

Unit-II

Physical Chemistry

Sem-3

#

Mechanism of hydrogen evolution and oxygen evolution reactions.

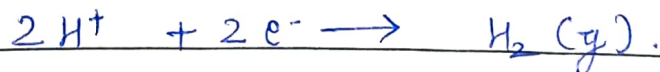
* The Hydrogen evolution reaction and oxygen evolution reaction are two fundamental half reactions that

* These play important roles in electrochemical energy conversion processes, such as water electrolysis and fuel cells.

● Hydrogen evolution Reaction:- (HER)

It involves the conversion of protons (H^+) in an aqueous solution to hydrogen gas (H_2) at a Cathode.

Reaction is :-



Multiple steps takes place to Complete Hydrogen evolution:-
~~Volmer/Steps~~

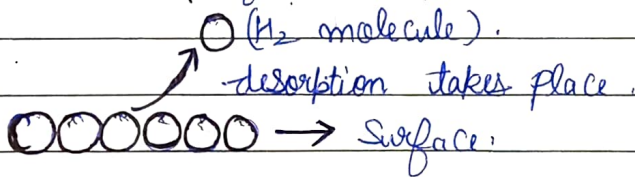
- * Adsorption protons (H^+) onto the electrode surface to form adsorbed hydrogen atoms.



- * Recombination of two adsorbed hydrogen atoms (H^+_{ads}) to form a neutral hydrogen molecule (H_2).



- * Desorption of a hydrogen molecule (H_2) from the electrode surface

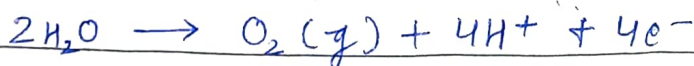


- * The Rate ~~determining~~ determining step of the Hydrogen evolution reaction depends on the electrode material and the electrolyte conditions.

● Oxygen Evolution Reaction :- (OER)

It involves the splitting of water molecules (H_2O) into oxygen gas (O_2) and protons (H^+) at an anode.

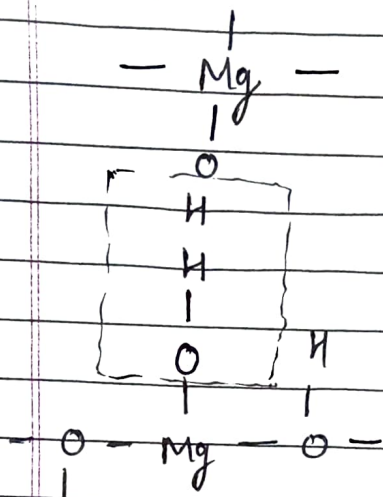
Reaction is :-



Multiple steps takes place to Complete Hydrogen evolution:-

Formation of surface hydroxyl groups:-

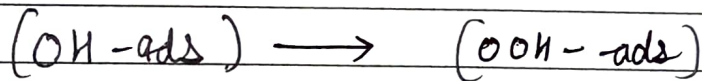
Adsorption of hydroxyl ion (OH^-) onto the electrode surface to form adsorbed hydroxyl groups (OH-ads).



[Surface hydroxyl groups on MgO]

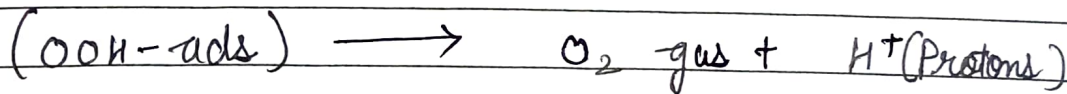
Formation of Surface hydroperoxide:-

oxidation of adsorbed hydroxyl groups (OH-ads) to form adsorbed hydroperoxide (OOH-ads)



oxygen evolution:-

Decomposition of adsorbed hydroperoxides (OOH-ads) to form oxygen gas (O_2) and protons (H^+).



Factors affecting the Mechanism (HER) and (OER)

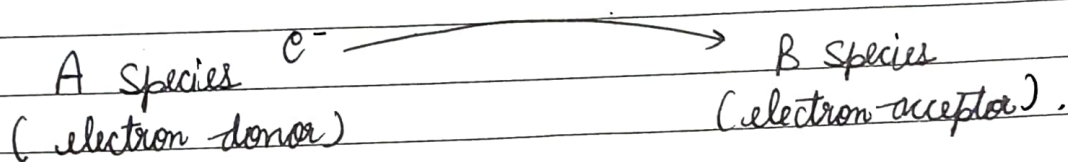
- ① Electrode material
- ② Electrolyte Composition
- ③ pH
- ④ Temperature

Marcus theory:-

* Marcus theory is a theory of electron transfer reactions in electrochemistry.

* It was developed by Rudolph A. Marcus in 1992.

* ~~xxx~~ This theory describes the rate at which an electron can move or jump from one chemical species (called the electron donor) to another (called the electron acceptor).



* Marcus theory states that the rate of an electron transfer reaction is determined by the free energy change of the reaction (ΔG°) and the reorganization energy (λ).

The Rate of an electron transfer reaction:-

$$k = k_0 \exp \left(\frac{\Delta G^\circ}{4 \lambda RT} \right)$$

where, k = Rate constant of the electron transfer reaction

k_0 = pre-exponential factor

ΔG° = Gibbs free energy

λ = Reorganization energy

R = Gas Constant

T = Temperature.

* It is a powerful tool for understanding the behaviour of electrochemical systems.

#

Current density

- * Current density is the amount of electric current passing through a unit area of an electrode.
- * The S.I unit of current density is A/m^2 [Amperes per unit meter square].
- * It determines the rate of electrochemical reaction.

Mathematical Expression of current density:-

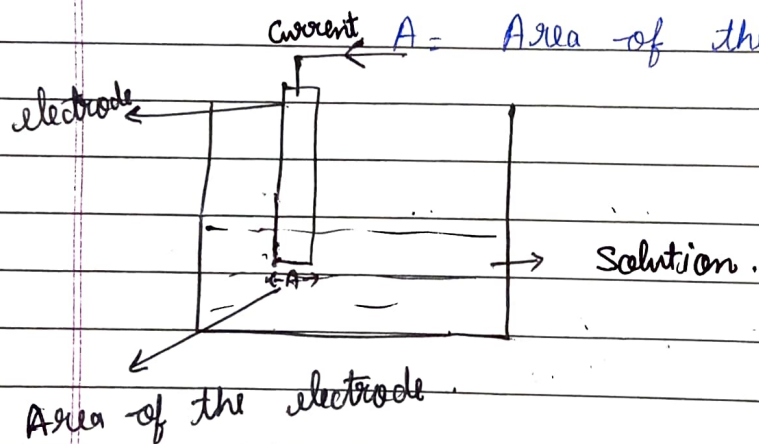
$$J = \frac{I}{A}$$

Where,

J = Current density

I = Total current

A = Area of the electrode



- * The J (current density) is directly proportional to the total current passing on electrode

$$J \propto I$$

- * It means if current increases the current density will increase.
- * if current decreases the current density will decrease.

* The J (Current density) is inversely proportional to the Area of the electrode

$$J \propto \frac{1}{A}$$

* If Area of electrode increase the Current density will decrease.

* If Area of electrode decrease the Current density will increase.

Factors affecting the Current density:-

- (1) Area of the electrode.
- (2) Current passing to the electrode.
- (3) The Conc. of the electrolyte.
- (4) Temperature of the solution.

#

Butler - Volmer equation

It is a fundamental equation in electrochemistry that describes the relationship between the Current density (i) of an electrode reaction and the over potential (η) of the electrode.

Mathematical expression of Butler - Volmer equation:-

$$i = i_0 \left[\exp \left(\frac{\alpha n F}{RT} \right) - \exp \left(-\frac{\beta n F}{RT} \right) \right]$$

Where, i_0 = Exchange current density.

α = Cathodic transfer coefficient.

β = Anodic transfer coefficient.

η = overpotential

F = Faraday Constant

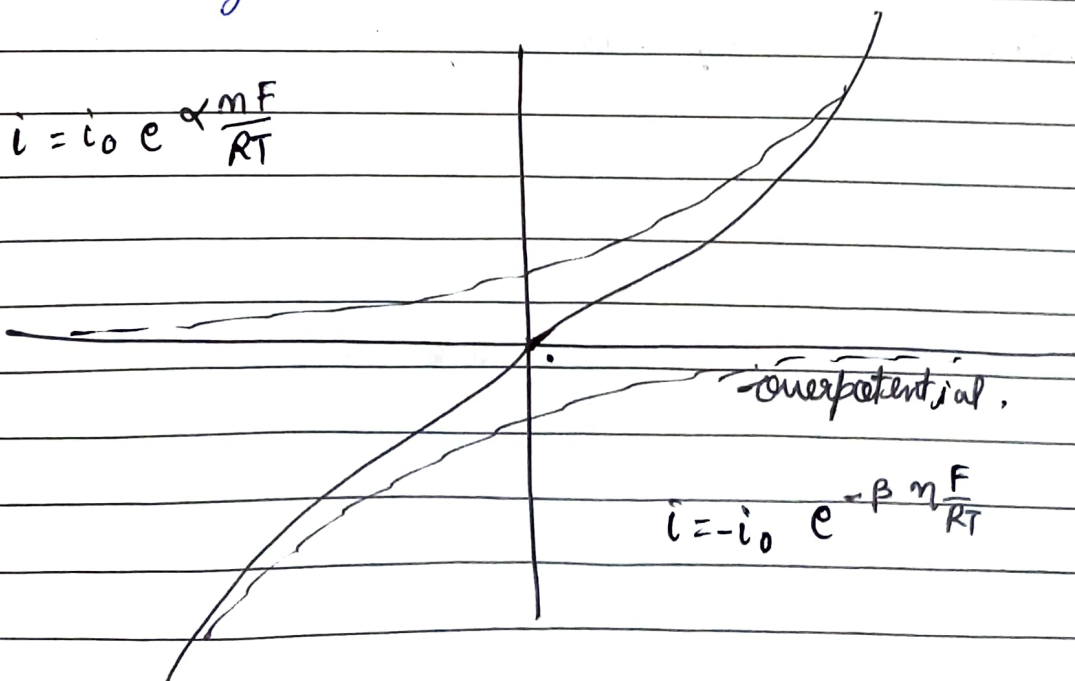
R = Gas Constant.

$T =$ Temperature in K.

- * The current density (i) depend on overpotential (η).
- * If overpotential (η) increase the current density will also increase.
- * If overpotential (η) decrease the current density will decrease.
- * These equation is used to determine the rate of the reaction.

Factors affect the current density in Butler Volmer equation:-

- (1) The temperature affect the current density if temperature increases the current density will change.
- (2) The overpotential (η) affect the current density.



Polarization and overvoltage

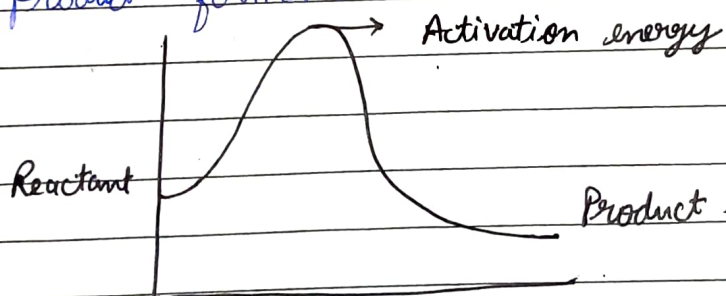
- * In electrochemistry both phenomenon Polarization and overvoltage affect the rate of the reaction.

Polarization:-

- * This is mechanical side effect that occurs at the interface between an electrode and electrolyte when an electric current is passed through the system.
- * This reduces the efficiency of the electrochemical process.
- * There are three main types of Polarization.

Activation Polarization:-

This is the minimum energy required to proceed the reaction from Reactant to product formation.



Concentration Polarization:-

This is the depletion of reactants or the Accumulation of products at the electrode surface.

Res Resistance Polarization:-

This is the Resistance to the flow of electrons through the electrolyte or the electrodes. It is usually negligible in most electrochemical reactions.

● OVERVOLTAGE:-

This occurs when the voltage applied is higher than the needed voltage for the electrochemical reaction.

Factors affect the overvoltage:-

* The nature of the electrode material

Different electrode material have different activation energy for proceeding the reaction. it means the overvoltage depend on the electrode material

* The Concentration of reactant and products

The Concentration can affect the rate of the reaction. it means overvoltage depend on the Concentration of reactant and product.

* The Current density

The Current density directly on the overvoltage. Higher Current density means the higher overvoltage.

* The temperature

The temperature of the electrolyte can affect the rate of the electrochemical reaction. this can also affect the overvoltage.

Methods of protection of metals from Corrosion.

Corrosion

- * It is the process in which metal get Corrode by chemical reaction with its environment.
- * In this process the metal loses the electron to form an ion. This ion react with other environment substance to form a Corrosion Product.
- * If metal is Iron then the Rust word is used. For Iron and Rusting Process take place with iron metal.

There are number of different methods.

* Barrier methods

This Can be done by applying Coating to the metal surface such as paint, plastic etc.

* Electroplating

In this process one metal layer fise to the surface of other metal by using electricity.

* ~~Anodizing~~ Anodizing

It is the electrochemical process that creates a thin oxide film on the surface of a metal. The oxide film Can protect the metal from Corrosion.

* Alloying

It is the process of mixing two or more metals together to form an alloy.

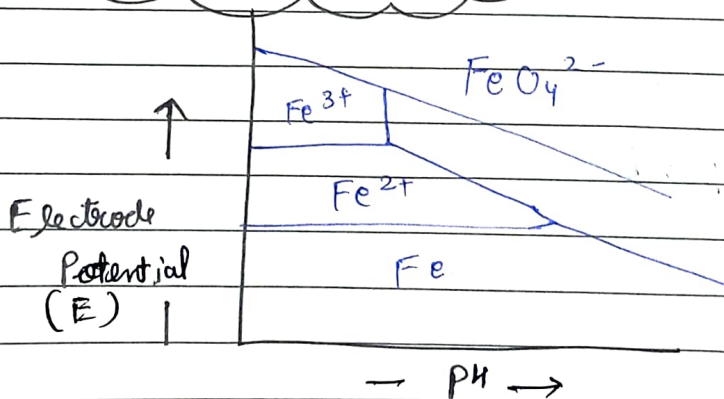
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Pourbaix and Evans diagrams.

* Pourbaix and Evans diagrams are graphical representations of the thermodynamic stability of different chemical species in a system as a function of the electrode potential (E) and pH.

* They are used in electrochemistry and Physical Chemistry to study the corrosion, redox reactions of elements in different environments.

● Pourbaix diagrams: of iron



Pourbaix diagram of iron.

* Pourbaix diagram, also known as E-h-pH diagram

* This graph is constructed between the electrode potential on the Y-axis and

the pH on the x-axis.

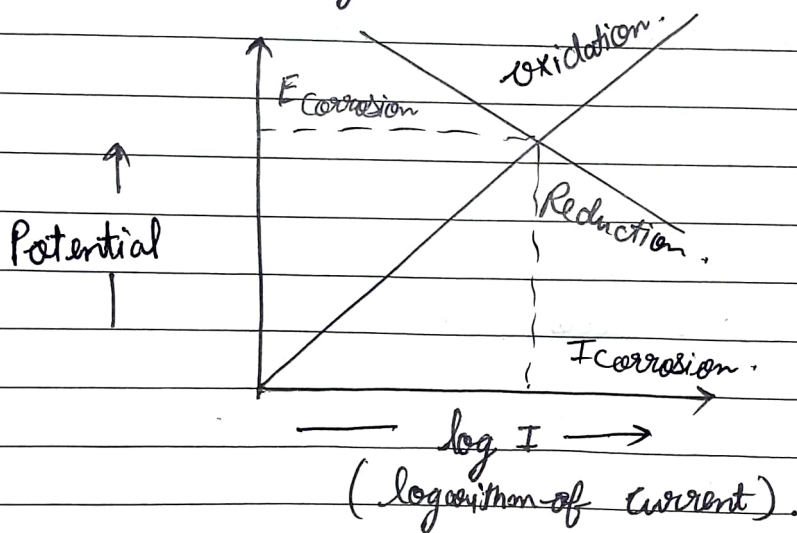
- * The Nernst equation is used to find the electrode potential of the Redox reaction.
- * The Pourbaix diagram can be used to predict the corrosion behavior of metals.

* For Example

→ If electrode potential value is low the metal will corrode.

→ If electrode potential value is high the metal will not corrode easily.

● Evans diagrams.



- * Evans diagram also known as potential - pH diagram.
- * This graph is constructed between the potential ~~and~~ on the Y-axis and logarithm of current on the X-axis.
- * The $E_{corrosion}$ ~~means~~ (corrosion potential) means the metal is just beginning to corrode.
- * The Evans diagram can be used to predict the corrosion behavior of metals.

● Applications of Pourbaix and Evans diagrams

→ Corrosion

Pourbaix and Evans diagram ^{are} ~~is~~ used to predict the corrosion behavior of metal.

→ Geochemistry

Pourbaix and Evans diagram ^{are} ~~is~~ used to predict ~~the~~ understand the behavior of pollutants and to study the formation of minerals.

→ Environmental Chemistry

Pourbaix and Evans diagram ^{are} ~~is~~ used to study the environmental pollutants.

#

Photovoltaic cells

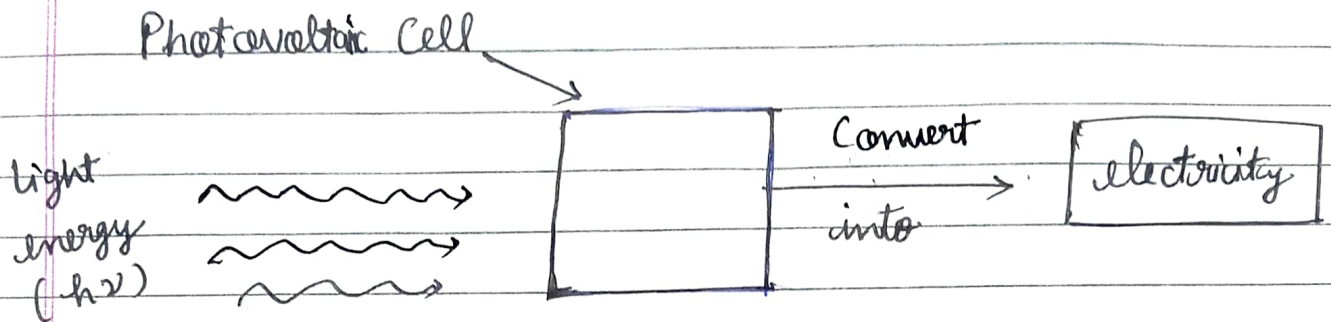
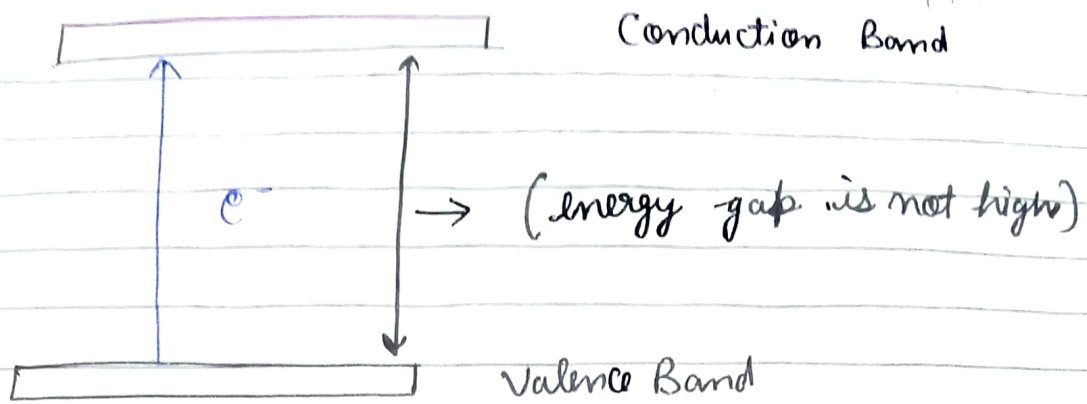
* Photovoltaic cells also known as Solar Cells.

* Photovoltaic cells are electronic devices that convert light energy directly into electricity.

* Photovoltaic cells are made up of semiconductor material.

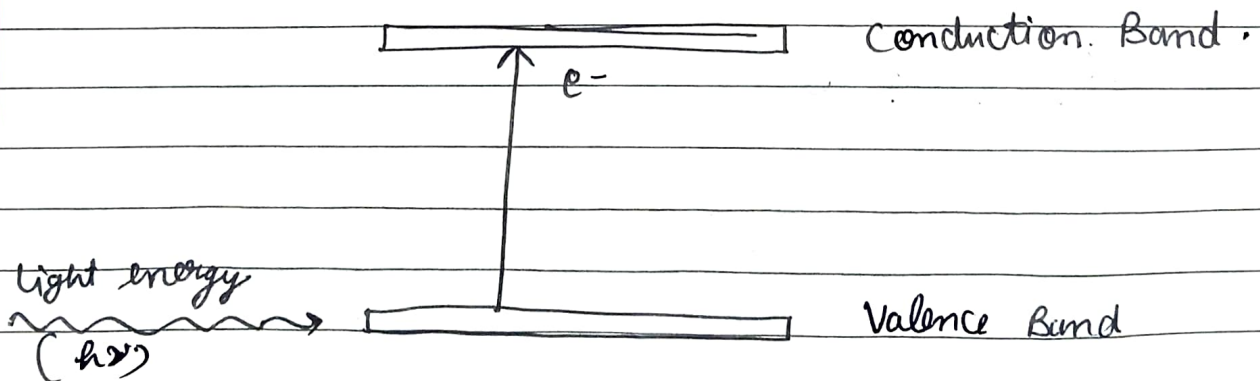
In Semiconductor

The e^- 's are present in valence band. When energy given to semiconductor the electron transfer from ~~semiconductor~~ valence band to conduction band in semiconductor.



Function of Photovoltaic cell

- * When light energy pass on the Photovoltaic Cell. the electron transfer from Valence band to conduction band



- * When e^- move from Valence Band. the +ve hole form.
- * The ~~trans~~ Due to the transfer of e^- from one point to another. the electricity ~~be~~ generate.

• Application of Photovoltaic Cells:-

(1) Solar Power Cell :-

Photovoltaic cell is used in Solar cell to generate electricity from light source.

(2) Portable Power Source :-

Photovoltaic cell is used in portable devices such as solar laptop charges, phones, batteries etc.

(3) Spacecraft Power Systems:-

Photovoltaic cells are used in space craft machinery robots to give power supply.

(4) Building roof cells:-

Now a days most of the private sector company buildings use cells on roof of the building to generate electricity.

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Fuel Cells:-

* Fuel cell is an electrochemical device which convert the ~~an~~ chemical energy into electrical energy by using fuel and an oxidizing agent.

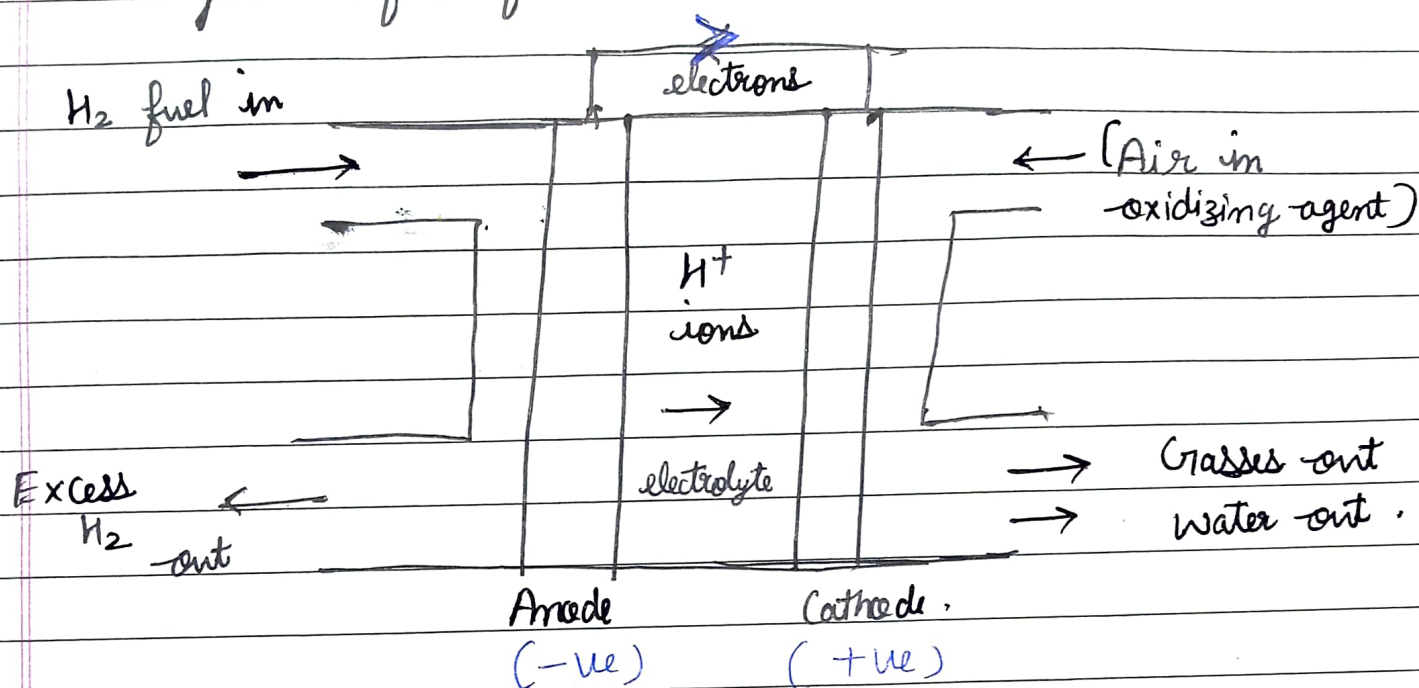
* The Redox reaction takes place in this energy production.

* Fuel cell is totally different from battery because through Fuel cell the continuous electric energy ~~will~~

Can be produce

- * The fuel and oxidizing agent continuously passing to the fuel cell to generate electricity.

Diagram for fuel cell :-



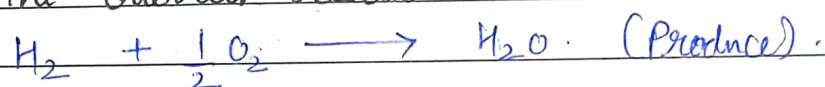
Construction :-

- * Electrodes [Anode and Cathode] are separated by electrolyte.
- * Electrolyte is used to transfer electron from Anode to Cathode.
- * In this Anode is -ve electrode ~~at~~ in this oxidation Reaction takes place means the loss of e^- which transfer to the Cathode.
- * In this Cathode is +ve electrode the Reduction Reaction takes place means the gain of e^- .

Function of fuel cell:-

- * Fuel is pass to the anode electrode
- * The fuel undergoes oxidation reaction at the anode and generate the electrons
- * The electrons transfer from anode to cathode by electrolyte
- * At Cathode Reduction ~~takes~~ Reaction takes place by ~~reducing agent~~ oxidising agent.

The overall reaction



When H_2 fuel is used the H_2O produce as a product.

Application:-

① Transportation

Fuel cells can be used to power vehicles such as cars, buses and trucks.

② Stationary power

Fuel cells can be used to generate electricity for homes, business and industries.

③ Portable power

Fuel cells can be used to power portable device such as laptops, cell phones etc.

④ Spacecraft craft fuel cell can be use.