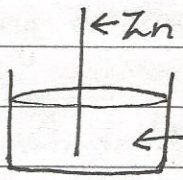
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2012 Eth. C. Grade 12. Chem.

Unit 4 ... continued. **Galvanic (Voltaic) Cells**

→ Electrochem. cells. Energy producers. Covert chem. energy into electrical energy by using spontaneous redox rxns.

→ When Zn metal is dipped into $CuSO_4(aq)$ solution, some Zn metal dissolves while some Cu metal is deposited on the Zn metal surface.




$Zn(s) \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ (Anode Rxn)

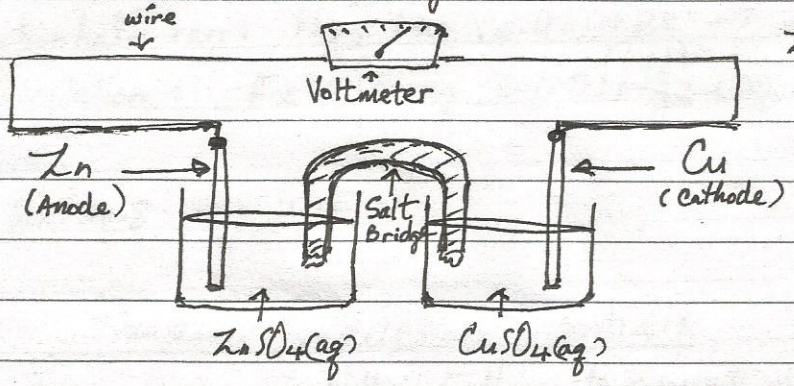
$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu(s)$ (Cathode Rxn)

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

The $CuSO_4(aq)$ is in contact with the Zn metal (electrode), electrons flow directly from the Zn metal to the $Cu^{2+}_{(aq)}$ ions without doing useful work. If the halve rxns could made to occur in separate compartments and the electrons were transferred through an external wire from one compartment to the other, then we would have a cell capable of doing electrical work (useful work). Such electrochemical cell = Galvanic (Voltaic) cell.

Galvanic cell was invented by the British chemist John Daniell in 1836.

Daniell cell




Zinc-copper Voltaic cell

Anode Compartment (Zinc half-cell)

$Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (oxidation)

Cathode Compartment (Copper half-cell)

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu(s)$ (Reduction)

Half-cell: an electrode dipping into an electrolyte solution

Salt-Bridge: electrolyte contained in an inverted U-tube (semi-solid electrolyte) electrically connects the anode compartment with the cathode compartment (completes the circuit). The electrolyte doesn't flow out. But ions can diffuse through it. i.e., from the electrolyte into the tube and from the tube into the electrolyte.

The essential components of a Galvanic cell: Two half-cells, salt bridge, conducting wire.

Oxidation occurs at anode = — electrode

Reduction occurs at cathode = + electrode

## Cell Notation

A cell notation allows to describe a Galvanic cell without drawing a diagram. The notation for any Galvanic cell has the following form:

Anode | Anode Electrolyte || Cathode Electrolyte | Cathode

The anode compartment is written on the left and the cathode compartment on the right. Single line stands for phase boundary and double lines represent the salt bridge.

Eg. Write the cell notation for the Galvanic cell based on the following rxn. $Fe(s) + Hg_2^{2+}(aq) \longrightarrow Fe^{2+}(aq) + 2Hg(l)$

Assume solution concentrations are 0.10M

oxidation half-rxn: $Fe(s) \longrightarrow Fe^{2+}(aq, 0.1M) + 2e^-$

Reduction half-rxn: $Hg_2^{2+}(aq, 0.1M) + 2e^- \rightarrow 2Hg(l)$

Cell notation: $Fe(s) \,|\, Fe^{2+}(aq, 0.1M) \,||\, Hg_2^{2+}(aq, 0.1M) \,|\, Hg(l)$

## Exercise

Do Ex. 4.8, page 190

## Standard Reduction Potentials

The purpose of a Voltaic Cell is to convert the free energy change of a spontaneous redox rxn into the kinetic energy of electrons moving through an external circuit (electrical energy). This electrical energy can do work and is proportional to the difference in the electrical potential b/n the two electrodes. This difference in the electrical potential of the electrodes is called the cell potential ($E^\circ_{cell}$), also called the voltage of the cell or the electromotive force (emf).

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

By convention the potential associated with electrode is the potential for reduction rxn to occur at the electrode at standard state condition.

## Determining $E^\circ_{half\text{-}cell}$

$E^\circ_{half\text{-}cell}$ of every half-cell is determined by using a standard reference half-cell.

The reference half-rxn (used internationally) is the reduction of $H^+_{(aq)}$ To $H_{2(g)}$ under standard state condition. It is assigned a standard reductional of exactly 0.00V.

$$2H^+_{(aq,\,1M)} + 2e^- \longrightarrow H_{2(g,\,1atm)},\ E^\circ_{red} = 0.00V.$$

An electrode designed to produce this half-rxn is a standard hydrogen electrode (SHE). SHE consists of Pt electrode dipping in 1M aqueous HCl solution. It is encased in a glass tube, so that $H_2$ gas can bubble over the Pt and the solution contains $H^+_{(aq)}$ under standard state condition.

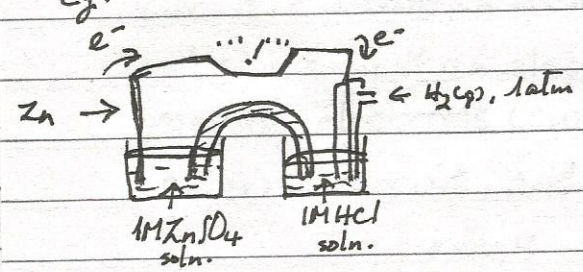
* When $H_2$ is oxidized, the reference half-cell is the anode. Reduction occurs at the unknown half-cell.

$$E^\circ_{cell} = E^\circ_{(cathode)} - E^\circ_{(anode)} = E^\circ_{(unknown)} - E^\circ_{reference}$$
$$= E^\circ_{unknown} - 0.00V$$
$$= E^\circ_{unknown}.$$

* When $H^+_{(aq)}$ is reduced, the reference half-cell is the cathode. Oxidation occurs at the unknown half-cell.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{reference} - E^\circ_{unknown}$$
$$= 0.00V - E^\circ_{unknown}$$
$$= -E^\circ_{unknown}$$

Eg.




$$2H^+_{(aq,\,1M)} + 2e^- \longrightarrow H_{2(g)},\ E^\circ_{reference} = 0.00V$$
$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq,\,1M)} + 2e^-,\ E^\circ_{Zn} = ?$$
$$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)},\ E^\circ_{cell} = 0.00V$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{reference} - E^\circ_{zinc}$$
$$= 0.00V - E^\circ_{zinc}$$

$$E^\circ_{zinc} = E^\circ_{(reference)} - E^\circ_{cell} = 0.00V - 0.76V = -0.76V$$

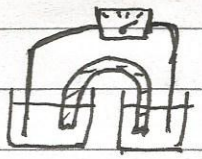
$Zn\,|\,Zn^{2+}_{(aq)}$ and $H^+_{(aq)}\,|\,H_{2(g)}$

$$Zn_{(s)}\,|\,Zn^{2+}_{(aq,\,1M)}\,//\,H^+_{(aq,\,1M)}\,|\,H_{2(g,\,1atm)}\,|\,Pt$$

$Zn^{2+}(aq, 1M) + 2e^- \longrightarrow Zn(s)$; $E^\circ_{red} = -0.76V$

Sample Problem

A Galvanic cell consists of a Mg electrode in 1.0M $Mg(NO_3)_2$ soln and a Ag electrode in 1.0M $AgNO_3$ soln. Calculate the standard cell potential (emf) of this cell at 25°C.



$Mg \mid Mg(NO_3)_2 (aq, 1M) \mid\mid AgNO_3 (aq, 1M) \mid Ag(s)$

or $Mg \mid Mg^{2+}(aq, 1M) \mid\mid Ag^+(aq, 1M) \mid Ag$

Anode (lower reduction potential) $Mg^{2+} + 2e^- \longrightarrow Mg(s)$, $E^\circ_{red} = -2.37V$

(Cathode: higher reduction potential) $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$, $E^\circ_{red} = 0.80V$

$E^\circ_{red} = E^\circ_{red}(Ag^+/Ag) - E^\circ_{red}(Mg^{2+}/Mg)$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{(anode)}$

$= [+0.80V - (-2.37V)] = +\underline{3.17V}$

OR $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$; $E^\circ_{red} = +2.37V$

$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$; $E^\circ_{red} = +0.80V$

$Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$; $E^\circ_{red} = \underline{3.17V}$

## EXERCISE

Do Ex. 3.9. Page 197.

The electromotive force in a Galvanic cell comes from the redox rxn that pushes electrons from the anode to the cathode through the external circuit. Electrons on the negative terminal repel each other and have more potential energy than electrons on the positive electrode. The energy of the moving electrons (current) is used to overcome the resistance in the external circuit, and it can do various forms of electrical work.

$Work = charge \times E_{cell}$

$= Q \times E_{cell}$

$Q = nF$, $1F = 96500\ c/mole^-$

$W_{electrical} = W_{max} = -nFE_{cell}$

The change in free energy ($\Delta G$) = $W_{max}$

$\Delta G = W_{max} = -nFE_{cell}$ (under standard state conditions)

$\Delta G < 0$ for spontaneous process, $\Delta E^\circ_{cell} > 0$ for spontaneous

$$\Delta G^\circ = -RT\ln K$$

$$nFE^\circ_{cell} = RT\ln K$$

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

When $T = 298K$,

$$E^\circ_{cell} = \frac{8.134 J/molK \times 298K}{n\ (96500 J/Vmol)}\ln K = \frac{0.0257V}{n}\ln K$$

$\ln x = 2.303 \log x$

$$E^\circ_{cell} = \frac{0.0257}{n} \times 2.303 \log K = \frac{0.0592V}{n}\log K$$

If anyone of the three quantities $\Delta G^\circ$, K or $E^\circ_{cell}$ is known, the other two can be calculated, using the equations $\Delta G^\circ = -RT\ln K$, $\Delta G^\circ = -nFE^\circ_{cell}$ or $E^\circ_{cell} = \frac{-\Delta G^\circ}{nF}$.

| $\Delta G^\circ$ | K | $E^\circ_{cell}$ | Rxn at standard state condition |
|---|---|---|---|
| $<0$ | $>1$ | $>0$ | spontaneous |
| 0 | 1 | 0 | At Equilibrium |
| $>0$ | $<1$ | $<0$ | Non-spontaneous |

## The Effect of concentration on cell Potential

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q \quad \text{(Nernst Equation)}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0592V}{n}\log Q \quad \text{at } 25^\circ C$$

$$Q = \frac{[\text{oxidized species}]}{[\text{Reduced species}]}$$

The Nernst equation gives the relationship b/n the cell potential and the concentration of the cell components.

## Sample Problem

1. Calculate the equilibrium constant for the following rxn at 25°C.

$$Sn_{(s)} + 2Cu^{2+}_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + 2Cu^{+}_{(aq)}$$

$$\ln K = \frac{nE^\circ_{cell}}{0.0257V} \Rightarrow K = e^{\frac{nE^\circ_{cell}}{0.0257V}}$$

$Sn^{2+}_{(aq)} + 2e^- \longrightarrow Sn_{(s)}$, $E^\circ_{red}$ (Anode) $= -0.14V$

$2Cu^{2+}_{(aq)} + 2e^- \longrightarrow 2Cu^{+}_{(aq)}$, $E^\circ_{red}$ (cathode) $= 0.15V$

$E^\circ_{cell} = E^\circ_{red(cathode)} - E^\circ_{red(anode)}$

$= 0.5V - (-0.14V) = 0.29V$

Charge = 2

Therefore $\frac{nE^\circ_{cell}}{0.0257V} = \frac{2 \times 0.29V}{0.0257V} = \frac{0.58}{0.0257} = 22.6$

$K_{standard} = e^{nE^\circ_{cell}/0.0257V} = e^{22.6} = (2.72)^{22.6} = 6.62 \times 10^9$

2. Calculate the free energy change for the following rxn at 25°C.

$2Au(s) + 3Ca^{2+}(1.0M) \rightarrow 2Au^{3+}(1.0M) + 3Ca(s)$

$\Delta G^\circ = -nFE^\circ_{cell}$

(Anode): $2Au(s) \longrightarrow 2Au^{3+}(aq) + 6e^-$, $E^\circ_{red} = 1.50V$

(Cathode): $3Ca^{2+}(aq) + 6e^- \longrightarrow 3Ca(s)$, $E^\circ_{red} = -2.87V$

$E^\circ_{cell} = E^\circ_{(cathode)} - E^\circ_{(anode)} = -2.87V - 1.50V = -4.37V$

$\therefore \Delta G^\circ = -6 \times 96500 C/mol \times (-4.37V)$, $C = J/V$

$= 2530230 J/mol = 2.53 \times 10^6 J/mol = 2.53 \times 10^3 KJ/mol$

The large positive value of $\Delta G^\circ$ indicates that the reaction favors the reactants. The forward rxn is non-spontaneous. That means Au cannot reduce Ca.

3. Calculate $\Delta G^\circ$ for the following rxn at 25°C.

$2Al^{3+}(aq) + 3Mg(s) \rightleftharpoons 2Al(s) + 3Mg^{2+}(aq)$

(Anode): $3Mg(s) \rightarrow 3Mg^{2+}(aq) + 6e^-$, $E^\circ_{red} = -2.37V$

(Cathode): $2Al^{3+}(aq) + 6e^- \rightarrow 2Al(s)$, $E^\circ_{red} = -1.66V$

$E^\circ_{cell} = E^\circ_{(cathode)} - E^\circ_{(anode)}$

$= -1.66V - (-2.37V) = 2.37V - 1.66V = 0.71V$

$\Delta G^\circ = -nFE^\circ_{cell} = -6 \times 96500 J/V \times 0.71V = -411090 J$

$= -4.11 \times 10^5 J = -4.11 \times 10^2 KJ/mol$

5. Predict whether the following would proceed spontaneously as written at 298K, given $[Co^{2+}] = 0.15M$ and $[Fe^{2+}] = 0.68M$

$Co(s) + Fe^{2+}(aq) \longrightarrow Co^{2+}(aq) + Fe(s)$

The Half-cell rxns are (Anode): $Co(s) \rightarrow Co^{2+}(aq) + 2e^-$, $E^\circ_{red} = -0.28V$

(Cathode): $Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$, $E^\circ_{red} = -0.44V$

$E^\circ_{cell} = E^\circ_{red(cathode)} - E^\circ_{red(anode)} = -0.44V - (-0.28V) = -0.16V$

$\Delta G^\circ = -nFE^\circ_{cell} = -2 \times 96500\ J/V \times (-0.16V) = 30880J$

$= 30.88KJ$

Not spontaneous as written.

OR $E_{cell} = E^\circ_{cell} - \frac{0.0592V}{n} \times \log Q = -0.16V - \frac{0.0592V}{2} \log \frac{0.15}{0.68}$

$= -0.16V + 0.019V$

$= -0.141V$

The rxn is not spontaneous as written. B/C cobalt can not reduce iron.

ASSIGNMENT

EXERCISE 4.11, Page 204.

## BATTERIES

A battery is a Galvanic cell or a series of combined Galvanic cells. They are used as sources of direct electric current at constant voltage. They are convenient and portable - Batteries can be:

(i) Primary - Not rechargeable (cell rxn irreversible)

(ii) Secondary - Can be recharged (rechargeable. B/C cell rxn reversible)

iii) Fuel Cell - Works by continuous supply of reactants from outside the cell

### Primary Batteries

→ not rechargeable (not renewable)

Eg. a) Dry cell (C-Zn battery) = Le Clanche cell

| Electrolyte | Anode | cathode |
|---|---|---|
| Moist: paste of $NH_4Cl$ + $ZnCl_2$ + $MnO_2$ | Zn | Graphite rod |

Anode Rxn: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $\quad Zn^{2+}(aq) + 2NH_3(aq) + 2Cl^-(aq) \rightarrow Zn(NH_3)_2Cl_2(s)$

Cathode Rxn: $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Overall Rxn: $2MnO_2(s) + 2NH_4Cl(aq) + Zn(s) \rightarrow Zn(NH_3)_2Cl_2(s) + H_2O(l) + Mn_2O_3(s)$, $E_{cell} = 1.5V$

Uses: Portable radios, flash lights.

Advantage: cheap, safe, available in many sizes

Disadvantage: Short shelf life b/c the Zn anode reacts with the acidic $NH_4^+$ ...

## b) Alkaline Battery

| Electrolyte | Anode | cathode |
|---|---|---|
| KOH paste + $MnO_2$ | Zn | graphite rod |

Anode Rxn: $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

Cathode Rxn: $MnO_{2(s)} + 2H_2O_{(l)} + 2e^- \rightarrow Mn(OH)_{2(s)} + 2OH^-_{(aq)}$

Overall Rxn: $Zn_{(s)} + MnO_{2(s)} + 2H_2O_{(l)} \rightarrow ZnO_{(s)} + Mn(OH)_{2(s)}$

$E_{cell} = 1.5V$

Uses: Same as dry cell

Advantage: No voltage drop and longer shelf life than dry cell, safe many sizes.

Disadvantages: More expensive than common dry cell.

## c) Mercury and Silver (Button) Batteries

The mercury battery and the silver Battery are similar. Both use zinc anode in basic medium. The mercury cell uses HgO cathode. The silver cell uses $Ag_2O$ cathode.

Mercury cell

Anode Rxn: $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

Cathode Rxn: $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)}$

Silver cell

Cathode Rxn: $Ag_2O + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-_{(aq)}$

overall cell Rxn:

Mercury cell: $Zn_{(s)} + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$, $E_{cell} = 1.3V$

Silver cell: $Zn_{(s)} + Ag_2O_{2(s)} \rightarrow ZnO_{(s)} + 2Ag_{(s)}$, $E_{cell} = 1.6V$

Uses: The mercury cell is used in watches and calculators; the silver cell in cameras, heart peacemakers, and hearing aids

Advantage: Both are very small, with relatively large voltage. The silver cell has a steady output

Disadvantage: Discarded mercury cells release the toxic metal. Silver cells are expensive.

## Secondary (Rechargeable) Batteries

### 1. Lead-Acid Battery

A typical 12 V lead acid car battery has six cells connected in series, each of which delivers about 2.1 V. Each cell contains two lead grids packed with the electrode materials; the anode is spongy, powdered Pb and the cathode is powdered $PbO_2$. The grids are immersed in an electrolyte solution of about 4.5 M $H_2SO_4$. Fiberglass sheets b/n the grids prevent shorting due to physical contact.

→ When the cell discharges

Anode Rxn: $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$

Cathode Rxn: $PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall Rxn: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$, $E_{cell} = 2.1\,V$

→ When the cell is recharging it uses electrical energy as electrodaytic cell and the half-cell and overall reactions are reversed.

$$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq).$$

**Uses**

* In automobiles and trucks

→ Advantage:- provids a large burst of current to the engine starter motor; is reliable and has a long life; is effective at low temperature.

→ Disadvantage: ① Loss of capacity ② Safety hazard

### 2. Nickel-Metal Hydride (Ni-MH) Battery

The nickel-metal hydride is replacing the nicked-cadmium battery.

Anode Rxn: $MH(s) + OH^-(aq) \rightarrow M(s) + H_2O(l) + e^-$

Cathode Rxn: $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

Overall Rxn: $MH(s) + NiO(OH)(s) \rightarrow M(s) + Ni(OH)_2(s)$; $E_{cell} = 1.4\,V$

The cell rxn is reversed during recharging.

Uses: cordless razors, photo flash units and power tools.

Advantage: Lightweight; high power, avoids the toxicity of cadmium in Nicad battery.
Disadvantage: Discharge upon storage.

3. Lithium-Ion Battery

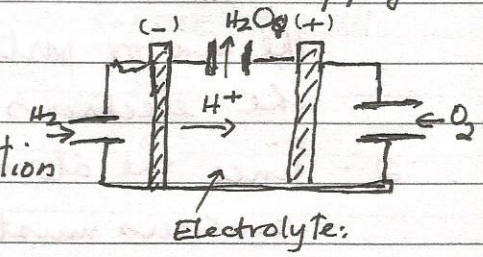
Anode: $Li_x$(graphite) or Lithium in graphite
Cathode: $LiMn_2O_4$
Electrolyte: 1M $LiClO_4$ in ethylene carbonate
Anode Rxn: $Li_x(graphite) \rightarrow xLi^+ + xe^-$
Cathode Rxn: $Li_{1-x}Mn_2O_4(s) + xLi^+ + xe^- \rightarrow LiMn_2O_4(s)$
Overall Rxn: $Li_x(graphite) + Li_{1-x}Mn_2O_4(s) \rightarrow LiMn_2O_4(s)$; $E_{cell} = 3.7V$
The cell rxn is reversed when recharging.
Uses: Laptop computers, cell phones and camcorders
Advantages: Extremely high energy/mass ratio
Disadvantage: Expensive, organic solvent may be flammable.

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## Fuel Cells (Flow Batteries)

A fuel cell is a Galvanic cell that requires a continuous supply of reactants to keep functioning.

Eg. ① Hydrogen-Oxygen Fuel cell




Electrolyte: NaOH solution or KOH solution
Anode: Porous C containing Ni
Cathode: Porous C containing Ni and NiO

Anode Rxn: $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$ $E_{red} = -0.83V$
Cathode Rxn: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$ $E_{red} = 0.40V$
Overall Rxn: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$, $E^\circ_{cell} = 1.23V$
Uses:- for transportation, residential and business electric power; currently provide electricity and pure water during spaceflights.
Advantage: ① clean and portable, produce no pollutants. ② convert about 75% of bond energy in fuel into electricity
Disadvantages: ① Fuel cells operate with continuous supply (flow) of reactants. They cannot store electrical energy ② Electrode catalysts are expensive.