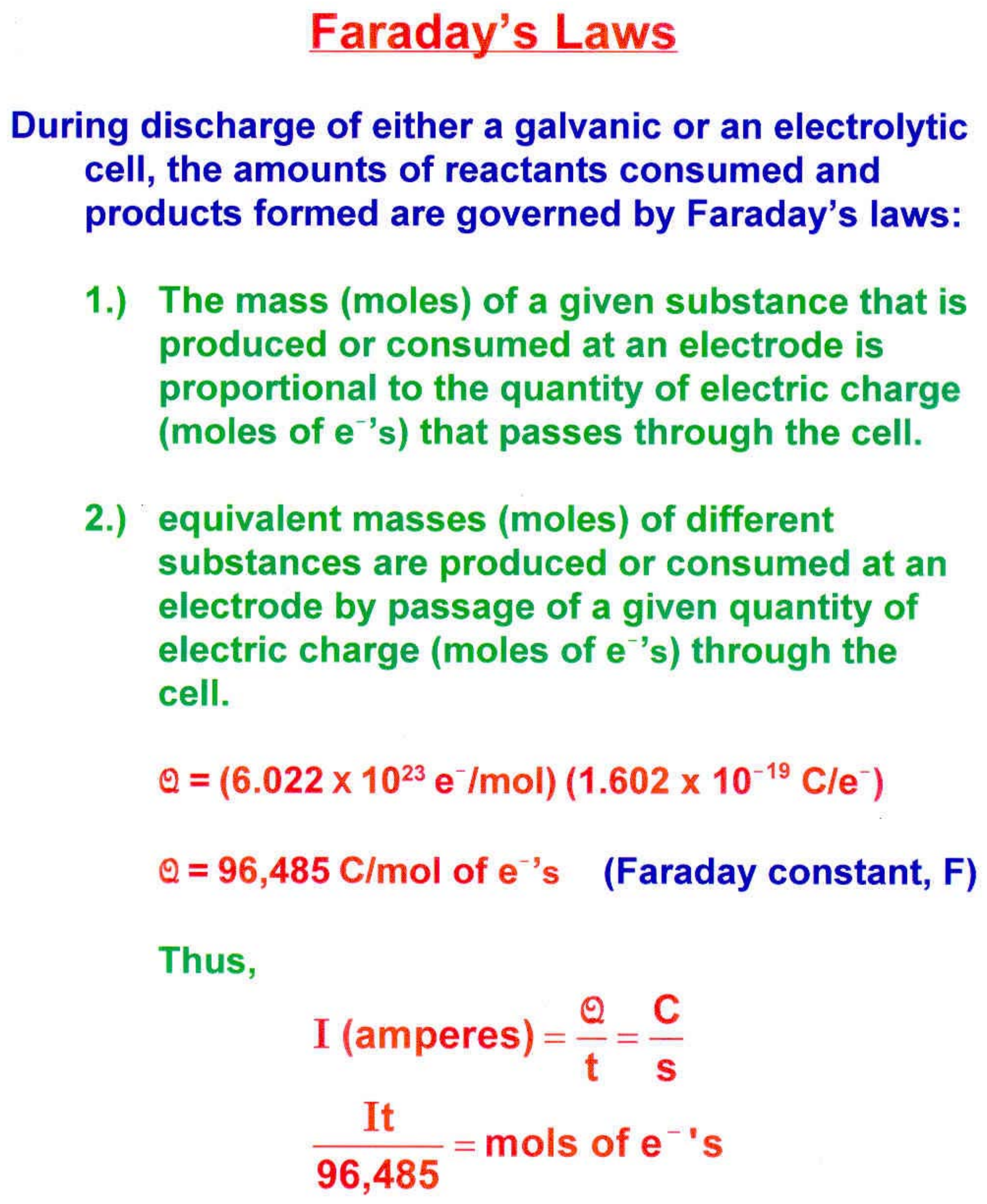
Topic 6O - Electrolysis



Faraday's Laws

During discharge of either a galvanic or an electrolytic cell, the amounts of reactants consumed and products formed are governed by Faraday's laws:

1.) **The mass (moles) of a given substance that is produced or consumed at an electrode is proportional to the quantity of electric charge (moles of e^-'s) that passes through the cell.**

2.) **equivalent masses (moles) of different substances are produced or consumed at an electrode by passage of a given quantity of electric charge (moles of e^-'s) through the cell.**

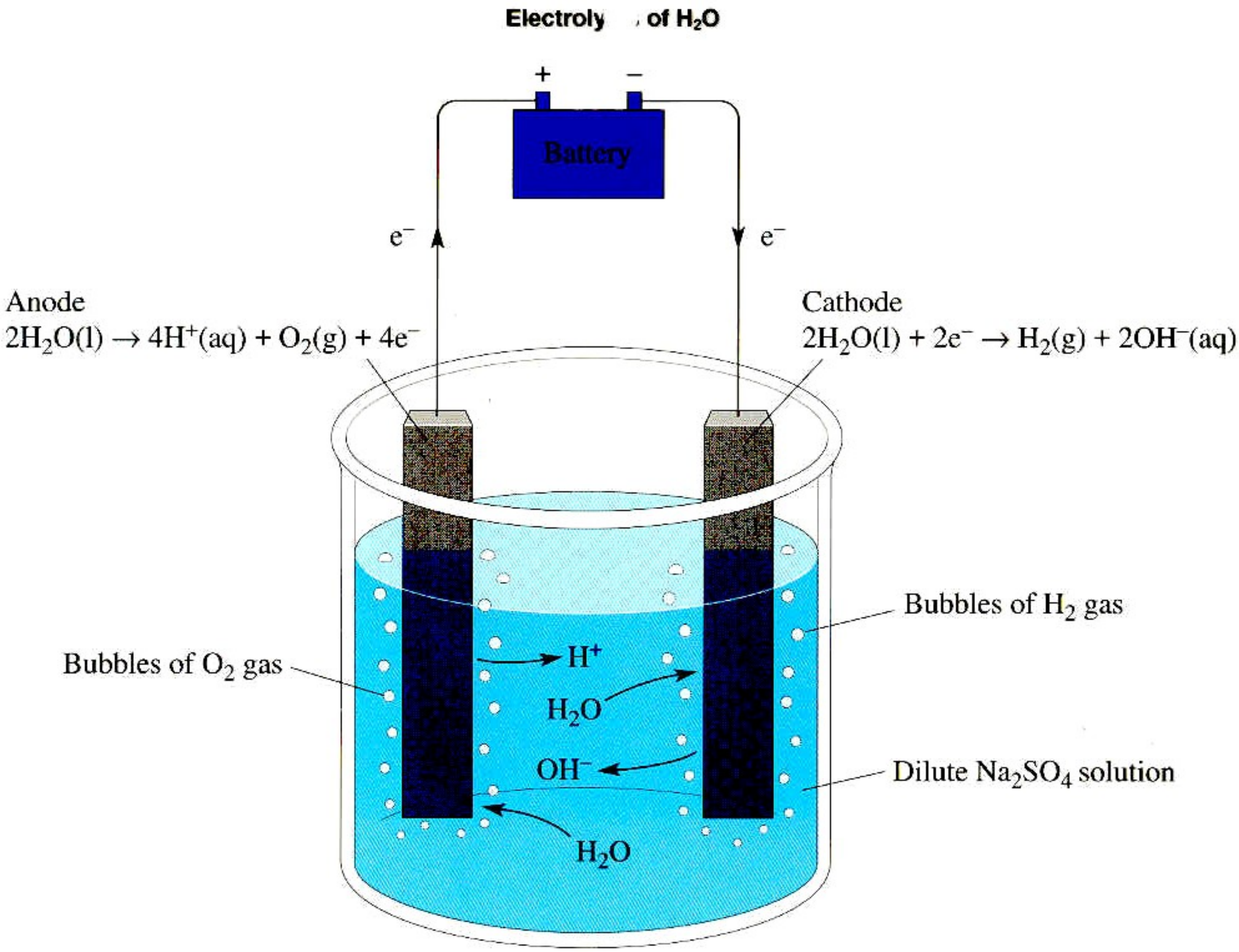
$$Q = (6.022 \times 10^{23}\ e^-/\text{mol})\ (1.602 \times 10^{-19}\ \text{C}/e^-)$$

$Q = 96{,}485$ C/mol of e^-'s **(Faraday constant, F)**

Thus,

$$\text{I (amperes)} = \frac{Q}{t} = \frac{C}{s}$$

$$\frac{It}{96{,}485} = \text{mols of } e^-\text{'s}$$



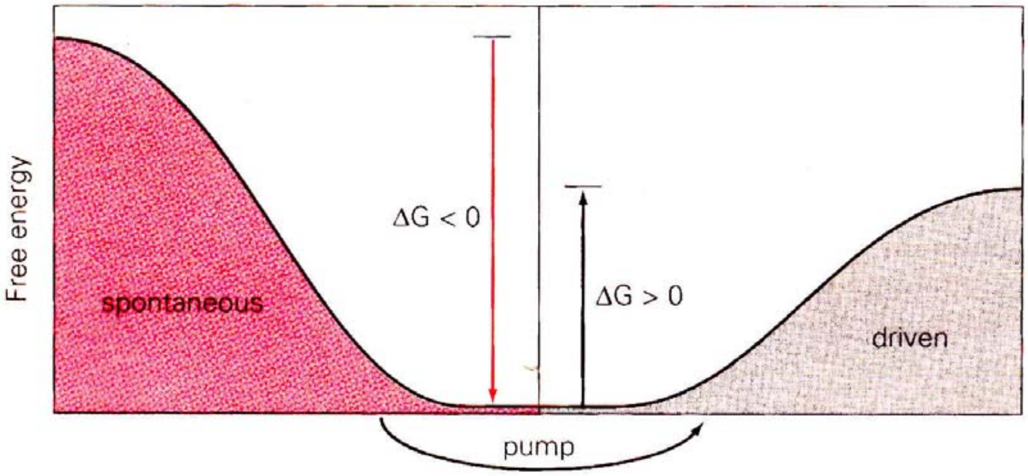


FIGURE 17-8. No free lunch: The energy to push a nonspontaneous process up the hill must come from somewhere else—from a downhill, spontaneous process that adds to the entropy of the universe. Local order is purchased at the cost of global disorder.

Applications of Electrochemistry

Production of Useful Products by Electrolysis

$NaOH + Cl_2$ (Chlor-Alkali Process) **$\Delta G° = +422$ kJ**

$2\,Cl^- (aq) \rightarrow Cl_2 (g) + 2\,e^-$ $E° = -1.36$ V
$\underline{2\,H_2O (l) + 2\,e^- \rightarrow H_2 (g) + 2\,OH^-}$ $\underline{E° = -0.83 \text{ V}}$
$2\,H_2O (l) + 2\,Cl^- (aq) \rightarrow 2\,OH^- (aq) + Cl_2 (g)$ $E° = -2.19$ V

Aluminum (Hall-Héroult Process) **$\Delta G° = +2000$ kJ**

$Al^{3+} (melt) + 3\,e^- \rightarrow Al (l)$ $E° = -1.66$ V
$\underline{2\,O^{2-} (melt) + C (gr) \rightarrow CO_2 (g) + 4\,e^-}$
$4\,Al^{3+} (melt) + 6\,O^{2-} (melt) + 3\,C (gr) \rightarrow 4\,Al (l) + 3\,CO_2 (g)$

$[2\,Al_2O_3 (l)]$ anode molten

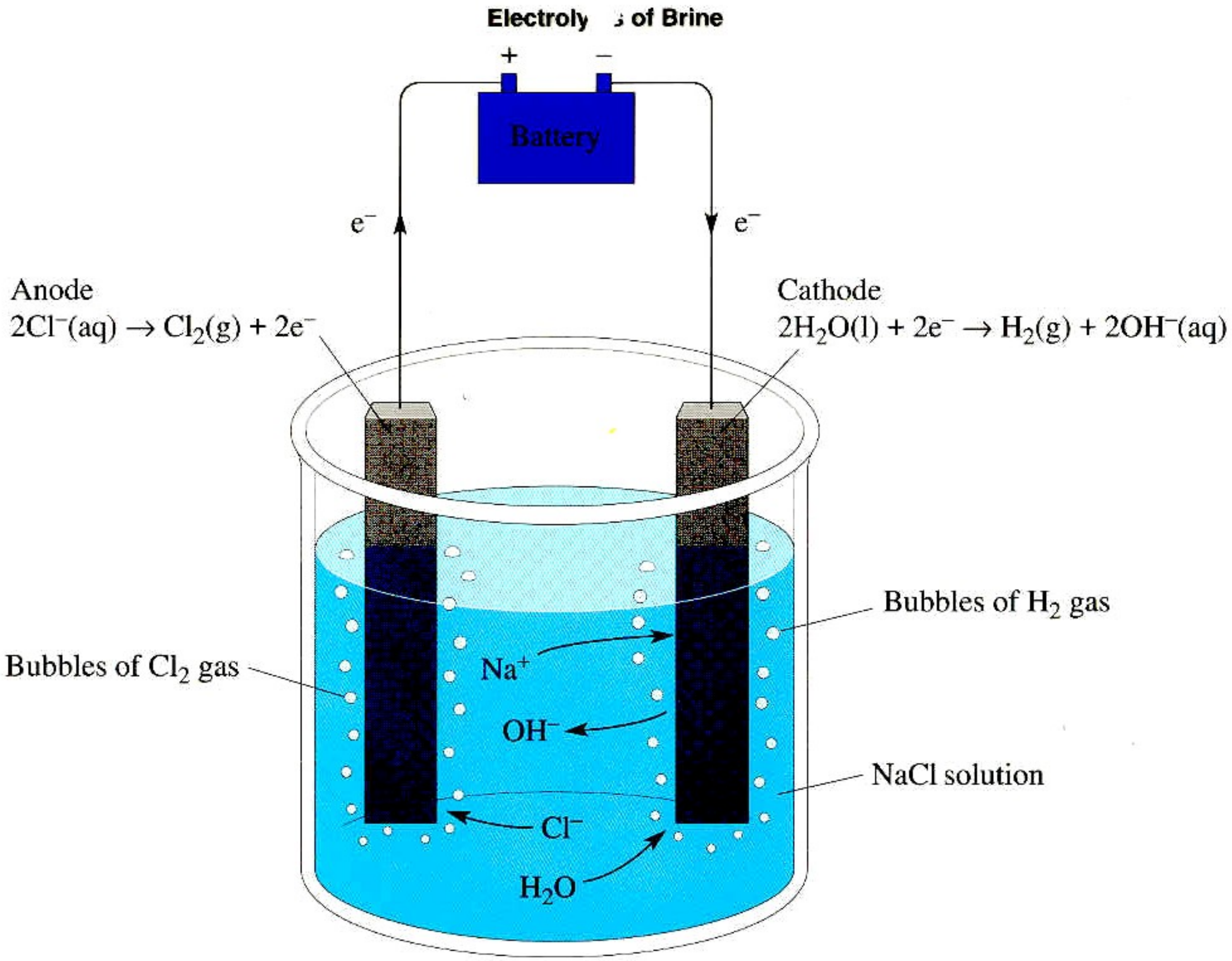
Pure Al_2O_3 (bauxite) melts at 2050°C, but it dissolves readily in molten Cryolite (Na_3AlF_6), which melts at “only” 950°C.

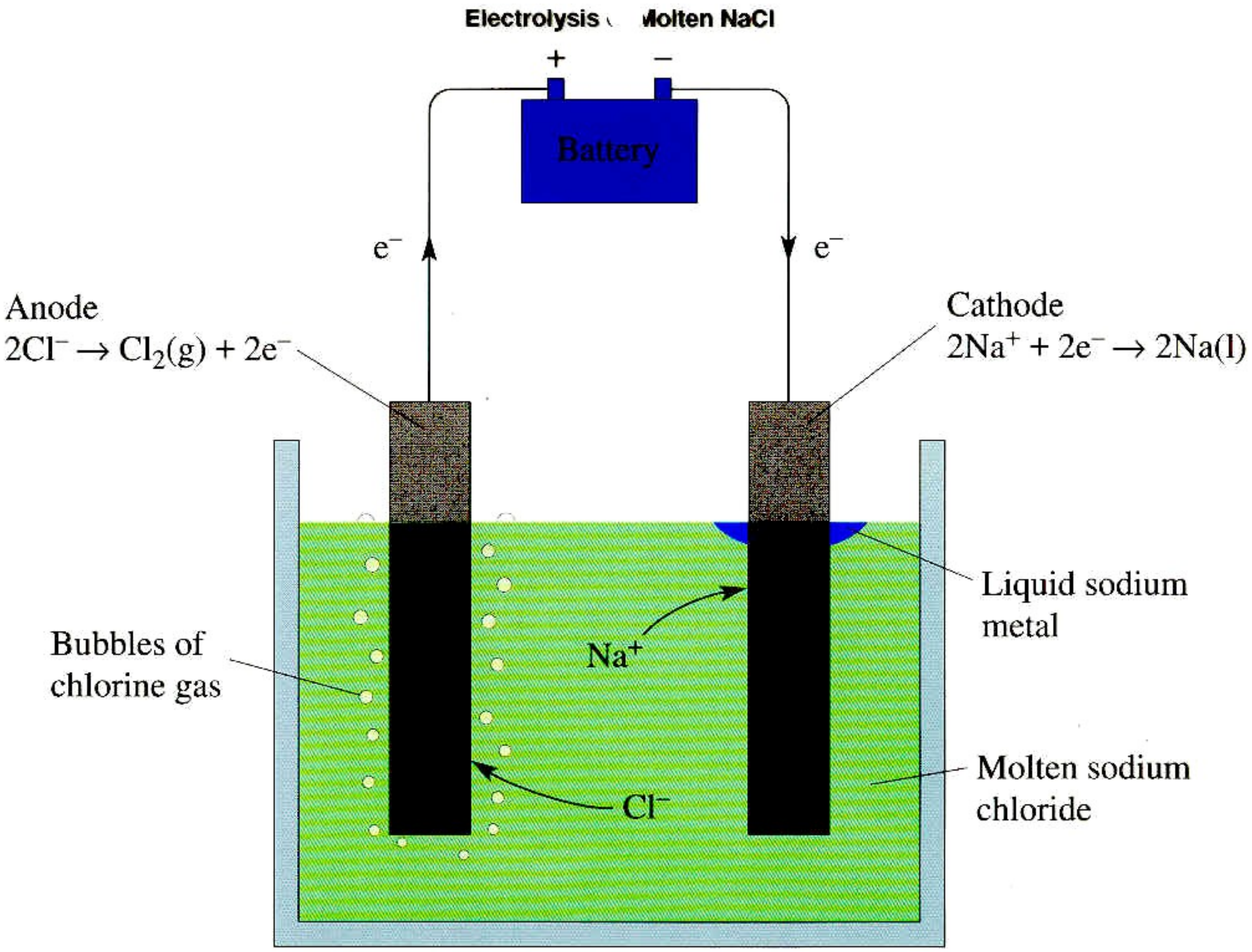
Batteries

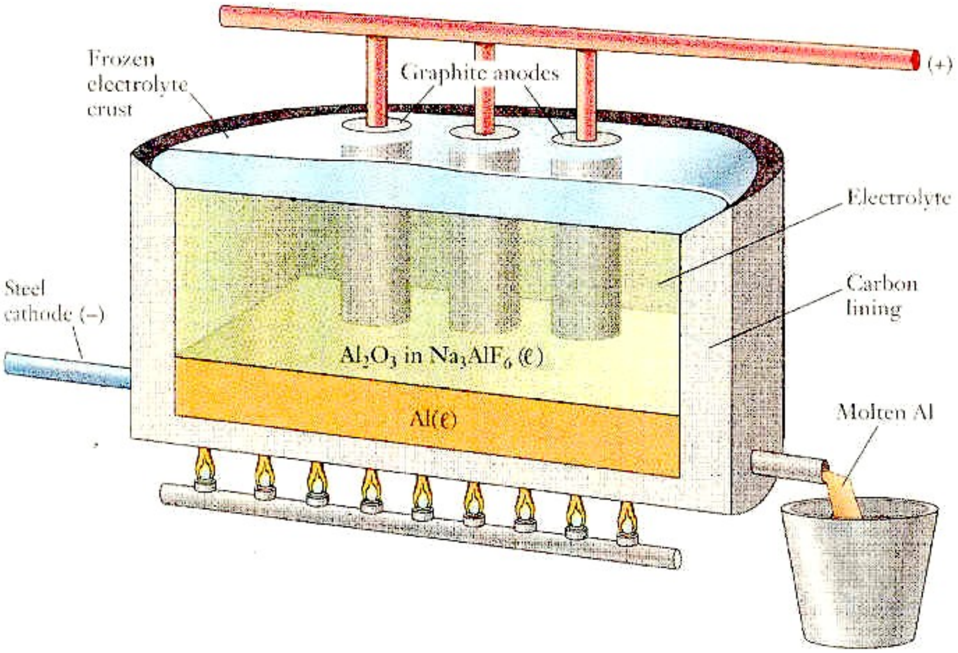
Primary
Secondary

Fuel Cells

Controlled combustion (oxidation)


Electroly ; of Brine
+
−
Battery
e^-
e^-
Anode
$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
Cathode
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
Bubbles of H_2 gas
Bubbles of Cl_2 gas
Na^+
OH^-
NaCl solution
Cl^-
H_2O


Electrolysis (Molten NaCl
+
–
Battery
e^-
e^-
Anode
$2Cl^- \rightarrow Cl_2(g) + 2e^-$
Cathode
$2Na^+ + 2e^- \rightarrow 2Na(l)$
Liquid sodium metal
Na^+
Bubbles of chlorine gas
Molten sodium chloride
Cl^-


Frozen electrolyte crust
Graphite anodes
(+)
Electrolyte
Carbon lining
Steel cathode (–)
Al_2O_3 in Na_3AlF_6 (ℓ)
Al(ℓ)
Molten Al

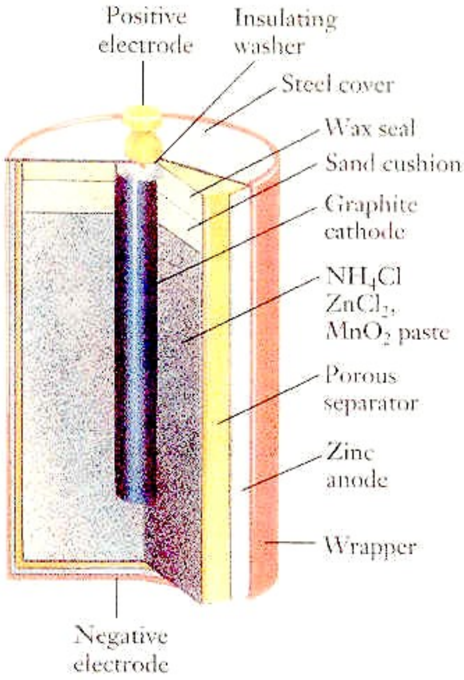


FIGURE 12.6 In a Leclanché dry cell, electrons are released to an external circuit at the anode and enter the cell again at the cathode, where the reduction of MnO_2 occurs.

Conventional Leclanché Dry Cell

$$Zn\ (s) + 2\ MnO_2\ (s) + 2\ NH_4^+\ (aq) \rightarrow Zn^{2+}\ (aq) + Mn_2O_3\ (s) + H_2O\ (l) \qquad E° = +1.50\ V$$

Alkaline Dry Cell (NH$_4$Cl replaced by KOH)

$$Zn\ (s) + 2\ MnO_2\ (s) + H_2O\ (l) \rightarrow Zn(OH)_2\ (s) + Mn_2O_3\ (s) \qquad E° = +1.50\ V$$

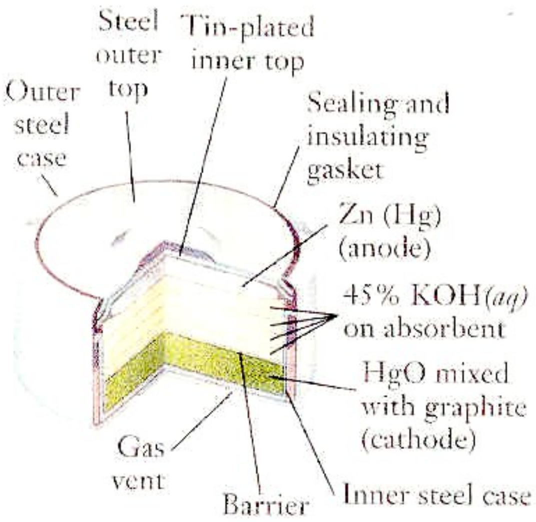


FIGURE 12.7 A zinc–mercuric oxide dry cell, used in electric watches and cameras.

Anode is a mixture of Hg and Zn; cathode is steel in contact with solid HgO. Electrolyte is 45% KOH solution that saturates an absorbent material.

$$\text{Zn}\ (s) + \text{HgO}\ (s) + \text{H}_2\text{O}\ (l) \rightarrow \text{Zn(OH)}_2\ (s) + \text{Hg}\ (l) \qquad E^\circ = +1.34\ \text{V}$$

Rechargeable Batteries

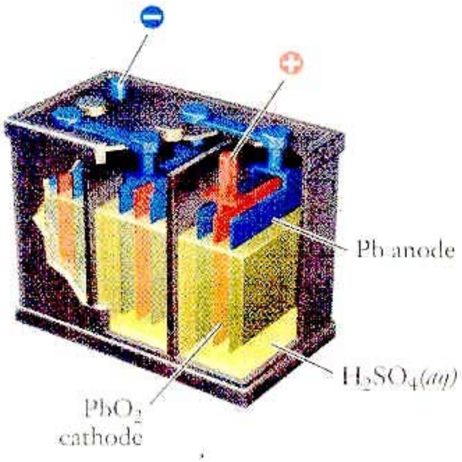


FIGURE 12.9 In a lead–acid storage battery, anodes made of Pb alternate with cathodes of Pb coated with PbO_2. The electrolyte is sulfuric acid.

$Pb\ (s)\,|\,PbSO_4\ (s)\,|\,H_2SO_4\ (aq)\,|\,PbSO_4\ (s)\,|\,PbO_2\ (s)\,|\,Pb\ (s)$

$$Pb\ (s) + PbO_2\ (s) + 2\ HSO_4^- + 2\ H_3O^+\ (aq) \rightarrow 2\ PbSO_4\ (s) + 3\ H_2O\ (l) \qquad E^\circ = 2.0\ V$$

Nickel-Cadmium

$$Cd\ (s) + 2\ NiO(OH)\ (s) + 2\ H_2O\ (l) \rightarrow Cd(OH)_2\ (s) + 2\ Ni(OH)_2\ (s) \qquad E = +\ 1.34\ V$$

Li-Ion Batteries

Both the anode and cathode are materials into which, and from which, lithium ions can migrate. During insertion (or intercalation) lithium ions move into the electrode. During the reverse process, extraction (or deintercalation) lithium ions move back out. When a lithium-based cell is discharging, the lithium is extracted from the anode and inserted into the cathode. When the cell is charging, the reverse occurs.

The cathode half-reaction (with charging being left-to-right) is:

$$\mathrm{LiCoO_2} \rightleftharpoons \mathrm{Li_{1\text{-}\mathit{x}}CoO_2} + x\,\mathrm{Li^+} + x\,\mathrm{e^-}$$

The anode half-reaction is:

$$x\,\mathrm{Li^+} + x\,\mathrm{e^-} + 6\,\mathrm{C} \rightleftharpoons \mathrm{Li_{\mathit{x}}C_6}$$

Because of the low density of lithium, Li-ion batteries have the lowest attainable weight-to-power ratio of any commercial batteries, making them particularly useful for mobile devices, such as laptop computers, cameras, and cell phones.

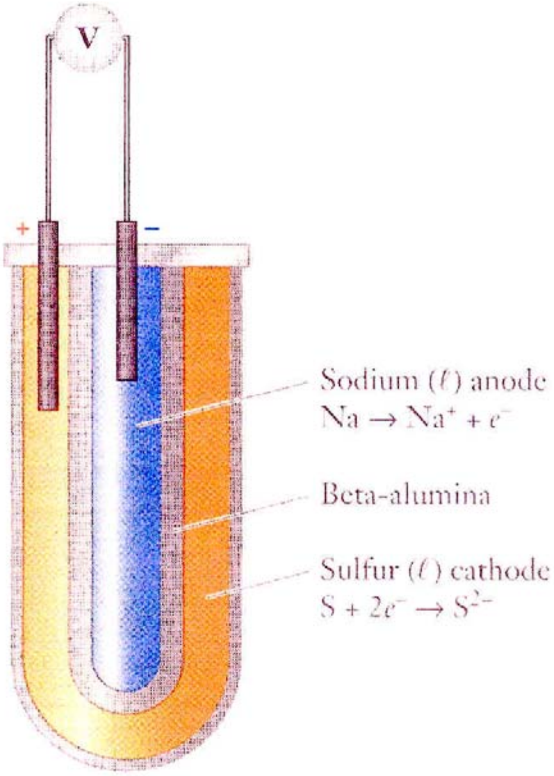
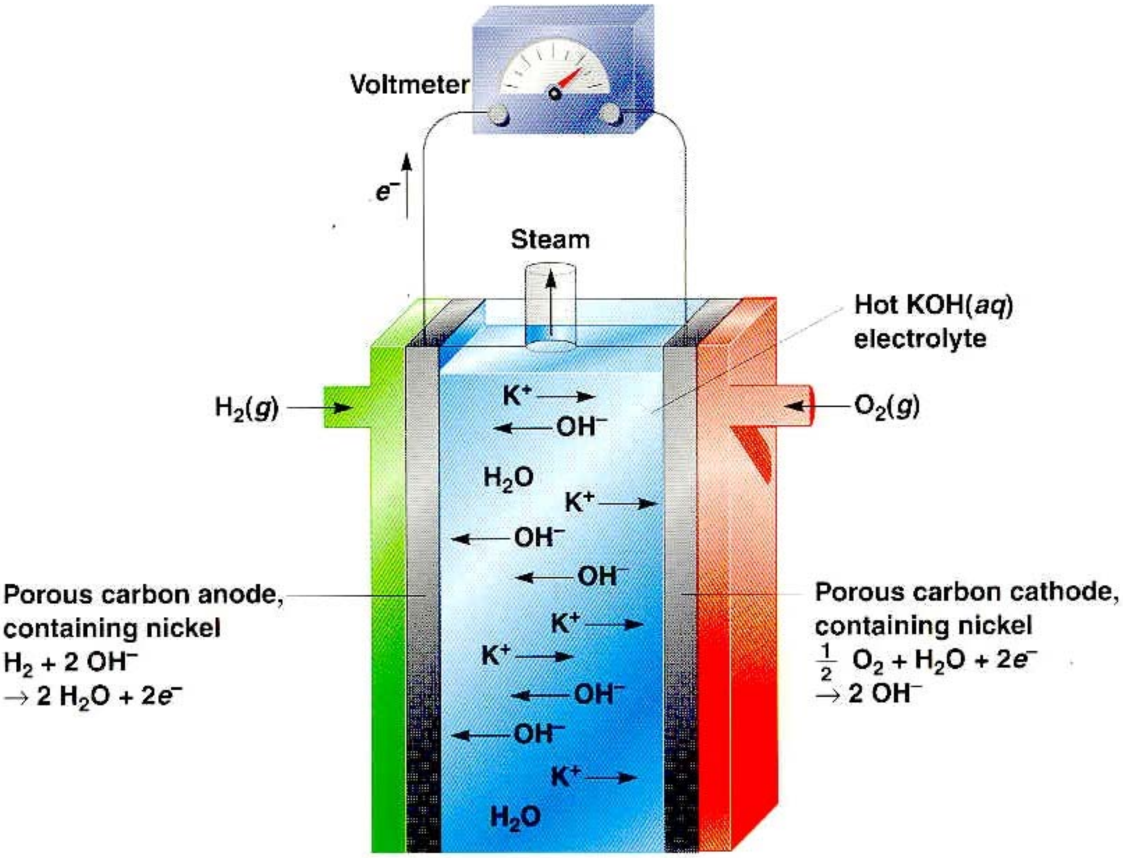
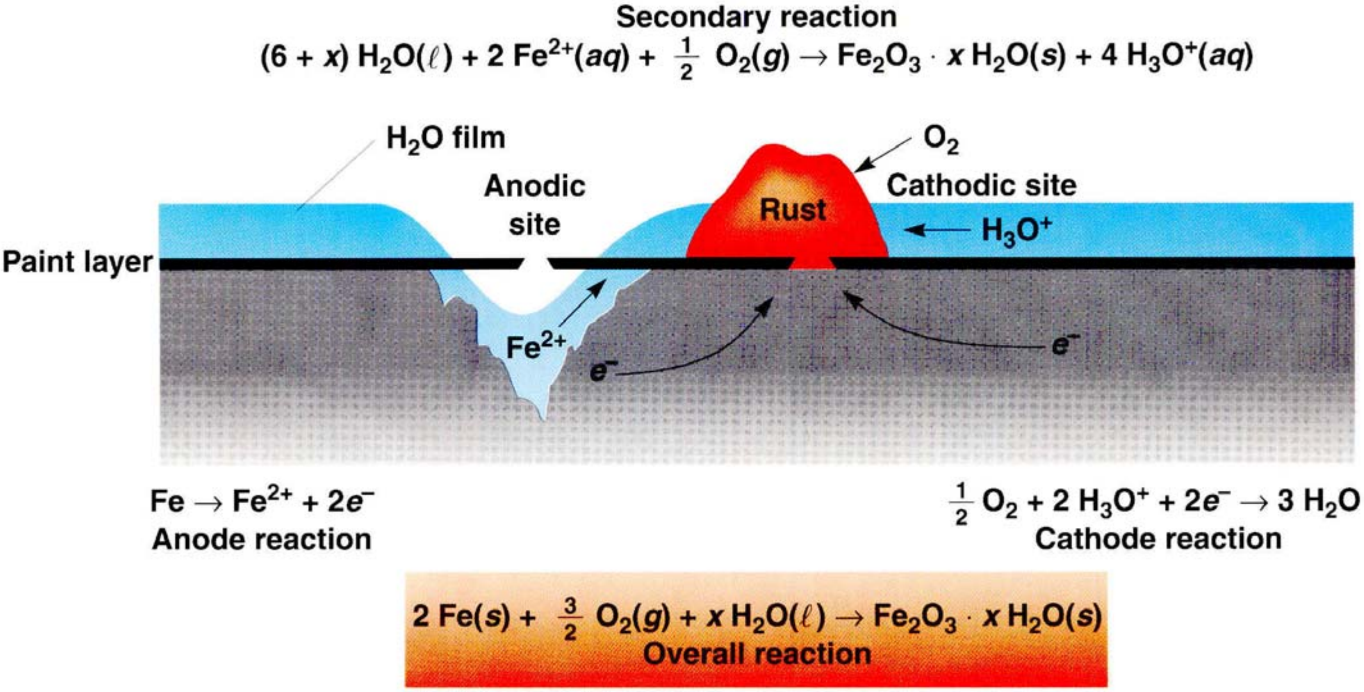


FIGURE 12.10 In a sodium–sulfur battery, Na^+ ions migrate through beta-alumina to the cathode to equalize the charge as electrons flow spontaneously from the anode to the cathode through the external circuit.

$$2\ \mathrm{Na}\ (s) + \mathrm{S}\ (s) \rightarrow 2\ \mathrm{Na}^{+}\ (aq) + \mathrm{S}^{2-} \qquad E° = +2.20\ \mathrm{V}$$

$$\mathrm{S}^{2-} + n\ \mathrm{S}\ (s) \rightarrow \mathrm{S}_{n+1}^{2-}\ (aq) \quad \textbf{(Polysulfides)}$$


Voltmeter
e^-
Steam
Hot KOH(aq) electrolyte
$H_2(g)$
$O_2(g)$
K^+
OH^-
H_2O
Porous carbon anode, containing nickel
$H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2e^-$
Porous carbon cathode, containing nickel
$\frac{1}{2}\ O_2 + H_2O + 2e^- \rightarrow 2\ OH^-$


Secondary reaction
$(6 + x)\ H_2O(\ell) + 2\ Fe^{2+}(aq) + \frac{1}{2}\ O_2(g) \rightarrow Fe_2O_3 \cdot x\ H_2O(s) + 4\ H_3O^+(aq)$
H_2O film
Anodic site
O_2
Cathodic site
Rust
H_3O^+
Paint layer
Fe^{2+}
e^-
e^-
$Fe \rightarrow Fe^{2+} + 2e^-$
Anode reaction
$\frac{1}{2}\ O_2 + 2\ H_3O^+ + 2e^- \rightarrow 3\ H_2O$
Cathode reaction
$2\ Fe(s) + \frac{3}{2}\ O_2(g) + x\ H_2O(\ell) \rightarrow Fe_2O_3 \cdot x\ H_2O(s)$
Overall reaction