21.5 Galvanic Cells as Batteries

- **Primary cells** – can't be recharged
  - The battery dies when the reactants are exhausted

Example: The alkaline battery – a dry cell

Cathode (reduction):

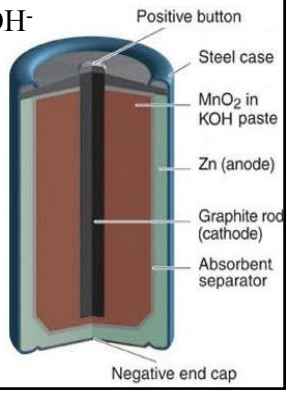
$2MnO_2(s) + H_2O + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-$

Anode (oxidation):

$Zn(s) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

Overall:

$2MnO_2(s) + Zn(s) \rightarrow Mn_2O_3(s) + ZnO(s)$

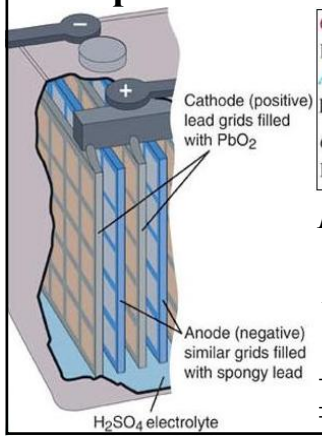


Since all reactants and products are solids (dry cell) → $Q = 1$

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln 1 = E^o_{cell} \approx 1.5\ \text{V}$$

- **Secondary cells** – can be recharged
  - The cell is periodically converted to an electrolytic cell in order to convert some of the products back to reactants

Example: The lead-acid battery



Cathode (reduction): $E^o = +1.685$ V

$PbO_2(s) + 3H^+ + HSO_4^- + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$

Anode (oxidation): $E^o = -0.356$ V

$Pb(s) + HSO_4^- \longrightarrow PbSO_4(s) + H^+ + 2e^-$

Overall (cell) reaction:

$PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$

$E^o_{cell} = 1.685 - (-0.356) = 2.041 \approx \mathbf{2\ V}$

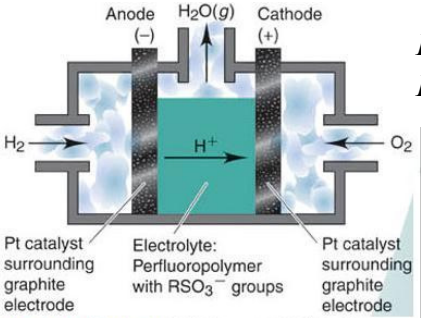
$$E_{cell} = E^o_{cell} - \frac{0.0257}{2}\ln\left(\frac{1}{[H_2SO_4]^2}\right)$$

→ As H_2SO_4 is consumed, E_{cell} drops

⇒ The cell needs to be recharged

- **Fuel cells** – use combustion reactions
  - The cell must be continuously provided with fuel and oxygen (**flow cells**)

Example: The hydrogen fuel cell



$E^o_{cell} = E^o_{cath} - E^o_{anod}$

$E^o_{cell} = 1.23 - (0.00) \approx \mathbf{1.2\ V}$

$$Q = \frac{P_{H_2O}}{P_{H_2}P_{O_2}^{1/2}}$$

$$E_{cell} = E^o_{cell} - \frac{0.0257}{2}\ln Q$$

Anode (oxidation): $H_2(g) \longrightarrow 2H^+ + 2e^-$

Cathode (reduction): $\frac{1}{2}O_2(g) + 2H^+ + 2e^- \longrightarrow H_2O(g)$

Overall (cell) reaction: $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$

⇒ ↑P_{H_2} and ↑P_{O_2} leads to ↑E_{cell}

21.6 Corrosion

- Unwanted oxidation of metals in the environment
  - If the metal (M) is in contact with water

Cathode, reduction:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $\quad E^o = -0.83$ V

(at $pH = 7$) → $\quad E = -0.42$ V

Anode, oxidation:

$M(s) \rightarrow M^{n+} + ne^-$ $\quad E^o < -0.42$ V

⇒Any metal with $E^o < -0.42$ V can be oxidized by H_2O

Cathode, reduction:

$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$ $\quad E^o = +1.23$ V

(at $pH = 7$) → $\quad E = +0.82$ V

Anode, oxidation:

$M(s) \rightarrow M^{n+} + ne^-$ $\quad E^o < +0.82$ V

⇒Any metal with $E^o < +0.82$ V can be oxidized by H_2O in the presence of O_2

– At ***pH* < 7** (acid rain, etc.), the reduction potentials of H_2O and O_2 are even higher

⇒ Easier oxidation of the metal

Example: Rusting of iron (Fe → E^o = -0.44 V)

Cathode, reduction:

$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$ $\quad E = +0.82$ V (***pH* = 7**)

Anode, oxidation:

$Fe(s) \rightarrow Fe^{2+} + 2e^-$ $\quad (\times 2)$ $\quad E^o = -0.44$ V

Overall:

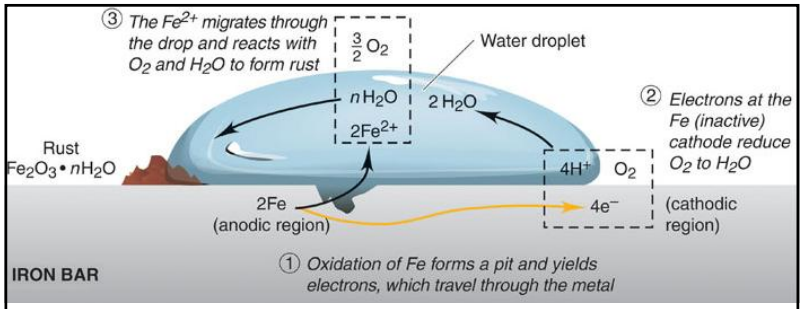
$2Fe(s) + O_2(g) + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O(l)$

$E^o_{cell} = E^o_{cath} - E^o_{anod} = +0.82 - (-0.44) = \mathbf{+1.26\ V}$

⇒ $E^o_{cell} > 0$ → spontaneous reaction

→ Further oxidation:

$2Fe^{2+} + \frac{1}{2}O_2(g) + (n+2)H_2O(l) \rightarrow \overbrace{Fe_2O_3 \cdot nH_2O(s)}^{\text{Rust}} + 4H^+$



→ Overall rusting process:

$2Fe(s) + O_2(g) + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O(l)$

$2Fe^{2+} + \frac{1}{2}O_2(g) + (n+2)H_2O(l) \rightarrow Fe_2O_3 \cdot nH_2O(s) + 4H^+$

$2Fe(s) + 3/2O_2(g) + nH_2O(l) \rightarrow Fe_2O_3 \cdot nH_2O(s)$

→ Corrosion is enhanced by acidic conditions (↑$[H^+]$) and by salty solutions (improved conductivity)

- **Corrosion protection**
  - **Anodic protection** – preoxidation of the metal by formation of a thin layer of protective metal oxide
  - **Cathodic protection** – connecting the metal to a more strongly reducing metal with lower E^o value called **sacrificial anode**

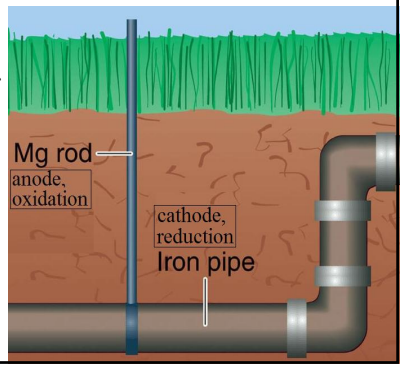
Example: Protecting **Fe** construction elements by connecting them to blocks of **Mg** or **Al** (sacrificial anodes)

$E^o_{Mg} = \mathbf{-2.36\ V}$

$E^o_{Fe} = \mathbf{-0.44\ V}$

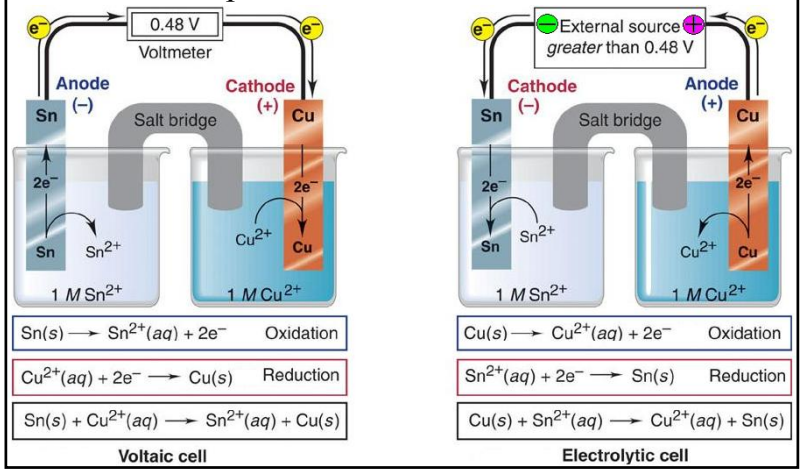
Example: Galvanization of **Fe** by coating it with **Zn**

$E_{Zn}{}^o = \mathbf{-0.76\ V}$



21.7 Electrolytic Cells and Electrolysis

- **Electrolytic cells** – use external electrical source to drive a non-spontaneous reaction



- **Electrolytic cells** act in reverse (non-spontaneous) direction compared to galvanic cells
  - $E^o_{cell} < 0$ and $\Delta G > 0$ (non-spontaneous reaction)
  - The **anode is positive** and the **cathode is negative**
- There are some **similarities** between **electrolytic** and **galvanic** cells
  - **Oxidation** is always on the **anode** and **reduction** is always on the **cathode**
  - Electrons always flow from anode toward cathode

			Electrode		
Cell Type	ΔG	E_{cell}	**Name**	**Process**	**Sign**
Voltaic	<0	>0	Anode	Oxidation	−
			Cathode	Reduction	+
Electrolytic	>0	<0	Anode	Oxidation	+
			Cathode	Reduction	−

- **Electrolysis** – the passage of electrical current through an electrolyte by applying external voltage (the process in electrolytic cells)
  - Electrolysis causes a non-spontaneous reaction (often a splitting of a substance to its elements)
  - The applied voltage must be greater than the cell potential of the reverse spontaneous reaction
  - The electrolyte can be a molten salt or an aqueous electrolyte solution
  - Salt bridges are often not necessary
  - During electrolysis the cations are attracted to the cathode (negative) and the anions are attracted to the anode (positive)