

The Formative Practical Investigation for the topic Electrochemistry requires three sequenced tasks:

- ❶ Displacement Reaction **observations** to determine chemical **activity** for metal / ionic solutions.
- ❷ Electrochemical **investigation** to collect information for **analysis** of battery properties.
- ❸ Science as Human Endeavour **applications** to **predict** displacement reaction outcomes.

On completion of these sequenced practical and written inquiry tasks you should be able to balance electro-chemical reaction equations **AND** be able to predict which reagents produce an electrochemical reaction.

Your **Formative Task** is to write **A Single Report** about how these sequenced investigations developed your skills and abilities in understanding chemical reactions as observed processes that can consequently have their trends predicted. In other words, did you notice how the displacement practical in ❶ had you recording lots and lots of chemical reaction observations; then had you deduce trends occurring within those reactions electrochemically in ❷; so that you could use those trends to predict the outcome of reactions in ❸ (and Extension) that you had not previously observed? The report should be approximately 200 words ($\pm 10\%$) including appropriate Tables of Data and Reaction Equations to support your discussion. Important criteria to consider in this report are as follows:

- Discuss how you went about physically obtaining the observations and safety precautions used.
- Summarise each of the three sequenced inquiry tasks by focusing on trends deduced from the tasks.
- Why were the three inquiry tasks presented in the order used?
- Provide a single conclusion for these three inquiry tasks based on the deduced trends.
- Comment on difficulties encountered and suggest how to improve the tasks to better achieve the desired outcomes or conclusions.
- Reference one industrial or commercial application for the chemical processes described in your Practical Report. Briefly discuss the benefits and hazards to society and the environment of this application.

Practical Investigation	Handed out:	Due Date:
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The practical investigation is sequenced to build upon initial ideas about electron transfer during chemical reactions:

<p>p2 - 5</p> <p>❶</p>	<ul style="list-style-type: none"> • Displacement Reaction Observations table to rank the ability of metals to displace other metal cations. • Using hydroxide precipitates as colour indicators for the presence of metal cation species. • Develop displacement reaction Activity series with application of simple balanced reaction equations.
<p>p6 - 11</p> <p>❷</p>	<ul style="list-style-type: none"> • Identify electric current nature of redox reactions using Ohm's Law $V = I \times R$ • Physically arrange redox reactants to produce an 'external' transfer of electrons as electrochemical cells. • Observe 'external' electron flow to measure the electrical potential of cell combinations E_{cell}^0
<p>p12 - 17</p> <p>❸</p>	<ul style="list-style-type: none"> • Comparison of Part ❶ and Part ❷ to develop idea of Activity Series and Reduction Potential $E_{1/2}^0$ • Part ❸ application of ideas about electrochemical cells into real world situations. <ul style="list-style-type: none"> ○ Further develop balancing of reaction equations by application of changing oxidation states. ○ Extension of previous ideas in ❶ ❷ ❸ into unfamiliar situations.

❹ (p18 – 20) Your **Summative SACE Task** is to write a 1000-word ($\pm 10\%$) referenced article about the development and applications of contemporary alkaline rechargeable batteries, such as Ni-MH or Lithium-ion.

- You must include examples from the Formative Practical Investigation ❸.
- You will need to research new and contemporary applications of electrochemistry for sustainable batteries.
- Your article will include a discussion about how science research interacts with applications in society.
- Assessment explanations and details are provided on page 16. Submission timeline to be set early next term.

ELECTROCHEMISTRY PRACTICAL INVESTIGATION

Name _____

Chemical reactions can be identified with a combination of observations:

Formation of:		Changes in:		
Gases ✓	Precipitates ✓	Colour ✓	Heat ✓	Oxidation State?

⚡ **Oxidation State?** A major aim of this practical investigation is to develop an ability to recognise Oxidation States: The name 'oxidation state' historically comes from a chemical ability to combine/uncombine with oxygen.

- Oxidation was a measure of increasing the mass of a compound by gaining oxygen during a reaction;
- Reduction was a measure of reducing the mass of a compound by losing oxygen during a reaction.

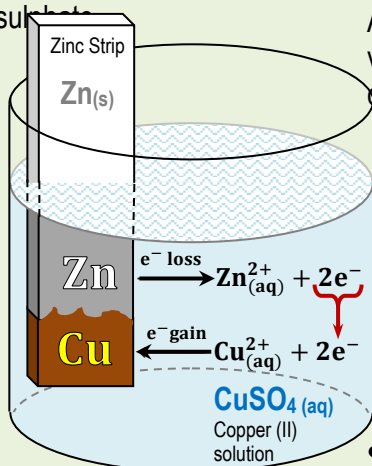
Oxidation State ($\pm n$) consists of two distinct components: sign (\pm) and value (n)

- (\pm) indicates **bond direction** as valence electrons **shift** between atoms during bond formation
- (n) represents **how many** primary (chemical) bonds an atom makes with **different** elements

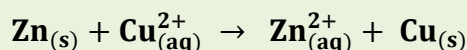
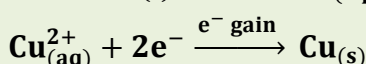
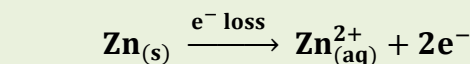
See Redox Topic work book for more details

Displacement Reactions occur when a solid metal is placed into a solution of another metal salt. The metal cation in the salt solution appears to be displaced from the solution as it forms a solid precipitate.

Example: A strip of zinc metal corrodes when placed in a solution of copper (II) sulphate.



The ability of one solid metal to 'displace' another metal cation from solution is called the '**activity**' of the solid metal. Different metals have different 'activity' strengths compared to each other because of electronegativity differences. An Activity Series can be developed by testing a variety of solid metals with an equal variety of different aqueous salt solutions of metal cations to observe their corresponding displacement reactions.



grey metal blue solution colourless solution brown precipitate

Half-equations represent the transfer of electrons as separate processes.

Full-equations represent the overall reagents when electrons are lost and gained in equal numbers during redox.

- The gain of electrons is known as **reduction**
- The loss of electrons is known as **oxidation**

Overall **Redox** reaction

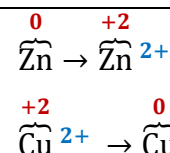
Solid $\text{Zn}_{(s)}$ metal can cause aqueous $\text{Cu}_{(aq)}^{2+}$ cations to be precipitated from solution as solid $\text{Cu}_{(s)}$ metal.

- This example of a Redox reaction is usually summarised as "**Zinc displaces Copper**".

- Blue copper (II) sulphate solution initially contains lots of **blue** $\text{Cu}_{(aq)}^{2+}$ cations in high concentration.
 - Addition of $\text{NaOH}_{(aq)}$ confirms presence with $\text{Cu}_{(aq)}^{2+} + 2\text{OH}_{(aq)}^{-1} \rightarrow \text{Cu}(\text{OH})_{2(s)}$ blue gel precipitate.
 - Solution becomes pale blue, until colourless, as less $\text{Cu}_{(aq)}^{2+}$ remains in solution following their **reduction**.
- Copper metal is initially deposited on the zinc strip as a coating of finely divided black particles.
 - Internal interference patterns of light that make the copper coating initially appear to be black.
 - The copper appears metallic brown and fall to the bottom of the beaker as particles become larger.
- The concentration of **colourless** $\text{Zn}_{(aq)}^{2+}$ cations increases from zero as the zinc metal is **oxidised**.
 - Addition of $\text{NaOH}_{(aq)}$ confirms presence with $\text{Zn}_{(aq)}^{2+} + 2\text{OH}_{(aq)}^{-1} \rightarrow \text{Zn}(\text{OH})_{2(s)}$ white gel precipitate.
 - Smooth flat surface of zinc metal strip becomes pitted and corroded as it is dissolved by displacement.

Zinc and Copper are both transition element metals with lower electronegativity than Oxygen:

- As elemental metals they form no bonds with other elements and have oxidation state **zero**
- When they form primary bonds with other elements, their oxidation state sign will be (+)
- They both form cations, making two **ionic bonds** for oxidation state value (2)



Both Zinc and Copper change their **oxidation states** during the displacement reaction.

TASK 1

DISPLACEMENT REACTIONS usually occur when one solid metal causes another metal salt solution to precipitate as a solid metal from the solution. For example, when solid zinc metal strip is placed in a solution of blue copper (II) sulphate to produce a precipitate of powdery particles that coalesced into shiny copper metal.

- This observation can be summarised as '*copper is displaced by zinc*'.

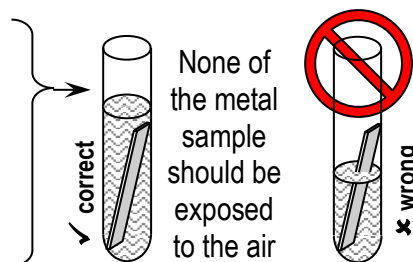
Your **task** is to test five solid metals with five corresponding salt solutions to observe a variety of rapid, and not so rapid, displacement reactions.

- Place a piece of paper between the test tubes and the test tube rack to designate each set of solutions with a test metal.
- Include your group name** on the pieces of paper.
 - Label the left-hand side of the test-tube rack as the $Mg_{(aq)}^{2+}$ salt solution provided: for example, $MgSO_4$ **or** $MgCl_2$ **or** $Mg(NO_3)_2$
 - Keep labels to the order shown to avoid confusion identifying reactions.
- Remove the 'oxide' layer (tarnish) from the solid metal using sandpaper.
 - This may have been done for you by a considerate Laboratory Manager.

Place the cleaned solid metal samples into each test salt solution.

- Place about 2 cm of salt solution in each test tube in the order shown.

- Ensure that all the metal sample is completely **covered** by the salt solution. This may require some 'topping up' of the salt solutions.
- This prevents unwanted side reactions with oxygen in the air.



Leave the five sets of five test tubes overnight!

- After **at least** one day, record observations, noting any changes:
 - Change in colour of the solution (original colour → new colour);
 - Bubbles formed and on what surfaces they appear;
 - Change in condition of the solid metal sample;
 - Precipitates formed before the addition of NaOH test solution.

Testing for cations in solution using NaOH

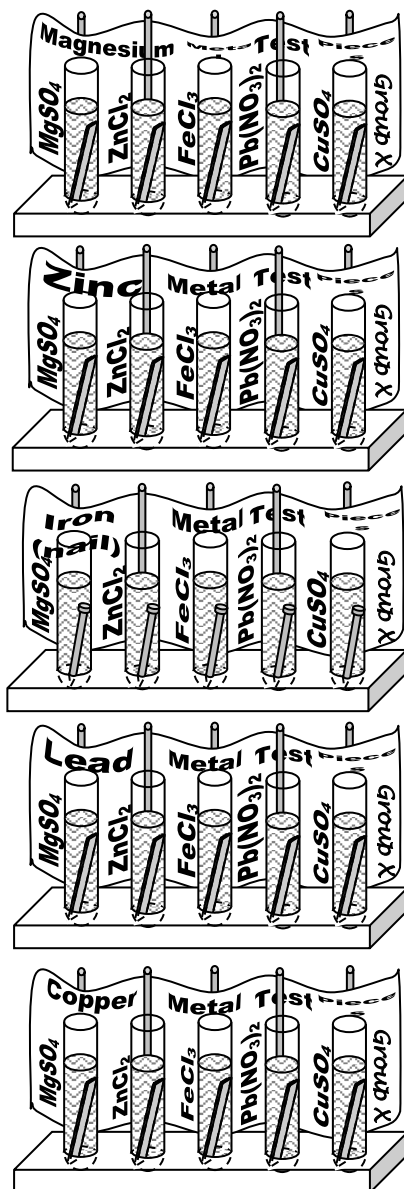
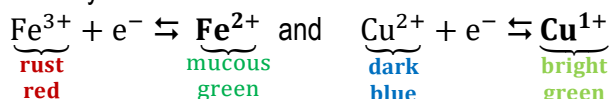
- Place the salt test solutions into new test tubes with **no** metals.
 - Add one or two drops of NaOH and record the precipitate properties.
 - These hydroxide precipitate observations let you know what cations were in solution **before** displacement.

- Precipitate observations;

- Colour**
- Type** = gel, powder, granule.
- Density** = opaque, partial, translucent.

Cation identified	Mg^{2+}	Zn^{2+}	Fe^{3+}	Fe^{2+}	Pb^{2+}	Cu^{2+}
Colour						Blue
Type						Gel
Density						Opaque
Precipitate formed	$Mg(OH)_2$	$Zn(OH)_2$	$Fe(OH)_3$	$Fe(OH)_2$	$Pb(OH)_2$	$Cu(OH)_2$

- Now add a few drops of NaOH to the displacement reaction test tubes and note any new precipitates.
 - These hydroxide precipitate observations let you know what cations are in solution **after** displacement.
 - Some new precipitate colours are:



¹ Continue with Part 2 SHE questions or Topic Book questions while waiting for the rather slow to develop observations.

**DISPLACEMENT
Reaction
Observations**

Displacement reactions occur between two different metals

METAL CATION SOLUTIONS: for example, $MgCl_2$ or $MgSO_4$ or $Mg(NO_3)_2$ to obtain $Mg^{2+}_{(aq)}$

Write the formula of the salt solution provided for each metal cation

Number of Displacement Reactions

SOLID METAL STRIPS		$Mg^{2+}_{(aq)}$	$Zn^{2+}_{(aq)}$	$Fe^{3+}_{(aq)}$	$Pb^{2+}_{(aq)}$	$Cu^{2+}_{(aq)}$	Complete	Partial	None
		<p>Mg Magnesium</p> <p>Mg will react with $H^{1+}_{(aq)}$ from ionisation of water at pH = 7: <ul style="list-style-type: none"> $H_2O \rightleftharpoons H^{1+}_{(aq)} + OH^{1-}$ $Mg + 2H^+ \rightarrow H_2 + Mg^{2+}$ Add NaOH: $\Rightarrow Mg(OH)_2$ translucent white gel </p>	<p>Before NaOH</p> <p>After NaOH</p>	<p>Before NaOH</p> <p>After NaOH</p>	<p>Before NaOH</p> <p>After NaOH</p>	<ul style="list-style-type: none"> Copper metal deposits Magnesium breaks into small pieces Blue \rightarrow colourless solⁿ Add NaOH $\Rightarrow Mg(OH)_2$ translucent white gel 			
		<p>Zn Zinc</p> <p>These are not displacement reactions</p>	<p>Should displacement reactions occur in the diagonal boxes?</p> <ul style="list-style-type: none"> Add NaOH: $\Rightarrow Zn(OH)_2$ opaque white gel from the original $Zn^{2+}_{(aq)}$ solⁿ 	<ul style="list-style-type: none"> Orange \rightarrow Less orange Zn pitted with holes Add NaOH: <ul style="list-style-type: none"> \Rightarrow white gel $Zn(OH)_2$ \Rightarrow dk green gel $Fe(OH)_2$ \Rightarrow brown gel $Fe(OH)_3$ 	<p>Before NaOH</p> <p>After NaOH</p>	<p>Before NaOH</p> <p>After NaOH</p>			
		<p>Fe Iron (nails)</p> <p>These are not displacement reactions</p>	<p>These are not displacement reactions</p>	<ul style="list-style-type: none"> Green and brown layers: <ul style="list-style-type: none"> $Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$ $Fe^{2+}_{\text{green}} \rightarrow Fe^{3+}_{\text{red}} + e^-$ Add NaOH: <ul style="list-style-type: none"> \Rightarrow dk green gel $Fe(OH)_2$ \Rightarrow rust brown gel $Fe(OH)_3$ 	<p>Before NaOH</p> <p>After NaOH</p>	<p>Before NaOH</p> <p>After NaOH</p>			
		<p>Pb Lead</p> <p>These are not displacement reactions</p>	<p>These are not displacement reactions</p>	<p>These are not displacement reactions</p>	<p>Why is no displacement reaction expected?</p> <ul style="list-style-type: none"> Add NaOH: $\Rightarrow Pb(OH)_2$ opaque white powder from the original $Pb^{2+}_{(aq)}$ solⁿ 	<p>Before NaOH</p> <p>After NaOH</p>			
	<p>Cu Copper</p> <ul style="list-style-type: none"> $H_2O \rightleftharpoons H^{1+}_{(aq)} + OH^{1-}$ $Mg + 2H^+ \rightarrow H_2 + Mg^{2+}$ $Mg^{2+} + 2OH^{1-} \rightarrow Mg(OH)_2$ <p>The white ppt is not from displacement between two different metals. Absence of blue $Cu(OH)_2$ shows that $Cu \rightarrow Cu^{2+}$ is not involved</p>	<p>These are not displacement reactions</p>	<p>These are not displacement reactions</p>	<p>These are not displacement reactions</p>	<ul style="list-style-type: none"> Green and blue layers: <ul style="list-style-type: none"> $Cu_{(s)} \rightarrow Cu^{1+} + e^-$ $Cu^{1+}_{\text{green}} \rightarrow Cu^{2+}_{\text{blue}} + e^-$ Dark red ppt Cu_2O Add NaOH: <ul style="list-style-type: none"> \Rightarrow blue gel $Cu(OH)_2$ 				

Activity Series

Ranking the number of activated reactions when a metal displaces another metal cation from solution for Mg, Zn, Fe, Pb and Cu can be summarised as an **Activity Series** ☞.

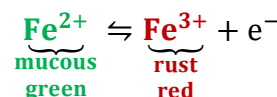
- Any metal in the Series can displace a metal below it in the series. For example, Magnesium metal will activate Copper (II) solution to precipitate Copper metal.
- Any metal in the Series cannot displace a metal above it in the series. For example, Lead metal will not activate Zinc cations to precipitate as Zinc metal.

Iron cations cannot gain electrons and be reduced back to iron metal in a test tube by displacement; reduction back to iron metal requires a blast furnace. However, iron ions can lose or gain electrons during displacement reactions with active metals.

Activity Series	Most Active	
	Magnesium	Mg
	Zinc	Zn
	Iron	Fe
	Lead	Pb
	Copper	Cu
	Least Active	

Lead (II) is displaced by Iron	Iron (III) is displaced by Magnesium
$\text{Pb}^{2+} + 2\text{e}^{-} \rightarrow \text{Pb}$ $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}$	$[\text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+}] \times 2$ $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^{-}$ <div style="display: flex; justify-content: space-between; align-items: center;"> LCM for e^{-} </div>
$\text{Pb}^{2+} + \text{Fe} \rightarrow \text{Pb} + \text{Fe}^{2+}$	$2\text{Fe}^{3+} + \text{Mg} \rightarrow 2\text{Fe}^{2+} + \text{Mg}^{2+}$

Two distinct colours are often blended with iron reactions:



- (a) Use the information from PART 1 **Displacement Reaction Observations** to complete the horizontal descending activity series shown below for the metals tested in this experiment, with special regard to how iron is behaving.

most active **Mg** > > > > least active

- (b) Explain the reasoning you used to obtain the Activity Series above by referring to the Displacement Observations.

- (c) Testing with more metals and their salt solutions produces a larger Activity Series as shown below.

Use this Activity Series to predict which combinations produce a displacement reaction and complete its equation.

A metal cation on the list will be displaced by a metal above it	Most Active	A solid metal on the list will displace any metal cation below it	
	Potassium K		ex: Tin in silver nitrate solution displaces silver because Sn is above Ag $\text{Sn} + 2\text{Ag}^{1+} \rightarrow \text{Sn}^{2+} + 2\text{Ag}_{(\text{s})}$ ppt
	Calcium Ca		(i) Calcium metal in aluminium chloride solution.
	Sodium Na		(ii) Iron metal in sodium chloride solution.
	Magnesium Mg		(iii) Zinc metal in Tin (II) chloride solution.
	Aluminium Al		H₂O reacts 'preferentially' with any metal above it before displacement ex: $\text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{H}_2(\text{g})$ eff
	Zinc Zn		and $\text{Ca} + \text{CuSO}_4 \rightarrow \text{CaSO}_4 + \text{Cu}_{(\text{s})}$ ppt
	Iron Fe		(iv) Zinc metal in potassium iodide solution.
	WATER H₂O		(v) Calcium metal in lead acetate solution.
	Tin Sn		ex: Aluminium in calcium nitrate solution will produce no reaction because Al is not above Ca on the Activity Series.
Lead Pb			
Copper Cu			
Silver Ag			
Gold Au			
Platinum Pt			
Least Active			

TASK 2 External electron e^- flow

Displacement reactions transfer electrons e^- between metals and metal cations with electronegativity differences $\Delta\chi$. Chemical reactions used to generate a flow of electricity are known as electrochemical reactions.

- Arranging reactants to make electrons move along an external circuit is known as **electrochemistry**.
 - A metal in its corresponding salt solution is a half-cell; **ex** Cu metal in CuSO_4 solution $\text{Cu} \mid \text{Cu}^{2+}$.
 - Two half-cells of different metals connected to produce a voltage is a full-cell; **ex** $\text{Cu}^{2+} \mid \text{Cu} \parallel \text{Zn} \mid \text{Zn}^{2+}$.
 - A group of cells connected to produce more current is a battery.

The same redox reaction, $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$, with different electrochemical physical arrangements		
Redox with e^- transfer	$\frac{1}{2}$ -cell Combinations for Voltage	Electrochemistry with external e^- flow
<p>The overall reaction is: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$</p>	<p>Combining solid metals with their corresponding salt solutions, such as $\text{Zn} \mid \text{Zn}^{2+}$ and $\text{Cu} \mid \text{Cu}^{2+}$ make 'half cells'. Two $\frac{1}{2}$-cells are used to study external e^- flow voltages, E_{cell}.</p> <ul style="list-style-type: none"> • Solvated ions act as electric charge carriers in aqueous solutions. • Free electrons e^- can only flow between separated reactants along external conducting wires. <p>Two $\frac{1}{2}$-cells connected by external circuitry is known as a full-cell.</p>	<p>The overall reaction remains as: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$</p>
<p>The $\overset{0}{\text{Zn}}$ solid and $\overset{+2}{\text{Cu}^{2+}}$ salt solution now have an external circuit for a redox e^- flow (aka electric current I).</p>		

Electrochemistry

The battery is producing a Direct Current (DC) flow of electricity coming from chemical reactions producing electricity. DC means the electrons flow in the same direction between reactants during production of the electrical current (I). These reactions follow the same rules and conventions for electronic circuits you would have learnt about in junior science or Technology Studies: DC circuits follow Ohm's Law $V = I \times R$ and can be arranged in series or in parallel.

- Electrical current (I) is the flow of electrons along metal wires towards a positively charged terminal, although the traditional current direction is defined as $(+) \rightarrow (-)$.
- The transfer of electrons e^- between reactants produces a difference in Electrical energy between them, known as the Voltage V . This is measured as the cell voltage E_{cell} .
- Electrical resistance (R) of the circuit is determined by molar [Concentration] of reactants: High concentration has a high rate of e^- flow; low concentration has a low rate of e^- flow.

These electrical characteristics are related by Ohm's Law,
 $V = I \times R$.

Setting Up and Measuring Cell Voltages E_{cell}

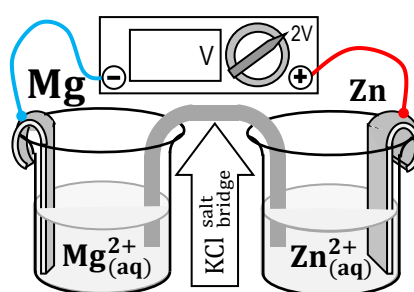
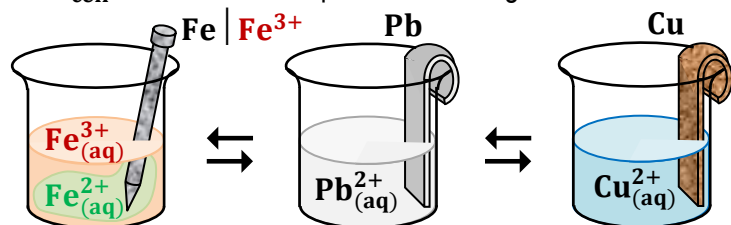
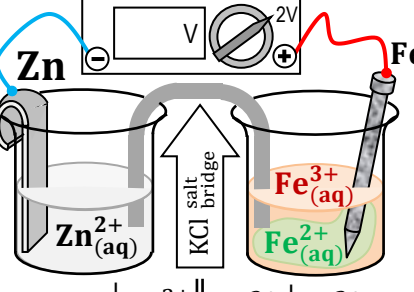
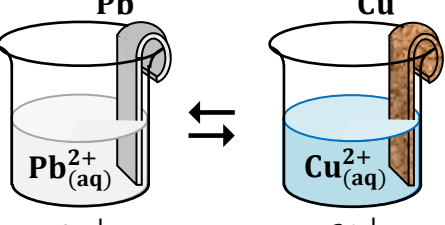
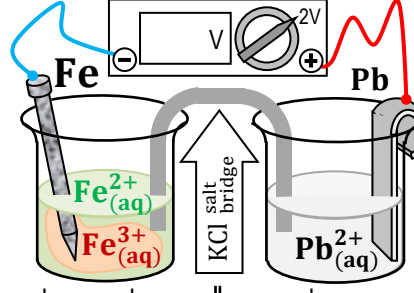
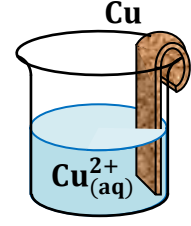
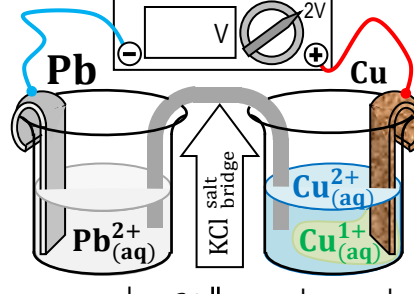
Assemble five half-cells as shown below to investigate which combination of them produces the highest voltage.

- Rank them in order of displacement activity based on the previous Displacement Observations table.

most active least active

Mg metal electrode	>	Zn metal electrode	>	Fe nail electrode	>	Pb metal electrode	>	Cu metal electrode
Mg \mid Mg^{2+} half cell		Zn \mid Zn^{2+} half cell		Fe \mid $\text{Fe}^{2+} \mid \text{Fe}^{3+}$ half cell		Pb \mid Pb^{2+} half cell		Cu \mid $\text{Cu}^{1+} \mid \text{Cu}^{2+}$ half cell

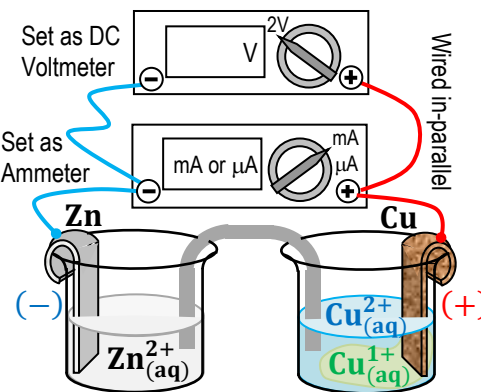
Reference Electrode	Half Cell Combinations in Activity Series order to obtain E_{cell} trends			
	E_{cell} with $\text{Zn}^{2+} \text{Zn}$	E_{cell} with $\text{Fe}^{3+} \text{Fe}^{2+}$	E_{cell} with $\text{Pb}^{2+} \text{Pb}$	E_{cell} with $\text{Cu}^{2+} \text{Cu}$
$\text{Mg} \text{Mg}^{2+}$	$\text{Mg} \text{Mg}^{2+} \text{Zn}^{2+} \text{Zn}$	$\text{Mg} \text{Mg}^{2+} \text{Fe}^{3+} \text{Fe}^{2+}$	$\text{Mg} \text{Mg}^{2+} \text{Pb}^{2+} \text{Pb}$	$\text{Mg} \text{Mg}^{2+} \text{Cu}^{2+} \text{Cu}$
$\text{Zn} \text{Zn}^{2+}$	No displacement with Zn	$\text{Zn} \text{Zn}^{2+} \text{Fe}^{3+} \text{Fe}^{2+}$	$\text{Zn} \text{Zn}^{2+} \text{Pb}^{2+} \text{Pb}$	$\text{Zn} \text{Zn}^{2+} \text{Cu}^{2+} \text{Cu}$
$\text{Fe} \text{Fe}^{2+}$	No displacement with Fe		$\text{Fe}^{2+} \text{Fe}^{3+} \text{Pb}^{2+} \text{Pb}$	$\text{Fe}^{2+} \text{Fe}^{3+} \text{Cu}^{2+} \text{Cu}$
$\text{Pb} \text{Pb}^{2+}$	No displacement with Pb			$\text{Pb} \text{Pb}^{2+} \text{Cu}^{2+} \text{Cu}$
$\text{Cu} \text{Cu}^{2+}$	Copper does not cause the other metal cations to be displaced; copper cations are displaced by the other metals			

<p>Magnesium $\text{Mg} \text{Mg}^{2+}$ Reference Electrode</p>  <p>$\text{Mg} \text{Mg}^{2+} \text{Zn}^{2+} \text{Zn}$</p>	<ul style="list-style-type: none"> Mg causes displacement for Zn^{2+}, Fe^{3+}, Pb^{2+} and Cu^{2+}. Record E_{cell} for each one compared to the magnesium half-cell.  <p>$\text{Fe}^{3+} \text{Fe}^{2+}$ $\text{Pb}^{2+} \text{Pb}$ $\text{Cu}^{2+} \text{Cu}$</p>
<p>Zinc $\text{Zn} \text{Zn}^{2+}$ Reference Electrode</p>  <p>$\text{Zn} \text{Zn}^{2+} \text{Fe}^{3+} \text{Fe}^{2+}$</p>	<ul style="list-style-type: none"> Zn displaces only Fe^{3+}, Pb^{2+} and Cu^{2+}. Record E_{cell} for each one compared to the zinc half-cell.  <p>$\text{Pb}^{2+} \text{Pb}$ $\text{Cu}^{2+} \text{Cu}$</p>
<p>Iron $\text{Fe} \text{Fe}^{2+}$ Reference Electrode</p>  <p>$\text{Fe} \text{Fe}^{2+} \text{Fe}^{3+} \text{Pb}^{2+} \text{Pb}$</p>	<ul style="list-style-type: none"> Fe^{2+} displaces only Pb^{2+} and Cu^{2+}. Need to use Iron (II) Sulphate half-cell when comparing to other half-cells. Keep a small beaker of saturated potassium chloride solution KCl and strips of chromatography paper with plastic tweezers for freshly prepared salt bridges with each E_{cell} reading.  <p>$\text{Cu}^{2+} \text{Cu}$</p>
<p>Lead $\text{Pb} \text{Pb}^{2+}$ Reference Electrode</p>  <p>$\text{Pb} \text{Pb}^{2+} \text{Cu}^{2+} \text{Cu}^{1+} \text{Cu}$</p>	<ul style="list-style-type: none"> Pb only displaces Cu^{2+} in the salt solutions tested; no other half-cells need to be tested for E_{cell} compared to the Lead half-cell. Make sure the salt bridge does not contact either of the two electrodes in each half-cell being tested to prevent a 'short' circuit reading. Cl^{1-} anions from the salt bridge may form precipitates with some of the test solutions alongside displacement reactions.

What to do about Voltage Drift? [Answer: wait until the Voltage becomes constant]

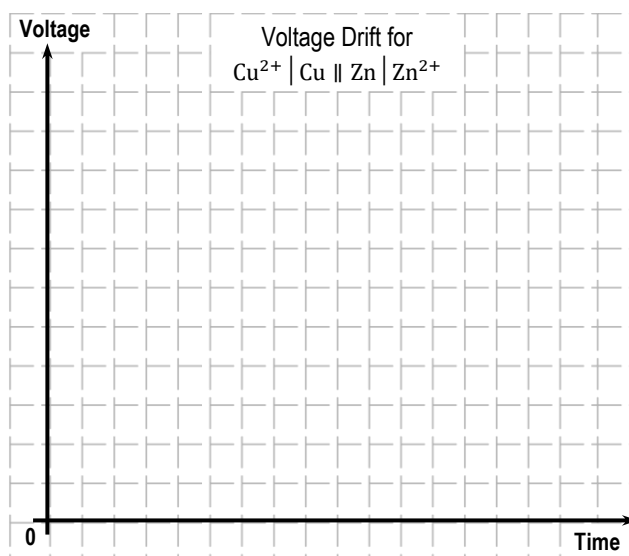
Voltage 'drift' is best measured using two multi-meters, one for Voltage **V** and one for current **I**, simultaneously.

- Set voltage (**V**) for Direct Current Voltage DCV on the multi-meter:
 - Use the 2 V (2000 mV = 2000 × 10⁻³V = 2.00 V) range.
- Set current (**I**) for DCV also on the other multi-meter:
 - Start at the highest range and step down until a reading is detected;
 - Should use milli-Amp mA (10⁻³A) or micro-Amp μA (10⁻⁶A) range.
- Record (**V**) and (**I**) values every 60 seconds until the voltage is constant.
 - Enter these values in the data table and determine electrical Resistance (**R**) using Ohm's Law in the last column.
 - Plot the voltage (**V**) values on the graph provided.



The voltage achieves a constant value after some time when chemical reactants have achieved an equilibrium state.

Time: (actually observed)	Observed Data		$R = \frac{V}{I}$
	Voltage (V)	Current (I)	
#1	0		
#2			
#3			
#4			
#5			
#6			
#7			
#8			



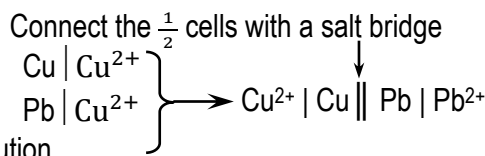
Explain why voltage drift indicates changing [molar] concentration of the electrochemical reagents to a constant equilibrium state.

Recording Cell Voltages E_{cell} for Displacement Reactions

Lead had one displacement reaction in PART 1.

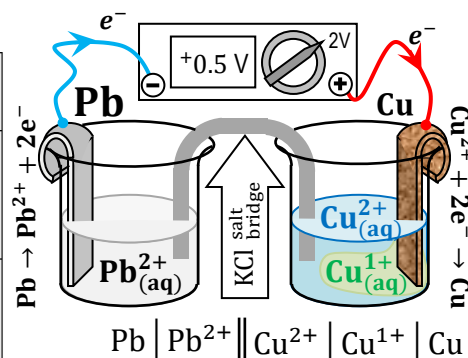
(Copper did not displace the other metal cations)

- Assemble two half-cells for each metal to make a battery.
 - Copper metal strip in copper (II) sulphate solution is written as: Cu | Cu²⁺
 - Lead metal strip in lead (II) nitrate solution is written as: Pb | Pb²⁺
- Connect each 1/2-cell solution with a 'salt bridge' soaked in KCl solution.
- Set the multi-meter for Direct Current Voltage DCV 2 V scale and adjust connectors for a positive voltage reading.
- Read the initial cell voltage and note the time take to achieve constant voltage.



Pb referenced 1/2-cell Series (with one reaction)

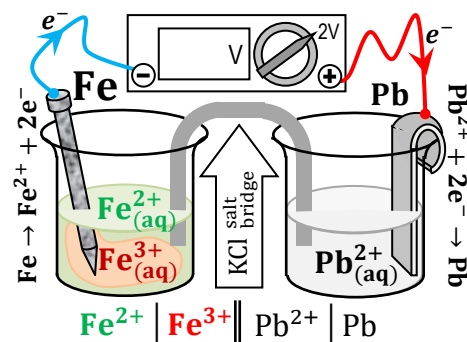
Lead with Copper		Pb Pb ²⁺ Cu ²⁺ Cu ¹⁺ Cu	
2 × E _{1/2}	(+)	Cu ²⁺ + 2e ⁻ → Cu	Two coloured regions: • Cu ²⁺ + e ⁻ → Cu ¹⁺ Green • Residual Cu ²⁺ blue
	(-)		
Voltage drift time		Pb + Cu ²⁺ → Pb ²⁺ + Cu	Cell Voltage E _{cell} ≈ 0.5V



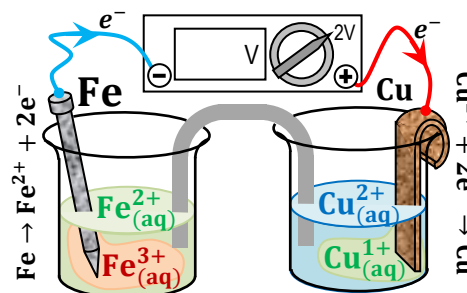
The next least active metal from PART 1 is Iron, with two reactions.

Iron referenced 1/2-cell Series (with two reactions)

Iron in Fe²⁺ solution with Lead		$\text{Fe}^{2+} \text{Fe}^{3+} \text{Pb}^{2+} \text{Pb}$	
$2 \times E_{1/2}$	(+) or (-)	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$ nail electrode	Two blended colours: • Original Fe ²⁺ green from half-cell salt • New Fe ³⁺ red
Voltage drift time		Cell Voltage $E_{\text{cell}} \approx \text{V}$	



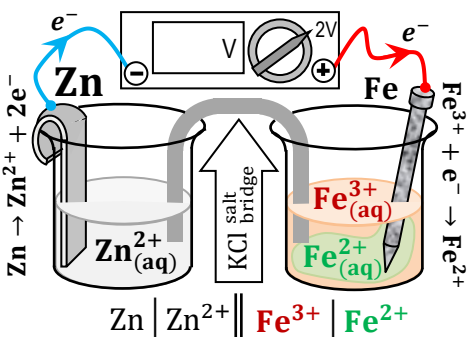
Iron in Fe²⁺ solution with Copper		$ $	
$2 \times E_{1/2}$	(+) or (-)	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ nail electrode	Two coloured regions: • Residual Cu ²⁺ blue • New Fe ²⁺ green
Voltage drift time		Cell Voltage $E_{\text{cell}} \approx \text{V}$	



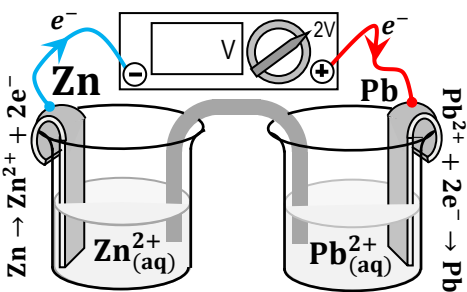
The next least active metal from PART 1 is Zinc, with three reactions.

Zinc referenced 1/2-cell Series (with three reactions)

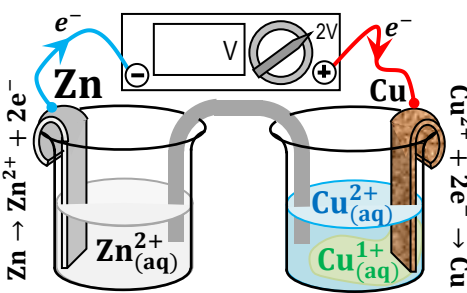
Zinc with Iron in Fe³⁺ solution		$\text{Zn} \text{Zn}^{2+} \text{Fe}^{3+} \text{Fe}^{2+}$	
$2 \times E_{1/2}$	(+) or (-)	$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ nail electrode	Two coloured regions: • Residual Fe ³⁺ red • New Fe ²⁺ green
Voltage drift time		Cell Voltage $E_{\text{cell}} \approx \text{V}$	



Zinc with Lead		$ $	
$2 \times E_{1/2}$	(+) or (-)	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$ nail electrode	
Voltage drift time		Cell Voltage $E_{\text{cell}} \approx \text{V}$	

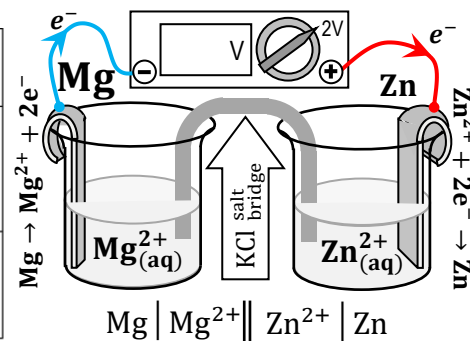


Zinc with Copper		$ $	
$2 \times E_{1/2}$	(+) or (-)	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ nail electrode	Two coloured regions: • Cu ²⁺ + e ⁻ → Cu ¹⁺ Green • Residual Cu ²⁺ blue
Voltage drift time		Cell Voltage $E_{\text{cell}} \approx \text{V}$	

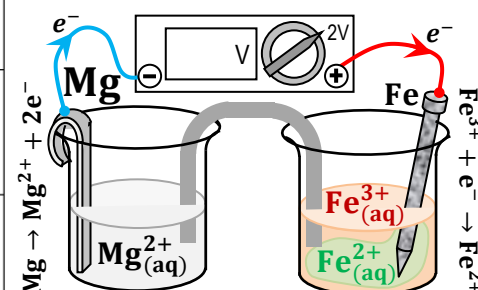


Magnesium referenced 1/2-cell Series (with four reactions)

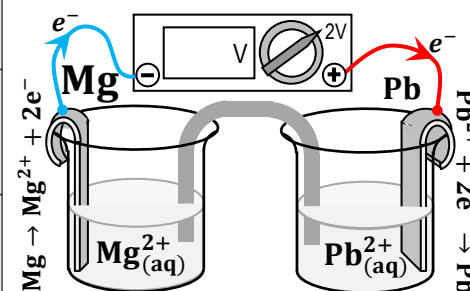
Magnesium with Zinc		$\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Zn}^{2+} \mid \text{Zn}$	
$2 \times E_{1/2}$	(+) or (-)	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$ $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	
Voltage drift time		Cell Voltage	$E_{\text{cell}} \approx \text{V}$



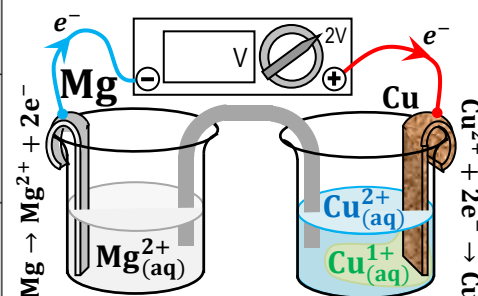
Magnesium with Iron <i>in Fe³⁺ solution</i>		$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	
$2 \times E_{1/2}$	(+) or (-)	Two coloured regions: • Residual Fe ³⁺ red • New Fe ²⁺ green	
Voltage drift time		Cell Voltage	$E_{\text{cell}} \approx \text{V}$



Magnesium with Lead		$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$ $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	
$2 \times E_{1/2}$	(+) or (-)		
Voltage drift time		Cell Voltage	$E_{\text{cell}} \approx \text{V}$



Magnesium with Copper		$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	
$2 \times E_{1/2}$	(+) or (-)	Two coloured regions: • $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^{1+}$ Green • Residual Cu^{2+} blue	
Voltage drift time		Cell Voltage	$E_{\text{cell}} \approx \text{V}$



Relation between Activity and E_{cell}

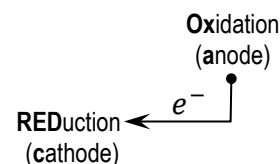
Comment on the relation between Activity series and E_{cell} values using the observations from this investigation.

(a) What do you notice about the half-cell combinations that give the largest E_{cell} values within each reference set?	_____
(b) What do you notice about the half-cell combinations that give the smallest E_{cell} values within each reference set?	_____
(c) What general trend is relating E_{cell} values with the position of metals in the displacement reaction Activity series?	_____

Active Metal Referenced Reduction Potentials (Voltage)

Copy the Cell Voltage E_{cell} values from your practical observations into the Table below:

- The connector arrows indicate half-cells being connected to form a full-cell;
- The arrows indicate direction of electron e^- transfer during redox;
 - Half-cells being reduced are labelled as cathodes (oxidation state is decreased);
 - Half-cells being oxidized are labelled as anodes (oxidation state is increased).



Magnesium referenced reduction of Zinc, Iron, Lead and Copper using Activity Series		Activity Series	Cell voltage, E_{cell} , increases as distance apart on the Activity Series increases.
	Reduction Oxidation $\text{Zn}^{2+} \text{Zn} \text{Mg} \text{Mg}^{2+}$ $E_{\text{cell}}^{\text{Zn Mg}} \approx$ $\text{Fe}^{3+} \text{Fe}^{2+} \text{Mg} \text{Mg}^{2+}$ $E_{\text{cell}}^{\text{Fe Mg}} \approx$ $\text{Pb}^{2+} \text{Pb} \text{Mg} \text{Mg}^{2+}$ $E_{\text{cell}}^{\text{Pb Mg}} \approx$ $\text{Cu}^{2+} \text{Cu} \text{Mg} \text{Mg}^{2+}$ $E_{\text{cell}}^{\text{Cu Mg}} \approx$	Mg	Conversely, E_{cell} decreases with closeness on the Activity Series
Zinc referenced reduction of Iron, Lead and Copper		For example, in the Mg referenced set of four reductions, Cu and Mg are farthest apart on the Activity Series above. Therefore, the $\text{Cu}^{2+} \text{Cu} \text{Mg} \text{Mg}^{2+}$ cell produces the largest electrical potential difference between electrodes, better known as Voltage.	
	Magnesium cannot be displaced (reduced) by Zinc Reduction Oxidation $\text{Fe}^{3+} \text{Fe}^{2+} \text{Zn} \text{Zn}^{2+}$ $E_{\text{cell}}^{\text{Fe Zn}} \approx$ $\text{Pb}^{2+} \text{Pb} \text{Zn} \text{Zn}^{2+}$ $E_{\text{cell}}^{\text{Pb Zn}} \approx$ $\text{Cu}^{2+} \text{Cu} \text{Zn} \text{Zn}^{2+}$ $E_{\text{cell}}^{\text{Cu Zn}} \approx$	In comparison, Zn and Mg are closest together in the Magnesium referenced set. $\therefore \text{Zn}^{2+} \text{Zn} \text{Mg} \text{Mg}^{2+}$ has the smallest reduction potential of the Mg set.	
Iron referenced reduction of Lead and Copper		This pattern is repeated in each of the reference sets for Zinc, Iron and Lead. The further apart two half-cells are in the Activity Series, the higher the voltage produced by their E_{cell} combination.	
	Magnesium and Zinc cannot be displaced (reduced) by Iron, as shown on the Activity Series above. Reduction Oxidation $\text{Pb}^{2+} \text{Pb} \text{Fe}^{2+} \text{Fe}^{3+}$ $E_{\text{cell}}^{\text{Pb Fe}} \approx$ $\text{Cu}^{2+} \text{Cu} \text{Fe}^{2+} \text{Fe}^{3+}$ $E_{\text{cell}}^{\text{Cu Fe}} \approx$		
Lead referenced reduction of Copper			
	Magnesium, Zinc and Iron cannot be displaced (reduced) by Lead, as indicated by their position above it in the Activity Series. Reduction Oxidation $\text{Cu}^{2+} \text{Cu} \text{Pb} \text{Pb}^{2+}$ $E_{\text{cell}}^{\text{Cu Pb}} \approx$		

Hydrogen Referenced Reduction Potential

All half-cells have been referenced against the **Standard Hydrogen Electrode (SHE²)** using $\text{H}_{2(\text{g})} \rightarrow 2\text{H}_{(\text{aq})}^{1+} + 2e^-$.

Each half-cell has a 'standardised' reduction potential, shown as $E_{\frac{1}{2}}^0$ with respect to SHE set as $E_{\frac{1}{2}}^{\text{H}_2|\text{H}^+} = 0.0 \text{ V}$.

² Aylward & Findlay, SI Chemical Data (Second Edition) page 116. John Wiley & Sons 1974.

TASK 3 Science as Human Endeavour: Harnessing Redox to Make Batteries

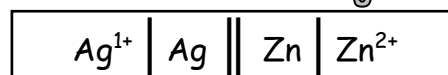
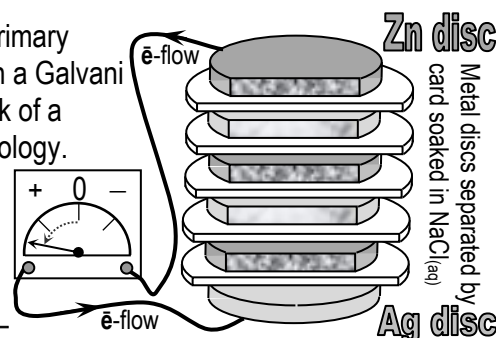
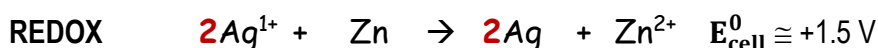
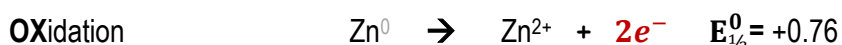
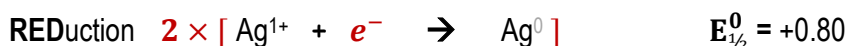
Electrochemical Reactions produce electricity as output to be collected as electro-motive force for work.

Professor Alessandro Volta was first to develop reproducible technology to safely release electricity 'on demand' by arranging metal / metallic cation $\frac{1}{2}$ -cells in a 'Voltaic Pile' to achieve an external e^- flow at the University of Pavia, Italy. It was much safer than Benjamin Franklin's idea to fly a kite in a lightning storm to collect electricity. Voltaic pile technology enabled many researchers to study electricity around the world under controlled laboratory conditions. Napoleon Bonaparte named the Italian professor Count Volta in honour of his research. The metric unit for electricity is called the volt **V**, named after this pioneering scientist.



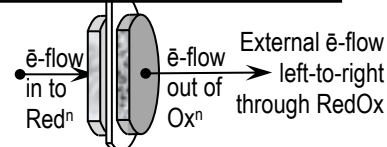
Complete the $\frac{1}{2}$ -cell reactions for the Voltaic Cells shown below. Include the direction of e^- flow on the schematic volt meter. These examples are for students to practice and interpret redox equation balancing in context. There is zero expectation for students to recite these as set problems. Understanding the process is what matters.

Ex: The Voltaic Pile was developed between 1790 and 1800 as the first Primary (aka non-rechargeable) battery. Its 'external' e^- flow was measurable with a Galvani designed frog leg 'voltmeter'. Scientists could produce electricity at the flick of a switch. Many new elemental metals were discovered using this new technology.



The redox 'mnemonic box' shown below the Voltaic Pile diagram opposite uses the following representational conventions

- Salt bridge $||$ in between Redox reagents
- Reduction reagent pair $\text{Red}^{\text{High}} | \text{Red}^{\text{Low}}$ on the left, Oxidation reagent pair $\text{Ox}^{\text{Low}} | \text{Ox}^{\text{High}}$ on the right
- e^- -flow left-to-right, into Red^{n} , out of Ox^{n} .

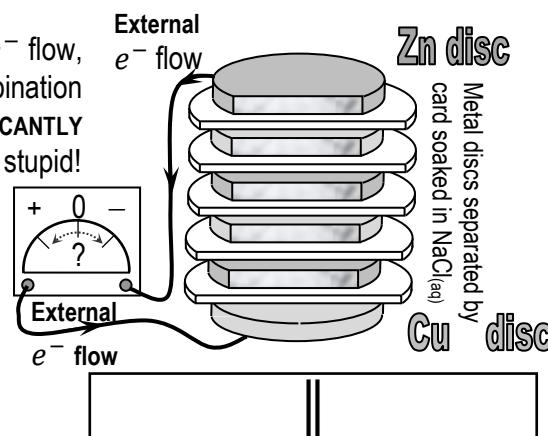
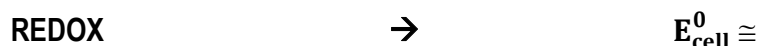


- In 1780 Luigi Galvani noted that dead frog legs twitched when their nerves were cut with a steel scalpel on a copper cutting board. Severed frog legs became the first volt-meters for testing electrical 'vitality' in Bologna, Italy.
- During the 1792 Reign of Terror in the French revolution F.X. Bicat unsuccessfully attempted to 'revitalise' guillotined aristocrats by reattaching their heads and then using a large Voltaic Pile to make them twitch back into life.
- In 1803 Giovanni Aldini (nephew of Galvani) used the body of the hanged English murderer Forster an hour after his death to test the 'precise effects of galvanism with a voltaic column of one hundred and twenty copper and zinc couples', to no effect except the odour of ozone produced by ionising oxygen in the surrounding air.
- In 1817 Mary Shelley wrote *Frankenstein* in Geneva, Switzerland, about an unscrupulous scientist working against nature by making a monster with a sewn-on head brought back to life by revitalizing electrical energy as a bolt of lightning.

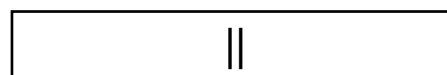
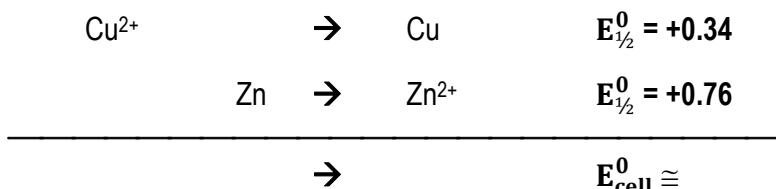
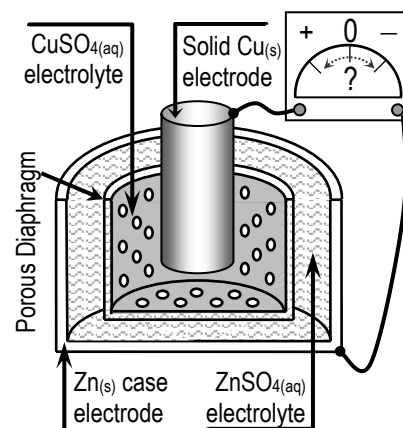


Young Frankenstein (1974)
"It's Alive!"

(a) The **Voltaic pile** used various metals to produce an electrochemical e^- flow, aka a battery. Giovanni Aldini used the slightly lower voltage $\text{Cu}|\text{Zn}$ combination compared to Volta's expensive $\text{Ag}|\text{Zn}$. The Aldini battery was **SIGNIFICANTLY** cheaper than the Volta version. Aldini may have been mad, but he wasn't stupid!



(b) The **Danielle Cell** was developed in 1830 as the first portable battery. They were used to provide electrical power to the then new telegraph relay stations. Electrolytes are aqueous solutions containing ions that can act as mobile charge carriers. Sulfuric acid H_2SO_4 was used to maintain high concentrations of $\text{CuSO}_4(\text{aq})$ and $\text{ZnSO}_4(\text{aq})$ to form aqueous $\frac{1}{2}$ -cells for $\text{Cu} | \text{Cu}^{2+}$ and $\text{Zn} | \text{Zn}^{2+}$. This was quite hazardous as the acidic electrolytes were prone to corroding the metal casings and leaking lots of acid and explosive hydrogen gas. Smoking was very popular at the time, despite the obvious health risks: there were frequent explosive 'accidents'.



Electrochemical reactions are best balanced using the five step $\frac{1}{2}$ -equation method.

- 1 Identify the redox species changing oxidation states as redox conjugate pairs [reactant | product].
 - Balance the number of atoms changing oxidation state on each side of [reactant \rightarrow product].
- 2 Account for missing Oxygen atoms between Reactants and Products.
 - Convert unaccounted Oxygen atoms to H_2O with the addition of H^{1+} ions (aka acidic conditions).
- 3 Determine the arithmetic value of total ionic charge on each side of [reactant \rightarrow product] the reaction.
 - Add \bar{e} electrons to the side with the lowest negative charge until both sides have equal total ionic charge.

Steps 1 to 3 will produce two redox $\frac{1}{2}$ -equations, with one showing Reduction while the other shows Oxidation.

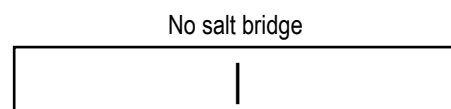
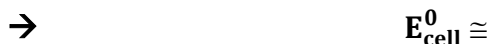
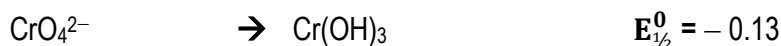
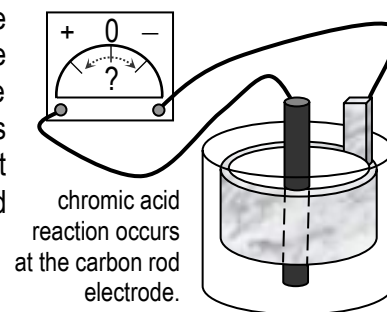
- 4 Determine the Lowest Common Multiple (LCM) for both $\frac{1}{2}$ -equations with respect to the \bar{e} electrons.
 - Use LCM to generate equal numbers of \bar{e} electrons on each side of [reactant \rightarrow product] for elimination.
- 5 Algebraically cancel excess H^+ and H_2O from each side of [reactant \rightarrow product] the reaction equation.
 - Add remaining reagents from each $\frac{1}{2}$ -equation to obtain a balanced Redox reaction equation.

Example: The Bichromate cell reacts chromic acid $\text{H}_2\text{CrO}_4(\text{aq})$ with zinc metal $\text{Zn}(\text{s})$.		
1	The chromic acid reactions is given $\underbrace{\text{CrO}_4^{2-}}_{\text{one Cr atom}} \rightarrow \underbrace{\text{Cr(OH)}_3}_{\text{one Cr atom}}$	The zinc reaction is given as $\underbrace{\text{Zn}}_{\text{one Zn atom}} \rightarrow \underbrace{\text{Zn}^{2+}}_{\text{one Zn atom}}$
2	$\underbrace{\text{CrO}_4^{2-}}_{\text{four O atoms}} \rightarrow \underbrace{\text{Cr(OH)}_3}_{\text{three O atoms}} + \text{H}_2\text{O}$ need to add one H_2O to balance O $\text{CrO}_4^{2-} \rightarrow \text{Cr(OH)}_3 + \text{H}_2\text{O}$ has 4xO each side. Add acid $\text{CrO}_4^{2-} + 5\text{H}^{1+} \rightarrow \text{Cr(OH)}_3 + \text{H}_2\text{O}$ There are now 5xH on each side.	There is no oxygen or hydrogen involved with the Zinc component, so there is no need to adjust for oxygen or hydrogen atoms. In other words, zero Oxygen and zero Hydrogen on each side.
3	$\underbrace{(\text{1} \times 2^-) + (\text{5} \times 1^+) = 3^+}_{\text{zero overall charge}}$ $\text{CrO}_4^{2-} + 5\text{H}^{1+} \rightarrow \text{Cr(OH)}_3 + \text{H}_2\text{O}$ $\underbrace{\text{CrO}_4^{2-} + 5\text{H}^{1+} + 3e^-}_{3^+ + 3^- = \text{zero}} \rightarrow \underbrace{\text{Cr(OH)}_3 + \text{H}_2\text{O}}_{\text{already zero}}$	$\underbrace{\text{Zn}}_{\text{zero}} \rightarrow \underbrace{\text{Zn}^{2+}}_{2^+}$ $\underbrace{\text{Zn}}_{\text{zero}} \rightarrow \underbrace{\text{Zn}^{2+} + 2e^-}_{2^+ + 2e^- = \text{zero}}$

$\frac{1}{2}$ -equations showing Reduction (gain of e^-) while the other shows Oxidation (loss of e^-), are ready for balancing

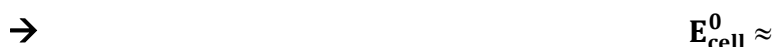
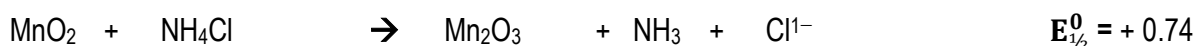
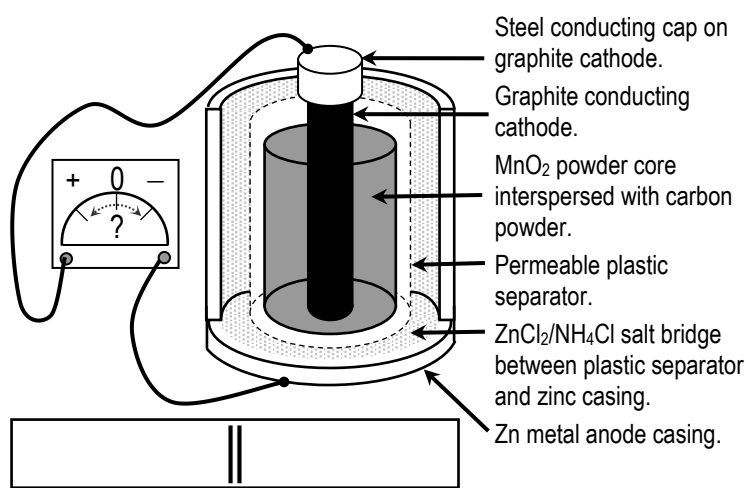
4	$[\text{CrO}_4^{2-} + 5\text{H}^{1+} + 3e^- \rightarrow \text{Cr(OH)}_3 + \text{H}_2\text{O}] \times 2$ $[\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-] \times 3$	$2\text{CrO}_4^{2-} + 10\text{H}^{1+} + \cancel{6e^-} \rightarrow 2\text{Cr(OH)}_3 + 2\text{H}_2\text{O}$ $3\text{Zn} \rightarrow 3\text{Zn}^{2+} + \cancel{6e^-}$
5	Mass and charge balanced reaction equation.	$\underbrace{2\text{CrO}_4^{2-} + 10\text{H}^{1+} + 3\text{Zn}}_{(2 \times 2^-) + (10 \times 1^+) = 6^+} \rightarrow \underbrace{2\text{Cr(OH)}_3 + 3\text{Zn}^{2+} + 2\text{H}_2\text{O}}_{(3 \times 2^+) = 6^+}$

(c) The **Bichromate Cell** was developed during the 1850's as a relatively safe alternative to earlier batteries which used a strong acid such as H_2SO_4 for the electrolyte. A zinc annular plate and an inert carbon rod were used as the electrodes immersed in weak chromic acid, $\text{H}_2\text{CrO}_{4(\text{aq})}$. No salt bridge was needed as the chromic acid doubled up as electrolyte and oxidising agent (e^- acceptor). Placing the zinc casing at the centre of a glass jar prevented leakage as the zinc corroded by acting as the reducing agent (e^- donor).



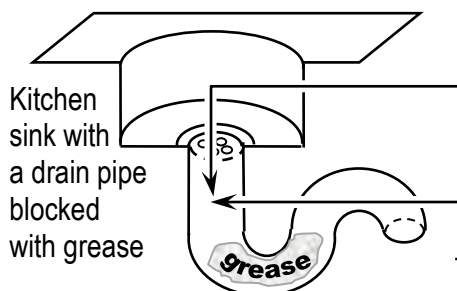
The Voltaic Pile, Daniell Cell and Bichromate Cell are all 'Wet Cells' with aqueous acid electrolytes. Problems with metal casing corrosion and $\text{H}_{2(\text{g})}$ side reactions with the acids led chemists to develop alkaline based electrolytes to avoid these quite real and dangerous problems.

(d) Georges Leclanché developed the **Dry Cell** circa 1860 to overcome the leaking liquid problem of Wet Cells. This was achieved by replacing the aqueous acid electrolytes with a gel like paste acting as a salt bridge. However, the NH_4Cl in the paste is converted to NH_3 during the reduction of MnO_2 . The NH_3 is then involved in the oxidation of Zn to form the transition metal complex zinc tetra amine (II) chloride, $\text{Zn}(\text{NH}_3)_4\text{Cl}_2$.



(e) **Drain Cleaner** uses a redox reaction to dislodge grease from blocked drain pipes. The dry drain cleaner mixture is poured down the drain followed by a small amount of water which becomes part of the electrochemical reaction.

Most commercial brands usually state a minimum caustic content of 55% w/w NaOH with aluminium pieces, indicating that $n(\text{NaOH}) : n(\text{Al})$ is approximately 4 : 1, making $\text{pH} \gg 7$ which is very alkaline. These conditions make water react electrochemically to produce hydrogen gas and hydroxide anions.

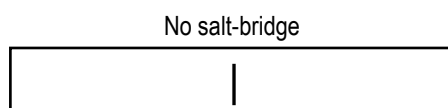


The drain cleaner solution is very alkaline with $[\text{NaOH}] \gg 1 \text{ mol L}^{-1}$



$\Delta H \gg 0$ (very hot) for this reaction:

- warming the grease to make it more fluid
- then dislodging the fluid grease with vigorous H_2 effervescence.



TASK 3 (Extension) New and Familiar Contexts

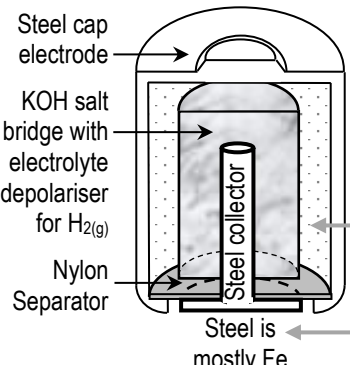
Alkaline Conditions: Ammonium chloride paste in 'Dry Cells' dissociates: $\text{NH}_4\text{Cl}_{(\text{aq})} \rightarrow \text{NH}_4^{1+}_{(\text{aq})} + \text{Cl}^{-1}_{(\text{aq})}$
 $\text{NH}_4^{1+}_{(\text{aq})}$ is acidic and reacts with the solid zinc metal casing: $2\text{NH}_4^{1+}_{(\text{aq})} + \text{Zn}_{(\text{s})} \rightarrow 2\text{NH}_3_{(\text{aq})} + \text{H}_{2(\text{g})} + \text{Zn}^{2+}_{(\text{aq})}$

The battery would leak when enough zinc metal casing had dissolved and formed a hole: messy! The production of hydrogen gas in enclosed spaces with electricity was downright hazardous. This problem is fixed with alkaline conditions when using metal casings for batteries. The chemical reactions are slightly more complex, but much safer.

Most contemporary batteries use 'alkaline conditions' with OH^{-1} to prevent these types of acid side reactions.

- This is achieved by balancing the half-reactions as before with initial acidic conditions. Ensure each $\frac{1}{2}$ -equation is correctly charge balanced and the following steps become incidental.
- Every remaining H^{1+} ion is then neutralised by adding OH^{-1} to convert into **water**: $\text{H}^{1+}_{(\text{aq})} + \text{OH}^{-1}_{(\text{aq})} \rightarrow \text{H}_2\text{O}$
The OH^{-1} must be added on both sides of the reaction equation to maintain mass and charge balance.
- Cancel excess species on each side, in particular extra H_2O .

DURACELL® and **ENERGIZER®** are contemporary alkaline batteries using this cell: $\text{NiO}_2 \mid \text{Ni}(\text{OH})_2 \parallel \text{Fe} \mid \text{FeO}_4^{2-}$



1 Balance for acid conditions as before by adding H^{1+} .

Write the redox pairs above as two $\frac{1}{2}$ -equations for balancing:

$$3 \times [\text{NiO}_2 + 2\text{H}^{1+} + 2\text{e}^- \rightarrow \text{Ni}(\text{OH})_2]$$

$$1 \times [\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{FeO}_4^{2-} + 8\text{H}^{1+} + 6\text{e}^-]$$

$$3\text{NiO}_2 + \text{Fe} + 4\text{H}_2\text{O} \rightarrow 3\text{Ni}(\text{OH})_2 + \text{FeO}_4^{2-} + 2\text{H}^{1+}$$

2 Neutralize acidity by adding OH^{-1} for excess H^{1+}

$$\text{H}^{1+}_{(\text{aq})} + \text{OH}^{-1}_{(\text{aq})} \rightarrow \text{H}_2\text{O}$$

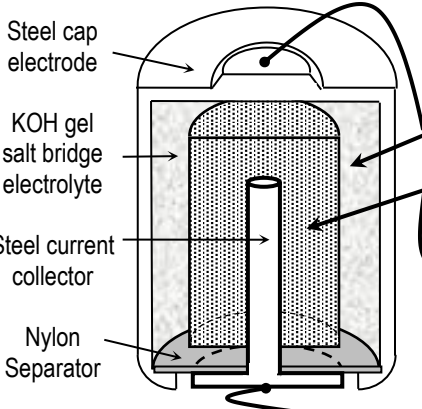
$$3\text{NiO}_2 + \text{Fe} + 4\text{H}_2\text{O} + 2\text{OH}^{-1} \rightarrow 3\text{Ni}(\text{OH})_2 + \text{FeO}_4^{2-} + 2\text{H}^{1+} + 2\text{OH}^{-1}$$

$$3\text{NiO}_2 + \text{Fe} + 4\text{H}_2\text{O} + 2\text{OH}^{-1} \rightarrow 3\text{Ni}(\text{OH})_2 + \text{FeO}_4^{2-} + 2\text{H}_2\text{O}$$

3 $3\text{NiO}_2 + \text{Fe} + 2\text{H}_2\text{O} + 2\text{OH}^{-1} \rightarrow 3\text{Ni}(\text{OH})_2 + \text{FeO}_4^{2-}$

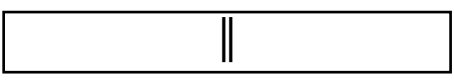
The hydroxide comes from the KOH salt bridge: $3\text{NiO}_2 + \text{Fe} + 2\text{H}_2\text{O} + 2\text{KOH} \rightarrow 3\text{Ni}(\text{OH})_2 + \text{K}_2\text{FeO}_4$

Label each electrode type, sign \pm and identify each $\frac{1}{2}$ -equation as either **RED**uction or **OX**idation.

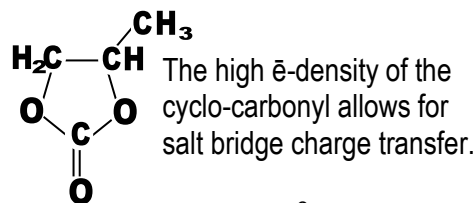
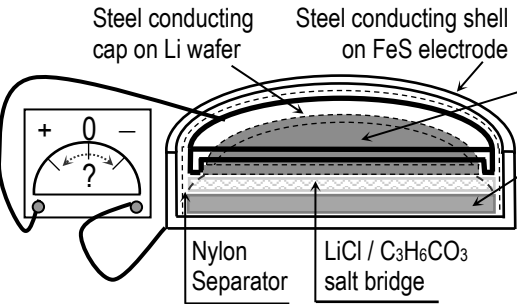


(e) ALKALINE BATTERY: developed in 1950's.

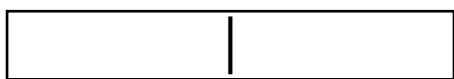
MnO_2	\rightarrow	$\text{Mn}(\text{OH})_2$	$E_{1/2}^0 = -0.05$
Zn powder	\rightarrow	ZnO_2^{2-}	$E_{1/2}^0 = +1.22$
	\rightarrow		$E_{\text{cell}}^0 \approx$



(f) LITHIUM BATTERY: uses a 1990's type solid polymer electrolyte, such as propylene carbonate matrix doped with LiCl.

Li	\rightarrow	Li^{1+}	$E_{1/2}^0 = +3.05$
FeS	\rightarrow	$\text{Fe} + \text{S}^{2-}$	$E_{1/2}^0 = -0.44$
	\rightarrow		$E_{\text{cell}}^0 \approx$



Re-Chargeable Batteries: Accumulators

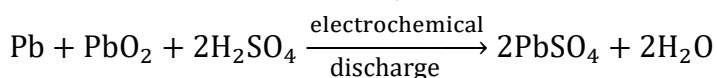
Primary cells use electrochemical reactions to **discharge** an electric current: also known as **Voltaic Cells**.

Secondary cells use electrolytic reactions to **recharge** the cell for discharging: also known as **Galvanic Cells**.

Accumulators physically arrange their chemical reagents to go through a **Discharge-Recharge** cycle.

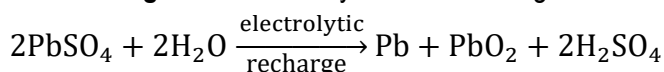
(g) **Lead Acid Accumulator** (Gaston Planté 1859) accumulates electrical energy (best known as the 'car battery').

- The **primary** cycle uses H_2SO_4 as the electrolyte in car batteries because lead metal Pb and lead dioxide PbO_2 both convert to Lead (II) cations in sulfuric acid during **discharge**. This arrangement creates insoluble lead sulfate PbSO_4 from both redox reactions, which then becomes adsorbed to the cell electrodes (car battery plates).



Oxidation States for Lead changes from:
 $0 \rightarrow +2$ for Pb **and** $+4 \rightarrow +2$ for PbO_2

- The **secondary** cycle reforms PbSO_4 to both PbO_2 and Pb states simultaneously (known as disproportionation). The **recharge** uses electricity from the moving car alternator to **accumulate** electrical energy in the battery.



Oxidation States disproportionate for Lead as:
 $+2 \rightarrow 0$ **and** $+4$ for simultaneous redox.

- Miniscule amounts of PbSO_4 fall off the cell plates during each cycle due to engine vibration. After about four years of average car usage, a substantial amount of PbSO_4 is deposited as sludge on the bottom of the battery. This effectively removes Pb and PbO_2 from the electrochemical Primary cycle: so the battery goes flat!

PRIMARY CYCLE: discharge

$$\begin{array}{l} \text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + \quad E_{1/2}^0 = + 0.36 \\ \text{PbO}_2 + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + \quad E_{1/2}^0 = + 1.88 \\ \hline \rightarrow \quad E_{\text{cell}}^0 \approx \end{array}$$

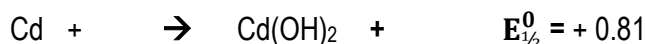
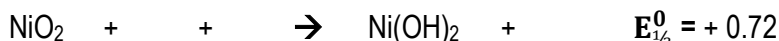
SECONDARY CYCLE: accumulation

$$\begin{array}{l} \text{PbSO}_4 + \quad \rightarrow \text{Pb} \\ \text{PbSO}_4 + \quad \rightarrow \text{PbO}_2 + \text{anode} \\ \hline \rightarrow \quad E_{\text{cell}}^0 \approx \end{array}$$

Primary Cycle

Secondary Cycle

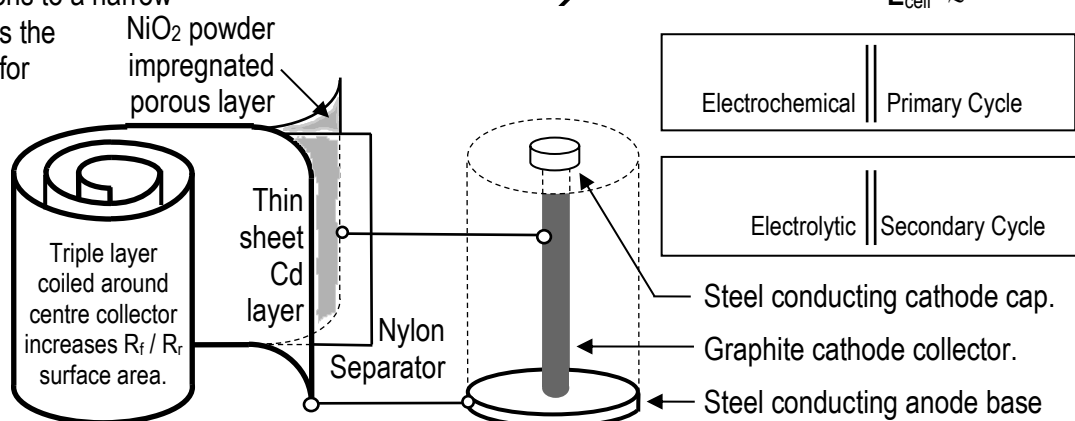
(h) **RECHARGEABLE BATTERY: NiCad**



All reactions occur within a thin layer over a large surface area. This physical confinement of all reactions to a narrow reaction pathway restricts the dispersal of all reagents for both R_f and R_r .

Once the Primary cycle has finished the NiCad is plugged into a recharger.

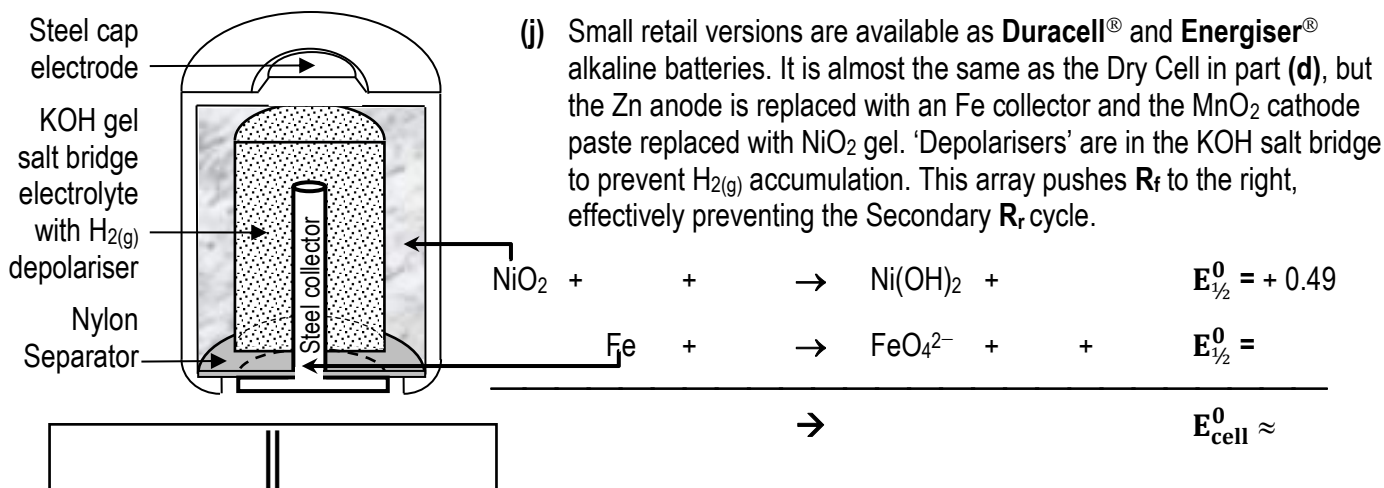
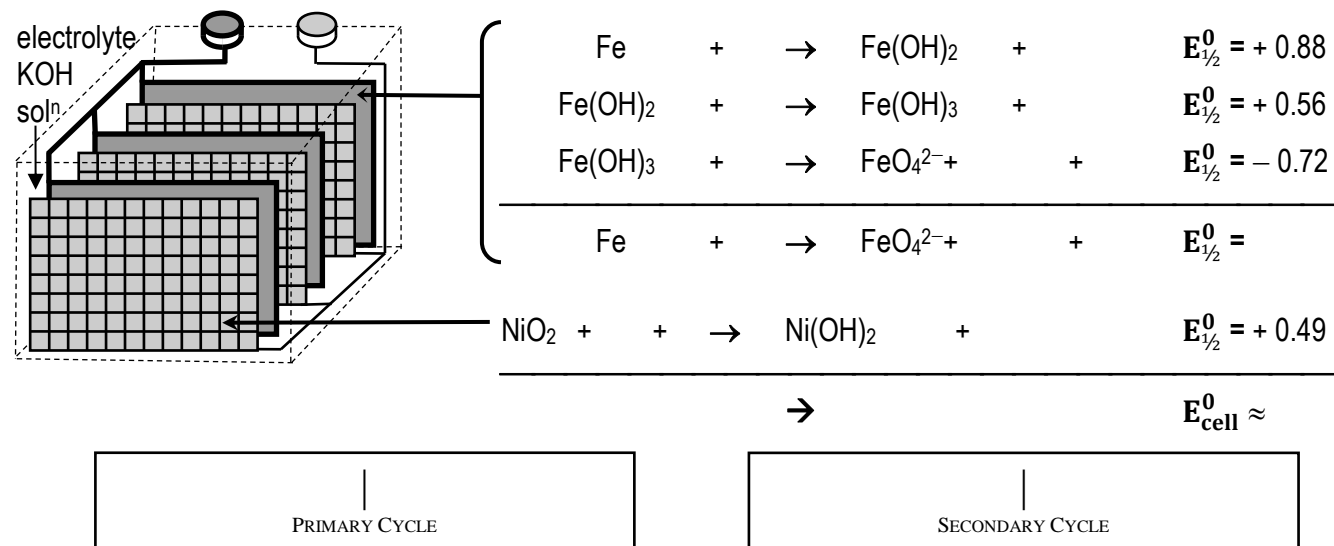
The Secondary R_r cycle then restores the oxidation states electrolytically for R_f .



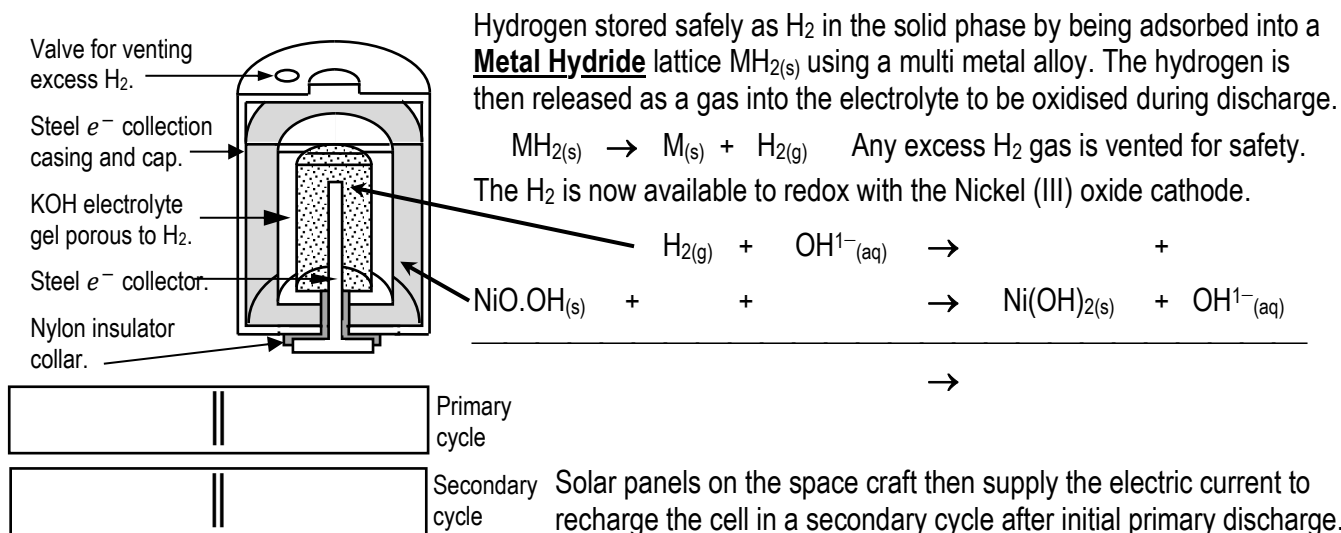
This can be repeated for about 1,000 cycles before the triple layer deteriorates and goes 'flat'!

(i) **INDUSTRIAL STORAGE: Edison Cell 1903.**

Thomas Edison developed the Nickel-Iron cell to provide a rugged long life battery for industry. The chemistry is intriguing because three reactions occur at the Anode during both cycles. This causes a slow overall Rate, high internal resistance and release of hazardous Hydrogen gas $H_{2(g)}$ near an electric current. But it lasts for ten years of continual use with a steady and constant current. These characteristics make it unsuitable for residential and office use but very cost effective in industry where safety measures can be enforced.



(k) Nickel-Hydrogen cells, with double the power and life of a NiCad, were developed for space craft.



TASK 4 Science as Human Endeavour (SHE) SACE Assessment

You have been commissioned by an online magazine to publish a 1000-word referenced article about the development and applications of contemporary alkaline rechargeable batteries, such as Ni-MH or Lithium-ion. Use the link given below to select one battery type from so many available.

- Select a recently developed battery not included in the previous examples (a)-to-(k).
 - Look at: https://en.wikipedia.org/wiki/Comparison_of_commercial_battery_types
 - Do not research photo-voltaic cells because they do not involve chemistry. However, you could research the storage batteries being developed to support solar energy cells, such as for the 'South Australian Grid-connected Battery Storage Project'.
- Choose examples from (a)-to-(k) to highlight why battery technology changed in response to safety and reliability concerns leading to the development of 'your' selected battery.

	Primary: discharge only	Secondary: Rechargeable
Acid	Voltaic Pile: (ex) Zinc-Silver / (a) Zinc-Copper Wet Cells: (b) Daniell Cell / (c) Bichromate Cell Dry Cells: (d) Leclanché Cell	(g) Lead-Acid Accumulator
Alkaline	(e) Alkaline Battery (f) Lithium Battery (i) Nickel-Iron: Industrial (Edison) / Commercial (Duracell)	(h) NiCad (k) Nickel-Hydrogen New industrial and commercial applications with Nickel-Metal Hydride Ni-MH / Lithium-ion batteries

- Discuss the current safety and reliability concerns with the selected battery.
 - Read about the 'UPS Airlines Flight 6' or the 'Galaxy S4 smartphone'.
- Identify which groups have been involved in the development of the selected battery.
 - Discuss why and how those groups were involved.
 - How has society benefitted from or been disadvantaged by the new technology?

The electrochemistry examples you select for the article must demonstrate at least one of these key concepts of Science as a Human Endeavour:

- Communication and collaboration of chemistry as a global enterprise.
- Development of chemistry models from evidence using new technologies across disciplines.
- Influence of chemistry across other areas of STEM and social influences on chemistry applications.
- Application and limitation of chemistry knowledge in benefitting society and the environment.

Design of High Energy Density Batteries

● Re-chargeable **Nickel Metal Hydride Batteries**, Ni-MH, have two reaction cycles, $R_{\text{forward}}^{\text{discharge}} \rightleftharpoons R_{\text{reverse}}^{\text{recharge}}$:

• Primary discharge electrochemical reaction $\boxed{\text{NiO.OH} \mid \text{Ni(OH)}_2 \parallel \text{MH} \mid \text{M}}$ produces an electric current:

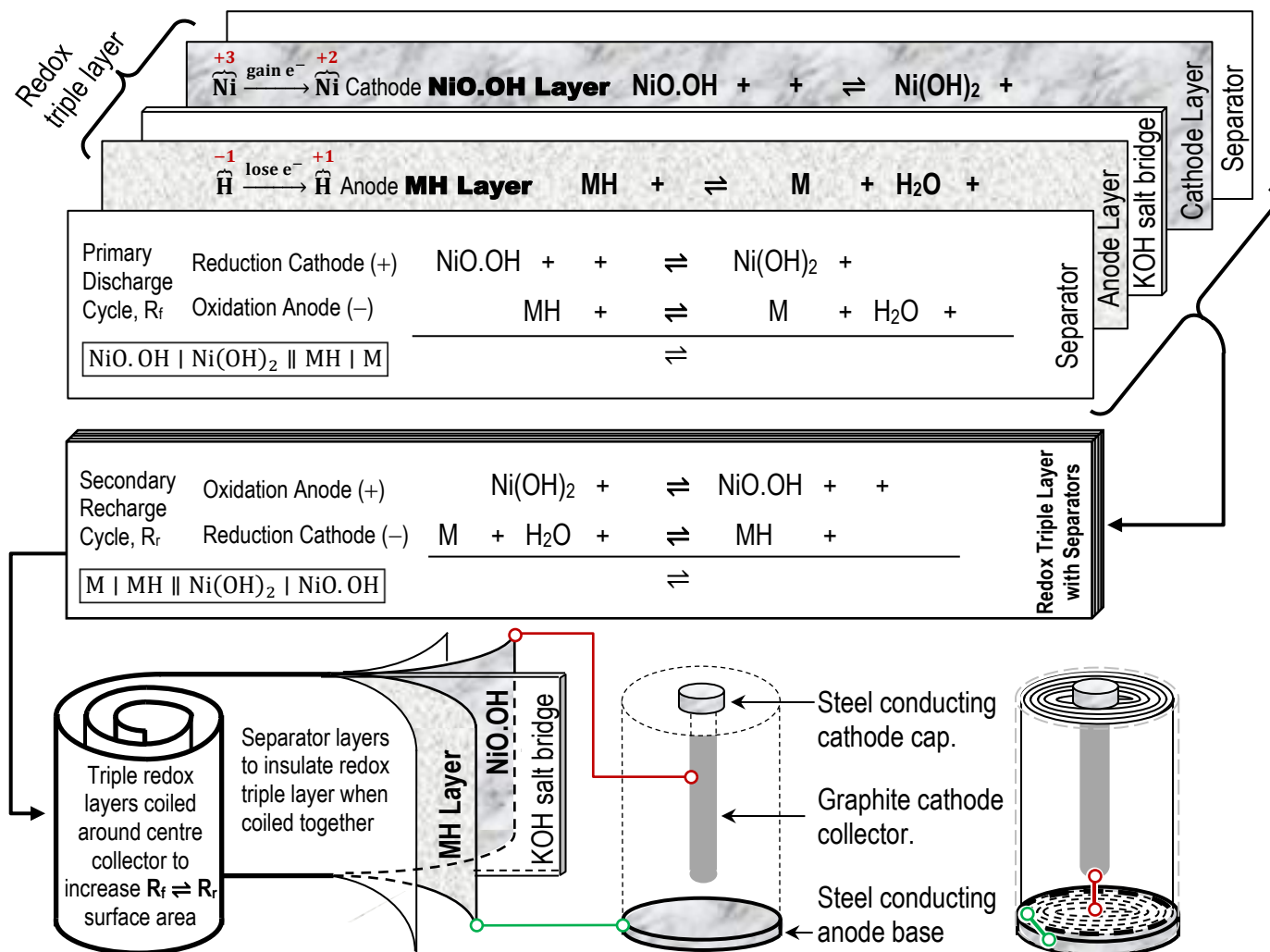
- 1^o Reduction at the (+) cathode of nickel (III) as NiO.OH to nickel (II) as Ni(OH)₂; $\overset{+3}{\text{Ni}} \xrightarrow{\text{gain } 1 \times e^-} \overset{+2}{\text{Ni}}$
- 1^o Oxidation at the (-) anode of hydrogen from a metal hydride MH to water H₂O; $\overset{-1}{\text{H}} \xrightarrow{\text{lose } 2 \times e^-} \overset{+1}{\text{H}}$

• Secondary recharge electric current produces an electrolytic reaction $\boxed{\text{M} \mid \text{MH} \parallel \text{Ni(OH)}_2 \mid \text{NiO.OH}}$:

- 2^o Oxidation at the (+) anode as nickel (II) becomes nickel (III) again; $\overset{+2}{\text{Ni}} \xrightarrow{\text{lose } 1 \times e^-} \overset{+3}{\text{Ni}}$
- 2^o Reduction at the (-) cathode as hydrogen in water becomes a metal hydride again; $\overset{+1}{\text{H}} \xrightarrow{\text{gain } 2 \times e^-} \overset{-1}{\text{H}}$

The discharge reaction occurs across very thin layers so that reagents can be electrolytically restored to their initial location. The large surface area of thin flat layers increases overall electric current flow. These planar thin layers can then be rolled into a compact cylindrical shape by coiling the layers around a central cathode collector.

- The redox triple layer provides a large surface area with a small cross-section for reversible redox reactions.
 - Metal Hydride MH layer to store Hydrogen as H¹⁻ hydride anion adsorbed to a metal alloy substrate M.
 - Salt bridge layer using absorbed KOH for 1/2-cell charge balancing and alkaline conditions (no H_(aq)¹⁺).
 - Nickel (III) oxy-hydroxide NiO.OH layer for reduction to nickel (II) hydroxide Ni(OH)₂
- Separator layers prevent short-circuits between redox layers when coiled around central cathode collector.
 - High density cross-linked polyolefin sulphate film insulates the electrically conductive layers.



Alternatively, the layers can be left as flat planes for a commercial or industrial scale rectangular shaped battery.

② **Lithium Ion Batteries** produce high voltage currents with reduction potential $E_{1/2}^0 = -3.04 \text{ V}$ for $\text{Li}^{1+} | \text{Li}$

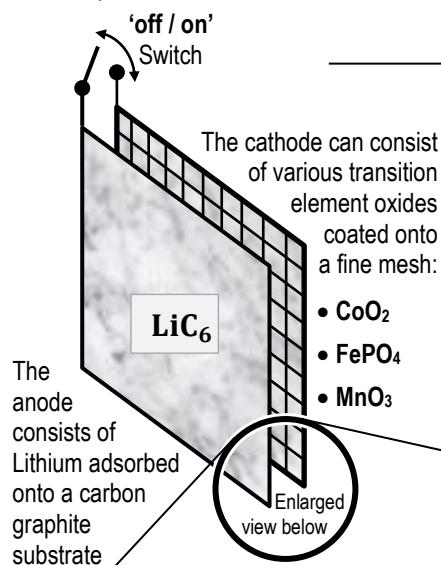
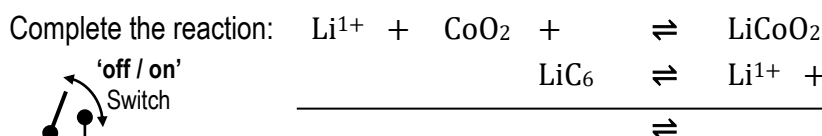
- A big problem with using Lithium is its ability to explode on contact with moisture when reduced to a metal.
- Lithium is observed with non-metal behaviour as covalent Li_2 gaseous molecules³. This non-metallic behaviour allows for covalent bonding with carbon and polar-covalent bonding with transition elements, such as cobalt.
- Lithium is able to change oxidation states without becoming a pure metal in Lithium Ion Batteries.

Lithium ion batteries avoid the moisture problem by providing a reaction pathway for Li^{1+} salt electrolytes in organic (non-aqueous) solvents such as ethylene carbonate. Furthermore, the redox reactions cause Li^{1+} to be adsorbed (not a spelling mistake) as Lithium atoms covalently bond with the electrodes during each cycle ☺!

• Primary discharge reaction $\text{CoO}_2 | \text{LiCoO}_2 \parallel \text{LiC}_6 | \text{C}_6$ produces an electric current:

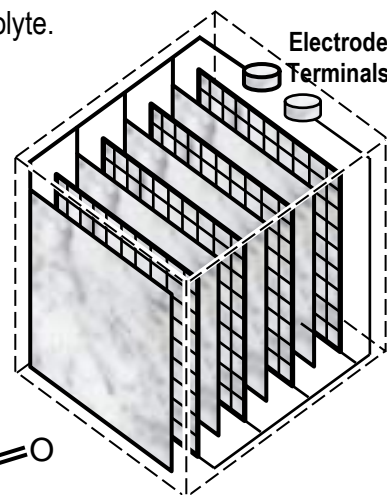
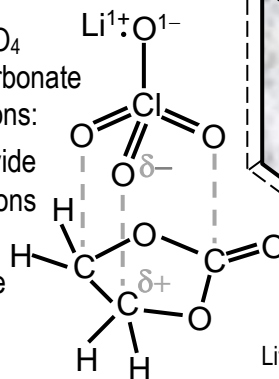
- 1^o Reduction at the (+) cathode of cobalt (IV) to cobalt (III); $\overset{+4}{\text{Co}}\text{O}_2 \xrightarrow{\text{gain } e^-} \overset{+3}{\text{LiCo}}\text{O}_2$
The Li^{1+} ion from the electrolyte forms a polar covalent bond with the CoO_2 substrate.
- 1^o Oxidation at the (-) anode of carbon as LiC_6 to elemental graphite C_6 substrate; $\overset{-1}{\text{LiC}}_6 \xrightarrow{\text{lose } 6 \times \frac{1}{6} e^-} \overset{0}{\text{C}}_6$
The Li was covalently bonded to C_6 graphite before being released into the electrolyte as Li^{1+} ion.

• A fully sealed battery has the half-cell electrodes set as alternating parallel plates connected to common electrode terminals. The spaces between the half-cells are packed with the gelatinous electrolyte.

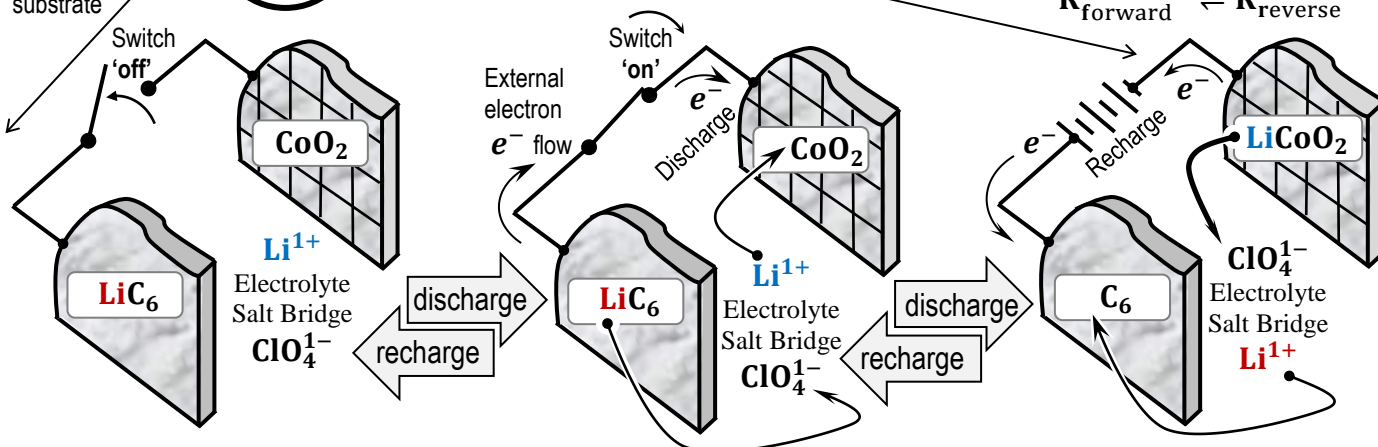
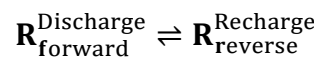


Lithium perchlorate LiClO_4 dissolved in ethylene carbonate $\text{C}_2\text{H}_4\text{CO}_3$ has two functions:

- As a salt bridge to provide charge balancing Li^{1+} ions between electrodes.
- Electrolyte to exchange Li^{1+} redox reactants at electrodes.



Lithium ions are redistributed during the secondary cycle



Tesla Inc. has produced an industrial sized battery for South Australian power networks to accumulate electrical charge from solar panels in a secondary recharge cycle and then discharge emergency power during blackouts.

Alternatively, the electrodes can be formed in long thin layers separated by an electrolyte salt bridge and coiled around a central collector cathode for miniaturised cylindrical batteries for use in portable electrically powered devices.

³ <https://en.wikipedia.org/wiki/Dilithium> notes that Li_2 molecules exist outside the Star Trek® 'universe' of Warp Drive dilithium crystals.