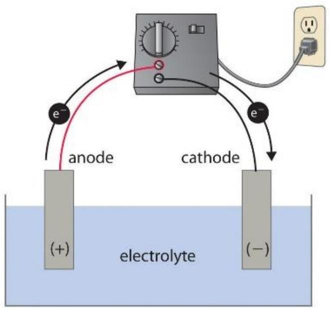
Redox reactions in electrolytic cell and chemical cell

-reactions that occur in electrolytic cells and chemical cells are redox reactions (involving transfer of electrons)

-whether it is an electrolytic cell or chemical cell, oxidation occurs at the anode and reduction occurs at the cathode

Redox reaction in an electrolytic cells



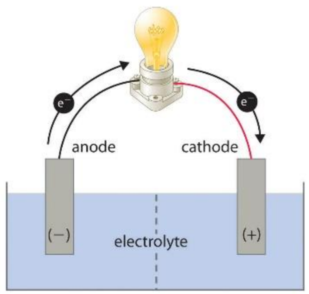
i. external circuit: during electrolysis, e^- flow from the anode (positive terminal) to cathode (negative terminal)

ii. anode (positive terminal)
-anion (negative ions) move towards the anode
-anions release e^- at the anode
-oxidation occurs at the anode

iii. cathode (negative terminal)
-cation (positive ions) move towards the cathode
-cations accept e^- from the cathode
-reduction occurs at the cathode

iv. electrolyte
-cations move towards the cathode
-anions move towards the anode
-the flow of ions to the electrode constitute the flow of electric current in the electrolyte

Redox reaction in chemical cells



i. external circuit
-electric current is produced because e^- flow from the more electropositive electrode (negative terminal) to the less electropositive electrode (positive terminal)

ii.anode (negative terminal)
-zinc dissolves to form zinc ions with the release of e^-

$Zn \rightarrow Zn^{2+} + 2e^-$

-the e^- flow through the external circuit to the copper electrode
-oxidation occurs at anode

iii. cathode (positive terminal)

-H^+ ions accept e^- from zinc to form hydrogen gas

$2H^+ + 2e^- \rightarrow H_2$

-effervescence occurs around the copper electrode
-reduction occurs at the cathode

iv. electrolyte
-the concentration of Zn^{2+} ions increases, while the concentration of H^+ ions decreases
-the overall reaction that occurs in the chemical cell

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

-zinc acts as the reducing agent and hydrogen ions acts as the oxidising agent

Redox reaction in electrolyte cells

-at anode: oxidation

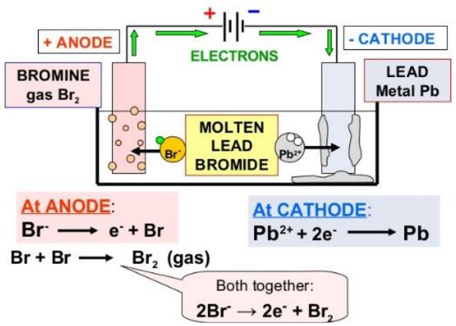
$A^{n-} \rightarrow A + ne^-$

-at cathode: reduction

$B^{n+} + ne^- \rightarrow B$

-e^- flow from the anode (positive electrode) to the cathode (negative electrode) through the connecting wire

I. electrolysis of molten lead(II) bromide



i.anode
- Br^- ions lose e^- to form bromine molecule

$2Br^- \rightarrow Br_2 + 2e^-$

-oxidation process
-oxidation number from -1 to 0
ii. cathode
-Pb^{2+} ions gain e^- to form lead metal

$Pb^{2+} + 2e^- \rightarrow Pb$

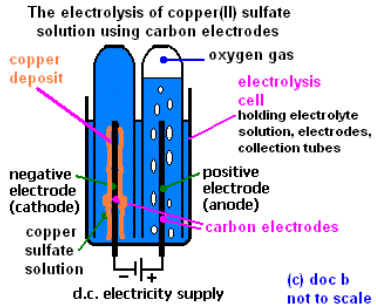
-reduction process
-oxidation number from +2 to 0

overall reaction

-breakdown of lead (II) bromide to give lead and bromine

$PbBr_2 \rightarrow Pb + Br_2$

II. electrolysis of copper (II) sulphate solution



i. anode:

OH^- are selectively discharged

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

-OH^- ions are oxidised to oxygen gas
-SO_4^{2-} ions remain in solution

ii. cathode:

-Cu^{2+} ions are selectively discharge at cathode

$Cu^{2+} + 2e^- \rightarrow Cu$

-Cu^{2+} ions are reduced to copper metal

-H^+ ions remain in solution

Overall reaction

-copper metal is deposited at cathode, oxygen has given off at anode and solution become more acidic

$$2CuSO_4 + \overbrace{2H_2O \rightarrow 2Cu}^{\text{reduction}} + O_2 + 2H_2SO_4$$

$$2CuSO_4 + 2H_2\underbrace{O \rightarrow 2Cu + O_2}_{\text{Oxidation}} + 2H_2SO_4$$

III. electrolysis of copper (II) sulphate solution using copper electrodes

i. anode: (oxidation)
-copper anode dissolves (corrodes) to form copper(II) ions
$Cu \rightarrow Cu^{2+} + 2e^-$

-electrode becomes thinner

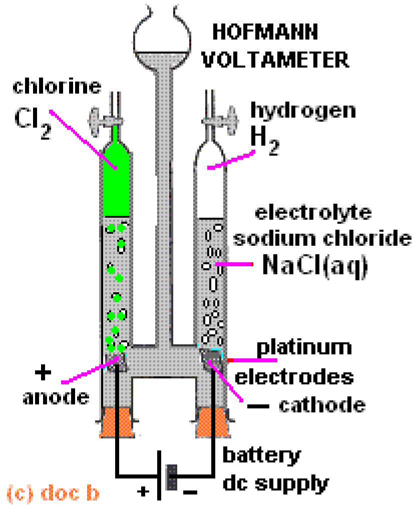
ii. cathode: (reduction)

$Cu^{2+} + 2e^- \rightarrow Cu$

-Cu^{2+} ions are selectively discharge to form copper atom

iii. overall reaction
-transfer of copper e^- from anode to cathode
-concentration of copper (II) sulphate does not change and blue colour electrolyte does not fade

IV. electrolysis of concentrated sodium chloride solution



i.anode: chloride ions(Cl^-) is selectively discharged at anode

$2Cl^- \rightarrow Cl_2 + 2e^-$
-Cl^- ions are oxidised to chlorine gas
-OH^- ions remain in the solution

ii.cathode:

-hydrogen ions (H^+) is selectively discharged at cathode

$2H^+ + 2e^- \rightarrow H_2$

-at cathode, H^+ ions are reduced to hydrogen gas
-Na^+ ions remain in the solution

iii. overall reaction

oxidation

$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$

Reduction

-electrolysis of concentrated sodium chloride solution produces one volume of hydrogen at the cathode, one volume of chlorine at the anode and sodium hydroxide solution

V. electrolysis of dilute sodium chloride solution

i. anode:

-OH^- ions donate e^- to the anode to form oxygen and water

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

ii.cathode:
-H^+ ions gain e^- from the cathode to form hydrogen gas
$2H^+ + 2e^- \rightarrow H_2$

iii.overall reaction

oxidation

$2H_2O \rightarrow 2H_2 + O_2$

Reduction

-electrolysis of dilute sodium chloride solution produces two volume of hydrogen at the cathode and one volume of oxygen at the anode

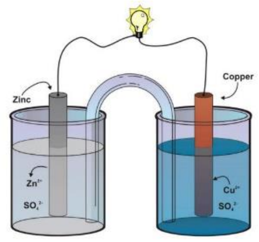
-since water is being removed (by decomposition to form H_2 and O_2) the concentration of sodium chloride increases gradually

Redox reaction in chemical cells

I. Daniell cell

-function of porous pot
i. separate two different solution
ii. complete the electric circuit by allowing the ions to pass through it

-salt bridge can be used to replace porous pot for same function



i.anode (oxidation)
-negative electrode
-zinc is more electropositive than copper
∴ greater tendency to donate e^-
$Zn \rightarrow Zn^{2+} + 2e^-$
ii. cathode (reduction)
-positive electrode Cu^{2+} ions gain e^- from zinc is reduced to copper metal
$Cu^{2+} + 2e^- \rightarrow Cu$
-Cu^{2+} act as oxidizing agent

iii. overall reaction

$$\overbrace{Zn + Cu^{2+}}^{\text{oxidised}} \rightarrow Zn^{2+} + Cu$$

$$Zn + \underbrace{Cu^{2+} \rightarrow Zn^{2+} + Cu}_{\text{reduced}}$$

-displacement reaction occurs
-concentration of Zn^{2+} ions in the solution increase
-blue colour of copper(II) sulphate solution fades gradually as more copper is deposited and concentration of Cu^{2+} decreases
-mass of zinc electrode decreases
-mass of copper electrode increases

Cell symbol
-used to represent chemical cells
-symbol '// ' represents the porous pot/ salt bridge

eg.

$Zn / Zn^{2+} // Cu^{2+} / Cu$

anode (-)

cathode (+)

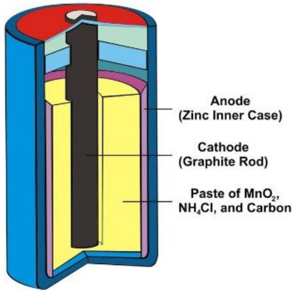
electrolyte at anode

electrolyte at cathode

voltage of Daniell cell
-if the concentration of both $ZnSO_4$ & $CuSO_4$ solution are 1.0mol dm^{-3} , the maximum voltage =1.10V

note
-the voltage of cell will decrease with time when the cell is being used because concentration of Cu^{2+} ions decreases

II Dry cell



i.anode (negative terminal)
-zinc container as anode
-zinc oxidised to Zn^{2+}
$Zn \rightarrow Zn^{2+} + 2e^-$
-oxidation occurs
-e^- flow from zinc container to carbon rod
ii. cathode (positive terminal)
-carbon rod as cathode
-NH_4^+ is reduced to NH_3 and H_2
$2NH_4^+ + 2e^- \rightarrow 2NH_3 + H_2$

note

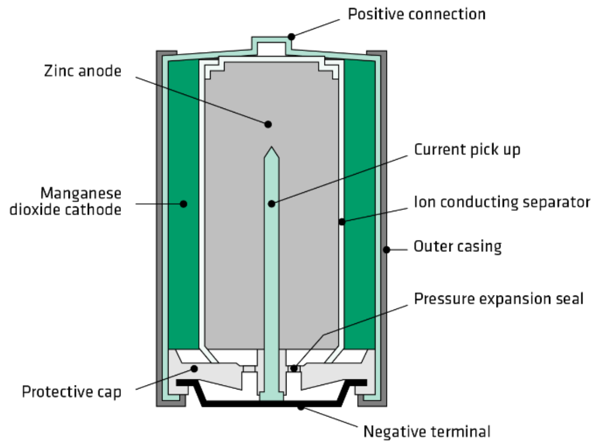
H_2 gas is removed by MnO_2

$2MnO_2 + H_2 \rightarrow Mn_2O_3 + H_2O$

iii. overall reaction
$Zn + 2NH_4^+ + 2MnO_2 \rightarrow Zn^{2+} + 2NH_3 + MnO_2 + H_2O$

Oxidizing agent = NH_4^+
reducing agent = zinc

III Alkaline cell



i.anode : (negative terminal)
-zinc container
-zinc oxidised to Zn^{2+}

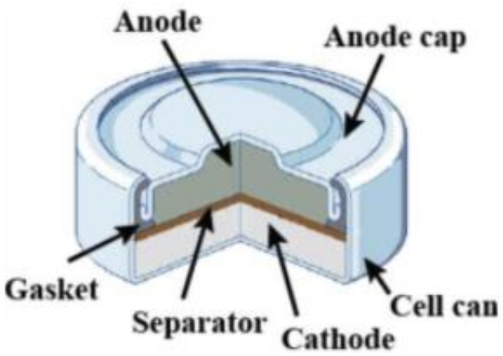
$Zn \rightarrow Zn^{2+} + 2e^-$
-e^- flow from zinc container to MnO_2
-acts as reducing agent, oxidation occurs

ii. cathode (positive terminal)
-manganese (IV) oxide powder
-MnO_2 reduced to manganese (III) oxide Mn_2O_3

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

iii. overall reaction
$Zn + 2MnO_2 + H_2O \rightarrow Zn^{2+} + Mn_2O_3 + 2OH^-$

IV. mercury cell



i. anode (negative terminal)

-zinc metal as anode
-zinc oxidise to Zn^{2+}

$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$

-e^- flow from zinc electrode to HgO
-oxidation occurs, zinc act as reducing agent

ii. cathode (positive terminal)

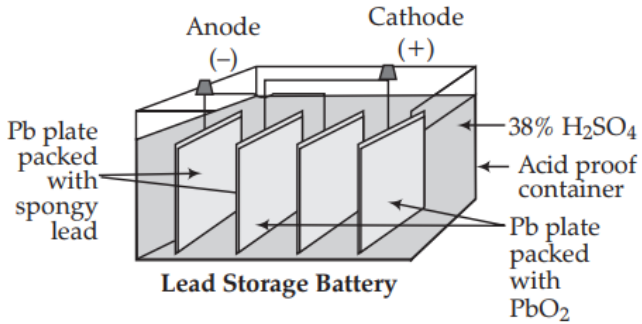
-mercury (II) oxide, HgO as cathode
- HgO reduced to mercury
$HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$

-reduction occurs, mercury (II) oxide acts as oxidizing agent

iii. overall reaction

$Zn + HgO + H_2O \rightarrow Zn(OH)_2 + Hg$

V. Lead-acid accumulator



-knows as car battery
-can be recharge by passing a current through it

i. anode (negative terminal)
-lead plate as anode
-lead oxidise to lead (II) ions
$Pb \rightarrow Pb^{2+} + 2e^-$
-oxidation occurs, lead act as reducing agent
-e^- given out at cathode flow through external circuit to positive terminal

-white precipitate $PbSO_4$ is produced when Pb^{2+} ions react with SO_4^{2-} ions

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

∴negative electrode become white solid

-overall reaction at anode:
$Pb \rightarrow Pb^{2+} + 2e^-$

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

(grey) (white)

ii. cathode (positive terminal)

-lead plate with coat PbO_2 as cathode
-lead (IV) oxide is reduced to Pb^{2+} ions by accepting e^-

$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$

-white solid produced when Pb^{2+} ions react with SO_4^{2-} ions in sulphuric acid to form lead (II) sulphate
$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

-white solid, lead (II) sulphate deposit on surface of positive electrode to form white coating
-overall reaction at cathode
$Pb_2O + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$
$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$
(brown) (white)

iii. overall reaction
$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$

note

-sulphuric acid is used up when discharge

recharging lead acid accumulator

-dc current passed through in direction opposite to the discharge

I. negative terminal (reduction)

$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$

white grey

∴ lead (II) sulphate reduced to lead

II. positive terminal (oxidation)

white brown

$PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-}$

∴ lead (II) sulphate oxidised to lead (IV) oxide

Overall reaction

$$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 \underbrace{+4H^+ + 2SO_4^{2-}}_{2H_2SO_4}$$

Comparison between electrolytic cell and chemical cell

Electrolytic cell	Chemical cell
Anode -positive and terminal in electrolytic cell -oxidation occurs -anions release e^- from cathode to anode	Anode -negative terminal in chemical cell -oxidation occurs -release e^-
Cathode -negative terminal in electrolytic cell -reduction occurs -cations accept e^-	Cathode -positive terminal in chemical cell -reduction occurs -accept e^-
-for both cells, anions move to anode while cations move to cathode	

Changes of oxidation number in a substance

i. extracting metal from its ore
ii. corrosion of metal
iii. preventing corrosion of metal
iv. generation of electricity by cells
v. recycling of metals