent, capable of reducing an acceptor A to A^-. The vacancies (holes) left behind can now accept electrons, which make them stronger oxidizing agents, capable of oxidizing a donor D to D^+.

◆ Direct photoelectrochemical water splitting by wide bandgap semiconductors (TiO_2 or $SrTiO_3$)

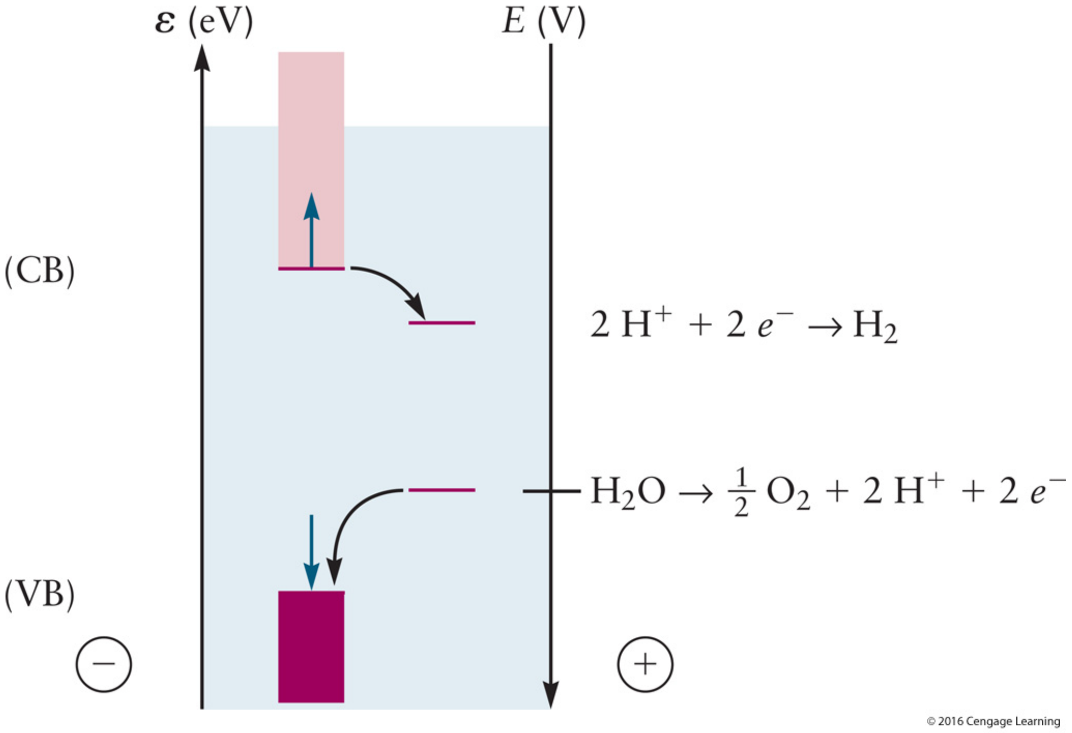

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Fig. 17.14 The potential of the conduction band of wide bandgap semiconductors is sufficiently negative to reduce hydrogen ions and that of the valence band sufficiently positive to oxidize water.

- Overall process with CB electrons reducing protons and VB holes oxidizing water:

  $4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2(g)$

  $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$

- Standard Gibbs free energy of formation of water:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta G_f^o = -237.18\ \text{kJ mol}^{-1}$$

- The maximum amount of energy available becomes the difference in energies of the hydrogen and oxygen redox levels:

$$\Delta G^o = -nFE^o = -(1\ \text{mol})(96{,}585\ \text{kJ mol}^{-1}\text{eV}^{-1})(1.299\ \text{eV}) = -125.3\ \text{kJ}$$

  per mole of electrons.

- Water splitting is a four-electron redox process that proceeds through a series of electron transfer reactions involving several intermediates.

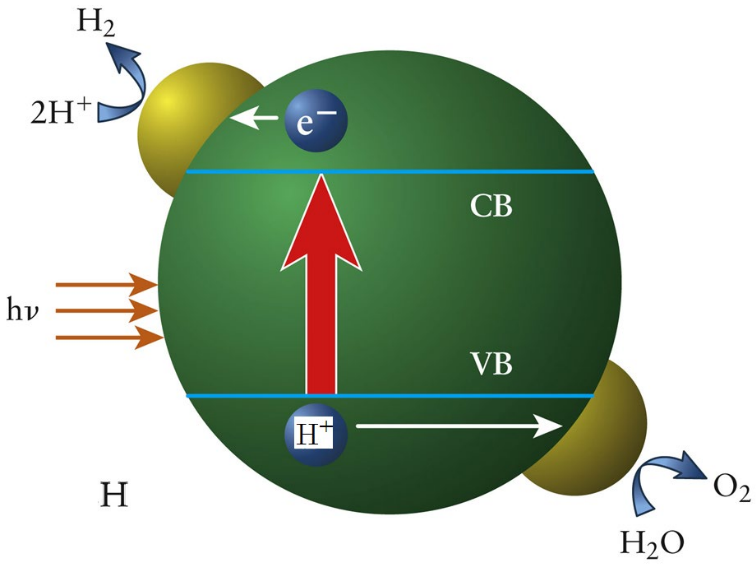


Fig. 17.15 Direct photoelectrochemical water splitting by colloidal TiO_2, shown with hydrogen and oxygen evolution catalyst particles attached.

- **Wide bandgap semiconductors** (TiO_2, $SrTiO_3$)
  - Absorb radiation only in the UV region

    → Only 10% of the energy provided by sunlight
  - C B with potentials sufficiently negative to reduce water
  - VB located at much more positive potentials than necessary to oxidize water → Most of energy absorbed is lost as heat

17.5 BATTERIES AND FUEL CELLS (optional*)

◆ Batteries

~ ***Primary cells, Secondary cells*** (rechargeable)

- **Zinc-carbon "Dry" cell**
  (Leclanché cell): 1.55 V

Cathode: graphite rod
MnO_2 + graphite powder
(large surface area)

$$2\ MnO_2(s) + 2\ NH_4^+(aq) + 2\ e^- \rightarrow Mn_2O_3(s) + 2\ NH_3(aq) + H_2O(l)$$

Salt bridge:
moist paste of $ZnCl_2$ + NH_4Cl

Anode: zinc shell
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$$

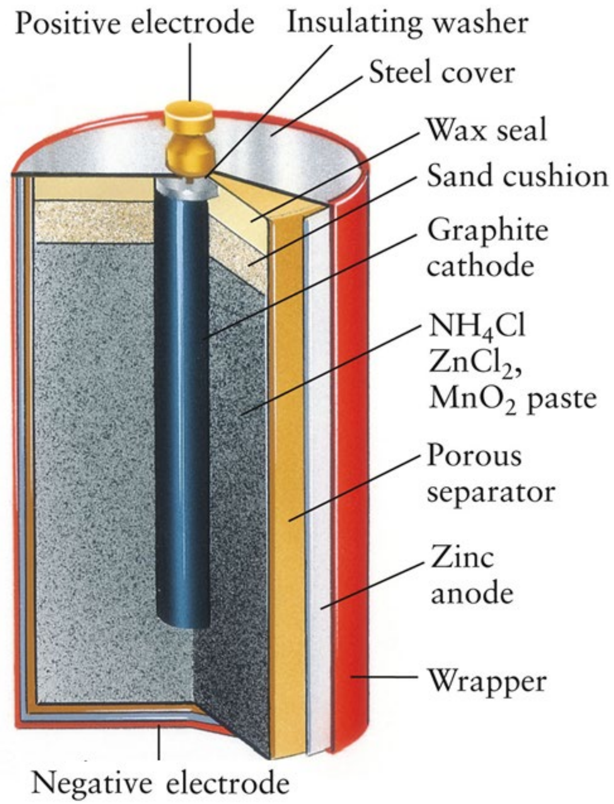


Fig. 17.21 Leclanché "dry" cell

Overall reaction:

$$Zn(s) + 2\ MnO_2(s) + 2\ NH_4^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2\ NH_3(aq) + \mathbf{H_2O(l)}$$

- Disadvantage

  $[NH_4^+]$ decreases with time → Battery's voltage falls with time

  Zinc anode corrodes as it oxidizes

  Electrolyte leaks out

Alkaline dry cell:

KOH instead of NH_4Cl, 1.5 V ($E^o = 1.364$ V)

Cathode: $2\ MnO_2(s) + H_2O(l) + 2\ e^- \rightarrow Mn_2O_3(s) + 2\ OH^-(aq)$

Anode: $Zn(s) + 2\ OH^-(aq) \rightarrow Zn(OH)_2(s) + 2\ e^-$

Overall: $Zn(s) + 2\ MnO_2(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s)$

No dissolved species: Constant concentration → **steadier voltage**

➢ Zinc-mercuric oxide cell

Very stable, 1.34 V, Camera, watch, calculators

Electrolyte: 45% KOH solution

Cathode: Steel & $HgO(s)$

$HgO(s) + H_2O(l) + 2\,e^-$

$\rightarrow Hg(l) + 2\,OH^-(aq)$

Anode: Mixture of Hg & Zn

$Zn(s) + 2\,OH^-(aq)$

$\rightarrow Zn(OH)_2(s) + 2\,e^-$

Overall:

$Zn(s) + HgO(s) + H_2O(l)$

$\rightarrow Zn(OH)_2(s) + Hg(l)$

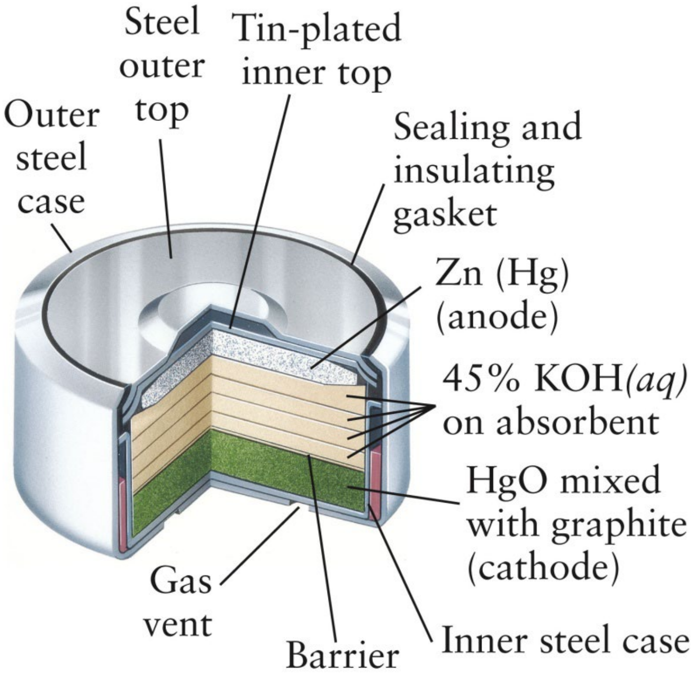


Fig. 17.22 A zinc-mercury oxide dry cell.

Lithium battery

Replacing zinc-mercuric oxide dry cell due to environmental reason

Battery voltage: 3 V

Electrolyte: $LiClO_4$ dissolved in a mixture of propylene carbonate and 1,2-dimethoxyethane

(anode) $Li \rightarrow Li^+ + e^-$

(cathode) $(Mn^{4+})O_2 + Li^+ + e^- \rightarrow (Mn^{3+})O_2(Li^+)$

(overall) $Li + (Mn^{4+})O_2 \rightarrow (Mn^{3+})O_2(Li^+)$

→ Voltage is the difference in charge between two points.
→ Current is the rate at which charge is flowing. (watt = 1J/s)

◆ Rechargeable Batteries

- Characterized by:

  Voltage, maximum current available, total energy stored

- Capacity: Amount of charge [current (*i*) × time (*t*)] available

  in a battery before it must be recharged

- 100 amph$\overset{**}{e}$re hour ($\overset{**}{A}$h) battery: delivers 5 A for 20 hours

- 3500 mAhr battery: provides 3.5 A for an hour or 1 A for 3.5 hour

  Energy available from a battery before it must be recharged

  = capacity × voltage = itV = (3500 mAhr)(10 V) = 127 kJ

- Volumetric energy density = energy per unit volume, Wh/L

  Gravimetric energy density = energy per unit weight, Wh/kg

  Ex. Modern Li-ion laptop batteries achieve 200 Wh/kg

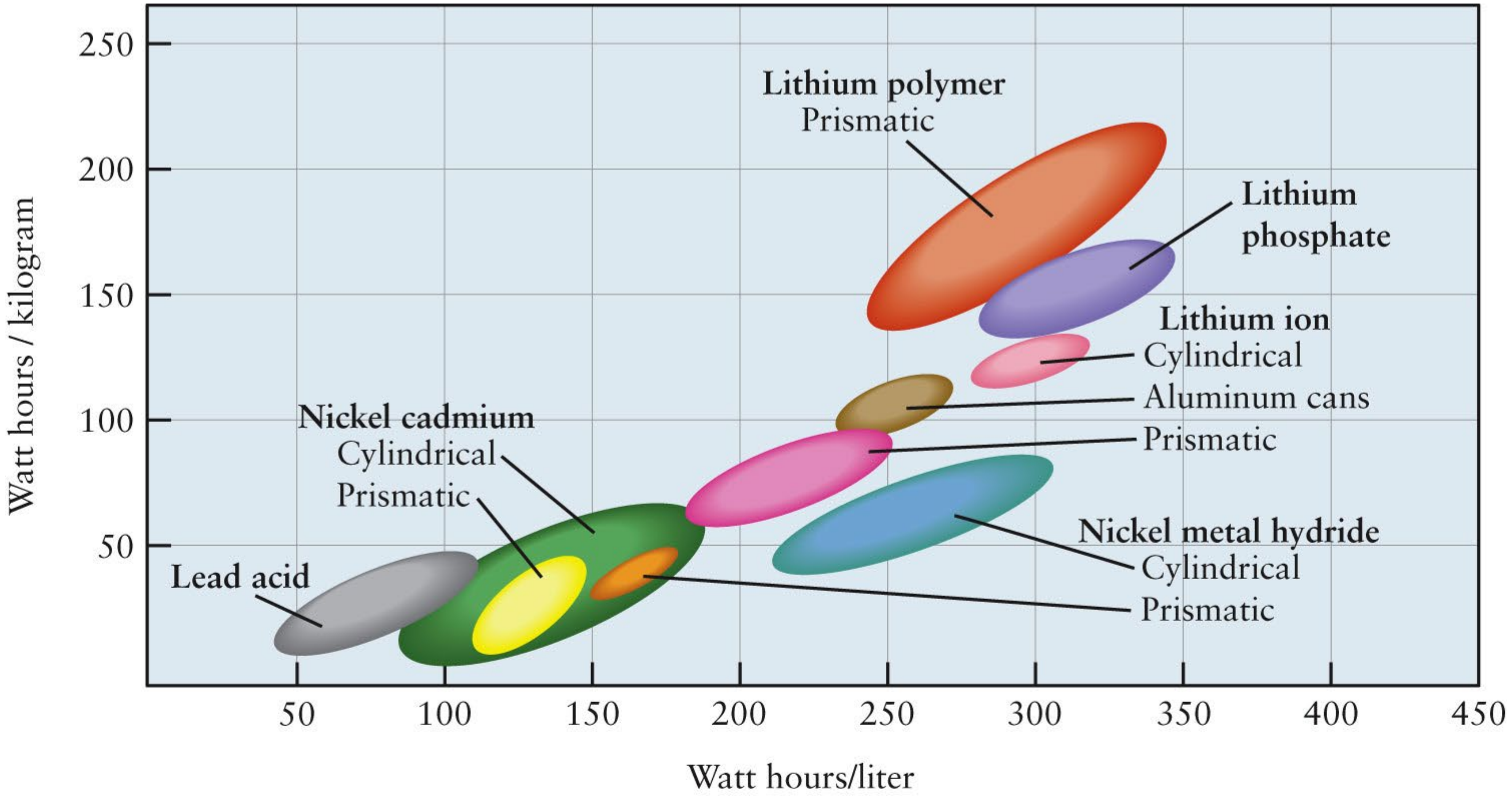


Fig. 17.23 Ranges of typical energy densities for different classes of batteries.

➢ Lead-acid storage battery:

6 × 2.0 V = 12 V

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4\ H_3O^+(aq) + 2\ e^- \rightarrow PbSO_4(s) + 6\ H_2O(l)$

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2\ e^-$

Overall: $Pb(s) + PbO_2(s) + 2\ SO_4^{2-}(aq) + 4\ H_3O^+(aq) \rightarrow 2\ PbSO_4(s) + 6\ H_2O(l)$

0 +4 common electrolyte +2

Many cycles of charge-discharge, Large current as large as 100 A,
Heavy (low energy density) → limits the range of the electric vehicles

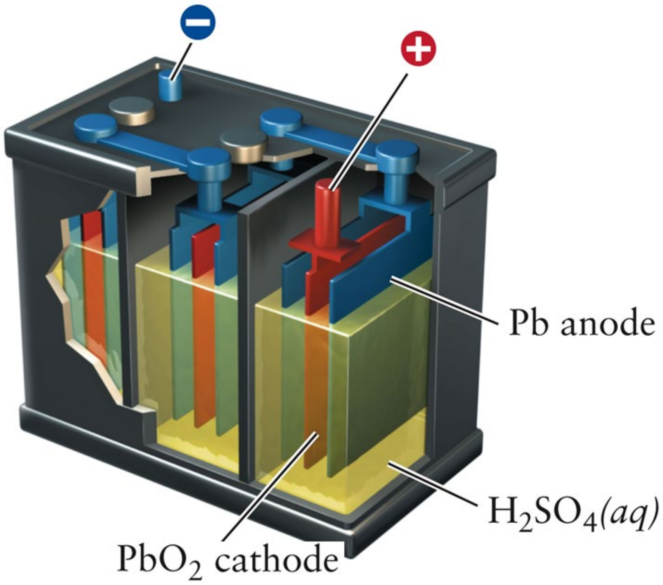


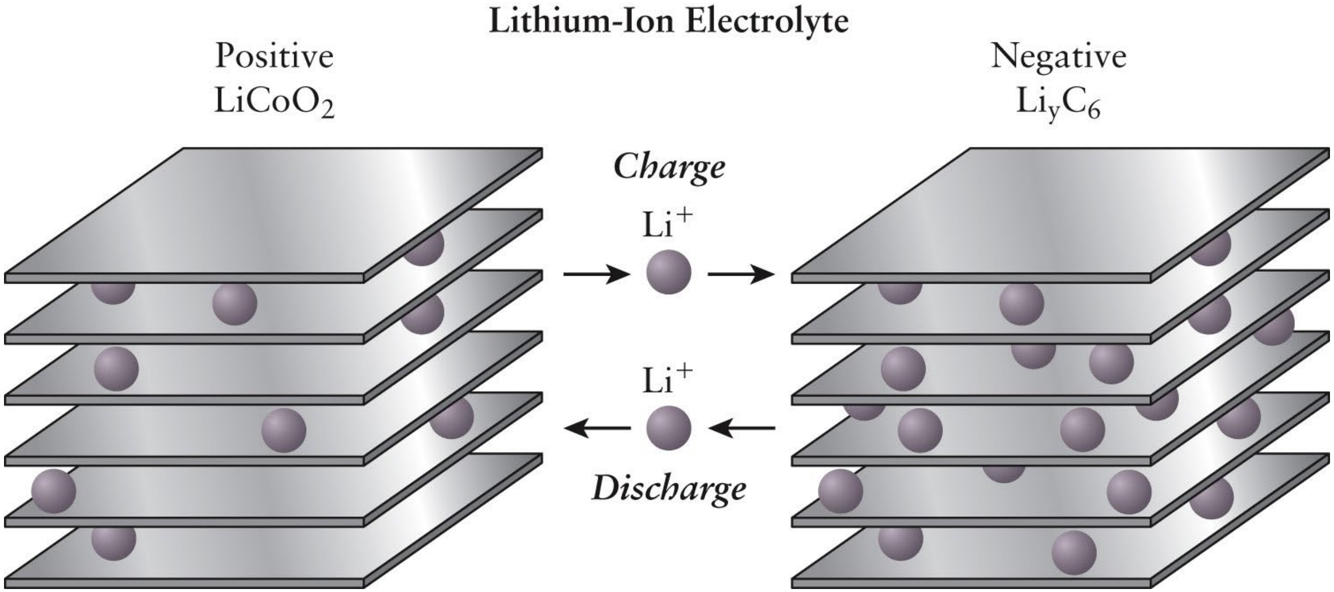
Fig. 17.24 A lead-acid storage battery consists of several cells connected in series. The electrodes are both constructed from lead grids filled with spongy Pb (cathode) and PbO_2 (anode) and the electrolyte is sulfuric acid.

Lithium-ion battery

High energy density (light Li)

Much safer than lithium battery (no elemental Li, only Li^+ ions)

Electrodes: $LiCoO_2$ (cathode), Li_yC_6 (graphite anode)



$$\mathrm{Li}_y\mathrm{C}_6 \longrightarrow y\,\mathrm{Li}^+ + y\,e^- \qquad \text{(anode)}$$

$$\mathrm{Li}_{1-y}\mathrm{MO}_2 + y\,\mathrm{Li}^+ + y\,e^- \longrightarrow \mathrm{LiMO}_2 \qquad \text{(cathode)}$$

$$\overline{\mathrm{Li}_y\mathrm{C}_6 + \mathrm{Li}_{1-y}\mathrm{MO}_2 \longrightarrow \mathrm{LiMO}_2}$$

$$\begin{array}{rcll} Li_yC_6 & \longrightarrow & y\ Li^+ + y\ e^- & \text{(anode)} \\ Li_{1-y}MO_2 + y\ Li^+ + y\ e^- & \longrightarrow & LiMO_2 & \text{(cathode)} \\ \hline Li_yC_6 + Li_{1-y}MO_2 & \longrightarrow & LiMO_2 & \end{array}$$

Single Li^+ ions shuttle back and forth:

$$\begin{array}{rcll} LiC_6 & \rightarrow & Li^+ + e^- + C_6 & \text{(anode)} \\ LiM^{n+}O_2 + Li^+ + e^- & \rightarrow & Li_2M^{(n-1)+}O_2 & \text{(cathode)} \\ \hline LiC_6 + LiM^{n+}O_2 & \rightarrow & Li_2M^{(n-1)+}O_2 + C_6 & \end{array}$$

➢ Alkali metal batteries (Na/S *battery*)

High energy density, high *T* (250°C) cells

Cathode: $S + nS + 2\,e^{-} \rightarrow S_{n+1}^{2-}$
Anode: $2\,Na \rightarrow 2\,Na^{+} + 2\,e^{-}$

Overall: $S + nS + 2\,Na \rightarrow S_{n+1}^{2-} + 2\,Na^{+}$

β-alumina ($NaAl_{11}O_{17}$):

- Ion-conducting solid electrolyte
- Only Na^{+} can migrate

CaF_2 solid electrolyte:

- Only F^{-} can migrate through

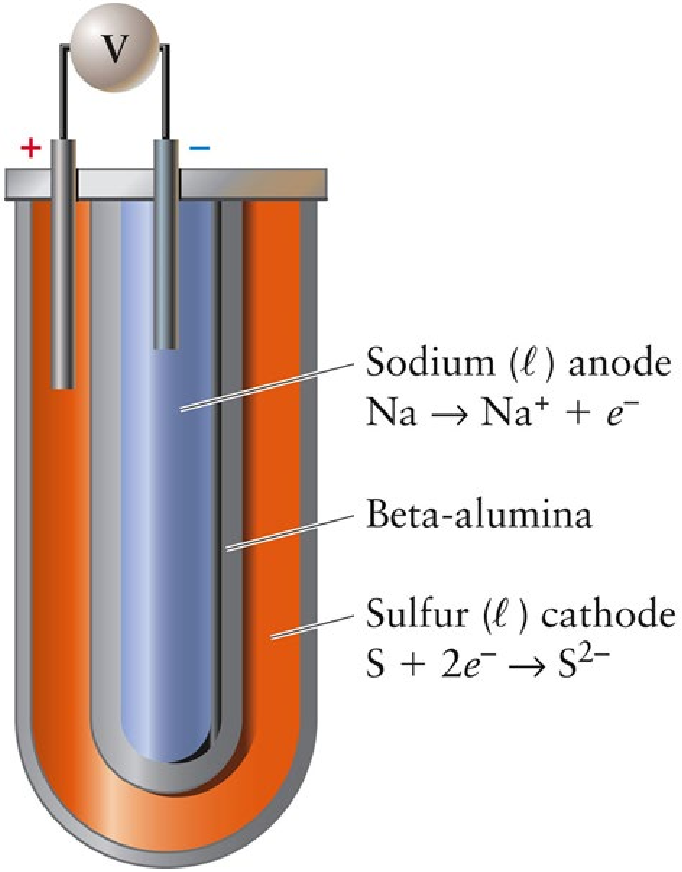
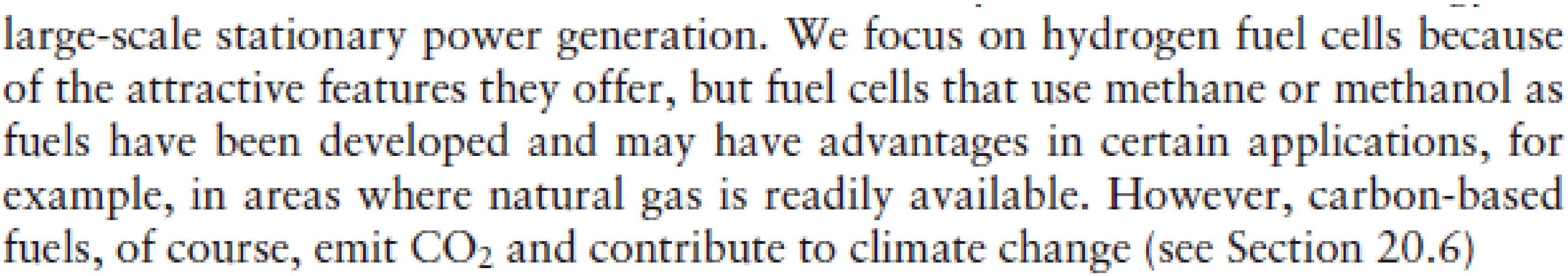


Fig. 17.26 Schematic of a sodium-sulfur battery.


large-scale stationary power generation. We focus on hydrogen fuel cells because of the attractive features they offer, but fuel cells that use methane or methanol as fuels have been developed and may have advantages in certain applications, for example, in areas where natural gas is readily available. However, carbon-based fuels, of course, emit CO_2 and contribute to climate change (see Section 20.6)

◆ Fuel Cells

- **Batteries:**

  Closed system, recharged or discarded after use

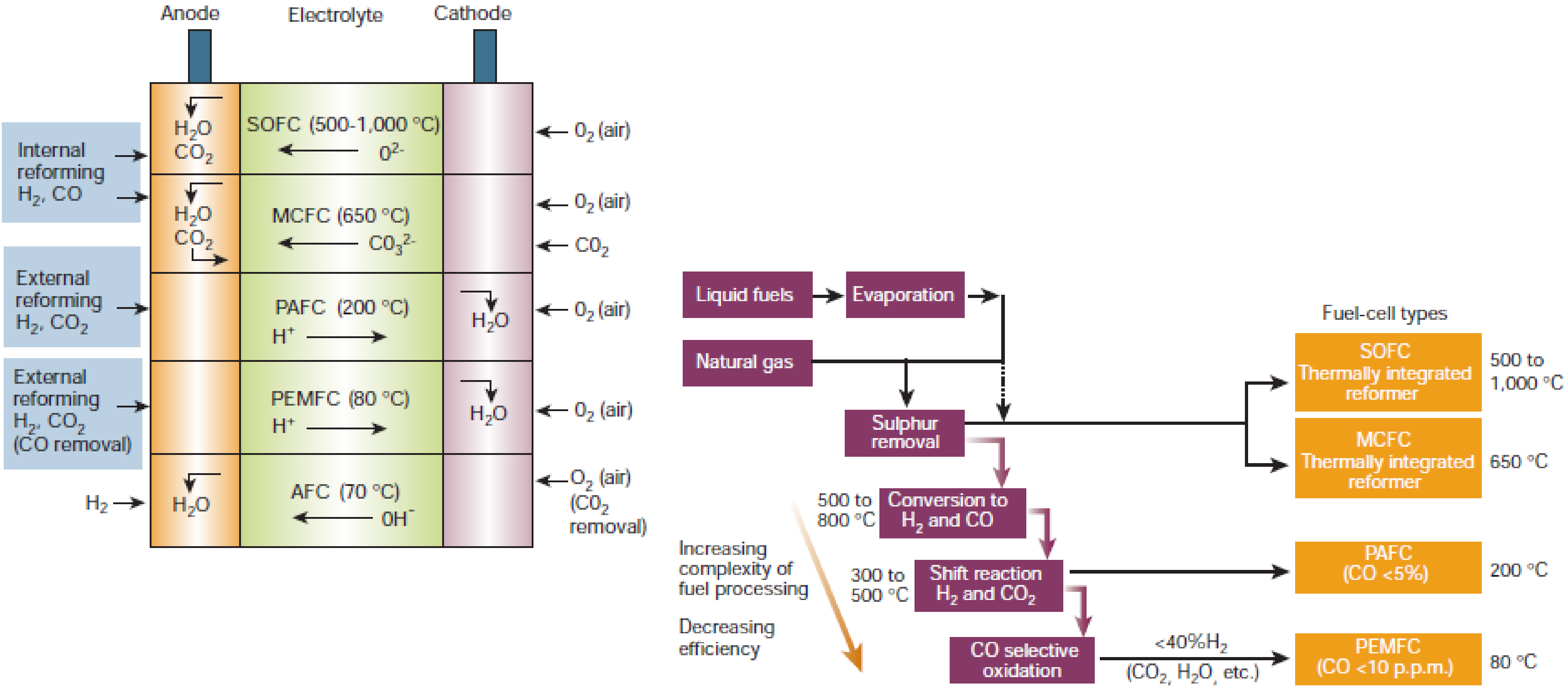
- **Fuel cell:** Energy converter
  - ~ Continuous operation,
  - ~ Supplying reactants and removing products

❖ Two classes of fuel cells

(1) Polymer electrolyte membrane (PEM) fuel cells

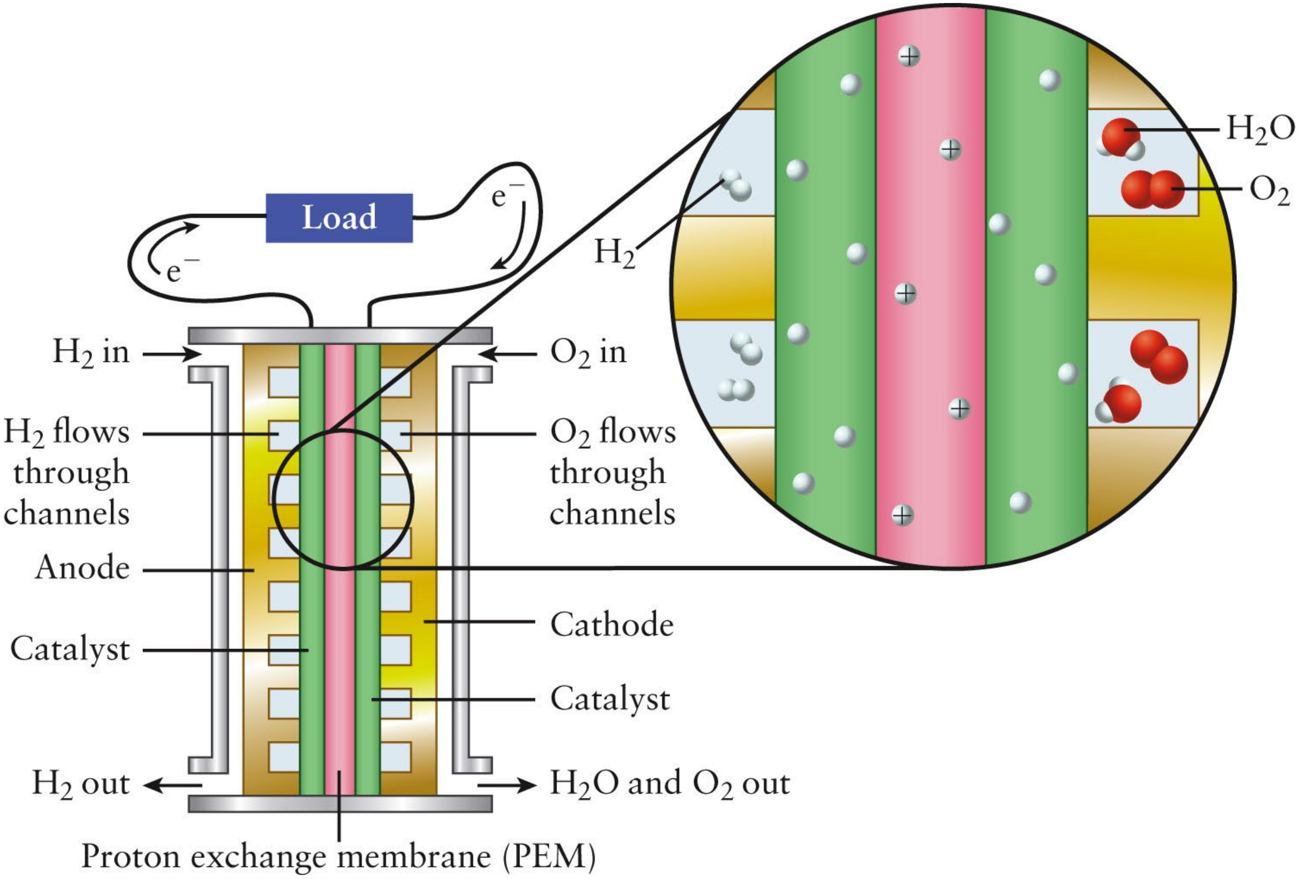
(2) Solid oxide fuel cells (SOFC)

Types of Fuel Cells



Steele, B. C. H. *et al. Nature* 2001, **414**, 345-352

➢ Polymer electrolyte membrane (PEM) fuel cell



Anode: $H_2(g) + 2\ H_2O(l) \rightarrow 2\ H_3O^+ + 2\ e^-$ $E^o = 0.000$ V

Cathode: $O_2(g) + 4\ H_3O^+ + 4\ e^- \rightarrow 6\ H_2O(l)$ $E^o = 1.229$ V

Overall: $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ $E_{cell}^o = 1.229$ V

➢ Maximum work available from combustion:

$$-w_{\text{max}} = \varepsilon q_{\text{P}} = (1 - T_{\text{l}} / T_{\text{h}})\Delta H_{\text{f}}^{\text{o}}$$

ε : Carnot efficiency of an internal combustion engine (~45%)

q_{P}: heat transferred at constant pressure

T_{l}: temperature of the exhaust gas

T_{h}: operating temperature of the internal combustion engine

$$\therefore \quad -w_{\text{max}} = (-0.4)(-241.8\ \text{kJ mol}^{-1}) = +96\ \text{kJ mol}^{-1}$$

➢ Maximum work available from a fuel cell:

$$-w_{\text{max}} = \Delta G_{\text{f}}^{\text{o}} = -228.6\ \text{kJ mol}^{-1}$$

❖ Comparison of the “Tank-to-wheel” efficiency

† Mechanical efficiency of the engines: combustion(75%), fuel cell(90%)

$$\frac{\text{Overall efficiency fuel cell vehicle}}{\text{Oveall efficiency internal combustion engine vehicle}} = \frac{(0.9)(228.6\ \text{kJ mol}^{-1})}{(0.75)(96\ \text{kJ mol}^{-1})} = 2.89$$

➢ Solid oxide fuel cell (SOFC)

~ Large scale stationary power generation for hospitals and remote towns, providing 250 kW~1 MW power

Electrolyes: Oxide ceramics, ZrO_2, doped with Y_2O_3

$$H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_f^\circ = -245.8\ \mathrm{kJ\ mol^{-1}}$$