Batteries (cells with spontaneous redox reactions)

Dry Cell

Alkaline Battery

uses KOH instead of NH $_4^+$ and ZnCl₂

anode: $Zn(s) + 2OH(aq) \times ZnO(s) + H_2O(l) + 2e^{-r}$

cathode: $2MnO_2(s) + H_2O(l) + 2e^{\frac{1}{2}} \times Mn_2O_3(s) + 2OH(aq)$

 $E_{\text{cell}} = 1.54 \text{ V}$

lasts longer, but slightly more expensive because of the construction

Mercury Battery

anode: $Zn(s) + 2OH(aq) \times ZnO(s) + H₂O(l) + 2e^{-r}$

cathode: $HgO(s) + H₂O(l) + 2e^- \times Hg(l) + 2OH(aq)$

 $E_{cell} = 1.34$ V

More current for a given size (used for calculators, watches, hearing aids, cameras). More expensive because of the Hg.

 E_{cell} constant during discharge because cell reaction doesn't change cell electrolyte composition.

Not rechargeable. Disposal of Hg is also a problem.

Nickel-Cadmium (nicad) & Nickel-Metal Hydride (NiMH) Batteries

Lithium Ion Battery

anode: Li(in polymer) λ Li⁺ (in polymer) + e⁻ cathode: $(in CoO₂) + e + CoO₂ \times LiCoO₂$ Rechargeable, long life, higher voltage ($E_{cell} = 3.4 V$). Used in portable computers, cellular phones, cameras.

Lead Storage Battery

anode (porous Pb): $Pb(s)$ + $HSO₄(aq)$ \times $PbSO₄(s)$ + $H⁺$ + 2e⁻ cathode (PbO₂): PbO₂(s) + 3H⁺(aq) + HSO₄⁻(aq) + 2e⁻ X PbSO₄(s) + 2H₂O(l)

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E_{cell} = 2.0 V
$$

Car battery has six cells in series to provide 12 V.

Rechargeable, since $PbSO₄$ sticks to electrodes.

Fuel Cells

Involve the direct conversion of chemical energy γ electrical energy (~70% efficiency) (otherwise, chemical Y heat Y electrical energy is only \sim 30% efficient)

Reactants are continuously supplied.

Example:

H₂ fuel anode: $H_2(g) + 2OH$ (aq) \times 2H₂O(l) + 2e⁻ cathode: $O_2(g) + 2H_2O(l) + 4e^- \times 4OH^ E_{cell}^0 = 1.23 \text{ V} (E_{cell} \sim 0.7 \text{ V})$

The Direct Fuel Cell installation on campus works in the following way.

Electrolysis - reactant-favored reactions

 $H₂O$ (basic/neutral solution)

anode: X O₂(g) + 2H₂O(l) + 4e⁻ E^o_{ox} = -0.40 V cathode: 2H₂O(I) + 2e χ H₂(g) + OH (aq) E⁰_{red} = -0.83 V ____________________________ overall: 2H₂O \times O₂(g) + 2H₂(g) $E^0 = -1.23$ V

Must have mobile ions in solution so that charge balance can be maintained.

Electrolysis of 1.0 M CuSO₄ at pH = 5.0, P_{H2} = 1 atm, P_{O2} = 1 atm

possible cathode reactions

 $Cu^{2+}(aq)$ + 2e⁻ \times Cu(s) $E_{\text{red}} = 0.34 \text{ V} - (0.0592/2) \log 1/[\text{Cu}^{2+}] = 0.34 \text{ V}$ 2H⁺(aq) + 2e \times H₂(g) $E_{\text{red}} = 0.00 \text{ V} - (0.0592/2) \log P_{\text{H2}} / [\text{H}^+]^2 = -0.296 \text{ V}$ Cu^{2+} is reduced (Cu will plate out on cathode) because it has the more favorable E_{red} . possible anode reactions

 $2SO_4^2$ ² \times $S_2O_8^2$ (aq) + 2e E_{ox}^0 = -2.00 V 2H₂O(I) X O₂(g) + 4H⁺(aq) + 4e⁻ E_{ox} = -1.23 V - (0.0592/4)logP_{O2}[H⁺]⁴ = -0.93 V $O₂$ is produced at the anode because it has the more favorable E_{ox} .

Electrolysis of 1.0 M ZnSO₄ at pH = 5.0, P_{H2} = 1 atm, P_{O2} = 1 atm

possible cathode reactions

 $Zn^{2+}(aq)$ + 2e^{- χ} $Zn(s)$ E_{red} = -0.76 V - (0.0592/2)log1/[Zn²⁺] = -0.76 V 2H⁺(aq) + 2e \times H₂(g) $E_{\text{red}} = 0.00 \text{ V} - (0.0592/2) \log P_{\text{H2}} / [\text{H}^+]^2 = -0.296 \text{ V}$

H₂ should form (it has the more favorable E_{red}), but Zn plates out due to **overvoltage**.

For Zn: $E_{\text{red}} = -0.76 \text{ V} - \text{overvoltage(Zn)}$

For H₂: $E_{\text{red}} = -0.296 \text{ V} - \text{overvoltage(H}_2)$

Overvoltage is a kinetic effect. Electron transfer is inhibited at the electrode. It is usually small for the deposition of metals, but often large (~1 V) for the evolution of gases. This explains why you can plate out Cr^{3+} and Ni²⁺, and produce $Cl_2(g)$ in the electrolysis of NaCl(aq), even though they have unfavorable half-cell potentials.