Electrochemistry

Element	Oxidation number	Exceptions
Group 1	Always +1	–
Group 2	Always +2	–
Group 13	Always +3	–
Group 17	Usually −1 (F is always −1)	forming compounds with more electronegative atom. $F > O > N > C > H$ more EN atom takes −ve charge, less EN atom takes +ve charge.
Hydrogen	Usually +1	−1 in metal hydrides (eg. NaH) ↳ Na more electropositive than H.
Oxygen	Usually −2	−1 in peroxides (eg. H_2O_2, BaO_2) peroxide ion is O_2^{2-}
		−0.5 in KO_2 (superoxide) superoxide is O_2^-
		+2 in OF_2 (monoxide) F > O

Balancing Redox Steps

1) Construct unbalanced oxidation and reduction half-equations.

To each half-equation, under ACIDIC medium

2) Balance the element reduced or oxidised in each half equation.
3) Balance oxygen atoms by adding H_2O
4) Balance hydrogen atoms by adding H^+ ions
5) Balance overall charges by adding e^-
   ↳ e^- on RHS of oxidation eqn, e^- on LHS of reduction eqn.
6) Multiply by appropriate integer so that no. of e^- gained = no. of e^- lost
7) Combine both eqns & eliminate common terms for overall equation (no e^-)

under ALKALINE medium → continue i)–iii) after step 5 then back to 6 & 7.

i) Neutralise H^+ ions by adding OH^- ions on both side of half equation
ii) Combine H^+ and OH^- on SAME side to form H_2O
iii) Re-balance half eqn by eliminating common terms.

Oxidation	Reduction
Increase in O.N.	Decrease in O.N.
Gain of O	Loss of O
Loss of H	Gain of H
Loss of e^-	Gain of e^-
Occurs at ANODE	Occurs at CATHODE

An Ox Red Cat

Anode → Oxidation Reduction is Cathode

Electrolytes: A compound which conducts electricity in an aqueous solution or molten state.
An electrolyte conducts electricity due to the flow of charge carried by ions.

strong electrolyte: fully ionised	weak electrolyte: partially ionised	non-electrolyte: does not ionise

① Galvanic cell
- chemical energy to electrical energy
- spontaneous

② Electrolytic cell
- electrical energy to chemical energy
- non-spontaneous

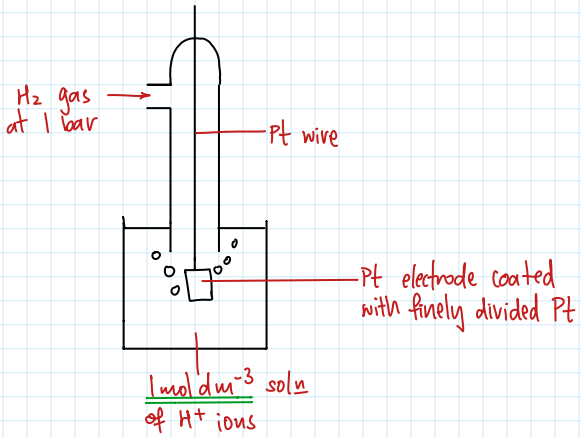
Electrode Potentials:

- Half equations show dynamic equilibrium

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$

- how readily a substance gains e^-
- Half-equations are always reduction reactions

Standard Hydrogen Electrode (SHE):



standard conditions
Temperature: 25°C (298K)
Pressure: 1 bar
$[H^+]$: 1 mol dm^{-3}

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E^\ominus = 0V$$

$E^\ominus$: potential difference between SHE and half-cell at $\ominus$

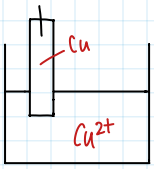
More positive $E^\ominus$ ⇒ reduction favoured

More negative $E^\ominus$ ⇒ oxidation favoured

Common half-cells:

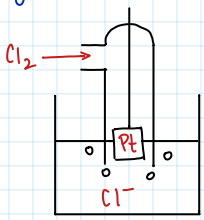
① metal/metal ion

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$



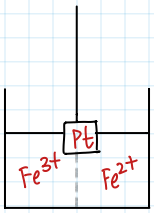
② gas/ion

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$



③ ion/ion

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

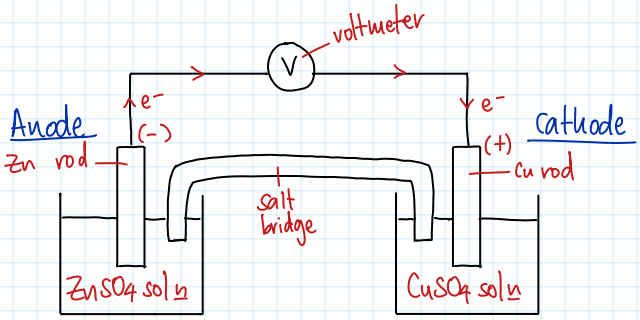


* Manganate(VII) is more oxidising than dichromate(VI).
It has more positive $E^\ominus$ than dichromate(VI). Hence, Manganate(VII) is more easily reduced.

* Most powerful reducing agent has the most negative $E^\ominus$ value. ⇒ most readily oxidised.

Galvanic Cell

Daniell cell:



reduced form | oxidised form || oxidised form | reduced form

Oxidation → Reduction →

Anode half-cell ↳ (−) electrode

Cathode half-cell ↳ (+) electrode

| → boundary
|| → salt bridge
, → 2 oxidation states sharing same homogeneous aq. phase
( ) → conditions

Cell diagram:

$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

Half-cell :	$Zn^{2+}(aq) \mid Zn(s)$ (Zn electrode)	$Cu^{2+}(aq) \mid Cu(s)$ (Cu electrode)
Data :	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^\ominus = -0.76V$	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34V$
Half-eqn :	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ (more −ve $E^\ominus$, oxidation occurs, Anode)	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ (more +ve $E^\ominus$, reduction occurs, cathode)

e^- flow : From $Zn^{2+}(aq) \mid Zn(s)$ to $Cu^{2+}(aq) \mid Cu(s)$ half-cell, a current is generated

Polarity : Zn is the −ve electrode (e^- released)
Cu is the +ve electrode (e^- absorbed)

Overall eqn: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Salt bridge: salt soln eg. KCl, Na_2SO_4, $NaNO_3$, KNO_3

- release of Zn^{2+} from $ZnSO_4$ $\Rightarrow$ Zn^{2+} cation surplus $\Rightarrow$ Zn^{2+}/Zn half-cell +vely charged.
- anions (NO_3^-) from salt bridge released into $ZnSO_4$ to balance surplus of Zn^{2+}
- removal of Cu^{2+} from $CuSO_4$ $\Rightarrow$ SO_4^{2-} anion surplus $\Rightarrow$ Cu^{2+}/Cu half-cell -vely charged
- cations (K^+) from salt bridge released into $CuSO_4$ to balance surplus of SO_4^{2-}

* prevent direct mixing of $ZnSO_4$ and $CuSO_4$

* Complete circuit $\Rightarrow$ maintain electrical neutrality

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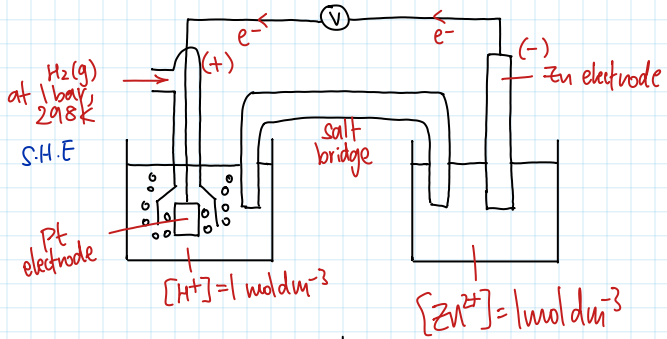
① S.H.E and Metal/Metal ion

i) $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^\ominus = -0.76V$



$Zn^{2+}(aq) \mid Zn(s)$ (with Zn electrode) | $H^+(aq) \mid H_2(g)$ (with Pt electrode)

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ | $2H^+(aq) + 2e^- \longrightarrow H_2(g)$

Oxidation, Anode | Reduction, Cathode

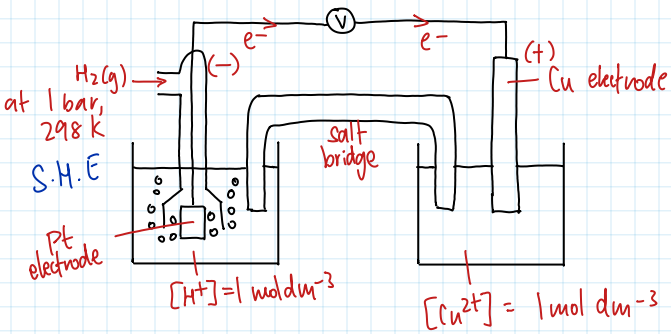
e^- flow from $Zn^{2+}(aq) \mid Zn(s)$ to $H^+(aq) \mid H_2(g)$ half-cell

Zn is the -ve electrode

Pt of S.H.E is the +ve electrode

H^+ is more easily reduced than Zn^{2+}

(ii) $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34V$



$H^+(aq) \mid H_2(g)$ (with Pt electrode) | $Cu^{2+}(aq) \mid Cu(s)$ (with Cu electrode)

$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$ | $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Oxidation, Anode | Reduction, Cathode

e^- flow from $H^+(aq) \mid H_2(g)$ to $Cu^{2+}(aq) \mid Cu(s)$ half-cell

Pt of S.H.E is the -ve electrode

Cu is the +ve electrode

Cu^{2+} is more easily reduced than H^+

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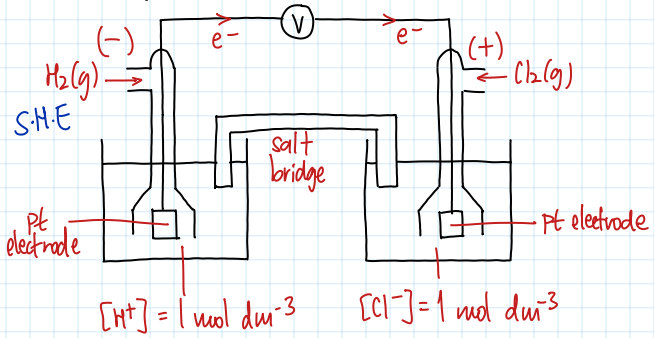
② S.H.E and Gas/Ion

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36V$



$H^+(aq) \mid H_2(g)$ (with Pt electrode) | $Cl_2(g) \mid Cl^-(aq)$ (with Pt electrode)

$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$ | $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$

Oxidation, Anode | Reduction, Cathode

e^- flow from $H^+(aq) \mid H_2(g)$ to $Cl_2(g) \mid Cl^-(aq)$ half-cell

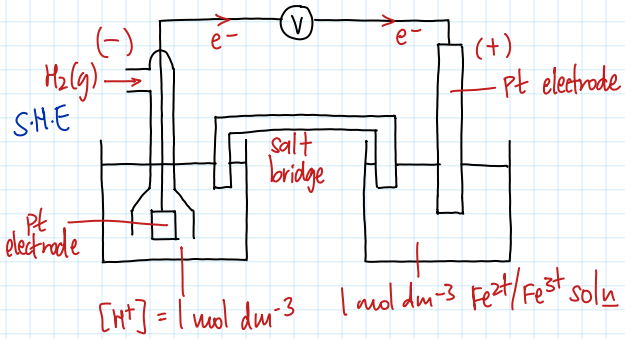
Pt of S.H.E is the -ve electrode

Pt of $Cl_2(g) \mid Cl^-(aq)$ is the +ve electrode

Cl_2 is more easily reduced than H^+

③ S.H.E and Ion/Ion

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad E^\ominus = +0.77V$



$H^+(aq) \mid H_2(g)$ (with Pt electrode)

$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

Oxidation, Anode

$Fe^{3+}(aq) \mid Fe^{2+}(aq)$ (with Pt electrode)

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$

Reduction, Cathode

e^- flow from $H^+(aq) \mid H_2(g)$ to $Fe^{3+}(aq) \mid Fe^{2+}(aq)$ half-cell

Pt of S.H.E is the -ve electrode

Pt of $Fe^{3+}(aq) \mid Fe^{2+}(aq)$ is the +ve electrode

Fe^{3+} is more easily reduced than H^+

$E^\ominus_{cell}$: e.m.f of a galvanic cell which consists of 2 half-cells at $\ominus$.

It is the difference between the 2 electrode potentials.

Units for $E^\ominus_{cell}$ = V

$$E^\ominus_{cell} = E^\ominus_{cat} - E^\ominus_{an}$$

$$\Delta G^\ominus_{cell} = -nFE^\ominus_{cell}$$

$F = 9.65 \times 10^4$ C mol^{-1}

Units for $\Delta G^\ominus_{cell}$: J mol^{-1}

$E^\ominus_{cell} > 0$, $\Delta G^\ominus_{cell} < 0$ $\Rightarrow$ Spontaneous

$E^\ominus_{cell} = 0$, $\Delta G^\ominus_{cell} = 0$ $\Rightarrow$ equilibrium

$E^\ominus_{cell} < 0$, $\Delta G^\ominus_{cell} > 0$ $\Rightarrow$ non-spontaneous

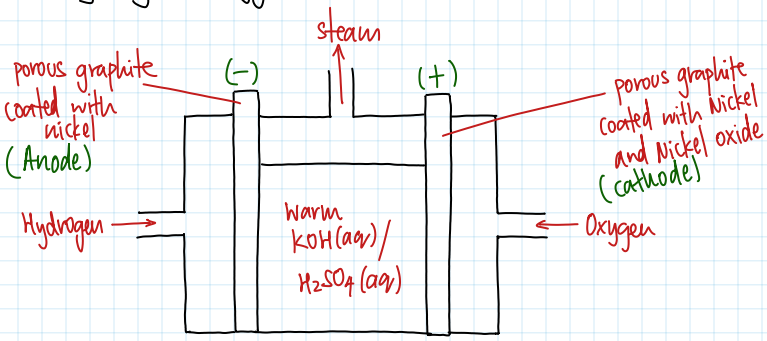
Factors affecting $E^\ominus_{cell}$:

1. Ion concentration
2. Gas pressure
3. Temperature

Limitations of $E^\ominus_{cell}$:

- reaction has very high Ea $\Rightarrow$ kinetically not favourable
- actual conditions are not $\ominus$

① Hydrogen-Oxygen fuel cell:



$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Alkaline electrolyte (eg. KOH (aq)):

Anode: $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

$E^\ominus_{cell} = +0.40 - (-0.83)$

$= +1.23V$

Acidic electrolyte (eg. H_2SO_4(aq)):

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

Cathode: $O_2(g) + 4H^+(aq) + e^- \longrightarrow 2H_2O(l)$

Overall: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

$E^\ominus_{cell} = +1.23 - 0.00$

$= +1.23V$

Advantages:

- Noiseless, pollution-free
- Good energy to mass ratio
- Easy maintenance ⇒ lack of moving parts
- high efficiency ~ 70%. ⇒ twice the efficiency of internal combustion engine.

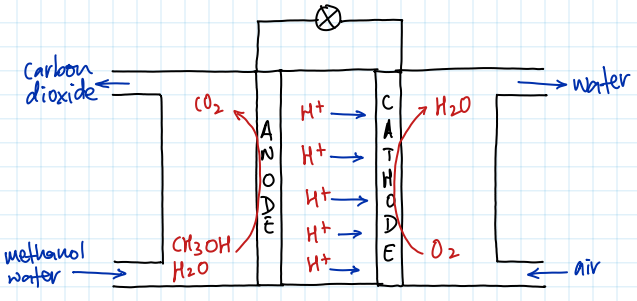
Disadvantages:

- Expensive as Pt catalyst becomes "poisoned" over time
- Hydrogen transported in heavy pressurised cylinders / very low temperature as liquid ⇒ troublesome

Uses:

- Space vehicles, EVs, Submarines, railway locomotives, lights

② Methanol fuel cell:



$CH_3OH + 3O_2 \longrightarrow 2CO_2 + 4H_2O$

Alkaline electrolyte (eg. dilute NaOH):

Anode (−): [O] $CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^-$

Cathode (+): [R] $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Acidic electrolyte (eg. dilute H_2SO_4):

Anode (−): [O] $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathode (+): [R] $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Primary cell

Electrolyte: Paste of NH_4Cl, $ZnCl_2$ and water

Anode (−): Zinc casing

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

Cathode(+): Carbon rod surrounded by MnO_2 layer

$$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \longrightarrow 2NH_3(aq) + 2MnO(OH)(s)$$

Overall:

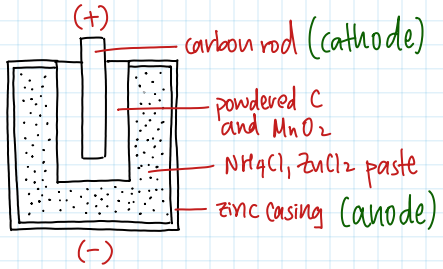
$$Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \rightarrow Zn^{2+}(aq) + 2NH_3(aq) + 2MnO(OH)(s)$$

Advantages:

- conveniently portable ⇒ tightly sealed, no leak

Disadvantages:

- Zn corroded by acidic electrolyte
- Voltage drops – rapid discharge (product build-up at electrolyte)
- Cannot be recharged



Secondary cells

Electrolyte: sulfuric acid

Discharging

Anode (−): Lead

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

Cathode (+): PbO_2

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(aq) + 2H_2O(l)$$

Overall discharging equation:

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(aq) + 2H_2O(l)$$

Recharge (external energy to reverse)

$$2PbSO_4(aq) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^-(aq)$$

$$PbO_2, Pb \underset{\text{recharge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_4$$

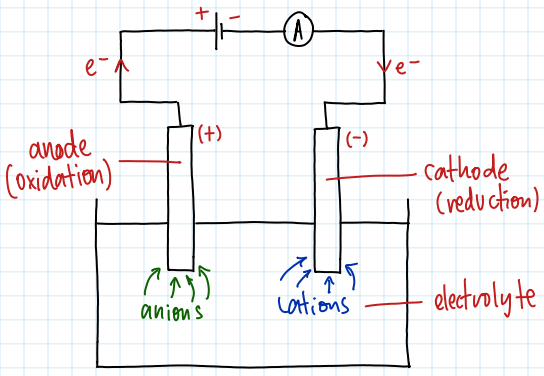
Advantage:

- can be recharged
- relatively inexpensive

Disadvantage:

- very heavy due to lead

Electrolysis: A current is passed through the electrolyte to decompose it.



Factors affecting selective discharge:

① Electrolyte state

NaCl (l) ⇒ molten

Species: $Na^+(l)$, $Cl^-(l)$

Electrodes: Graphite

Cathode (−): $Na^+(l)$ migrates to cathode & is reduced

$Na^+(l) + e^- \rightarrow Na(l)$

Anode (+): $Cl^-(l)$ migrates to anode & is oxidised

$2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$

Overall: $2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$

NaCl (aq) ⇒ aqueous

Species: $Na^+(aq)$, $Cl^-(aq)$, $H_2O(l)$

Electrodes: Graphite

Cathode (−): [R] of $Na^+(aq)$: $Na^+(aq) + e^- \rightarrow Na(s)$

[R] of $H_2O(l)$: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Anode (+): [O] of $Cl^-(aq)$: $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

[O] of $H_2O(l)$: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

② $E^\ominus$

More positive vs. Less positive (−ve)

↳ reduced ↳ oxidised

③ Concentration of ions

Cathode (−):

- increased $[Na^+]$ increases tendency for reduction of Na^+
- Making $E^\ominus$ of Na^+/Na more positive
- but NOT to the extent that it's higher than $E^\ominus$ of H_2O/H_2
- Hence, water preferentially discharged

Anode (+):

- increased $[Cl^-]$ increases tendency for oxidation of Cl^-
- Making $E^\ominus$ of Cl^-/Cl_2 more positive
- shifts to the extent that it's higher than $E^\ominus$ of H_2O/O_2
- Hence, chlorine is preferentially discharged.

④ Electrode

Inert: no effect on electrolysis

Reactive: eg. $CuSO_4(aq)$ Species: $Cu^{2+}(aq)$, $SO_4^{2-}(aq)$, $H_2O(l)$

electrodes: Copper

Cathode (−): $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34V$

$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83V$

- $E^\ominus$ of Cu^{2+}/Cu is more positive ⇒ more readily reduced ⇒ preferentially discharged
- Cu cathode size and mass increase

Anode (+): $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23V$

$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$ $E^\ominus = +2.01V$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34V$

- $E^\ominus$ of Cu^{2+}/Cu is more positive ⇒ more readily reduced ⇒ preferentially discharged
- Cu cathode size and mass increase

Electrolyte	**molten NaCl (l)**	**dil NaCl (aq)**	**Conc NaCl (aq) (brine)**		**$CuSO_4$(aq)**	
Ions/species present	$Na^+(l)$, $Cl^-(l)$	$Na^+(aq)$, $Cl^-(aq)$	$Na^+(aq)$, $Cl^-(aq)$, $H_2O(l)$	$Na^+(aq)$, $Cl^-(aq)$, $H_2O(l)$	$Cu^{2+}(aq)$, $SO_4^{2-}(aq)$, $H_2O(l)$	$Cu^{2+}(aq)$, $SO_4^{2-}(aq)$, $H_2O(l)$
Electrode	C (inert)	C	C	C anode, Hg cathode	Pt (inert)	Cu (reactive)
Anode Reaction	$2Cl^-(l) \rightarrow Cl_2 + 2e^-$	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$	$2Cl^- \rightarrow Cl_2 + 2e^-$	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Cathode Reaction	$Na^+(l) + e^- \rightarrow Na(s)$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$Na^+ + e^- \rightarrow Na$	$Cu^{2+} + 2e^- \rightarrow Cu$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Overall reaction	$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$	$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$	$2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$	–	$2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2(g) + 4H^+$	–
Remarks	Generally, electrolysis of molten ionic compounds, the metal is discharged at the cathode as solid or liquid metal and the non-metal is discharged at the anode as $X_2(g)$	A colourless gas is evolved at each electrode. 2 volumes of H_2 for 1 volume of O_2 The auto-ionisation of water gives too low (10^{-7} mol dm^{-3}) each of H^+ and OH^- for pure water to conduct electricity appreciably.	Cl_2 selectively discharged instead of O_2 due to high $[Cl^-]$.	Na selectively discharged instead of H_2 as Hg is used as electrode. Na/Hg amalgam formed.	Pink/brown metal Cu deposited on cathode Colourless gas relights a glowing splint is liberated at the anode Blue Solution decolourises.	Cu cathode increases in size and Cu anode decreases in size. $[CuSO_4]$ remains unchanged. The colour intensity of the solution remains unchanged.

Electrolyte	**H_2SO_4(aq)**			**molten $PbBr_2$**	**molten PbO**	**Na_2SO_4(aq)**
Ions/species present	H^+, SO_4^{2-}, H_2O	H^+, SO_4^{2-}, H_2O	H^+, SO_4^{2-}, H_2O	$Pb^{2+}(l)$, $Br^-(l)$	$Pb^{2+}(l)$, $O^{2-}(l)$	Na^+, SO_4^{2-}, H_2O
Electrode	Pt	C	Pt cathode, Ag anode	C	C	Pt
Anode Reaction	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ **$2C + O_2 \rightarrow 2CO$** **$C + O_2 \rightarrow CO_2$**	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ **$2Ag + O_2 \rightarrow Ag_2O$**	$2Br^- \rightarrow Br_2 + 2e^-$	$2O^{2-} \rightarrow O_2 + 4e^-$ **$2C + O_2 \rightarrow 2CO$** **$C + O_2 \rightarrow CO_2$**	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
Cathode Reaction	$2H^+ + 2e^- \rightarrow H_2$	$2H^+ + 2e^- \rightarrow H_2$	$2H^+ + 2e^- \rightarrow H_2$	$Pb^{2+} + 2e^- \rightarrow Pb$	$Pb^{2+} + 2e^- \rightarrow Pb$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Overall reaction	$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$	$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$	–	$Pb^{2+}(l) + 2Br^-(l) \rightarrow Pb(l) + Br_2(l)$		$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
Remarks	H_2SO_4 slowly becomes more concentrated.	O_2 liberated oxidises C anode to CO and CO_2	O_2 liberated oxidises Ag anode to Ag_2O.	–	O_2 liberated oxidises C anode to CO and CO_2.	Solution slowly becomes more concentrated.

$Q = It$

Q = charge (C)
I = current (A)
t = time (s)

$F = Le^-$

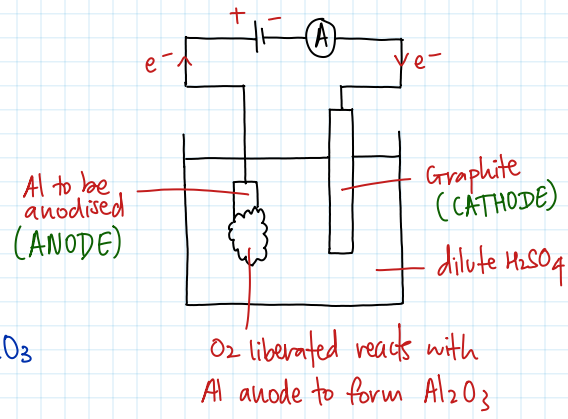
$1F = 96500\ C\ mol^{-1}$
$L = 6.02 \times 10^{23}$
$e^- = -1.60 \times 10^{-19}\ C$

$Q = n_{e^-}F$

$F = 96500C$
n_{e^-} = no. of moles of e^-

Industrial Uses :

① Anodising of Aluminium



Electrolyte : dilute H_2SO_4 (aq)

Anode (+) : Al subject to be anodised

Oxidation occurs ; O_2 liberated

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$$

Liberated O_2 reacts with Al anode to form Al_2O_3

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

Cathode (−) : Graphite

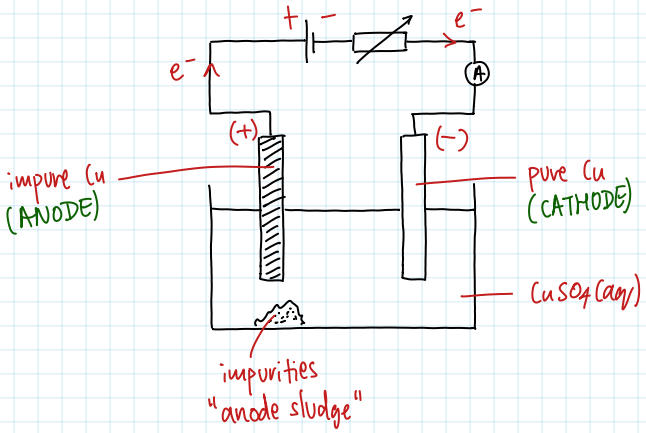
Reduction occurs ; H_2 liberated

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

Advantage : resists corrosion, lightweigh, decorative as oxide layer is hydrated and can absorb dyes

Examples : Window grills, drink cans, utensils, kitchen appliances

② Electrolytic purification of Copper



Electrolyte : $CuSO_4$ (aq)

Anode (+) : impure Cu ⇒ copper dissolves

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E^\ominus = +0.80V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\ominus = +0.34V$$
$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^\ominus = -0.44V$$
$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\ominus = -0.76V$$

- Zn & Fe with $E^\ominus$ less positive than Cu dissolve as ions before Cu.
- Ag with $E^\ominus$ more positive than Cu remain solid ; drop to the bottom as "anode sludge"

Cathode (−) : pure Cu ⇒ Cu^{2+} preferentially discharged over Zn^{2+} and Fe^{2+}

- $E^\ominus$ of Cu^{2+}/Cu is the most positive
- pure Cu cathode increases in size and mass
- $[CuSO_4]$ remains constant