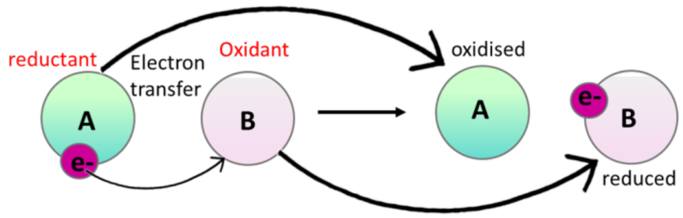
NCEA Chemistry 3.7 REDOX AS 91393

This achievement standard involves demonstrating understanding of oxidation-reduction processes

Demonstrate comprehensive understanding (Excellence) involves:

- ❑ *1. Identify the species oxidised and reduced*
- ❑ *2. Identify oxidation numbers in relation to species*
- ❑ *3. Write balanced half and full oxidation-reduction equations*
- ❑ *4. Give a conventional cell diagrams (not required for assessment)*
- ❑ *5. Calculate cell potentials using data provided*
- ❑ *6. Make and explain links between the calculations and spontaneity of the reactions*
- ❑ *7. Elaborate on the recharge process of batteries.*
- ❑ *8. Justify why the recharge process is necessary in terms of amount of species*
- ❑ *9. Compare and contrast the discharge and recharge processes in the battery*

1. Identify the species oxidised and reduced



LEO (loss electrons oxidation) A	GER (gain electrons reduction) B
Reductant	Oxidant
Acts as a reducing agent to B	Acts as an oxidising agent to A
❑ is oxidised	❑ is reduced
❑ loses electrons	❑ gains electrons

2. Identify oxidation numbers in relation to species

Elements	Hydrogen atom (not as element)	Oxygen atom (not as element)
Oxidation number = 0	Oxidation number = +1	Oxidation number = -2
For example Fe H_2 0 0	For example HCl H_2SO_4 +1 +1	For example MnO_4^- CO_2 -2 -2
	Except Hydrides Oxidation number = -1 For example LiH -1	Except peroxides Oxidation number = -1 for example H_2O_2 -1

Monatomic ions	Polyatomic ions	Molecules
Oxidation number = charge	Sum of Oxidation number = charge	Sum of Oxidation number = 0
For example Fe^{2+} Cl^- +2 -1	For example MnO_4^- +7 -2 Because Total charge = -1 And Oxygen = -2 +7 + (4x -2) = -1 Mn O	For example CO_2 +4 -2 Because Total charge = 0 And Oxygen = -2 +4 +(2x-2) = 0 C O

STEP ONE – write the ON for each atom using rules (not oxygen or hydrogen unless it is in elemental form)

$$\underline{Cr}_2O_7^{2-} + I^- \rightarrow Cr^{3+} + I_2$$

+6   -1   +3   0

Decrease - reduction   Increase - oxidation

STEP TWO – Identify the atom that has had its ON increased. It is Oxidised

I- has increased ON (-1 to 0) so *I-* is *Oxidised. (the reductant)*

STEP THREE – Identify the atom that has decreased ON. It is reduced.

Cr has decreased ON (+6 to +3) so $Cr_2O_7^{2-}$ is *Reduced. (the oxidant)*

<u>3. Write balanced half and full oxidation-reduction equations</u> e.g. $Cd + NiO(OH) \rightarrow Cd(OH)_2 + Ni(OH)_2$

Redox reaction in a discharging NiCad battery

$Cd \rightarrow Cd(OH)_2$	$NiO(OH) \rightarrow Ni(OH)_2$
1. Assign oxidation numbers and identify element oxidised or reduce (0) (+2) (oxidised) $Cd \rightarrow Cd(OH)_2$ 2. Balance atom no. for element oxidised or reduced (other than oxygen and hydrogen) 3. Balance the Oxygen using H_2O $Cd + 2H_2O \rightarrow Cd(OH)_2$ 4. Add H^+ to balance the hydrogen $Cd + 2H_2O \rightarrow Cd(OH)_2 + 2H^+$ 5. Add OH^- (in alkaline conditions) to cancel any H^+ [same amount on both sides] and cancel excess water $Cd + 2H_2O + 2OH^- \rightarrow Cd(OH)_2 + 2H_2O$ $Cd + 2OH^- \rightarrow Cd(OH)_2$ 6. Balance charge by adding electrons (LHS on oxidants RHS on reductants) $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$ 7. Check balance of elements and charges	1. Assign oxidation numbers and identify element oxidised or reduced. (+3) (+2) (reduced) $NiO(OH) \rightarrow Ni(OH)_2$ 2. Balance atom no. for element oxidised or reduced (other than oxygen and hydrogen) 3. Balance the Oxygen using H_2O $NiO(OH) \rightarrow Ni(OH)_2$ 4. Add H^+ to balance the hydrogen $NiO(OH) + H^+ \rightarrow Ni(OH)_2$ 5. Add OH^- (in alkaline conditions) to cancel any H^+ [same amount on both sides] and cancel excess water $NiO(OH) + H_2O \rightarrow Ni(OH)_2 + OH^-$ 6. Balance charge by adding electrons (LHS on oxidants RHS on reductants) $NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ 7. Check balance of elements and charges

Joining 2 half equations

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

$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

1. The two half equations must have electrons on <u>opposite</u> sides of the equation

2. Place the two equations one under the other

3. The electron numbers must equal each other – if not multiply one or both equations to the lowest common denominator (multiply every reactant/product)

$$2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$$

4. Cancel out the electrons

$$Cd + 2OH^- \rightarrow Cd(OH)_2 + \cancel{2e^-}$$

$$2NiO(OH) + 2H_2O + \cancel{2e^-} \rightarrow 2Ni(OH)_2 + 2OH^-$$

5. Cancel out the same number of H^+, OH^- and/or H_2O if present on both sides

$$Cd + \cancel{2OH^-} \rightarrow Cd(OH)_2$$

$$2NiO(OH) + 2H_2O \rightarrow 2Ni(OH)_2 + 2OH^-$$

6. Join the remainder together

$$Cd + 2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$$

4. Give a conventional cell diagrams (not required for assessment)

Galvanic cells can be represented using cell diagrams. This is a type of short hand notation that follows a standard IUPAC convention. For the NiCad battery cell the standard cell diagram is

Electron flow

$Cd/Cd(OH)_2//NiO(OH)/\ Ni(OH)_2$

oxidation **reduction**

The vertical lines represent phase boundaries and || represents the salt bridge.

The cathode (reduction reaction) is always shown on the right hand side and the anode (oxidation) on the left in a standard cell diagram. The electrons thus move from left of the II to right in the standard cell diagram, representing a spontaneous redox reaction. The electrodes are always written in at the beginning and end of a cell diagram. In each half cell the reactant appears first, followed by the product.

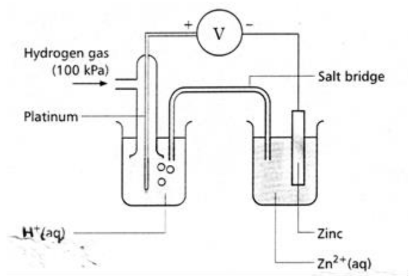
An inert electrode must be used in cells in which both species in a redox couple are in aqueous solution (MnO_4^- and Mn^{2+}). The inert electrodes are commonly either platinum, Pt*(s)* or graphite, C*(s)* electrodes. Since the two species in the redox couple are in solution, they are separated by a comma rather than a vertical line.

$Pb\ /\ Pb^{2+}//PbO_2, Pb^{2+}/Pb$

The cell diagram shows two half cells linked. Each half cell consists of the oxidant, the reductant and the electrode (which may be the oxidant or reductant). The two half cells above are Pb(*s*)|Pb^{2+}(*aq*) and PbO_2(s) Pb^{2+}(*aq*)|Pb (*s*).

5. Calculate cell potentials using data provided

For any redox couple, the standard electrode (reduction) potential is the voltage obtained under standard conditions when that half-cell is connected to the standard hydrogen electrode (value 0v).
For example, the electrode potential of a Zn^{2+}|Zn electrode can be measured by connecting it to a hydrogen electrode.



Experimentally, the more positive terminal is always where reduction is occurring in a spontaneous reaction. In example (a) reduction occurs in the hydrogen electrode (positive electrode) while oxidation occurs in the Zn^{2+}|Zn compartment (negative electrode). The cell diagram for this electrochemical cell is

Flow of electrons **Flow of electrons**

Zn*(s)* | Zn^{2+}*(aq)* || H^+*(aq)*, H_2*(g)* | Pt*(s)*

oxidation reduction

Using the standard reduction potentials for many half reactions have been measured under standard conditions (at 25 ^{o}C). Standard reduction potentials are provided in the Internal Assessment.

The table can be used to decide the relative strength of species as oxidants or reductants. The species on the left in the couple with the most positive reduction potential, will be the strongest oxidising agent or oxidant. E.g it is PbO_2*(g)* (NOT PbO_2 / Pb^{2+}). This means PbO_2 has the greatest tendency to gain electrons. As the electrode potential decreases, the strength as an oxidant decreases.

	Redox couple	Standard reduction potential (V)
1	PbO_2/Pb^{2+}	1.69
2	MnO_2/Mn^{3+}	0.74
3	$NiO(OH)/Ni(OH)_2$	0.48
4	HgO/Hg	0.098
5	I_2/I^-	0.54
6	Pb^{2+}/Pb	-0.36
7	Zn^{2+}/Zn	-0.76
8	$Cd(OH)_2/Cd$	-0.82
9	Li^+/Li	-3.10

When 2 couples are placed together, because they are all shown as reduction reactions, the lower value couple will be reversed into an oxidation reaction (the charge will stay the same on the SRP). All of these couples show reduction from left to right. i.e redox couple 1. PbO_2 is reduced to Pb^{2+}. If redox couple 6. was placed with 1. then it would have a lower reduction potential and therefore be reduced. Pb is therefore oxidised to Pb^{2+} (the order of the couple is reversed)

It is possible to use E^o values to predict whether a reaction will occur. This simply involves identifying which species must be reduced and which species must be oxidised if the reaction is to proceed spontaneously. The appropriate reduction potentials are then substituted into the equation.

$$E^o_{cell} = E^o_{(reduction)} - E^o_{(oxidation)}$$

$$\text{higher } E^o - \text{lower } E^o$$

where $E^o_{(cathode)}$ is the reduction potential for the half cell where reduction occurs and $E^o_{(anode)}$ is the reduction potential for the half cell where oxidation occurs. If the E^o_{cell} calculated is positive, then the reaction will occur spontaneously. Conversely, a negative cell potential means the reaction will not proceed.

6. Make and explain links between the calculations and spontaneity of the reactions

Consider the lead acid battery cell Pb*(s)* | Pb^{2+}*(aq)* || PbO_2, Pb^{2+}| Pb *(s)*

Reduction reaction is $PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$ $E^o(PbO_2/Pb^{2+}) = +1.69V$

Oxidation reaction is $Pb_{(s)} \rightarrow Pb^{2+} + 2e^-$ $E^o(Pb^{2+}/Pb) = -0.36V$

$E^o_{cell} = E^o(PbO_2/Pb^{2+}) - E^o(Pb^{2+}/Pb) = +1.69 - (-0.36)\ V = +2.05V$

This E^o_{cell} is positive therefore this redox reaction will occur spontaneously

7. Elaborate on the recharge process of batteries.

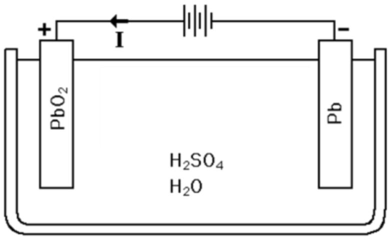
Eventually if the discharging of a battery continues (while supplying energy to the vehicle or appliance) the reactants will "run out" as they are changed into products during the redox reaction.

Some types of batteries can be charged – this involved supplying an external source of energy to power a reverse of the discharging reaction. The built up products will then be changed back into the original reactants to enable the battery to be discharged once more.

An electrochemical cell that undergoes a redox reaction when electrical energy is applied is called an *electrolytic cell*

The discharging oxidation reaction will become a reduction reaction during charging

The discharging reduction reaction will become an oxidation reaction during charging



With energy from the charging battery, the lead sulfate is broken down and with oxygen from ionized water, lead oxide is deposited on the positive electrode and lead is deposited on the negative electrode

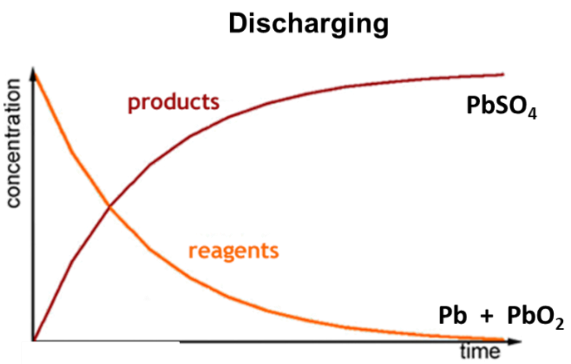
E^o_{cell} in Charging Batteries non-spontaneous Redox reactions

The E^o_{cell} for the charging battery "swaps around" the reduction potentials to give a negative value – which indicates the redox reaction is not spontaneous

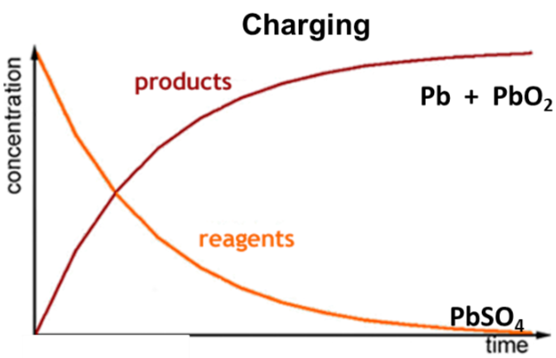
Charged E^ocell = E^o(reduction half-cell) - E^o(oxidation half-cell)

= lowest reduction potential –highest reduction potential

8. Justify why the recharge process is necessary in terms of amount of species



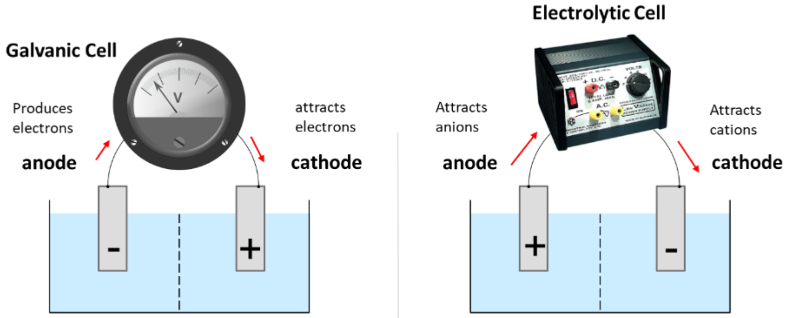
During **discharge** of a battery the amount of reactants (both the oxidant and reductant) will be decreased and the products formed increased. In the case of the lead-acid battery the Pb and PbO_2 will be decreased (the anode and cathode respectively) and the solid $PbSO_4$ will increase. Without enough reactants the Redox reaction will stop and the battery will stop producing voltage and become 'flat'



During **charging** of a battery the products from the discharging are now the reactants. In the case of the lead-acid battery the amount of $PbSO_4$ will be decreased and deposited back on the anode and cathode as Pb and PbO_2 respectively. Substances will now be in sufficient supply to begin discharging the battery once more.

9. Compare and contrast the discharge and recharge processes in the battery

Summary of charging and discharging a battery

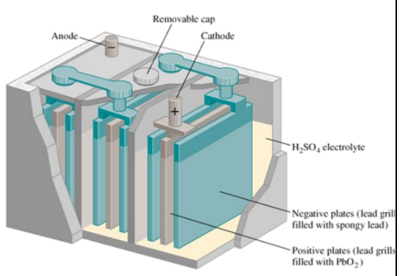


	Oxidation	Reduction		Oxidation	Reduction	
	reductant	**oxidant**		**reductant**	**oxidant**	
	Discharging Battery where energy is released by spontaneous redox reaction and converted to electrical energy			**Charging Battery** where energy is used to drive non-spontaneous redox reaction		
$Pb / Pb^{2+} // PbO_2, Pb^{2+} / Pb$	$Pb_{(s)} \rightarrow Pb^{2+}$	$PbO_2 \rightarrow Pb^{2+}$	Lead acid battery	$Pb^{2+} \rightarrow PbO_2$	$Pb^{2+} \rightarrow Pb$	$Pb / Pb^{2+}, PbO_2 // Pb^{2+} / Pb$
$Cd/Cd(OH)_2//NiO(OH)/ Ni(OH)_2$	$Cd \rightarrow Cd(OH)_2$	$NiO(OH) \rightarrow Ni(OH)_2$	NiCad battery	$Ni(OH)_2 \rightarrow NiO(OH)$	$Cd(OH)_2 + \rightarrow Cd$	$Ni(OH)_2/ NiO(OH)//Cd(OH)_2 / Cd$

Data Sheets for Batteries

Rechargeable Batteries - Lead Acid battery example

This is the redox reaction that occurs when the battery is **discharging** – and the **energy produced** is used to power electrical systems (usually inside a vehicle)



The oxidation and reduction reactions that occur at the electrodes are called **half-cell reactions**.

reductant

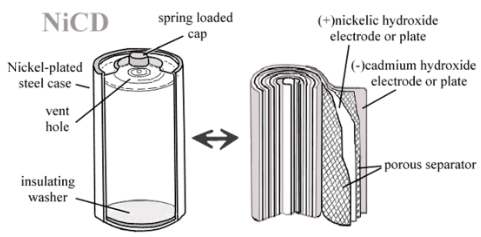
Anode (oxidation) $Pb_{(s)} \rightarrow Pb^{2+}$

Cathode (reduction) $PbO_2 \rightarrow Pb^{2+}$

oxidant

Rechargeable Batteries - NiCad Battery (nickel cadmium)

NiCad batteries are rechargeable batteries. The redox reaction shown is the spontaneous reaction when the battery is **discharging** and producing energy



The oxidation and reduction reactions that occur at the electrodes are called **half-cell reactions**.

reductant

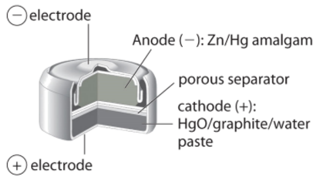
Anode (oxidation) $Cd \rightarrow Cd(OH)_2$

Cathode (reduction) $NiO(OH) \rightarrow Ni(OH)_2$

oxidant

Non-Rechargeable Batteries - Mercury Zinc Battery

This is the redox reaction that occurs when the battery is **discharging** – and the **energy produced** is used to power electrical systems (usually a small appliance or toy)



cell reaction:
$Zn(s) + HgO(s) \rightarrow Hg(l) + ZnO(s)$

The oxidation and reduction reactions that occur at the electrodes are called **half-cell reactions**.

reductant

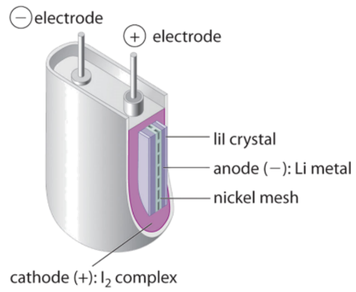
Anode (oxidation) $Zn_{(s)} \rightarrow ZnO$

Cathode (reduction) $HgO \rightarrow Hg$

oxidant

Non-Rechargeable Batteries - Lithium–iodine Battery

This is the redox reaction that occurs when the battery is **discharging** – and the **energy produced** is used to power electrical systems (used in pacemakers as they last up to 10 years and very reliable)



The oxidation and reduction reactions that occur at the electrodes are called **half-cell reactions**.

reductant

Anode (oxidation) $Li_{(s)} \rightarrow Li^{+}$

Cathode (reduction) $I_2 \rightarrow 2I^{-}$

oxidant