# Batteries (cells with spontaneous redox reactions)

# Dry Cell

anode:	$Zn(s) \times Zn^{2+}(aq) + 2e^{-}$
cathode:	$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \times Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$
$E_{cell} = 1.5 V$	(Indep. of cell size. Current output depends on cell size. As cell vol. increases, $R_{int}$ decreases and $I_{cell}$ increases; V=IR)
Problems:	Can't recharge because Zn <sup>2+</sup> diffuses away. Acidic NH <sub>4</sub> <sup>+</sup> corrodes Zn, leading to poor shelf life.

## Alkaline Battery

uses KOH instead of NH<sub>4</sub><sup>+</sup> and ZnCl<sub>2</sub>

anode:  $Zn(s) + 2OH(aq) \times ZnO(s) + H_2O(l) + 2e^{-1}$ 

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

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

lasts longer, but slightly more expensive because of the construction

## Mercury Battery

anode:  $Zn(s) + 2OH(aq) \times ZnO(s) + H_2O(l) + 2e^{-1}$ 

cathode: HgO(s) +  $H_2O(l)$  +  $2e^- \times Hg(l)$  +  $2OH^-(aq)$ 

 $E_{cell} = 1.34 \text{ V}$ 

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

 $\mathsf{E}_{\mbox{\tiny cell}}$  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

anode (nicad):  $Cd(s) + 2OH^{-}(aq) \times Cd(OH)_{2}(s) + 2e^{-}$ (NiMH)  $MH(s) + OH^{-}(aq) \times M(s) + H_{2}O(l) + e^{-}$ cathode:  $NiO(OH)(s) + H_{2}O(l) + e^{-} \times Ni(OH)_{2}(l) + OH^{-}(aq)$ Ecell = 1.2-1.4 V (fairly constant during discharge) Products adhere to electrodes - reactions can be reversed by charging. Disposal of cadmium a problem (nicad). Used in calculators, cordless appliances and portable power tools.

#### Lithium Ion Battery

anode: Li(in polymer)  $\times$  Li<sup>+</sup> (in polymer) + e<sup>-</sup> cathode: Li<sup>+</sup> (in CoO<sub>2</sub>) + e<sup>-</sup> + CoO<sub>2</sub>  $\times$  LiCoO<sub>2</sub> Rechargeable, long life, higher voltage (E<sub>cell</sub> = 3.4 V). Used in portable computers, cellular phones, cameras.

#### Lead Storage Battery

anode (porous Pb):  $Pb(s) + HSO_4^{-}(aq) \times PbSO_4(s) + H^+ + 2e^$ cathode (PbO<sub>2</sub>):  $PbO_2(s) + 3H^+(aq) + HSO_4^{-}(aq) + 2e^- \times PbSO_4(s) + 2H_2O(l)$  $E_{cell} = 2.0 V$ 

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

Rechargeable, since PbSO<sub>4</sub> sticks to electrodes.

# Fuel Cells

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

Reactants are continuously supplied.

Example:

 $\begin{array}{rll} {\sf H}_2 \mbox{ fuel} & \mbox{anode:} & {\sf H}_2(g) \ + \ 2 {\sf OH}^{-}({\sf aq}) \ \times \ 2 {\sf H}_2 {\sf O}({\sf I}) \ + \ 2 {\sf e}^{-} \\ & \mbox{cathode:} & {\sf O}_2(g) \ + \ 2 {\sf H}_2 {\sf O}({\sf I}) \ + \ 4 {\sf e}^{-} \ \times \ 4 {\sf OH}^{-} \\ & {\sf E}^0_{\ \mbox{cell}} = 1.23 \ {\sf V} \ ({\sf E}_{\mbox{cell}} \sim 0.7 \ {\sf V}) \end{array}$ 

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



# **Electrolysis - reactant-favored reactions**

$H_2O$ (acidic solution)					
anode:	2H <sub>2</sub> O(I) X	$O_2(g)$ + $4H^+(aq)$ + $4e^-$	$E^{0}_{ox} = -1.23 V$		
cathode:	2H <sup>+</sup> (aq) +	2e <sup>-</sup> X H <sub>2</sub> (g)	$E^{0}_{red} = 0.00 V$		
overall:	$\overline{2H_2O(I)}$ X	$O_2(g) + 2H_2(g)$	E <sup>0</sup> = -1.23 V		

#### H<sub>2</sub>O (basic/neutral solution)

anode:  $4OH^{-} \times O_2(g) + 2H_2O(I) + 4e^{-} = E^{0}_{ox} = -0.40 \text{ V}$ cathode:  $2H_2O(I) + 2e^{-} \times H_2(g) + OH^{-}(aq) = -0.83 \text{ V}$ overall:  $2H_2O \times O_2(g) + 2H_2(g) = -1.23 \text{ V}$ 

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

Electrolysis of 1.0 M CuSO<sub>4</sub> at pH = 5.0,  $P_{H2}$  =1 atm,  $P_{O2}$  = 1 atm

possible cathode reactions

 $Cu^{2+}(aq) + 2e^{-} \times Cu(s)$  $E_{red} = 0.34 \text{ V} - (0.0592/2)\log 1/[Cu^{2+}] = 0.34 \text{ V}$  $2H^{+}(aq) + 2e^{-} \times H_2(g)$  $E_{red} = 0.00 \text{ V} - (0.0592/2)\log P_{H2}/[H^+]^2 = -0.296 \text{ V}$  $Cu^{2+}$  is reduced (Cu will plate out on cathode) because it has the more favorable  $E_{red}$ .

possible anode reactions

 $2SO_4^{2-} \times S_2O_8^{2-}(aq) + 2e^- = E_{ox}^0 = -2.00 V$   $2H_2O(I) \times O_2(g) + 4H^+(aq) + 4e^- = -1.23 V - (0.0592/4)logP_{O2}[H^+]^4 = -0.93 V$  $O_2$  is produced at the anode because it has the more favorable  $E_{ox}$ .

Electrolysis of 1.0 M ZnSO<sub>4</sub> at pH = 5.0,  $P_{H2}$  =1 atm,  $P_{O2}$  = 1 atm

possible cathode reactions

 $Zn^{2+}(aq) + 2e^{-} X Zn(s) \qquad E_{red} = -0.76 V - (0.0592/2) log 1/[Zn^{2+}] = -0.76 V$  $2H^{+}(aq) + 2e^{-} X H_{2}(g) \qquad E_{red} = 0.00 V - (0.0592/2) log P_{H2}/[H^{+}]^{2} = -0.296 V$ 

 $H_2$  should form (it has the more favorable  $E_{red}$ ), but Zn plates out due to **overvoltage**.

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

For  $H_2$ :  $E_{red} = -0.296 \text{ V} - \text{overvoltage}(H_2)$ 

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  $Ni^{2+}$ , and produce  $Cl_2(g)$  in the electrolysis of NaCl(aq), even though they have unfavorable half-cell potentials.