BATTERIES

In a galvanic cell, electrical energy is produced by the spontaneous chemical reactions. Battery is a single or a combination of two or more galvanic cells, which act as a source of direct current (DC)

- Batteries are of two types, depending on their ability to be recharged. They are -

i> Primary battery

ii> Secondary battery

PRIMARY BATTERY

Primary batteries (or cells) are primary sources of electricity. They are not rechargeable. Once a primary battery is completely discharged, it can not be returned to it's original state by recharging.

Ex: Daniell cell, Mercury cell, Lelanche cell, Weston cell etc.

Dry cell :-

These types of cells are widely used in torchlights, transistors, clocks, toys etc. These cells are called 'dry cell' because they do not contain fluid components.

Construction →

A dry cell consists of a circular zinc container, which acts as the anode (negative pole) and a graphite rod, placed at the centre of the zinc container, acts as the cathode.

The cathode (positive pole) is surrounded by MnO_2 (Powdered Manganese dioxide) and carbon [it is used to prevent polarisation]. Between the cathode & the anode, a moist plate of Zinc Chloride ($ZnCl_2$) and Ammonium Chloride (NH_4Cl) is filled in. This moist paste serves as the electrolyte.

The upper surface of the paste is covered by pitch and the graphite rod is covered by a metallic cap at the top.

Reactions occuring in the cell :-

① Anode reaction →

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

② Cathode reaction →

$$2MnO_2(s) + 2NH_4^+(aq.) + 2e \longrightarrow Mn_2O_3(s) + 2NH_3(aq.) + H_2O(l)$$

③ Overall reaction →

$$Zn(s) + 2MnO_2(s) + 2NH_4^+(aq.) \longrightarrow Zn^{2+}(aq.) + Mn_2O_3(s) + 2NH_3(aq.) + H_2O(l)$$

→ NH_3, produced in the reaction reacts with $Zn^{2+}(aq.)$ to form the complex $[Zn(NH_3)_4]^{2\oplus}$. The potential of the cell is 1.5 V.

SECONDARY BATTERY

This type of battery is called - accumulator or Storage cell. When a secondary battery is connected to an outer circuit, energy released due to chemical reaction in the cell is converted to electrical energy. This is known as - discharging. A discharged secondary battery can be recharged by applying an external voltage. Due to recharging, the cell reaction occurs in the reverse direction, leading to regeneration of the reactant.

Ex: Acid accumulators, alkali accumulators OR Edison nicad battery.

Lead - Acid Accumulator :-

Such batteries are used in motor vehicles, inverters etc. This is also known as lead storage cell. The vessel is made up of glass. The (+ve) & (-ve) plates are not of pure Pb, but of Pb & Sb alloy. The plates are covered with PbO_2. [redacted] 20% H_2SO_4 behaves as the electrolyte.

In case of lead-storage battery, the electrolyte is 38% aqueous H_2SO_4 solution. The anode is a lead-plate (made of lead grid packed with spongy lead) connected together & the cathode is a series of lead plates in which lead oxide (PbO_2) is impregenated. The acid is kept in a strong bakelite box & the electrodes are immersed in it.

⊙ Cell reaction →

① During discharging of the cell :-

i) Anode reaction →

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

ii) Cathode reaction →

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

iii) Overall cell reaction →

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq.) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

② During Charging of the cell :-

During charging, the cell functions as an electrolytic cell.

i) Anode reaction →

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

ii) Cathode reaction →

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

iii) Overall cell reaction →

$$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq.)$$

- EMF of the fully charged cell is ~2V. If there are twelve plates (equivalent to six cells joined in series), then the EMF of the battery becomes ~12 V.

⊙ Electrode potential :-

Here, ~~oxidation~~

$$PbSO_4 + 2e \longrightarrow Pb + SO_4^{2\ominus} \quad [\text{in (-ve) half-cell}]$$

$$4H^+ + SO_4^{2-} + PbO_2 + 2e \longrightarrow PbSO_4 + 2H_2O \quad [\text{in (+ve) half-cell}]$$

The corresponding electrode potentials are -

$$E_\ominus = E^\circ_{PbSO_4 \to Pb} - \frac{RT}{2F} \ln \frac{a_{SO_4^{2-}} \times a_{Pb}}{a_{PbSO_4}}$$

$$\text{or, } \boxed{E_\ominus = E^\circ_{PbSO_4 \to Pb} - \frac{RT}{2F} \ln a_{SO_4^{2-}}} \quad [\because a_{Pb} = a_{PbSO_4} = 1]$$

$$E_\oplus = E^\circ_{PbO_2 \to PbSO_4} - \frac{RT}{2F} \ln \frac{a_{PbSO_4} \times a^2_{H_2O}}{a^4_{H^+} \times a_{SO_4^{2-}} \times a_{PbO_2}}$$

$$\text{or, } \boxed{E_\oplus = E^\circ_{PbO_2 \to PbSO_4} + \frac{RT}{2F} \ln (a^4_{H^+} \times a_{SO_4^{2-}})} \quad \left[\because a_{PbSO_4} = a_{PbO_2} = a_{H_2O} = 1\right]$$

Therefore, the cell EMF can be represented as,

$$E_{cell} = E_\oplus - E_\ominus$$

$$\text{or, } E_{cell} = \left[E^\circ_{PbO_2 \to PbSO_4} + \frac{RT}{2F} \ln (a^4_{H^+} \times a_{SO_4^{2-}})\right] - \left[E^\circ_{PbSO_4 \to Pb} - \frac{RT}{2F} \ln a_{SO_4^{2-}}\right]$$

$$\text{or } E_{cell} = \left[E^\circ_{PbO_2 \to PbSO_4} - E^\circ_{PbSO_4 \to Pb}\right] + \frac{RT}{2F} \ln (a^4_{H^+} \times a^2_{SO_4^{2-}})$$

$$\text{or, } E_{cell} = E^\circ_{cell} + \frac{RT}{2F} \ln a^2_{H_2SO_4}$$

$$\text{or, } \boxed{E_{cell} = E^\circ_{cell} + \frac{RT}{F} \ln a_{H_2SO_4}}$$

⊙ Discussion :-

i) The EMF of this cell shows its origin to the formation of $PbSO_4$ from Pb & PbO_2 of negative & positive electrode respectively. This is known as - 'double separation theory'.

ii) The Ecell should depend on the activity / concentration of H_2SO_4 at a particular temperature.

Hence, at standard condition,

for 7.5% H_2SO_4 → $E_{cell} = 1.9$ V

for 20% H_2SO_4 → $E_{cell} = 2.05$ V to 2.07 V

iii) Due to discharging, H_2SO_4 is consumed, hence $a_{H_2SO_4}$ is decreased, consequently E_{cell} decreases and ultimately the cell ceases to operate.

iv) When the discharged cell is connected with a D.C. supply or A.C. supply with rectifier, having EMF of supply-source greater than EMF of cell, $[E_{supply} > E_{accumulator}]$, generally 3-4 volt per cell, the (+ve) plate being connected to the positive pole of supply source.

➡ Both of the cells are reversible. Hence, during recharging, the following reaction takes place –

$$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4$$

– During charging, Pb gets deposited at the negative electrode & PbO_2 is formed at the positive electrode, H_2SO_4 is regenerated, so E_{cell} increases. This is continued untill the specific gravity of H_2SO_4 reaches upto the desired point.

v) Overcharging is not a good practice. If charging is carried out beyond the saturation point of specific gravity of H_2SO_4, all the Pb^{2+} ions of the solution are completely deposited. After this, due to electrolysis of H_2SO_4, H_2O and O_2 will evolve and activity of H_2SO_4 will decrease.

vi) The E_{cell} does not depend upon – a) size of the cell, b) size of the electrode. But, generally large electrodes are used to get cells of higher capacity.

vii) Due to formation of $PbSO_4$, the cell generally loses it's changes as a result of presence of impurities.

viii) The internal resistance of this cell is very small. So, when the cell is short-circuited, a large amount of current is passed through the cell and as a result of which the generated heat would change the electrodes.

FUEL CELL

In a conventional power plant for generating electricity a chemical fuel (mostly fossil-fuels) is burnted and the liberated thermal energy is utilized to drive a turbine. This turbine is coupled with a generator and electricity is produced. The maximum efficiency of such a process is usually 40%.

But if the free energy (G) of a chemical reaction can be directly converted to electricity as in a Galvanic cell, the efficiency of such a fuel cell becomes extremely high. Hence recently considerable efforts has been given to the construction of fuel cell.

- Defination :-

Fuel cells are the galvanic cells which converts the chemical energy of the redox reactions of fuels into electrical energy directly.

- Classification :-

Fuels are classified according to the temperature range in which they operate. These are -

i) Low temperature (25°c - 100°c) fuel cell
ii) Medium temperature (100°c - 500°c) fuel cell
iii) High temperature (500°c - 1000°c) fuel cell
iv) Very high temperature (>1000°c) fuel cell

- Uses :- Space craft

The oxidation of hydrogen by oxygen to form water was utilised to form a fuel cell & was used for electrical power supply in Apollo Space Programme. The water vapours produced during the reaction was condensed and added to drinking water supply for the astronauts.

- Example :- Hydrogen - Oxygen fuel cell is the most important fuel cell.

Construction :-

The cell is composed of a vessel containing concentrated solution of acid / alkali as the electrolyte.

The anode (i.e. (-ve) electrode) which acts as a source, is made up of porous carbon rod containing finely divided Pt or Pd as a catalyst.

The cathode (i.e. (+ve) electrode) which acts as a sink, is made up of porous carbon rod containing a mixture of CaO and Pt / Ag as catalyst.

H_2 and O_2 gases are passed at the anode & the cathode vessel respectively. The excess gases escape through the outlet.

Representation →

$$\text{Pt}, H_2(g) \left| \begin{matrix} \text{acid OR} \\ \text{alkali} \end{matrix} \right| O_2(g), \text{Pt}$$

Reactions & Cell EMF →

i) If the electrolyte is alkali :-

$$\left.\begin{array}{l} H_2(g) \longrightarrow 2H^{\oplus} + 2e \text{ -------} \\ 2H^{\oplus} + 2OH^{\ominus} \rightarrow 2H_2O(l) \text{ ------} \end{array}\right\} \text{at anode}$$

[redacted]

$$\overline{H_2(g) + 2OH^{\ominus} \rightarrow 2H_2O(l) + 2e}$$

$$\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^{\ominus} \text{ ------ at cathode}$$

∴ net cell reaction,

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

The EMF at anode -

$$E_{\ominus} = E^{\circ}_{H_2 \to H^{\oplus}} - \frac{RT}{2F} \ln \frac{a^2_{H^+}}{a_{H_2(g)}}$$

$$\text{or, } E_{\ominus} = -\frac{2RT}{2F} \ln a_{H^+} + \frac{RT}{2F} \ln a_{H_2} \quad \left[\because E^{\circ}_{H_2|H^+} = 0 \text{ V}\right]$$

$$\text{or, } E_{\ominus} = -\frac{RT}{F} \ln a_{H^+} + \frac{RT}{2F} \ln P_{H_2} \quad \left[P_{H_2} = \text{Parital pressure of } H_2(g)\right]$$

The EMF at cathode can similiary be -

$$E_{\oplus} = E^{\circ}_{O_2 \to OH^{\ominus}} - \frac{RT}{F} \ln a_{OH^{\ominus}} + \frac{RT}{2F} \ln P^{\frac{1}{2}}_{O_2} \quad \left[\begin{matrix} P_{O_2} = \text{Partial press} \\ \text{of } O_2(g) \end{matrix}\right]$$

∴ Net cell EMF –

$$E_{cell} = E_{\ominus} + E_{\oplus}$$

or, $E_{cell} = E^{0}_{O_2 \to OH^{\ominus}} - \frac{RT}{F}\left[\ln a_{H^+} + \ln a_{OH^-}\right] + \frac{RT}{2F}\left[\ln P_{H_2} + \ln P_{O_2}^{1/2}\right]$

or, $E_{cell} = E^{0}_{O_2 \to OH^{\ominus}} - \frac{RT}{F}\ln\left(a_{H^+} \times a_{OH^-}\right) + \frac{RT}{2F}\ln P_{O_2}^{1/2}\, P_{H_2}$

or, $E_{cell} = E^{0}_{O_2 \to OH^{\ominus}} - \frac{RT}{F}\ln k_w + \frac{RT}{2F}\ln P_{H_2} \times P_{O_2}^{1/2}$

If, $P_{H_2} = P_{O_2} = 1$ atm, $E^{0}_{O_2 \to OH^{\ominus}} = 0.403\ V$, $k_w = 10^{-14}$ at 25°C

then,

$E_{cell} = 0.403 - 0.509 \log 10^{-14}$

or, $E_{cell} = (0.403 + 0.826)$

or, $E_{cell} = 1.229\ V$

ii) If the electrolyte is acid:–

Reaction at anode →

$H_2(g) \longrightarrow 2H^+ + 2e$, $E^{0}_{H_2|H^+} = 0\ V$

Reaction at cathode →

$\frac{1}{2}O_2(g) + H_2O(l) + 2e \rightarrow 2\,OH^{\ominus}$

$2\,OH^{\ominus} + 2H^{\oplus} \longrightarrow 2H_2O(l)$

$\frac{1}{2}O_2(g) + 2H^+ + 2e \longrightarrow H_2O(l)$, $E^{0}_{\oplus} = 1.22V$

Net cell reaction,

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$, $E_{cell} = 1.229V$

- Discussion :–

Exchange of current density of the hydrogen is large but that of oxygen is very small (10^{-10} cm^2) so very limited amount of current is available from such cell. However, this problem can be overcomed by the following ways –

i) By using a long surface area of the electrodes.

ii) By using electrodes having catalytic Property to increase the current density.

iii) By heating the entire cell to improve the rate of reaction and the diffusion charecteristics (i.e. the rate of crossing the electrical double layers).

Advantages :-

i) Much more efficiency than thermal power plant sources like internal combustion engine. (generally 75% efficiency compared to heat engines having 40% efficiency)

ii) Less attention is required to maintain.

iii) The by products are harmless and do not need special arrangements for their removal. So pollution-free power is obtained.

Disadvantages :-

i) Low voltage (i.e. 1.229 V)

ii) Highly expensive

iii) Storage problem for fuels & oxidizers.

iv) Slow cell reaction

SOLAR CELL

Defination :- A solar cell (also known as a photovoltaic cell or PV cell) is defined as an electrical device that converts light energy into electrical energy through the photovoltaic effect.

A solar cell is basically a p-n-junction diode. Solar cells are one kind of photoelectric cells (a device whose electrical charecteristics i.e. current, voltage, resistance etc. vary when exposed to light).

Individual solar cells can be combined to form modules commonly known as solar panels. The common single-junction silicon solar cells can produce a maximum open-circuit voltage ~ 0.5 to 0.6 V. Although, this value is very small, but when these cells are combined in a solar panel, a considerable amount of renewable energy can be produced

Construction:-

A solar cell is basically a junction diode. Here, a very thin layer of p-type semiconductor is grown on a relatively wider/thicker n-type semiconductor. We then apply a few finer electrodes on the top of the p-type semiconductor layer.

These electrodes don't obstruct light to reach the thin p-type layer. Just below the p-type layer there is a p-n-junction. There is also a current carrying electrode present at the bottom of the n-type layer. The entire system is encapsulated by thin glass to protect the solar cells from any mechanical shock.

Working:-

① When light reaches the p-n-junction, the light-photons can easily enter in the junction, through very thin p-type layer.

② The light energy, in the form of photons, supplies sufficient energy to the junction to create a number of electron-hole pairs. The incident light breaks the thermal equilibrium condition of the junction. The free-electrons in the depletion region can quickly come to the n-type junction

③ Similiarly, the holes in the depletion layer can quickly come to p-type junction. The electrons in n-type side and the holes in p-type side can't further cross the junctions due to barrier potential of the junction.

④ As the concentration of electrons becomes higher in one side (n-type ~~junction~~) and the concentration of ~~electrons~~ holes becomes higher in another side (p-type) The p-n junction behaves like a small battery. A voltage is established. Such voltage is called- Photovoltage

⑤ If we connect a small load across the junction, then there will be flow of current.

Materials used :-

The semiconducting material which are used for this purpose, must have the band gap ~ 1.5 eV. Some commonly used materials are -

i> Silicon. ii> Ga-As iii> Cd-Te iv> Cu-In-Se_2

The materials ~~used~~ to be used in solar cells must satisfy the following criteria:

a> Must have band gap from 1 ev to 1.8 ev
b> It must have high electrical conductivity.
c> It must have high optical absorption.

Advantages :-

i> No pollution, ii> No maintenance cost, iii> Long-lasting.

Disadvantages :-

i> High installation cost.
ii> Low efficiency
iii> During cloudy days & at night the cells can't produce the electricity

Uses :-

i> It may be used to charge batteries.
ii> Used in ~~space~~ light-meters.
iii> It is used in wrist watches and power calculators.
iv> It can be used in spacecrafts to provide electrical energy

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Lithium - Ion Battery

A Lithium-ion battery or Li-ion battery is a type of ~~rechar~~ rechargable battery. Li-ions batteries are commonly used for portable electronics & electric vehicles. Just like dry cell batteries, Li-ion batteries provide power through the movement of Li⊕ ions.

Lithium is extremely reactive in it's elemental form. That's why Li-ion batteries don't use Lithium in elemental state. Instead, these batteries contain a lithium metal oxide such as, Lithium-cobalt oxide $(Li.CoO_2)$. This supplies the Li⊕ ion.

Lithium metal oxides are used as cathode and Lithium-carbon compounds are used in anode. These material are used because they allow for intercalation (intercalation means reversible inclusion / insertion of a molecule/ion into materials with layered structure)

Working :-

① At cathode :-

Reduction takes place at the cathode. Here, Cobalt oxide gets combined with Lithium ions to form Li-Co-oxide.

$$CoO_2 + Li^{\oplus} + e \longrightarrow LiCoO_2$$

② At anode :-

Oxidation takes place at anode. Here, the graphite intercalation compound (LiC_6) forms graphite (C_6) and $Li^{\oplus}$ ions.

$$LiC_6 \longrightarrow Li^{\oplus} + C_6 + e^{\ominus}$$

③ Net cell reaction :-

$$LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2$$

During discharging, positively charged $Li^{\oplus}$ ions move from the ~~negatively charged~~ anode to the cathode. Therefore, the electrons are moved from cathode to anode. The $Li^{\oplus}$ ions get deposited to the cathode, and this process continues. When the ~~batter~~ complete deposition of $Li^{\oplus}$ ion in cathode occurs, the battery gets exhausted.

During charging, the exact opposite process happens. The $Li^{\oplus}$ ions move back from cathode to anode.

- As long as the lithium ions are making the trek from one electrode to another, there is a constant flow of electrons. Since, this cycle can be repeated many times, this type of battery is rechargable.

Advantages :-

Li-ion batteries have the highest charge density. of any comparable system. This is due to two reasons-

i) Li is the most electropositive element, hence Li has a high tendency to lose electron. This means it can easily produce a lot of electrical energy

ii) Li is also the lightest of all metals. Hence, the batteries weigh much less than other type of batteries.

Disadvantages :-

i) Not very long-lasting and hence expensive

ii) The production & disposal of such batteries also has a big impact on the environment.

iii) For safety reasons, Li-ion batteries contain a separator. This prevents the electrodes of battery's cells from touching each other. But if this separator gets ripped or damaged, the electrodes then touch each other. This can cause a huge build-up of heat. If this build-up of heat produces a spark, the highly flammable electrolyte can catch on fire. This leads to severe explosion.

Uses :-

i) Mobile, laptops etc., electronic devices, which are portable.

ii) Electric vehicles (e.g. electric motorcycle, scooters, cars, wheel-chairs)

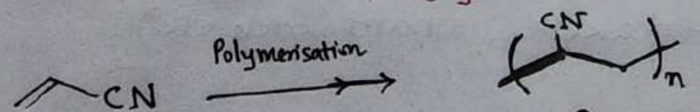
Lithium - Polymer Battery

A lithium-ion polymer battery (LiPo/LIP/Li-Poly etc.) is a rechargable battery of Lithium-ion technology using a polymer electrolyte instead of a liquid electrolyte. Highly conducting semi-solid polymers are used as electrolyte here. The specific energy of such batteries are also higher than normal Li-ion batteries.

Working :- Just like Li-ion battery, LiPo cells work on the theory of intercalation & de-intercalation of $Li^{\oplus}$ ion. To prevent the ~~liquid~~ touching of electrodes a microporous separator is used.

The only difference is that, instead of using a liquid Li-salt electrolyte (eg. $LiPF_6$ in dimethyl carbonate), this battery uses a Solid-polymer electrolyte; such as-

i) Poly ethylene oxide (PEO)
ii) Poly acrylonitrile (PAN)
iii) Poly methyl methacrylate (PMMA)
iv) Poly vinylidene fluoride (PVdf)



vinyl cyanide

Poly acrylonitrile (PAN)

Uses :- i) Mobile & Notebooks, ii) Radio-controlled equipment & aircrafts
iii) Electronic vehicles.

Solid - State battery

A solid-state battery uses solid electrodes & solid electrolytes. Generally, ceramics and solid polymers are used as material in these batteries. These batteries are used in pacemakers & Radio-frequency identifiers (RFID). They have high energy densities and are more safer.

Materials used :-

① ceramics like Lithium orthosilicates, glass & sulfides.

② cathodes can be prepared by the followings -

i> $LiCoO_2$
ii> $LiMn_2O_4$
iii> $LiNi_{\frac{1}{3}}Co_{\frac{1}{3}}Mn_{\frac{1}{3}}O_2$
iv> $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$

③ Anodes can be prepared by the followings -

i> Li_2FeS_2
ii> FeS
iii> Li_2SiS_3
iv> NiP_2
v> $SnS - P_2S_5$
vi> $SnO - B_2O_3$
vii> Ge_xSi_{1-x}

Advantages :-

i> Higher charge density
ii> No toxic materials are used.
iii> As most liquid electrolytes are flammable and most solid electrolytes are non-flammable, solid-state batteries have low risk of catching fire

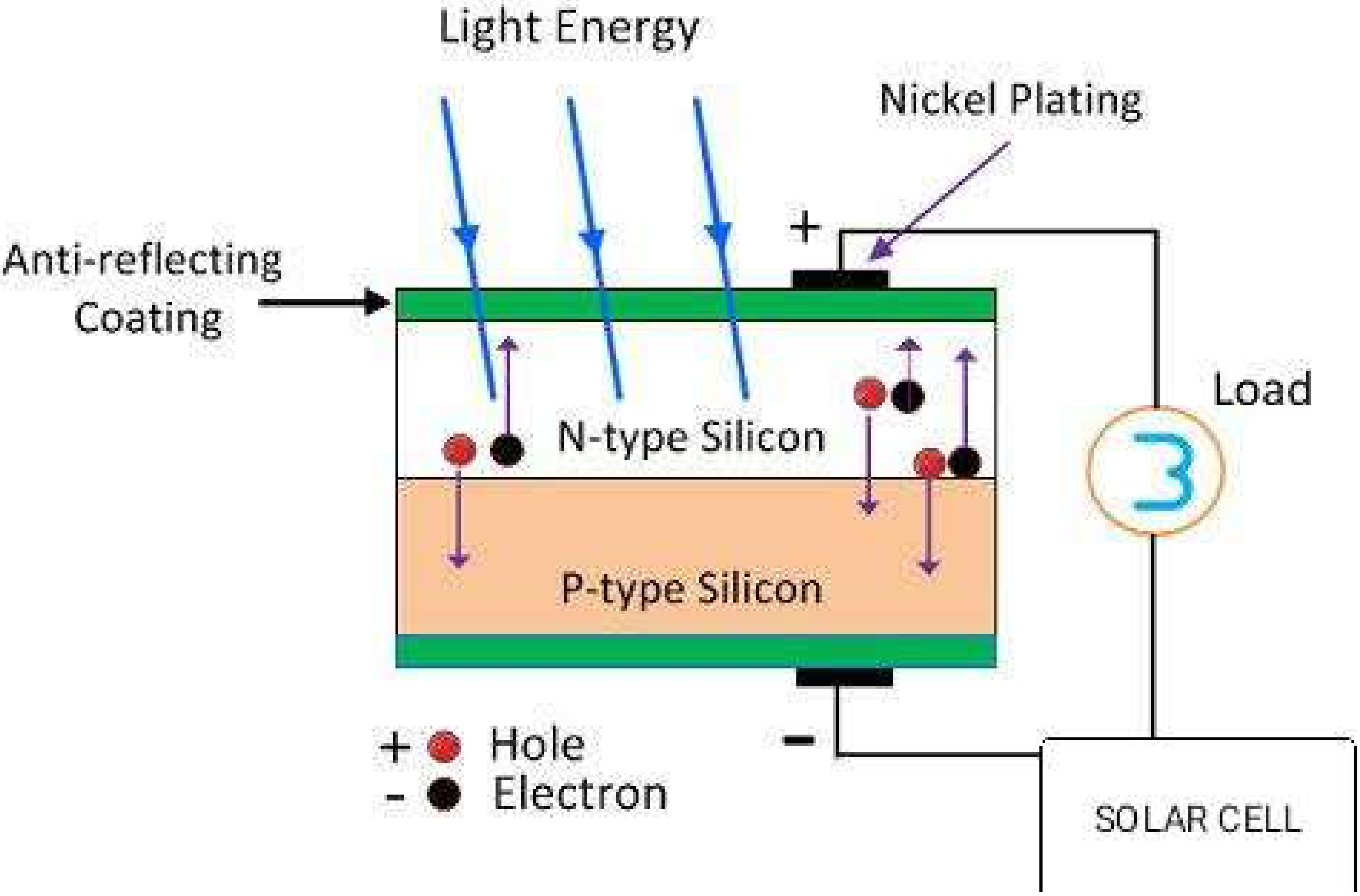
Disadvantages :-

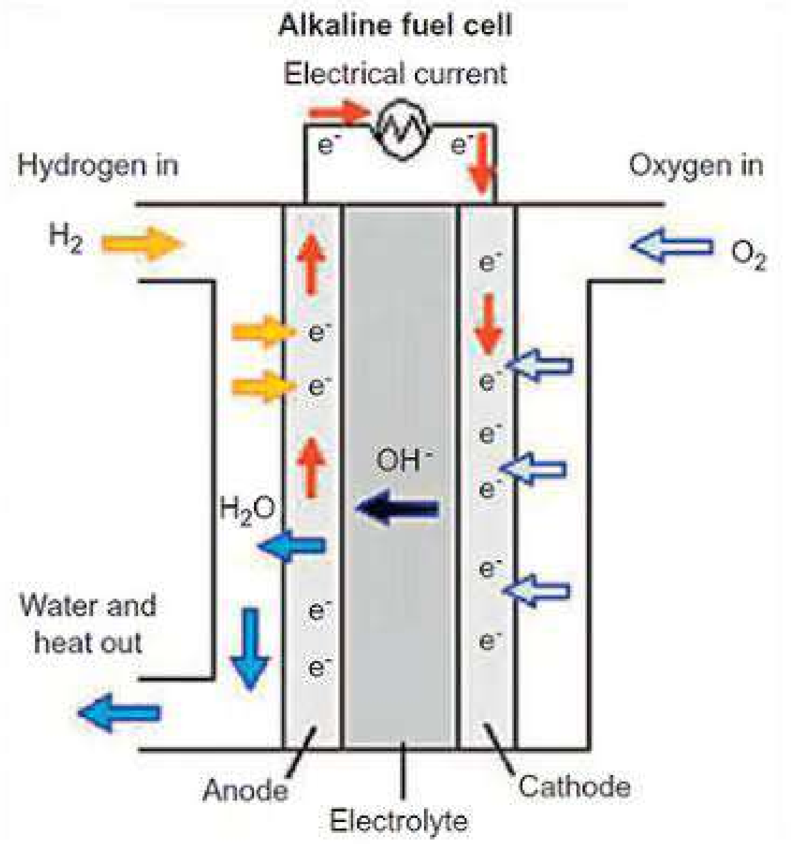
i> Highly expensive
ii> These batteries do not perform well sometimes in low temperature.

Uses :-

i> Used in Pacemakers, RFID and wearable devices (e.g. activity trackers, smartwatch etc)

ii> Electric vehicles.


Light Energy
Nickel Plating
+
Anti-reflecting Coating
N-type Silicon
P-type Silicon
Load
-
+ Hole
- Electron
SOLAR CELL


Alkaline fuel cell
Electrical current
e⁻
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Oxygen in
H₂
O₂
e⁻
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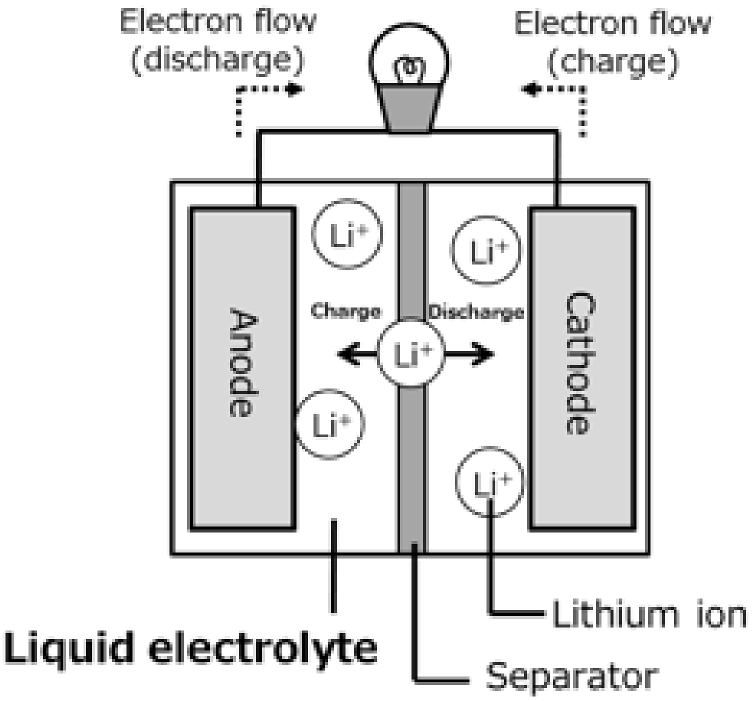
H₂O
Water and heat out
Anode
Electrolyte
Cathode


Electron flow
(discharge)
Electron flow
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Li+
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Anode
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Cathode
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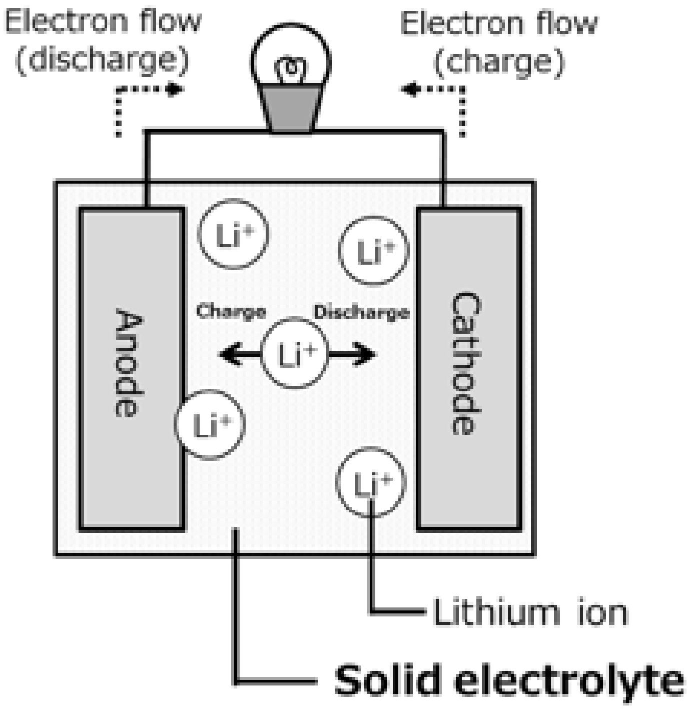
Li+
Lithium ion
Liquid electrolyte
Separator


Electron flow
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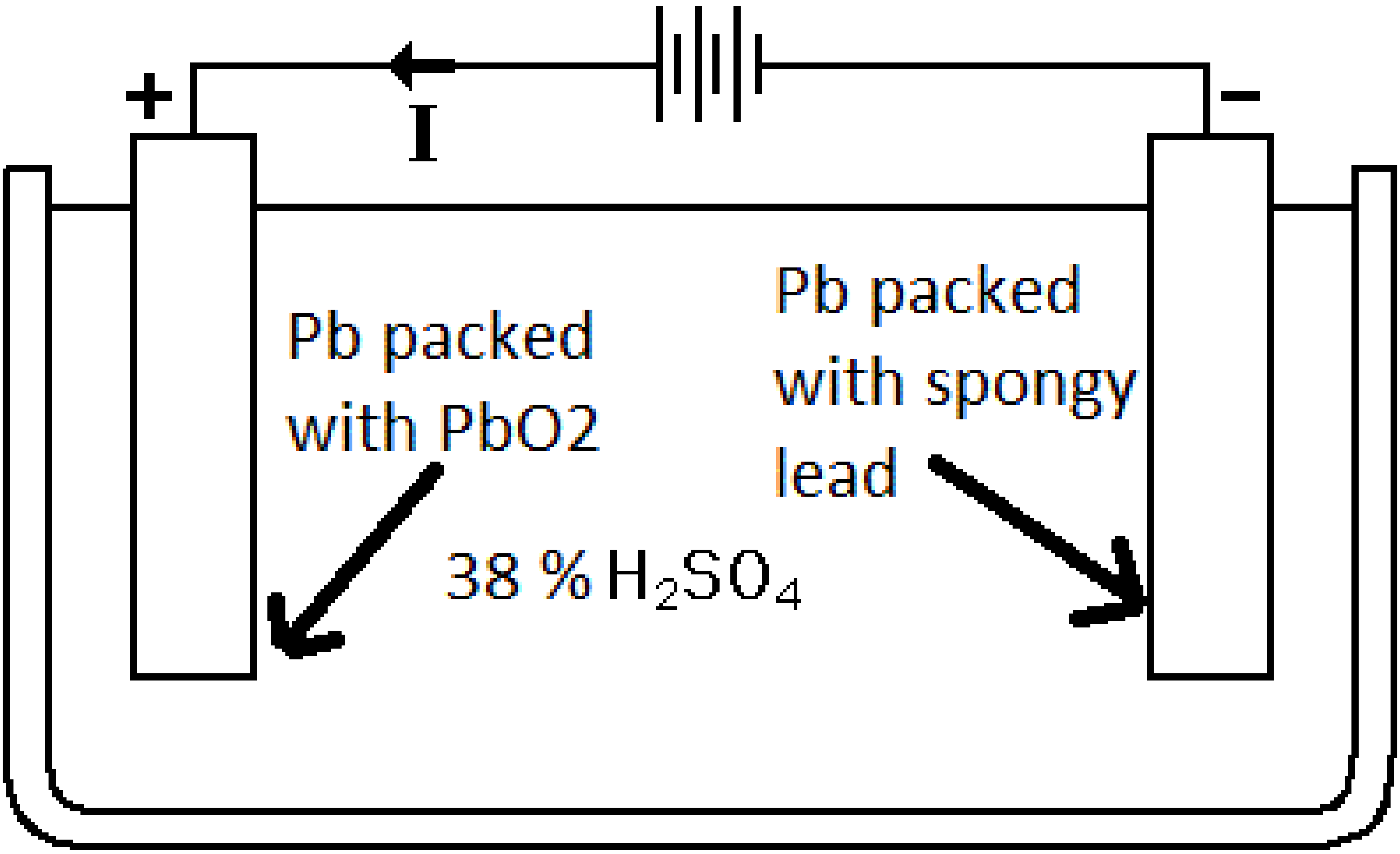
Lithium ion
Solid electrolyte


+
I
−
Pb packed with PbO2
Pb packed with spongy lead
38 % H_2SO_4