

Dry Cell	
Anode half-reaction	$Zn_{(s)} \rightarrow Zn_{(aq)}^{2+} + 2e^{-}$
Cathode half-reaction	$2MnO_{2(s)} + 2NH_{4(aq)}^{+} + 2e^{-} \rightarrow Mn_2O_{3(s)} + 2NH_{3(g)} + H_2O_{(l)}$

Alkaline Cell	
Anode half-reaction	$Zn_{(s)} + 2OH_{(aq)}^{-} \rightarrow ZnO_{(s)} + H_2O_{(l)}$
Cathode half-reaction	$2MnO_{2(s)} + H_2O_{(l)} \rightarrow Mn_2O_{3(s)} + 2OH_{(aq)}^{-}$

Silver Oxide Button Cell	
Anode half-reaction	$Zn_{(s)} + 2OH_{(aq)}^{-} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^{-}$
Cathode half-reaction	$Ag_2O_{(s)} + H_2O_{(l)} + 2e^{-} \rightarrow 2Ag_{(s)} + 2OH_{(aq)}^{-}$

Lithium Cell	
Anode half-reaction	$Li_{(s)} \rightarrow Li_{(aq)}^{+} + e^{-}$
Cathode half-reaction	$MnO_{2(s)} + Li_{(aq)}^{+} + e^{-} \rightarrow LiMnO_{2(s)}$

Lithium-Ion Cell	
Anode half-reaction	$Li_xC_{6(s)} \rightarrow xLi_{(aq)}^{+} + C_{6(s)} + xe^{-}$
Cathode half-reaction	$Li_{1-x}CoO_{2(s)} + xLi_{(aq)}^{+} \rightarrow LiCoO_{2(s)}$

Anode half-reaction	
Cathode half-reaction	

Anode half-reaction	
Cathode half-reaction	

Primary Cells

Set 12

Q: Everyday commercial galvanic cells can be classified as primary cells, secondary cells and fuel cells. Give an example of each and briefly describe how they differ.

In a primary cell there's a fixed amount of oxidant and reductant. Once this is used up, the cell no longer produces a voltage and is said to be "flat". Primary cells can't be recharged and so are discarded once they go flat. The dry cell is an example of a primary cell.

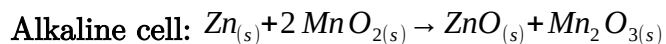
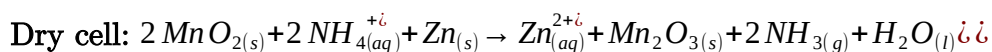
Secondary cells are galvanic cells that can be recharged. The recharging process involves applying a DC voltage to the cell. This regenerates the oxidant and reductant originally present in the charged cell.

The lead-acid accumulator battery is an example of a secondary cell.

Fuel cells are cells where the oxidant and reductant are continuously fed into the cell. Fuel cells have a very long life and can theoretically operate without limit as long as the oxidant and reductant are supplied into the cell.

The alkaline hydrogen fuel cell is an example of a fuel cell.

Q: While the alkaline cell is considered to be superior to the dry cell, they do share many common features. The overall discharge reactions for these 2 cells are shown here.



Answer the following questions about the operation of these cells.

[a] Both of these cells are referred to as primary cells. What does this mean?

Primary cells contain a fixed amount of oxidant and reductant and once this is consumed they can't be recharged.

[b] What's the oxidising agent and reducing agent for each of these cells?

In both cells the oxidising agent is MnO_2 and the reducing agent is Zn.

[c] One problem with the dry cell is the inclusion of NH_4Cl in the electrolyte paste.

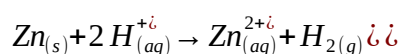
[i] What's the role of NH_4Cl in the dry cell?

NH_4Cl is the electrolyte, providing ions for the salt bridge and maintaining electrical neutrality. Also, the acidic NH_4^+ ions provide the protons necessary to reduce MnO_2 .

[ii] Why does its presence reduce the shelf life of these cells? Support your answer with the aid of an equation.

NH_4^+ ions are weakly acidic: $\text{NH}_{4(aq)}^+ \rightleftharpoons \text{NH}_{3(g)} + \text{H}_{(aq)}^+$

The resulting H^+ ions are in contact with the zinc metal, hence oxidising it:



This reaction slowly consumes the zinc, decreasing the dry cell's shelf life.

[d] One feature of the alkaline cell is a porous zinc anode. How is this different to the anode of the dry cell?

The zinc anode in the dry cell is a single solid sheet rolled into the shape of a can as opposed to the cylindrical plug of powdered zinc used in the alkaline cell.

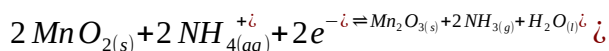
[e] The alkaline cell is suitable for applications like the power supply for a camera flash unit where a high current is required. Devices with high current demands essentially require a fast rate of supply of electrons. Write the anode half-reaction for both the dry cell and the alkaline cell. Refer to these equations and explain how the design of the anode in the alkaline cell allows a greater current to be produced (i.e., allows a faster rate of production of electrons) than the dry cell.

Anode half-reaction in both cells: $Zn_{(s)} \rightarrow Zn_{(aq)}^{2+} + 2e^{-}$

Since this half-reaction can only occur at the zinc surface, the higher zinc surface area of the alkaline cell (zinc powder as opposed to foil) promotes a faster rate of oxidation in the alkaline cell. This allows for a higher rate of production of electrons in the alkaline cell and hence a higher current flow.

[f] Another feature of the dry cell that limits its ability to produce high currents is the formation of ammonia gas within the cell as it discharges. Explain why ammonia gas will form as the cell operates. Use an equation to support your answer.

$NH_{3(aq)}$ is a by-product of the reduction of MnO_2 :



As ammonia is a gas at room temperature, it can be evaporated from solution to form ammonia gas: $NH_{3(aq)} \rightleftharpoons NH_{3(g)}$

2 changes that occur in a cell as it operates are a rise in temperature and an increase in $[NH_{3(aq)}]$. Both of these effects favour the production of more ammonia gas.

Q: What disposal problems are associated with silver button cells and lithium cells? DO the alkaline cells and dry cells have similar associated disposal issues?

AgO/Zn button cells may be considered toxic as some brands contain small amounts of mercury. These should be recycled appropriately. Lithium cells don't contain toxic components but are potentially dangerous (explosive and a fire hazard) as they may contain unreacted lithium metal, a strong reducing agent. They should be fully

discharged prior to disposal. Dry cells and alkaline cells aren't considered to contain toxic materials. Neither Zn nor Mn are considered toxic at low concentration.

Q: Primary lithium cells have a much higher energy density, up to 3 times more than alkaline cells. The following questions refer to these 2 cell types.

[a] Both cell types use MnO_2 as the oxidising agent. What's the reducing agent in each of these cells?

The oxidising agent in the lithium cell is lithium and in the alkaline cell it's zinc.

[b] Write the oxidation half-equation for lithium and zinc and give the oxidation potential for each half-reaction. How would the different oxidation potentials of these 2 elements contribute to the voltage of the 2 different cells and hence the energy available from the 2 cell types?

Alkaline cell: $\text{Zn}_{(s)} \rightarrow \text{Zn}_{(aq)}^{2+} + 2e^-$ $E^\circ = +0.76\text{V}$

Lithium cell: $\text{Li}_{(s)} \rightarrow \text{Li}_{(aq)}^+ + e^-$ $E^\circ = +3.05\text{V}$

The higher oxidation potential of lithium means the lithium cell should produce a higher voltage (around 2.29V higher at standard conditions).

[c] 2 moles of lithium metal in a primary lithium cell can produce the same electric current for the same length of time as 1 mole of zinc in an alkaline cell. How does this factor contribute to the energy density (in terms of available electrical energy per gram of metal) of the 2 cell types? Explain.

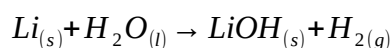
$$m(\text{Li}) = 2 \times 6.94 = 13.88\text{g}$$

$$m(\text{Zn}) = 1 \times 65.38 = 65.38\text{g}$$

To produce the same electrical current for the same length of time, a smaller mass of lithium is required. This means that the lithium cell has a higher energy density.

[d] Explain why the lithium cells can't contain water as the electrolyte solvent.

Lithium reacts spontaneously with water to produce LiOH and H₂ gas.



Q: Why are lead-acid batteries classified as hazardous waste?

Lead-acid batteries contain lead and concentrated (4.5mol/L) H₂SO₄. Lead and its compounds are acutely and chronically toxic. It should be recycled rather than carelessly released into the environment. H₂SO₄ is a hazardous, corrosive substance that should be recycled or neutralised before being released into the environment.

Q: An important feature of the lead-acid secondary cell is its ability to deliver a high current flow for long periods. This has made the lead-acid battery an ideal choice for motor vehicle ignition systems and as a power source for electric vehicles like electric wheelchairs, forklifts and golf carts. Unfortunately their very low energy density has limited their widespread use as a power source for electric powered vehicles.

[a] What design feature of the anode and cathode allows for the lead-acid battery to produce high currents i.e., fast reaction rates?

The Pb at the anode and PbO₂ at the cathode are present in a powdered, high surface area form. The oxidation of Pb and reduction of PbO₂ can only take place where the solid makes contact with the electrolyte. For this reason, a high surface allows for a high rate of oxidation and reduction i.e., high rate of production and consumption of electrons. This allows the cell to produce a high current.

[b] The oxidation of one mole of lead in a lead-acid battery can produce as much current (flow of electrons) as the oxidation of one mole of zinc in an alkaline cell. How does this one factor alone affect the mass and hence energy density of the lead-acid battery compared to an alkaline cell? Explain.

$$n(\text{Pb}) = 1 \times 207.2 = 207.2\text{g}$$

$$n(\text{Zn}) = 1 \times 65.38 = 65.38\text{g}$$

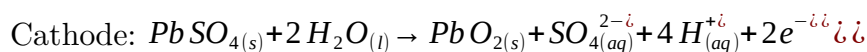
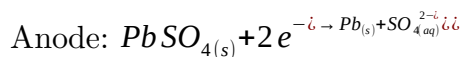
Therefore, to produce the same current, a much higher mass of lead is required, approximately 3.2 times higher. This means that the lead-acid battery has a lower energy density than an alkaline cell.

[c] The lead-acid cell is a secondary cell. Why is this an important feature in its use for motor vehicles and electric vehicles?

Secondary cells can be recharged once they go “flat”. That is, the oxidant and reductant can be regenerated by applying a suitable DC voltage. Being rechargeable means the cell can undergo many discharge-recharge cycles over a period of several years before eventually failing to recharge and requiring replacement.

Q: Lead-acid batteries are able to be recharged by attaching the electrodes to a DC power supply. The anode of the cell is connected to the negative terminal of the power supply while the positive terminal is attached to the cell’s cathode. This causes the discharge reactions at each of the electrodes to occur in the reverse direction. An undesirable side reaction that occurs during recharge is the electrolysis of water. The following questions refer to the recharge of a lead-acid cell.

[a] Write the recharge half-equations for the anode and cathode when a lead-acid cell is being recharged.



[b] How does the composition of the anode and cathode change during recharge and thus explain why the cell is now considered recharged.

Anode: Originally consists of Pb. During discharge Pb is converted to PbSO₄ and after recharge PbSO₄ is converted back to Pb.

Cathode: Originally consists of PbO₂. During discharge PbO₂ is converted to PbSO₄ and after recharge PbSO₄ is converted back to PbO₂.

During recharge, the oxidising agent (PbO₂) is regenerated at the cathode and the reducing agent (Pb) is regenerated at the anode, thus recharging the cell.

[c] Recharging the lead-acid battery of an electric wheelchair increases the enthalpy (stored energy) of the cell. Where does this energy come from?

The increase in enthalpy comes from the increase in electrical energy from the electric current used to recharge the cell.

[d] Describe what happens to the electrolyte pH as a lead-acid cell is recharged.

Overall reaction: $2 \text{PbSO}_{4(s)} + 2 \text{H}_2\text{O}_{(l)} \rightarrow \text{Pb}_{(s)} + \text{PbO}_{2(s)} + 2 \text{SO}_{4(aq)}^{2-} + 4 \text{H}_{(aq)}^{+}$

4mol of H⁺ ions are produced for every 2mol of PbSO₄ consumed. This means [H⁺] increases, thus decreasing pH.

[e] Why is it important to regularly check the water level inside a lead-acid battery?

An unwanted side reaction that occurs during the recharging process is the decomposition of water into O₂ gas and H₂ gas: $2 \text{H}_2\text{O}_{(l)} \rightarrow 2 \text{H}_{2(g)} + \text{O}_{2(g)}$

Hence water is lost.

[f] Why might it be dangerous to recharge lead-acid batteries of a dozen electric golf carts in a confined unventilated room?

The unwanted decomposition of water into H₂ gas and O₂ gas during the recharge of acid-lead accumulator batteries can produce an explosive mixture of H₂ gas and O₂

gas. This can be especially dangerous in a confined and unventilated space where the gases may accumulate and ignite explosively.

Q: Lithium-ion cells have now replaced lead-acid battery technology as the cell of choice in many types of electric vehicles. What features does the lithium-ion cell have that make it suited to this use and what significant advantage does the lithium-ion cell have over the lead-acid cells in this type of application? Explain.

The Li-ion cell has a very long shelf-life and requires no maintenance whereas the lead-acid cell may require addition of water to the electrolyte from time to time. The Li-ion cell's most important feature is its exceptional energy density, currently 3-5 times that of the lead-acid cell. This makes it ideal for all types of transportation applications where the overall mass of the battery system needs to be kept as low as possible whilst maximising the available electrical energy. Furthermore, the Li-ion cell doesn't have the same toxicity problems of lead and corrosion problems of H_2SO_4 as the lead-acid battery.

Q: The alkaline hydrogen-oxygen cell is referred to as a fuel cell. How does a fuel cell differ from other types of galvanic cells?

Fuel cells differ from primary cells and secondary cells in that they don't store the oxidising agent or reducing agent. Instead, the reactants are continuously fed into the cell to generate electricity. Chemical by-products of the cell reactions are expelled from the cell as it operates.

Q: The PEMFC is a promising though not yet widely commercialised fuel cell technology considered superior to alkaline fuel cells. A similar type of cell is now in commercial use in the Toyota FCV.

[a] How do the anode and cathode reactions of the PEMFC compare to those in the alkaline fuel cell?

Anode and cathode reactions are identical. In both cells, H_2 is oxidised and O_2 is reduced, forming H_2O as the only overall product.

[b] The polymer electrolyte membrane (PEM) of a PEMFC cell is considered to be a major improvement on the electrolyte from the alkaline fuel cell.

[i] What's the role of the PEM in a fuel cell?

The PEM acts as the electrolyte and electrode separator. It allows protons to transfer from the anode to the cathode. It also prevents H_2 or O_2 from moving across the membrane between the anode and the cathode.

[ii] How is the PEM considered to be an improvement on the alkaline fuel cell electrolyte?

The PEM is a solid polymer rather than a liquid as is the electrolyte in the alkaline hydrogen fuel cell. The PEM isn't corrosive as is the concentrated NaOH solution of the alkaline cell. The solid PEM can be extremely thin, which isn't possible with a liquid electrolyte and consequently allows a very compact, flexible design.

[c] What's the role of the nanoparticles of platinum present on the surfaces of both the anode and cathode and what's the advantage of having nanosized particles?

Platinum nanoparticles act as a catalyst by lowering the activation energy for the electrode half-reactions. The use of a catalyst like this increases the efficiency of enthalpy conversion into electrical energy so that less of the available energy is converted to heat and more as electrical energy. The small particle size (nanoparticles) gives the solid platinum a high surface area, allowing greater contact with both hydrogen and oxygen at the respective electrodes. This increases the reaction rate for each of the half-reactions, thus increasing the rate of electron supply and hence allowing a greater current to be produced.