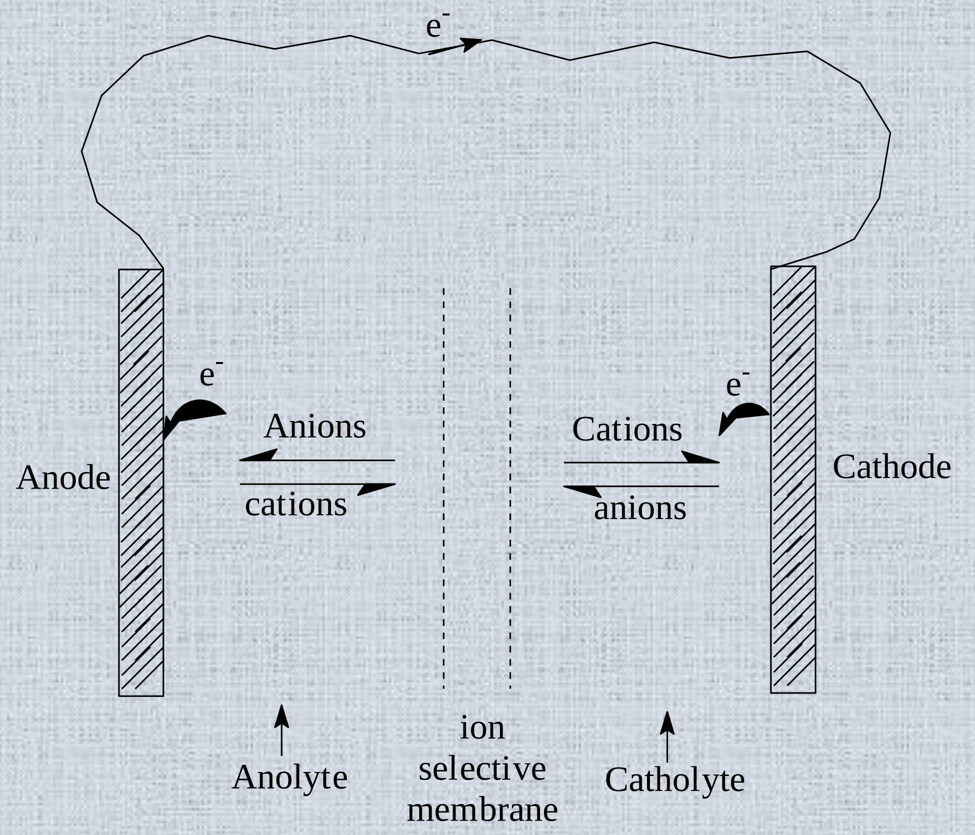
Chemists Online Seminar

Electrochemistry - Battery and Fuel Cell

An Electrochemical Cell



Schematic diagram of a charge transport process in a cell

Anode and Cathode

- Oxidation takes place at the anode
- Reduction takes place at the cathode

The Concept of Half Cell

In the electrolysis of water:

$$\text{anode: } 2H_2O - 4e^- \rightarrow O_{2(g)} + 4H^+$$

$$\text{cathode: } 2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-$$

Each of the anode and cathode reactions are half-cell reactions.

The overall cell reaction is:

$$2H_2O \rightarrow 2H_2 + O_2$$

Standard Electrode Potential E^o

Defined as the electrode potential of a half cell reaction (**under equilibrium condition**) versus the standard hydrogen electrode when all reactants and products exist at unit activity. It is often written in the form of reduction and is therefore also called `standard reduction potential'.

Standard Electrode Potential E^o

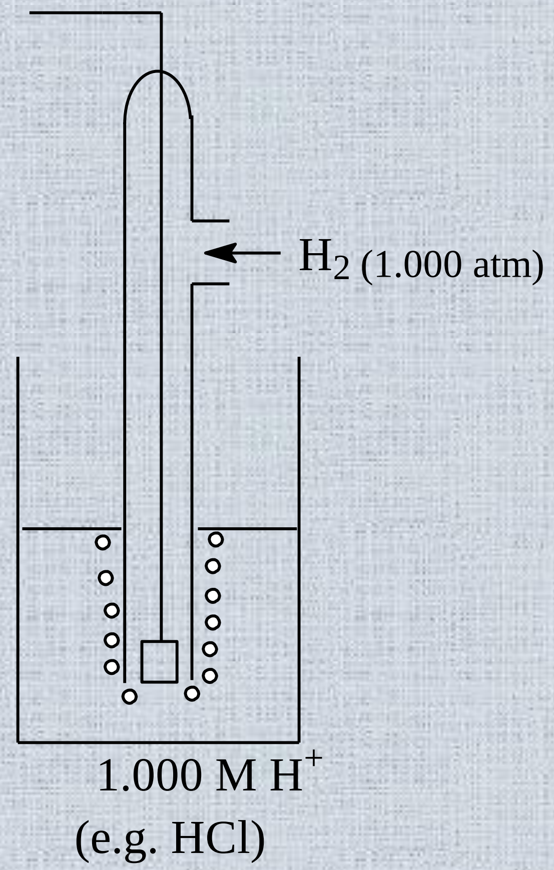
- A standard hydrogen electrode (SHE) consists of a platinum-black electrode immersed in a 1.000 M H^+ ion solution in contact with hydrogen gas at 1.000 atm pressure.

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2$$

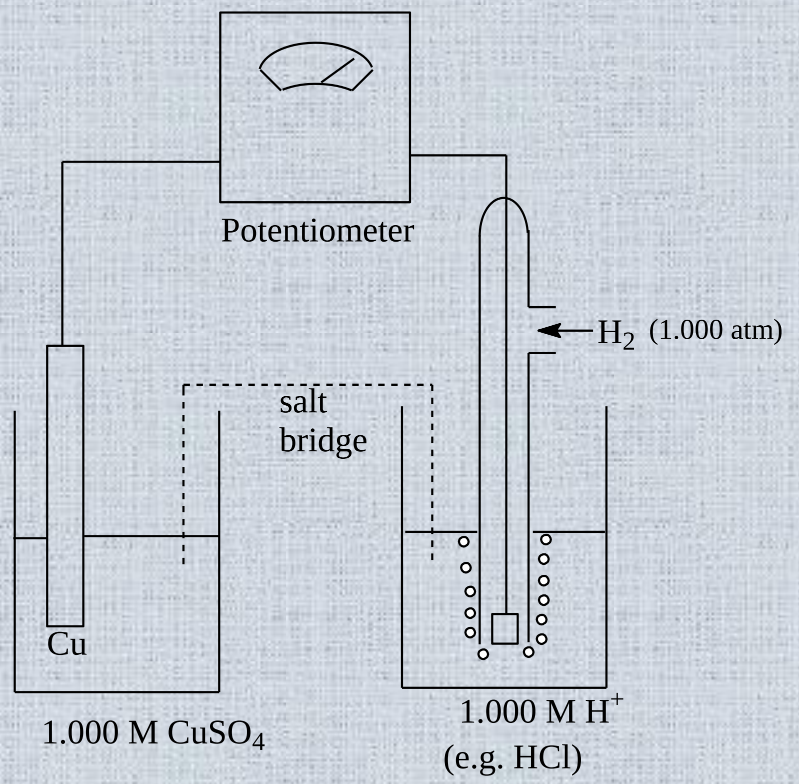
- The H^+ and H_2 are under **dynamic equilibrium**

- By convention, the standard electrode potential of a SHE is defined as exactly 0.000V.

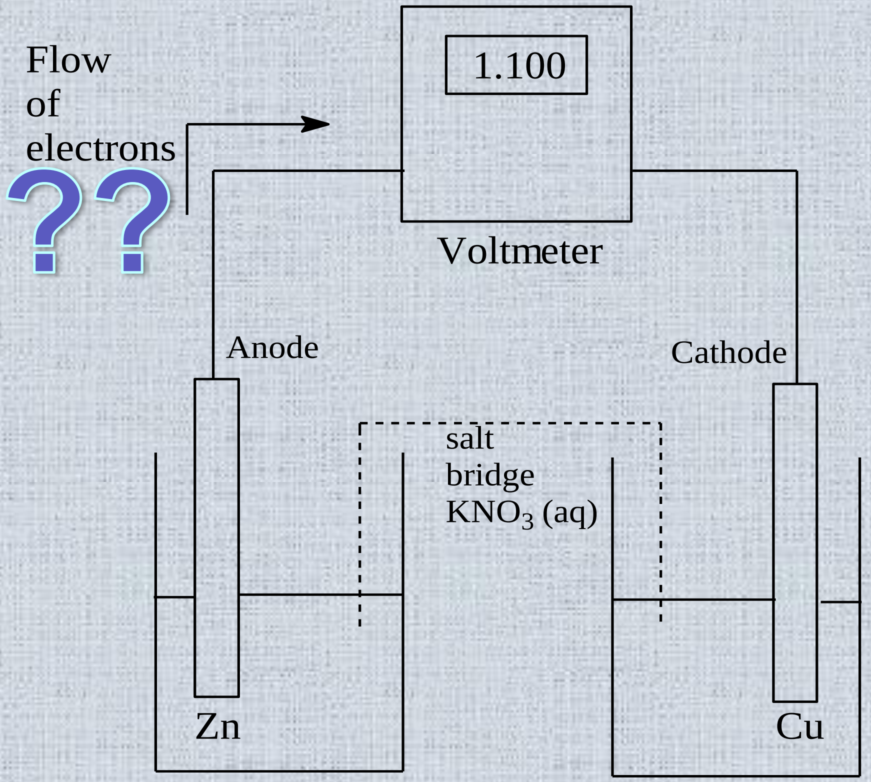
(a)



(b)



(a) The standard hydrogen electrode; (b) The standard electrode potential of Cu^{2+}/Cu versus the standard hydrogen electrode



$1.000\ M\ Zn(NO_3)_2\ (aq)$ $1.000\ M\ Cu(NO_3)_2\ (aq)$

$E^o_{Zn^{2+}/Zn} = -0.763V$ $E^o_{Cu^{2+}/Cu} = 0.337V$

$E_{cell} = E_c - E_a = 0.337 - (-0.763) = 1.100\ V$

The Concept of Overpotential (η)

- When current flows between two half cells
- $\Rightarrow$an overpotential exists on each of the half cell!

- The difference between the actual potential of a half cell electrode and its equilibrium potential (E^o) is the overpotential (η)

- e.g. the E^o for Cu^{2+}/Cu is 0.337 V

If the potential of a Cu^{2+}/Cu half cell has been lowered to 0.327 V when current flows, the overpotential is 0.327V - 0.337V = -0.010V

Polarization

- When the kinetics of an electrochemical reaction is slow (slow rate of reaction), the electrode is said to be polarized.

- Slow kinetics can be caused by:

1. Low concentration of reactant
2. High kinetic barrier on the electrode surface

Batteries

A battery is a device which can store chemical energy and, on demand, convert it into electrical energy to drive an external circuit.

Lead-Acid Batteries

Negative electrode :

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

$E_A^o = -0.346$ V

Positive electrode :

$Pb^{IV}O_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow Pb^{II}SO_4 + 2H_2O$

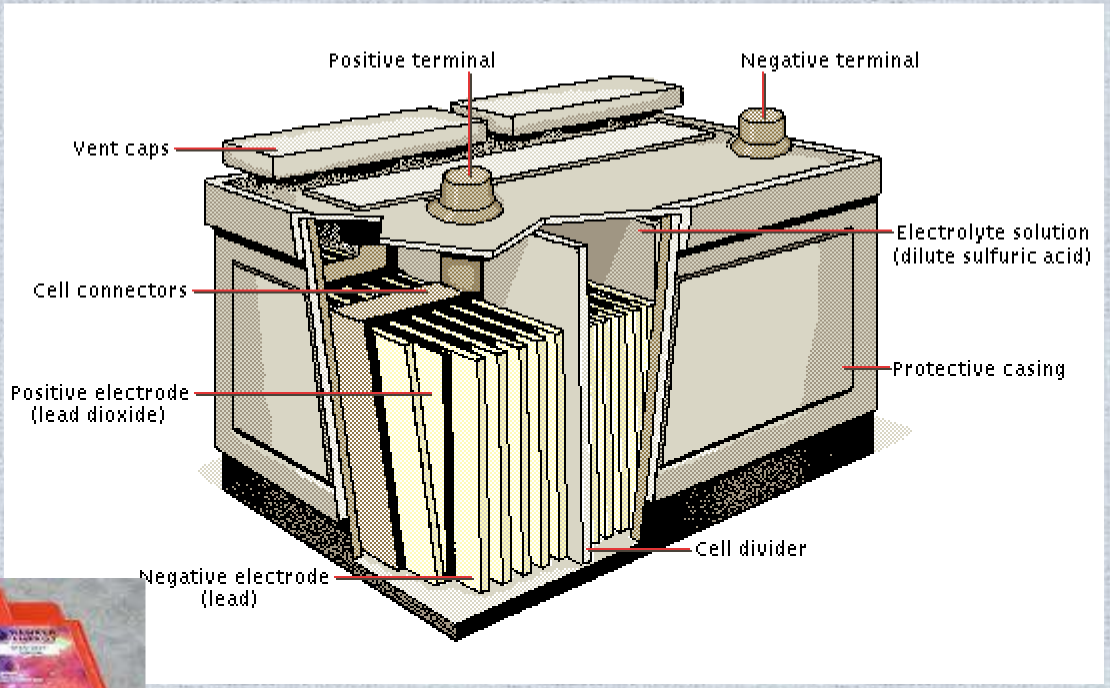
$E_c^o = 1.685$ V

$E^o_{cell} = E_c^o - E_A^o = 2.031$ V

Electrolyte: Sulfuric acid

Car Lead Acid Battery

- For starting, lighting and ignition
  6-12 volts (3-6 cells in series)
- Parallel pasted electrodes with separator



Development in the design of lead-acid batteries

1. Reduce the weight of grids (use lead alloys)

2. Change the case from hard rubber to the lighter polypropylene - improve the energy density from 24 to 32 $Whkg^{-1}$

3. If overcharging, water electrolysis $\rightarrow$ H_2 + O_2 (explosion)

   To build a catalyst for the recombination of H_2 & O_2 in the cell $\rightarrow$ maintenance-free sealed batteries

Valve-regulated lead acid (VRLA) batteries

Also known as *Maintenance Free (MF) battery*

Overcharging or misuse may cause the production of gases - hydrogen and oxygen

In VRLA battery the hydrogen and oxygen produced in the cells recombine back into water with the aid of a catalyst

If gases build up inside the battery, a valve is designed to vent the gas and thereby normalize the pressure $\Rightarrow$Valve-regulated

IV) Nickel-cadmium and Ni-metal hydride batteries

A) Nickel-cadmium electrode reactions

$$\text{Cathode: } NiOOH + H_2O + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Ni(OH)_2 + OH^-$$

$$\text{Anode: } Cd + 2OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Cd(OH)_2 + 2e^-$$

B) Ni-metal hydride electrode reactions

$$\text{Cathode: } NiOOH + H_2O + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Ni(OH)_2 + OH^-$$

$$\text{Anode: } MH + OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} M + H_2O + e^-$$

$LaNi_5H$ / $LaNi_5$ (alloy of rare-earth metal)

Electrolyte : aqueous KOH

Cell potential of both types of batteries ~1.3 V

Memory effect in Ni-Cd batteries

Sealed Ni-Cd cells exhibit an unfortunate characteristic known as the `memory effect'. When cells are only partially discharged, and then recharged, they progressively lose their capacity, cycle by cycle. In a sense, the cell `remembers' the lower capacity of the partial discharge. This could be caused by the formation of a passivating layer on the electrode, forming a barrier to further electrochemical reaction.

Priming New Batteries

- Manufacturers recommend to charge a nickel-based battery for 24 hours when new and after long storage. This service brings all cells to equal charge level and redistributes the electrolyte to remedy dry spots on the separator brought on by gravitation of the electrolyte.

- Nickel-based batteries are not always fully formed when leaving the factory. Applying several charge/discharge cycles through normal use completes the forming.

Lithium Ion Battery

Li^+ shuttling between anode and cathode during charging and discharging

Negative electrode: Graphite

$Li_yC_6 \rightarrow C_6 + yLi^+ + ye^-$

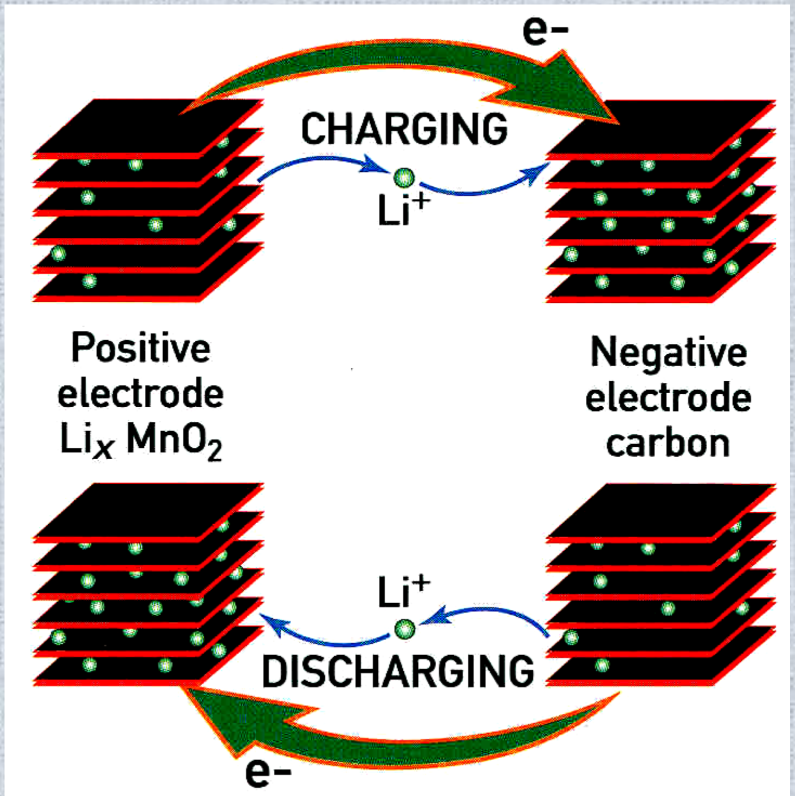
Positive electrode: Metal Oxide (MnO_2, CoO_2, NiO_2)

$xLi^+ + MO_2 + xe^- \rightarrow Li_xMO_2$

Intercalation of Li in the electrode materials

Electrolyte: Porous polymer saturated with an organic solvent containing the Li salt

Voltage: 3-4 V depending on the positive electrode material



$$Li_xMO_2 + yLi^+ + ye^- \longrightarrow Li_{x+y}MO_2 \qquad Li_yC_6 \longrightarrow C_6 + yLi^+ + ye^-$$

The rechargeable lithium battery.

On charging, Li^+ ions move from the Li_xMO_2 electrode to the carbon one.

At the same time, electrons move through the external circuit.

The reverse happen on discharge.

Batteries explosion

Dell laptop goes up in smoke

By Tony Smith [More by this author]
28th July 2006 09:46 GMT
Sign up to our newsletter

Another Dell laptop has undergone spontaneous combustion, p… office it was situated in and the urgent intervention of the local… incident point to a battery meltdown as the cause of the conflag…

Here's a picture, but there are plenty more over at Tom's Hardwa… shots were sent to first. Judging by the screen damage, the laptop… the fire.

Details… a Dell machine, and the battery compartment is now just so much… in an even worse state.

雜牌手機電池爆炸致居民家中失火

2007-09-22 東方今報

記者 王亞南 通訊員 鄭揚生

今報新鄉訊 昨日上午，家住新鄉市和平路的一戶居民家中突發火災，事後經消防人員勘察發現是由一塊正在充電的手機電池爆炸所引起的。

昨日上午10時25分，新鄉市紅旗區消防大隊官兵接到報警後，迅速趕到了和平路上的華中小… 在現場看到，戶主李飛（化名）已經用幹粉滅火器將火撲滅，客廳內的海綿沙發墊已被燒爛… 沙發也被燒成焦黑狀。

消防官兵在現場經仔細勘察，發現沙發對面的牆上有一塊正在充電的破碎手機電池，插… 有黑色印記，…爆炸過的跡象。

據李飛介紹，…睡覺，隱約聽見客廳里有"劈里啪啦"的聲音… 只見正充… 他就迅速拿起家中自備的幹粉滅火器… 稱，爆炸…

日兩iPod Nano過熱著火

http://www.wenweipo.com [2008-08-20]

放大圖片

■日本關注iPod Nano起火個案。

日本經濟產業省表示，東京接獲兩宗蘋果公司iPod Nano起火的個案，播放機起火後波及旁邊的紙張和地蓆，兩宗事件無人受傷。此外，還發生了兩宗因接觸發熱部位引起輕度燙傷的情況，以及12宗產品損壞事故。當局正調查iPod Nano的電池是否出現瑕疵，並下令日本蘋果公司找出肇事原因，並向當局匯報。

楊楊米焚毀 疑鋰電問題

中國 手機爆炸 焊工肋骨穿心亡

星島日報 SING TAO DAILY

手機爆炸 焊工肋骨穿心亡

2007-07-04

(綜合報道)(星島日報報道)繼廣州一名男子被爆炸手機炸掉乳頭後，內地又再發生手機爆炸事件。蘭州一名年輕焊工人，工作時把手機掛在胸前，疑手機受熱爆炸，機主肋骨當場被炸斷直插心臟，大量出血，送院搶救後終告不治。本港海關對接二連三發生的手機意外甚表關注，並部署加強堵截內地冒牌手機電池的流入。

蘭州發生全世界首宗手機爆炸「殺人」事件。據《蘭州晨報》報道，遭炸死的焊工人蕭金鵬，二十二歲，是金塔縣雙城鎮鑫盤鐵選廠的一名電焊工。

上月十九日端午節… 作時，他掛在胸前的手機突然… 工友見狀，立即代為報警及召… 證實不治。

醫生替死者檢查傷… 衣服當被燒毀，手機破爛，懷疑死者是遭掛在胸口的手機炸死，遂通知當… 的金塔縣警方，成…

廣告

本港一名二手電話店東主，展示正牌電池殼有短路裝置。

iPhone電池脹如氣球

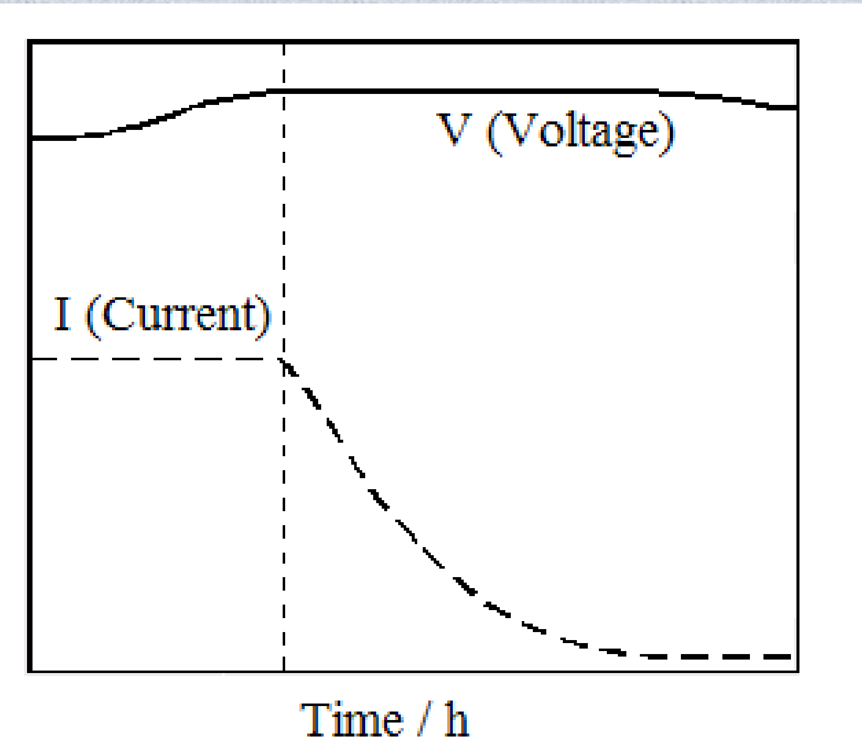
2012年03月11日

Safety issues related to lithium-ion batteries

- Lithium batteries are high-voltage batteries. Over-charging may lead to the decomposition of the electrolyte to generate gaseous products and hence explosion.
- Over-charging will generate excessive heat. The heat will cause decomposition of electrode material and vaporization of the organic solvent in the electrolyte to give gaseous products $\Rightarrow$ explosion.

Prevention of Over-charging

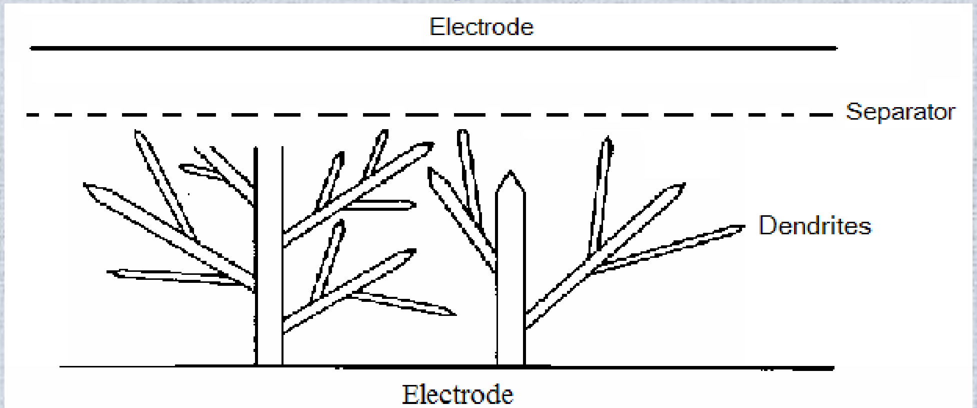
- **A good battery charger should be able to prevent over-charging, e.g. by constant-current-constant-voltage charging.**



The current is held constant until the battery voltage reaches a pre-defined value where side-reaction is likely to begin. At this point, the voltage is held constant and the current allowed to decline exponentially.

Safety issues related to lithium-ion batteries

- Impurities in the electrolyte and electrode material (e.g. those in poor quality batteries such as faked ones) will cause the formation of dendrites in repetitive charging-discharging cycles. The dendrites might penetrate the separator leading to short circuitry. Short circuit will lead to excessive heat which will decompose the lithium cobalt oxide electrode material and release the oxygen needed for combustion, hence explosion.



Zinc-carbon battery *vs.* Alkaline manganese battery

Advantages of the alkaline manganese battery:

- Mercury free
- Higher capacity and longer service time

I) Zinc-Carbon Primary Batteries

- Positive electrode

$2MnO_2(s) + 2\ e^- + 2NH_4Cl(aq) \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(aq) + 2\ Cl^-$ (Leclanché Cell)

or

$MnO_2 + H_2O + e^- \rightarrow MnO.OH + OH^-$ (Zinc Chloride Cell)

- Negative electrode

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

The pH in the vicinity of the negative electrode decreases due to hydrolysis of Zn^{2+}:

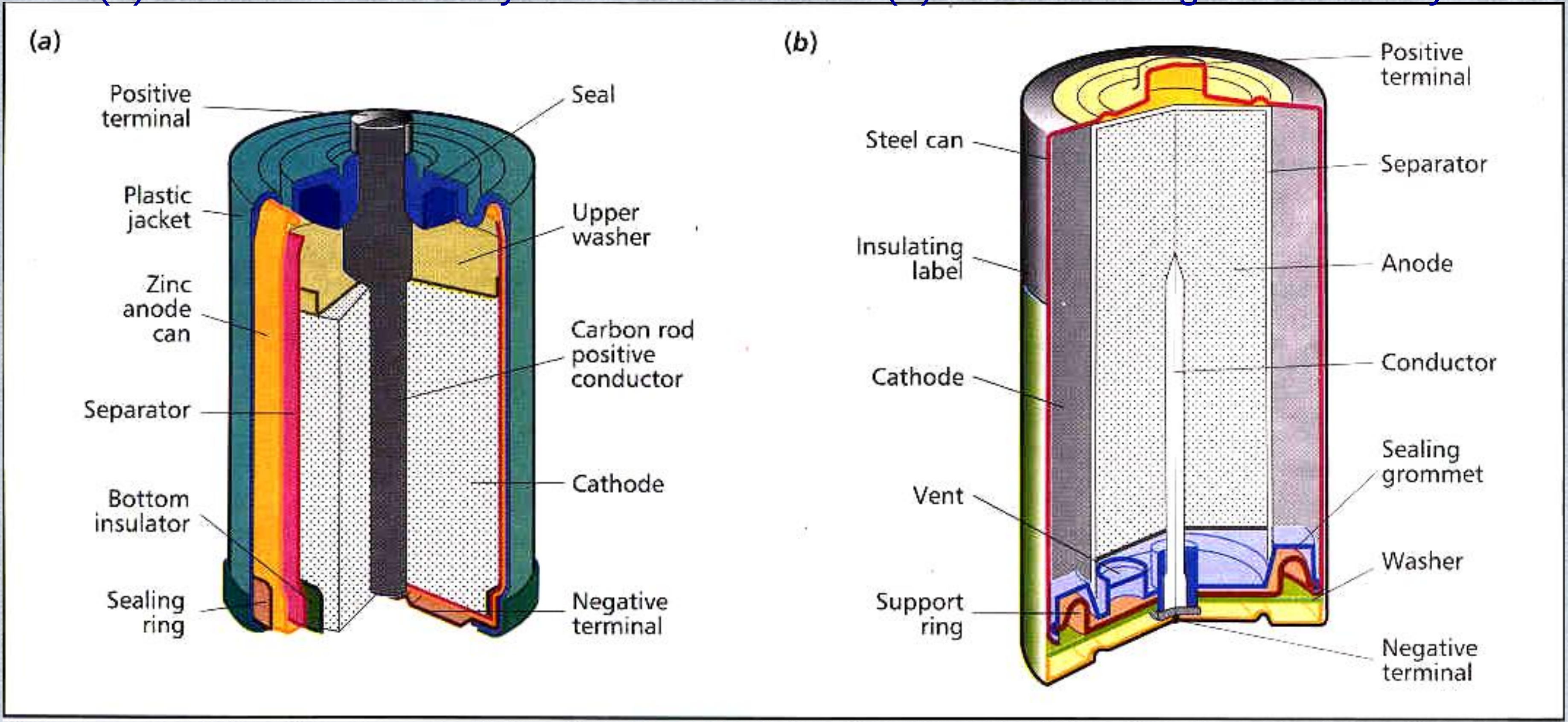
$Zn^{2+} + H_2O \rightarrow Zn(OH)^+ + H^+$

Hg may be added to the Zn metal to suppress the reaction of Zn with H^+ to give H_2.

II) Alkaline Manganese Cells

- Concentrated KOH (~30 wt.%) is used as electrolyte
- Negative electrode consists of finely-divided zinc powder packed around a current-collector positioned at the center of the cell
- The positive-electrode mix of MnO_2 and carbon is packed around the outside of the zinc negative and separator, and is in electrical contact with a nickel-plated steel can.

(a) Zinc-Carbon battery (b) Alkaline Manganese battery



Fuel Cells

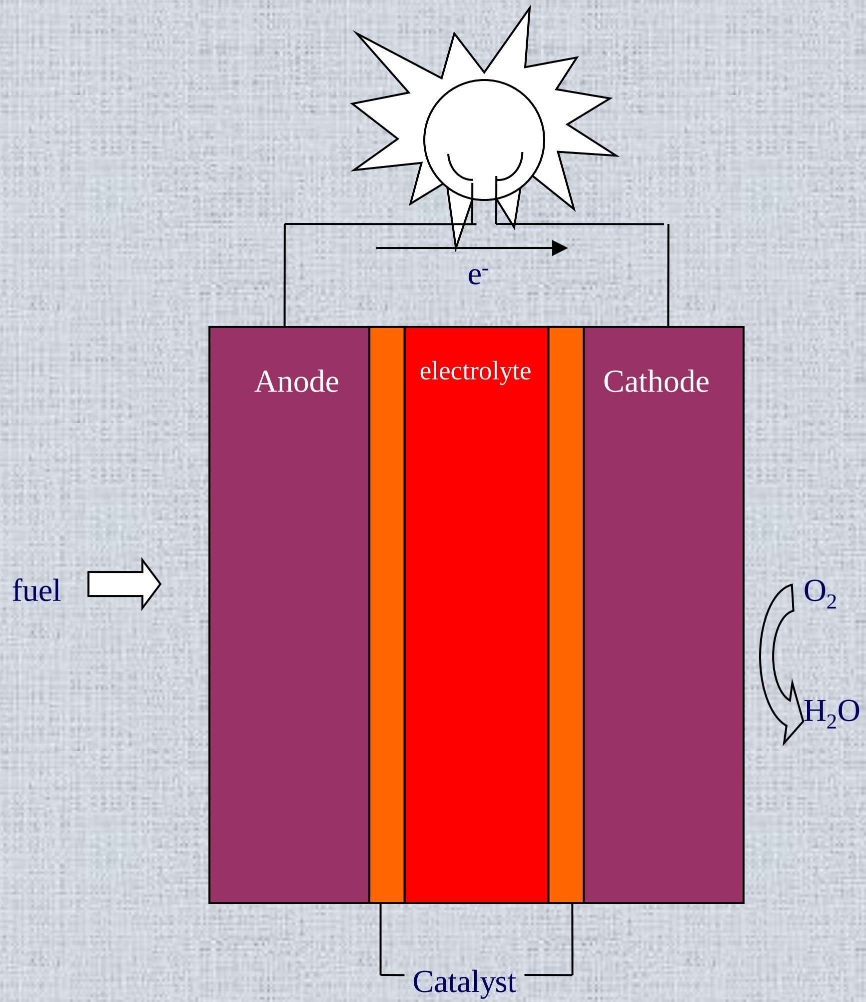
- Fuel is reacted with oxygen in an electrochemical cell to produce energy.
  - Electricity is generated from oxidation of fuel supplied to the anode and reduction of oxygen at the cathode.
- The H_2/O_2 fuel cell is considered environmentally friendly because H_2O is the product.

Working principle of fuel cell

- A fuel cell works by catalysis, oxidizing the fuel on anode, and forcing the electrons pass through a circuit, hence converting them to electrical power.

- At the cathode, the oxidant (oxygen) is reduced and takes the electrons back in, combining them with protons to give water.

- The waste product from the fuel cell is water when the fuel is hydrogen, and carbon dioxide plus water when the fuel is methanol.



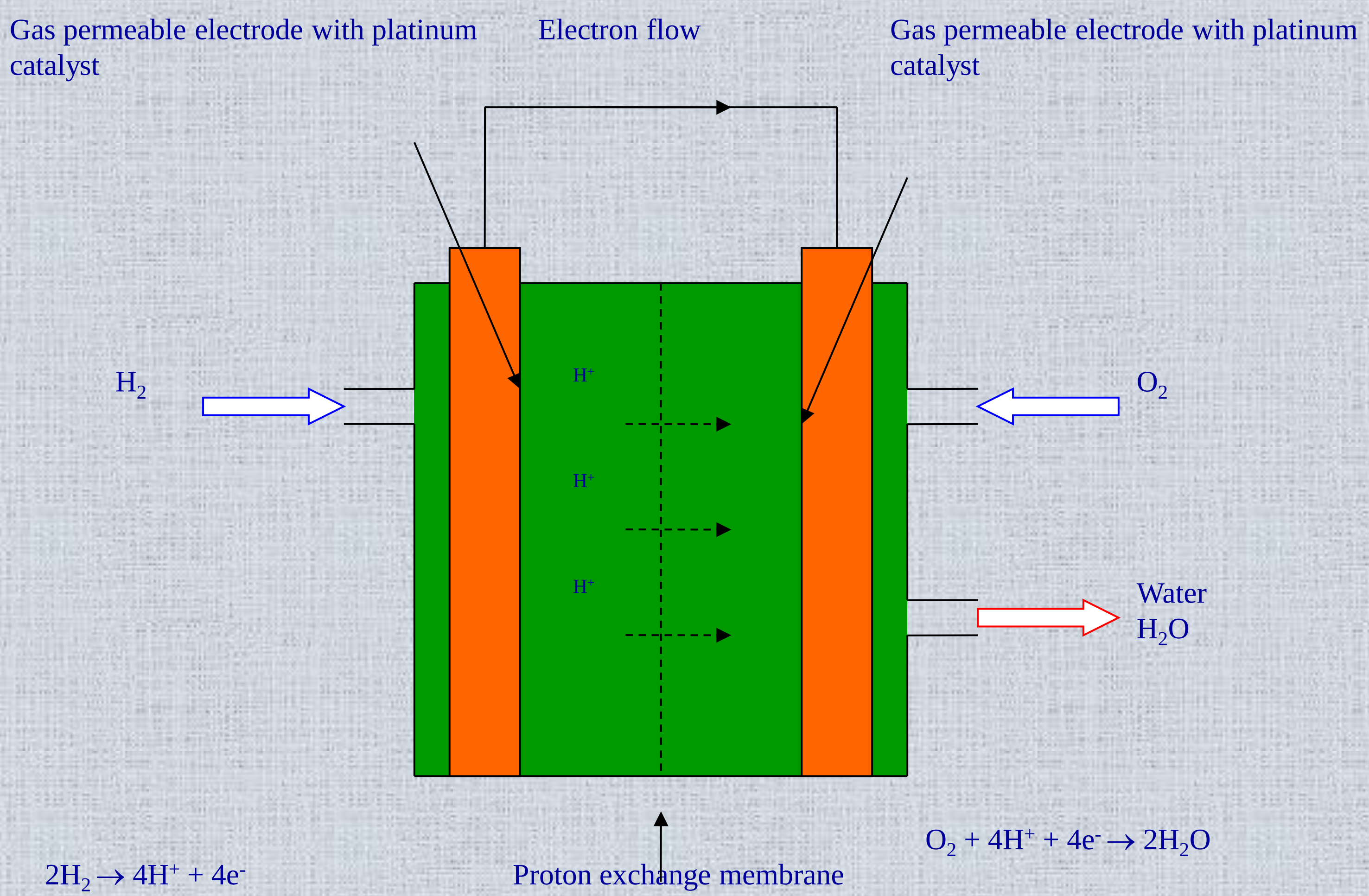
Schematic diagram of fuel cell

Hydrogen–Oxygen proton exchange membrane (PEM) fuel cell

- Hydrogen used as fuel
- A proton-exchange membrane (PEM) is used to separate the anode and cathode
  - Allows H^+ to pass through while keeping the gases apart
  - The protons reach cathode and react with oxygen to form water — the only waste product is water, which is environmentally benign.

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Overall: $2H_2 + O_2 \rightarrow 2\ H_2O$



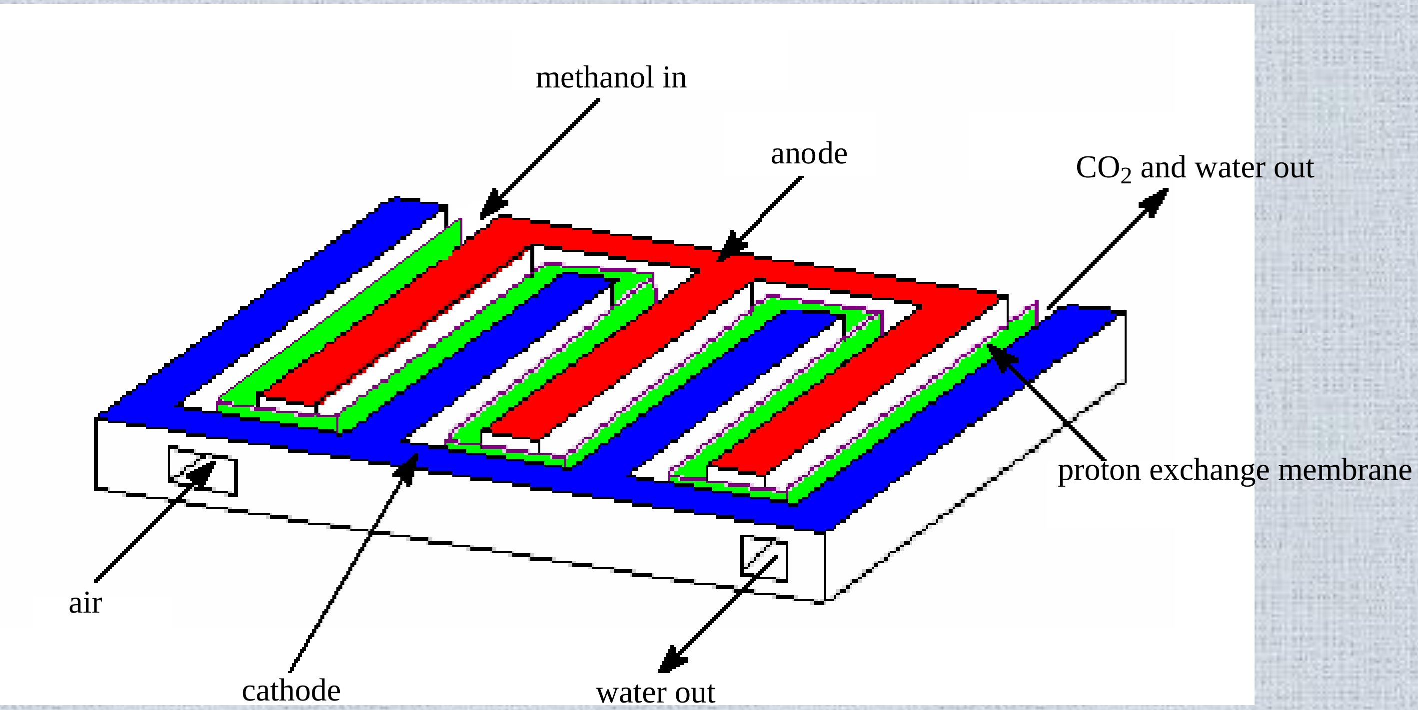
The PEM fuel cell

Direct methanol fuel cell (DMFC)

- Methanol used as fuel

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
Cathode: $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

Net reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$



Schematic diagram of a direct methanol fuel cell

Limitations of DMFC

- Efficiency is low due to the high permeation of methanol through the proton-exchange membrane (crossover effect) which then reacts directly with the oxygen at the cathode.
- A Pt/Ru catalyst is required to catalyze the oxidation of methanol at the anode (high cost).
- Current DMFCs are limited in the power they can produce, only suitable for use in certain consumer goods.

Recycle of Used Batteries

- Disposal of batteries containing toxic metals like lead, nickel, cadmium or mercury may be hazardous to human health and the environment.

- Recycling of used batteries becomes an important environmental issue in recent years.

Lead acid battery recycling

One of the most successful recycling programs in the world.

Steps:

1. Separation of non-metallic components
2. Smelting/reduction of lead-bearing products

$Na_2CO_3 + 2\ PbSO_4 + Fe + 9C \rightarrow 2Pb + FeS + Na_2S + 9CO + CO_2$

Refining the lead obtained by smelting to meet the market specifications.

Environmental issues

- Fuel cells and batteries are considered as environmentally friendly energy sources compared with fossil fuel
  - Reduce the production of greenhouse gases and smog-forming pollutants
- Application of fuel cells and batteries in vehicles to minimize the production of CO_2 and other pollutants from the combustion of fossil fuels.

Fuel cell powered vehicles

- A **hydrogen vehicle** uses a hydrogen-oxygen fuel cell to run the motor of the vehicle.

- The vehicle converts the chemical energy of hydrogen to mechanical energy by the electrochemical reaction in a fuel-cell.

Limitations of fuel cell powered vehicles

- Production of hydrogen is not convenient compared with coal or oil.
- Fuel cells (platinum catalysts) and hydrogen production (electricity) are relatively expensive.
- Problem in storage of hydrogen gas.
- Hydrogen infrastructure.

Battery powered vehicle

- Battery powered vehicles are powered by motors that draw electricity from on-board storage batteries

- Great potential to reduce greenhouse gases as no pollutants are generated.

Limitations of battery powered vehicles

- The cost is high, and the size of the battery is large.
- Lack of an adequate refueling (recharging) infrastructure.
- The batteries used in electric vehicles limit the average vehicle's driving range between 100 to 200 km.
- The batteries must be recharged often with long charging time.

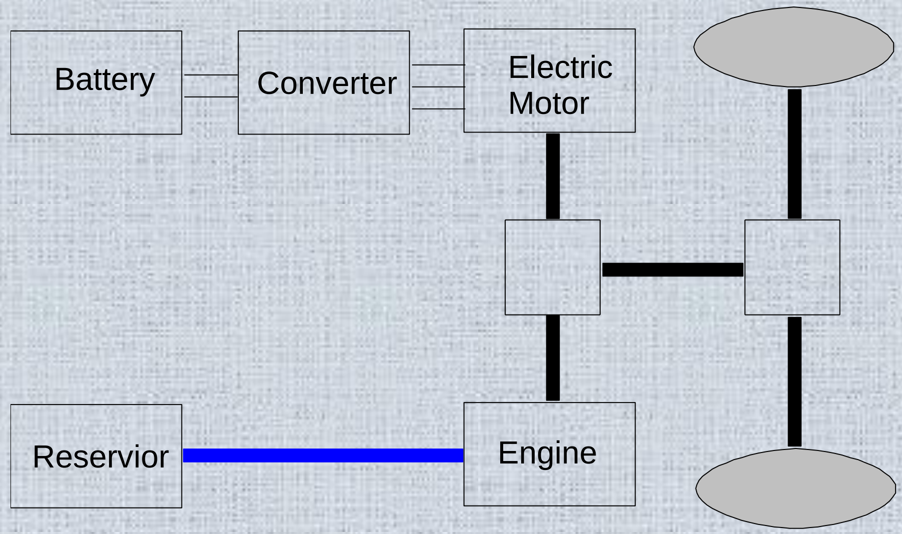
Hybrid-powered Vehicles

- Hybrid-powered vehicles make use of both an on-board rechargeable battery and a fueled power source.
  - generate less air pollutants.
  - reduce noise emissions, particularly at low operating speeds

Hybrid-powered Vehicles

- Contain both an internal combustion engine and an electric motor.
- Accessories such as power steering, air-conditioning are powered by electric motors instead of combustion engine.
- In some cases, combustion engine is the dominant while electric motors turns on when a boost is needed

Hybrid-powered Vehicles



Structure of a parallel hybrid electric vehicle

Thank you!