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Workshop on New Materials for Renewable Energy

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Photoelectrochemical solar energy conversion

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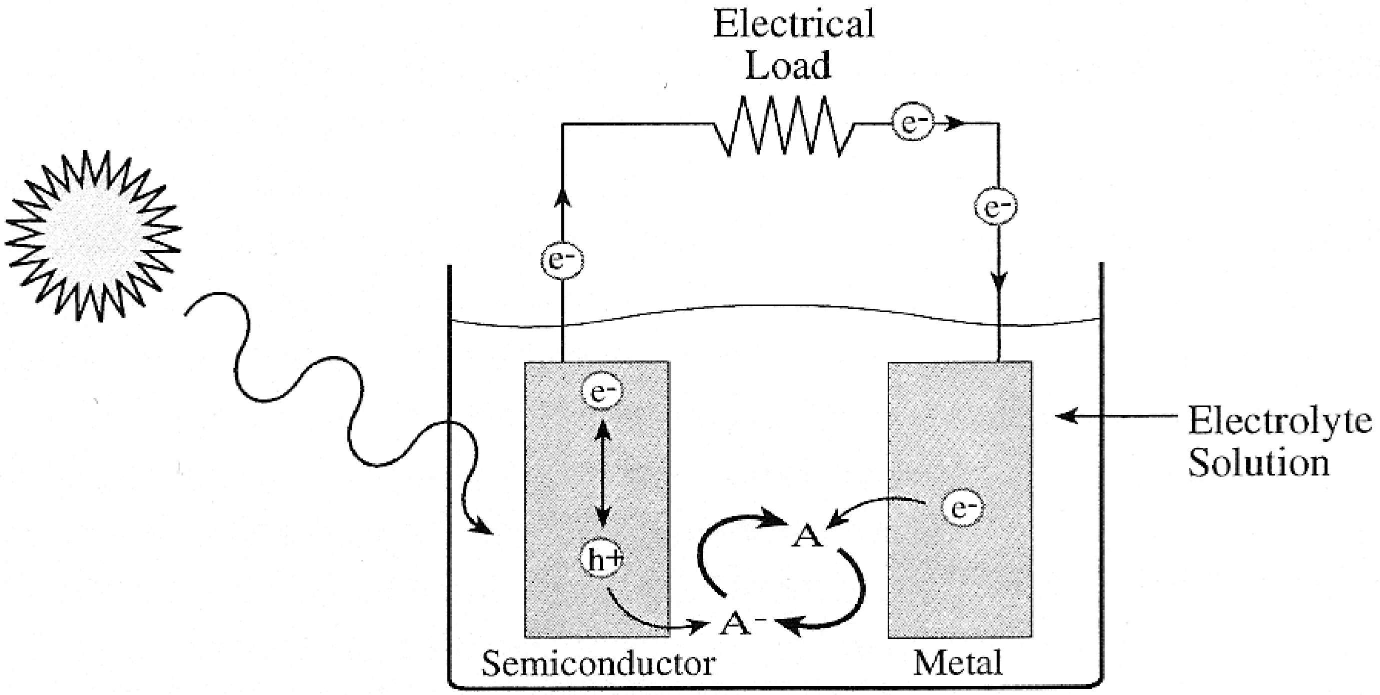
Outline

1. What are PEC cells?
2. Historical Background of PECs
3. The Semiconductor-Electrolyte Interface
4. Performance Characterization of PECs
5. Types of PECs
6. Semiconductor Electrode Stability
7. Semiconductor Electrode Stabilization Techniques
8. Conclusions

1. What are PECs?

PECs convert energy from the sun to electrical energy or to storable energy (chemical fuel)



Basic structure of the PECs

Operation principles

- Absorption of light by the semiconductor electrode creates electron and hole pairs
- The electron-hole pairs separate by the electric field created at the junction
- A voltage can be created as the electrons move towards the unilluminated (counter) electrode.
- The mediator is the electrolyte solution which allows the flow of electrons to proceed completing the circuit.
- Electron and holes drive chemical reactions.
- Light energy is converted into electrical energy or Chemical fuel.

Materials

Photoactive materials: Semiconductors with appropriate band gap and high absorption coefficient

- Inorganic Semiconductor:
  - Si, Ge, CdS, GaAs, CdTe, TiO_2, ZnO, $CuInSe_2$, etc.
- Organic Semiconductors:
  - Small molecules
    - phthalocyanines, porphyrins, etc.
  - Conducting polymers
    - Polythiophenes, polypyrrole, polyaniline, poly(p-phenylene), etc.

Redox couple & Counter Electrode

Redox couple

- Iodide/triiodide
- Eu^{3+}/Eu^{2+}
- Sulphide salt/sulphur
- $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$
- $SeCN^-/(SeCN)_2$
- $SCN^-/(SCN)_2$
- etc.

Counter electrode: Electrochemically stable materials
Usually: ITO, Au, Ag, etc.

If the redox couple is I/I_3^- the reaction at ITO is irreversible and an electrocatalyst coating is required. Commonly used ones Pt or PEDOT

PECs: Advantages

PECs are attractive because

- They can be fabricated with considerable ease since there are no solid-state junctions unlike the case of photovoltaic devices
- They can be used to store energy in the form of chemical fuels in addition to converting light to electricity
- are less expensive
- No front metallization required
- They do not have problems associated with different thermal expansion of solid-state junctions
- The band-bending characteristics of the semiconductor can be conveniently varied by suitable choice of redox couple or concentration of the redox couple
- No anti-reflection coating is required

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2. Historical Background of PECs

- In 1839 French physicist Alexandre-Edmond Becquerel observed and defined the first photovoltaic effect called Becquerel effect
- When Light shine over a chloride electrolyte containing Ag electrode, he observed creation of voltage and charge, call this photovoltaic effect.
- 1883 - first solar cell built, by Charles Fritts, coated semiconductor selenium with an extremely thin layer of gold to form the junctions.

Conti...

- 1952 Bell laboratories made a great success in photoelectrochemistry,
- In 1954, Brattain & Garrett showed how chemical reactions occurring at the surface of germanium semiconductor electrodes could be influenced by controlling the semiconducting properties of the germanium electrode, as well as by exposing the electrode to light.
- Following works on germanium studies of other semiconductor electrodes were continued on Si, CdS, ZnS, CdSe, ZnSe, ZnTe, GaAs, GaP, ZnO, $KTaO_3$, Ta_2O_5, $SrTiO_3$, and TiO_2

Conti...

- 1958 - US satellite *Vanguard1* became the first spacecraft to use solar boards

- In 1972, Fujishima and Honda constructed the first practical application of photoelectrochemical cell with TiO_2 irradiated electrode (photoanode) and Pt as counter electrode (photocathode) which involves photoxidation of water
- H. Gerischer, H. Tribusch, R. Memming, A. Nozik, A. Bard, M. Gratzel, etc.

Conti...

What facilitates situations for photoelectrochemistry to get more focus and wide acceptance?

- The energy crises around the 1970's due to Israeli- Arab conflict,
- Depletion of oil deposition
- The idea of clean hydrogen energy for green environment
- Growth of technology and associated energy demand

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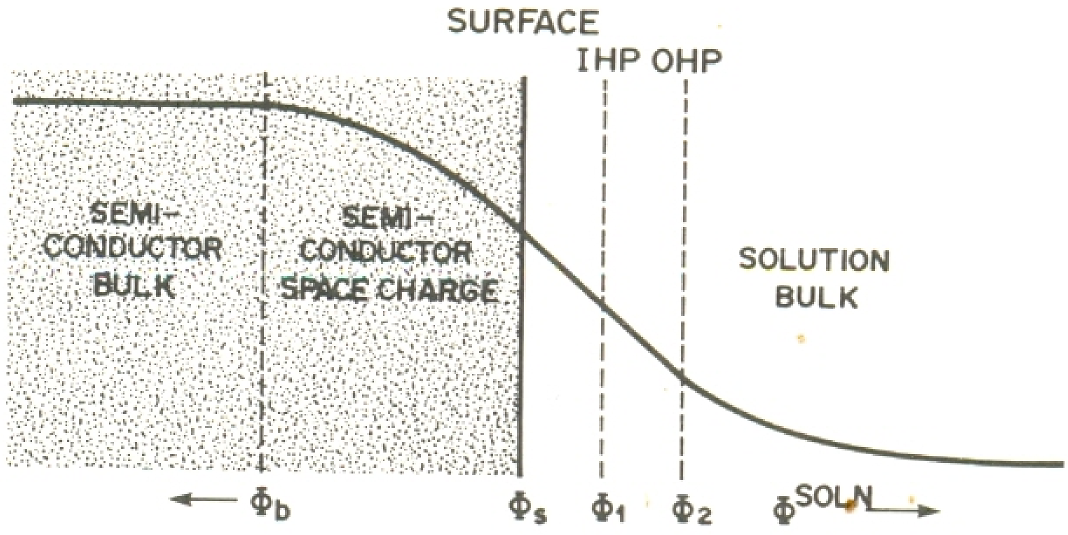
3. The Semiconductor-Electrloyte Interface

- A special relationship between the band energies of the semiconductor and the redox potential of the electrolyte is required to drive the reactions

- **For n-type:** A donor level above or equal to the valence band edge of the semiconductor must exist in the electrolyte

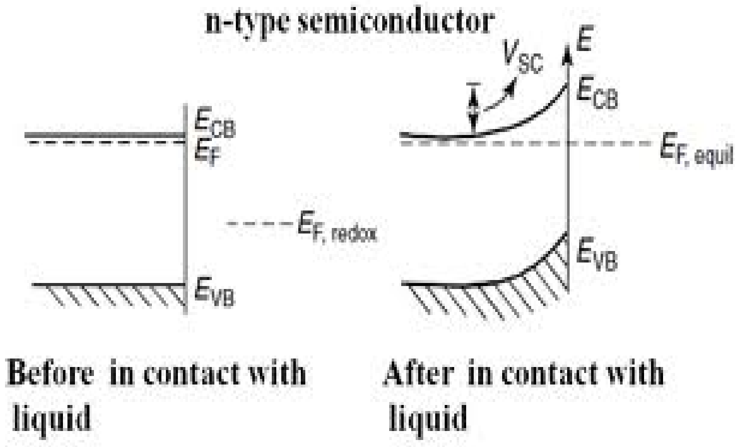
- **For p-type:** An acceptor level below or equal to the conduction band edge of the semiconductor must exist in the electrolyte

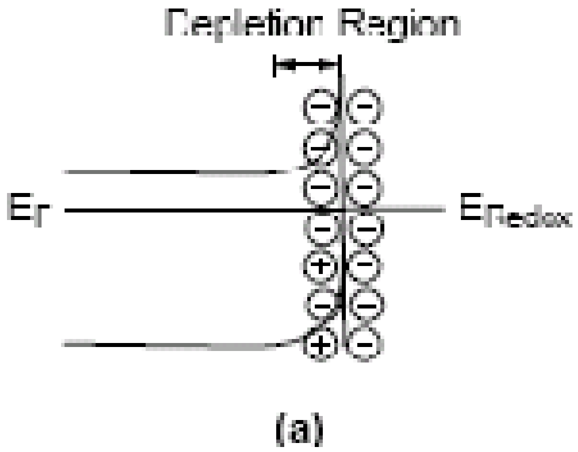
Model of the Semiconductor-Electrolyte interphase



- If the redox potential of the solution and the Fermi level do not lie at the same energy, movement of charge between the semiconductor and the solution takes place in order to equilibrate the two phases.
- Excess charge located on the semiconductor does not lie at the surface as it would for a metallic electrode, but extends into the electrode for a significant distance (100-10,000 Å) - *space charge region.*
- Hence, there are two double layers to consider: the interfacial (electrode/electrolyte) double layer, and the space charge double layer.

Conti...





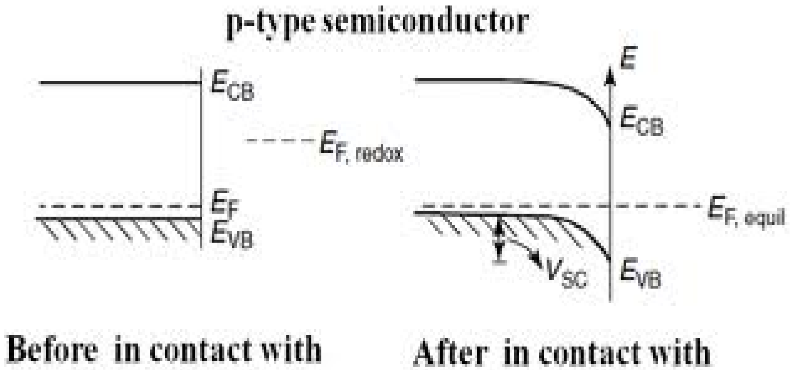
a) Band bending for an n-type semiconductor in equilibrium with an electrolyte

➔For an *n*-type semiconductor electrode at open circuit, the Fermi level is higher than the redox potential of the electrolyte, hence electrons will be transferred from the electrode into the solution

➔positive charge associated with the space charge region, causes an upward bending of the band edges

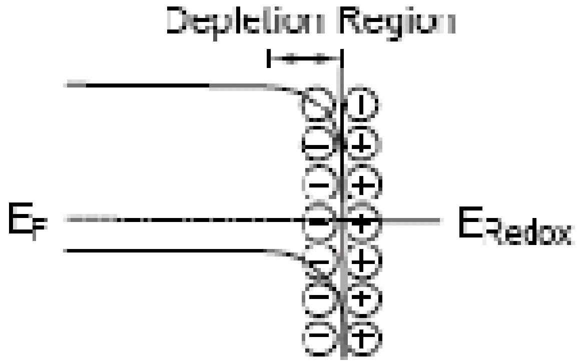
➔as majority charge carrier is removed from this region, this region is referred to as a *depletion* layer.

Conti...



Before in contact with liquid

After in contact with liquid



(b)

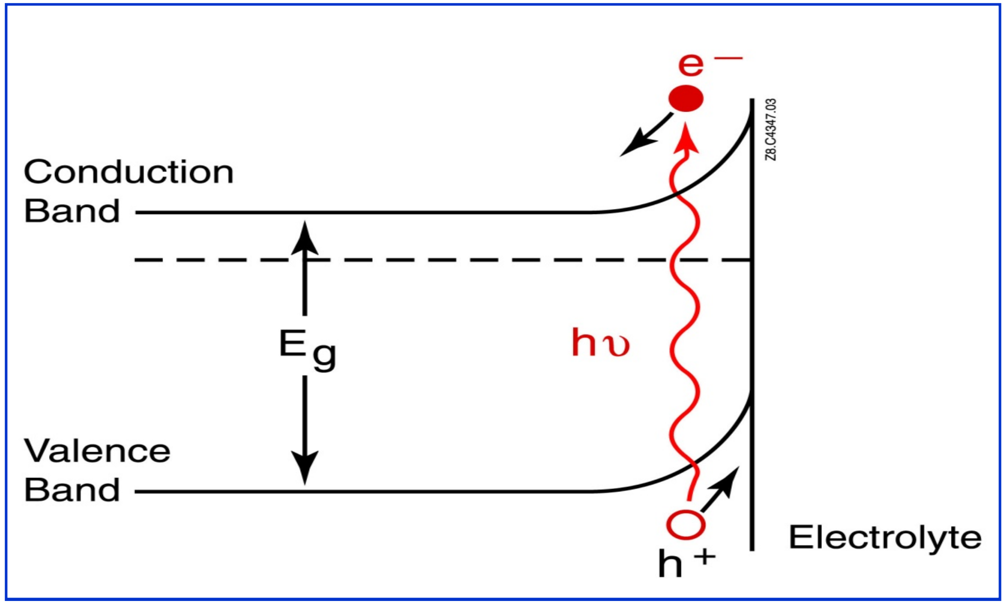
b) Band bending for a p-type semiconductor in equilibrium with an electrolyte

➔For a *p*-type semiconductor, the Fermi layer is lower than the redox potential, hence electrons must transfer from the solution to the electrode

➔generates negative charge in the space charge region, causes a downward bending in the band edges.

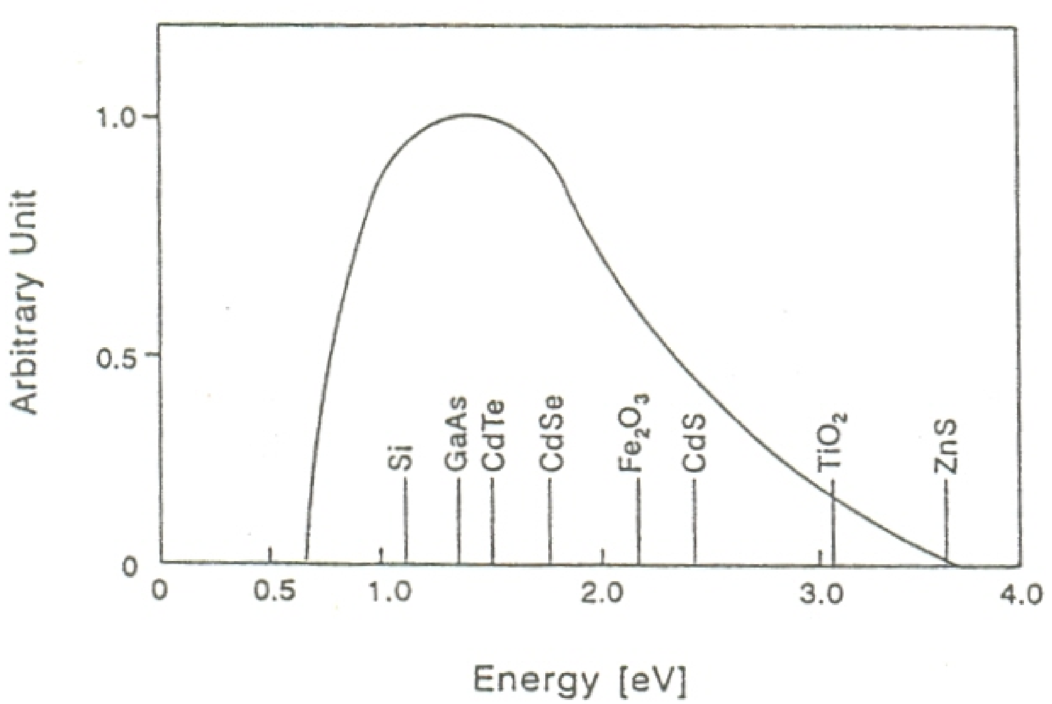
➔Since the holes in the space charge region are removed by this process, this region is again a *depletion layer.*

Photoeffects in Semiconductor-Redox Electrolyte Junction



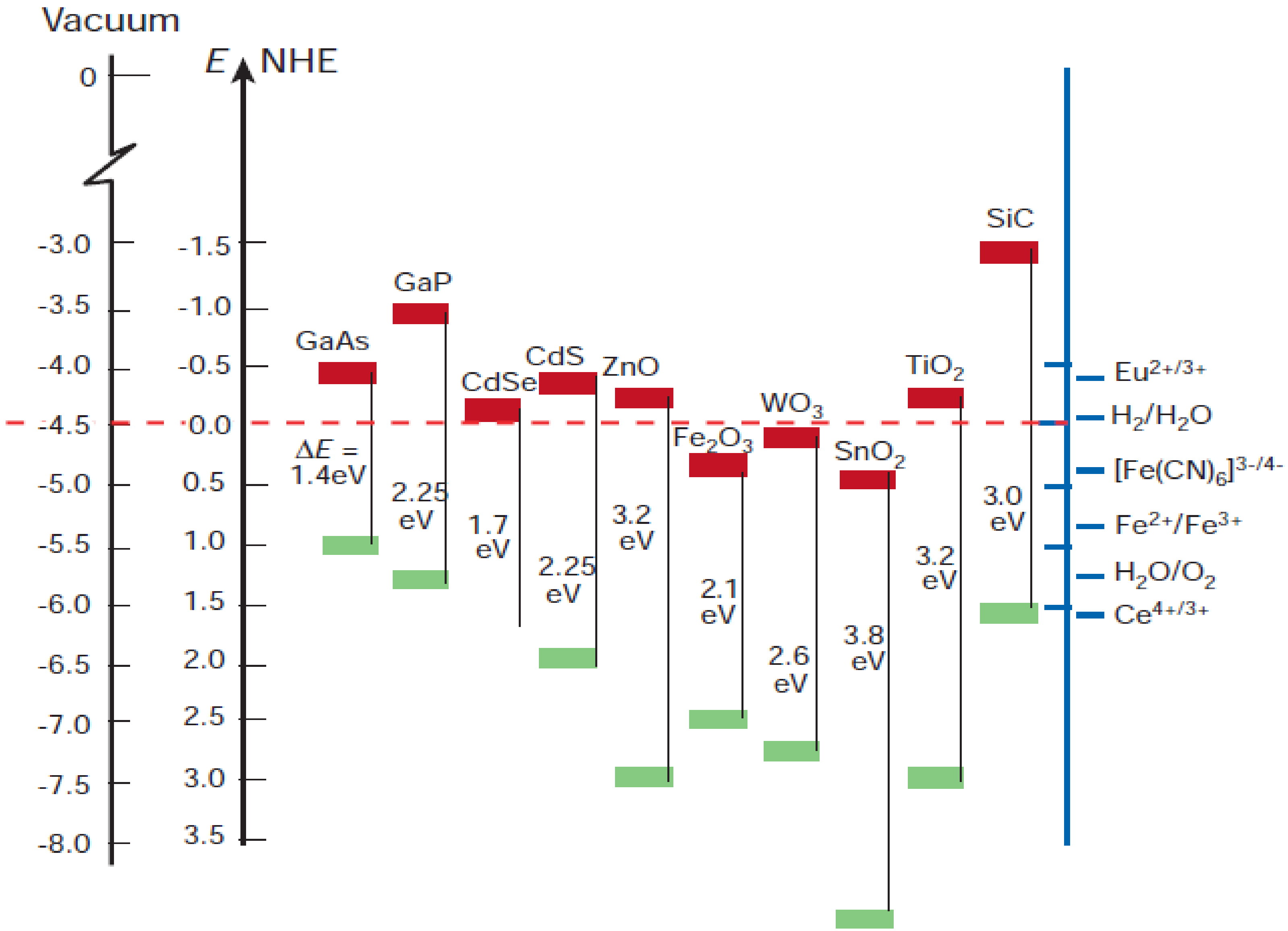
Absorption of light in depletion layer results in creation and separation of electron-hole pairs. For n-type semiconductors, holes move toward surface and electrons toward semiconductor bulk. For p-type semiconductors, reverse process occurs. Redox couples in electrolyte capture injected photogenerated carriers and reactions occur.

Solar Energy absorption by semiconductors of different band gaps



- low band gap materials absorb more of solar radiation, but are easily photodegradable.

Photoelectrochemical energetics of semiconductors



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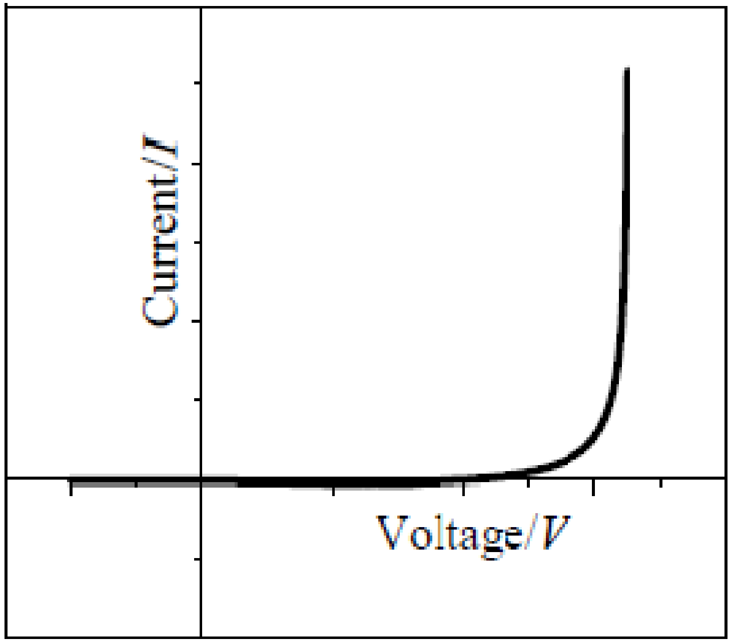
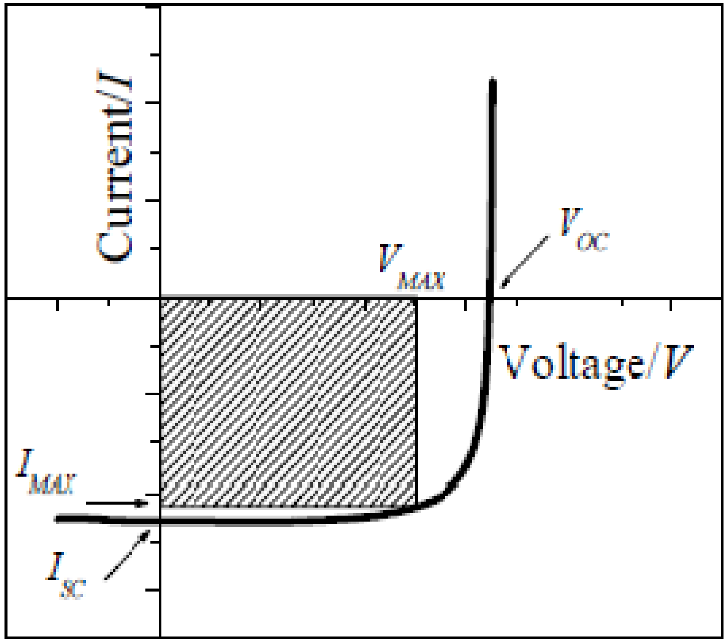
4. Characterization of PECs

There are different characterization techniques of which I-V curve characterization is the most commonly used.

- Upon illumination of solar radiation to the cell the I-V response is obtained



In the absence of light



With light

Conti...

a) Open Circuit Voltage (V_{OC})

- The max. voltage at zero current , V (at I=0) = V_{OC}

$$V_{oc} = \frac{nkT}{q}\ln\left(\frac{I_{ph}}{I_0}+1\right)$$

Where I_{ph} = photo-generated current

b) Short Circuit Current (I_{SC})

The max. current that can obtained when the cell potential is zero.

I (at V=0) = I_{SC} (μA/cm^2)

Conti...

c) Maximum Power (P_{MAX}),

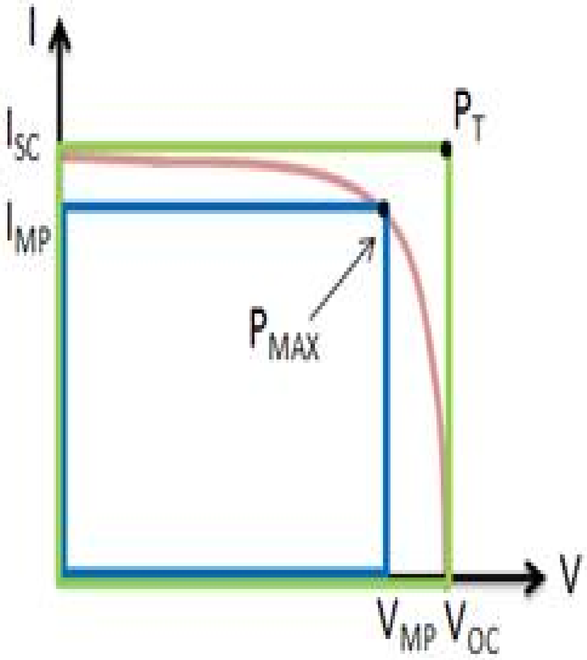
The max. power produced by the cell

$$P_{max} = V_{Max} I_{Max}$$

P_{max} is zero at I_{sc} and V_{oc}

d) Fill Factor (FF)

$$FF = \frac{P_{MAX}}{P_T} = \frac{\boxed{I_{MP} \cdot V_{MP}}}{\boxed{I_{SC} \cdot V_{OC}}}$$



P_T-Theoretical max. power

Conti...

e) Power Conversion Efficiency (η)

The ratio of electrical output to solar power input and mostly given in percent

$$\eta = P_{out}/P_{in} = (I_{max}V_{max})/P_{in}$$

$$\eta(\%) = \frac{P_{out}}{P_{in}} x\,100 = \frac{FF I_{sc} V_{oc}}{P_{in}} x\,100$$

Conti...

f) Incident Photon-to-current Conversion Efficiency IPCE (EQE)

- the ratio of the number of collected charge carriers to the number of incident photons at each wavelength

$$IPCE\% = \frac{E_{ph}(\lambda) I_{sc}}{I_{in}\, e} = \frac{1240 I_{sc}}{\lambda I_{in}}$$

Where E_{ph} (λ) is the energy of a photon,

I_{in}- intensity of incident photon,

λ- wavelength

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5. Types of PECs

PECs can be classified based on their Gibbs free energy change (ΔG) of the redox electrolyte as;

1) Photoelectrosynthetic PECs - have $\Delta G \neq 0$

Solar energy → chemical energy

a) Photoelectrolysis;

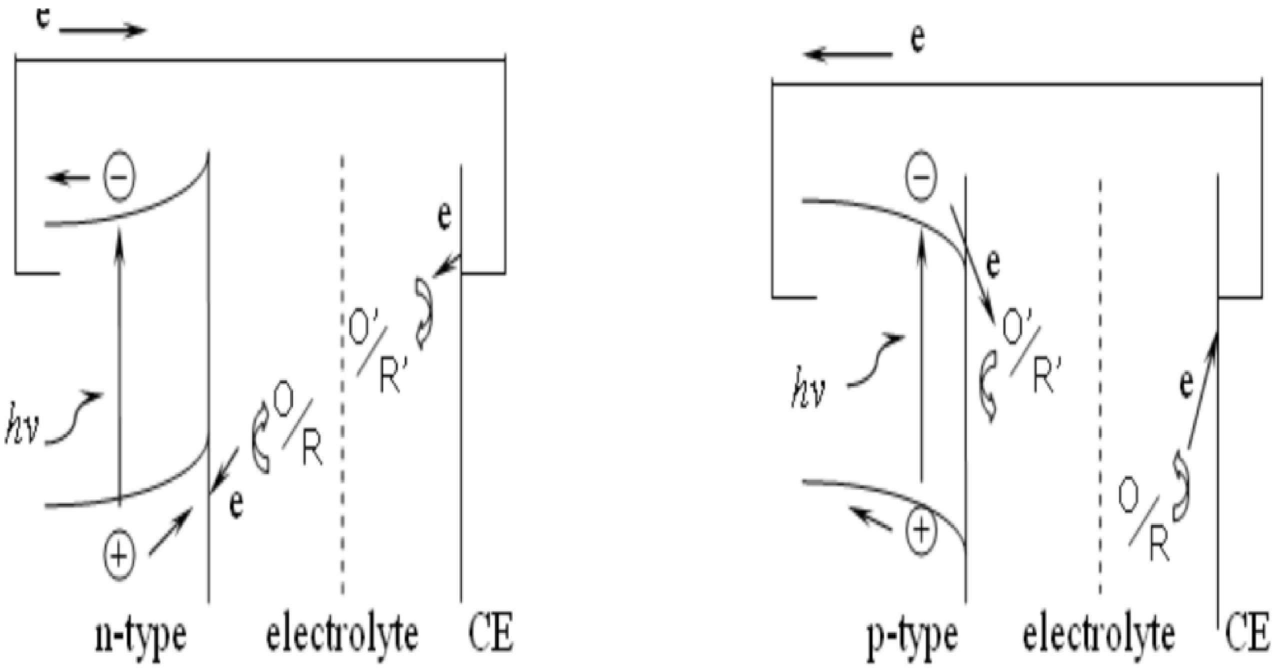
✓$\Delta G > 0$

✓The anodic reaction has more positive redox potential than the cathodic reaction so that the overall Gibbs free energy is +ve

$$\Delta G = -nFE^{o}$$

Conti…

- **Converts Solar energy as stored chemical energy**



Electrochemical photoelectrolytic cell

Conti…

There are two redox systems

e.g. For $2H_2O \rightarrow 2H_2 + O_2$ (the most important)

- one reacting with the holes at the surface of the semiconductor electrode (at the anode)

$$4OH^- + 4h^+ \rightarrow O_2 + 2H_2O\ ,\ E^o_{O2/OH-} = 0.401\ V_{NHE}$$

- the second reacting with the electrons entering the counter-electrode (at the cathode)

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-\ ,\ E^o_{H2O/H2} = -0.828\ V_{NHE}$$

The overall reaction is the cleavage of water by sunlight.

$$2H_2O \rightarrow O_2 + 2H_2 \qquad E^o_{cell} = 1.229\ V_{NHE}$$

Conti…

Attractive feature of water photoelectrolysis to hydrogen;

- Hydrogen can be stored much more easily than either electricity or heat
- Nonpolluting, renewable, inexhaustible, and very flexible with respect to conversion to other forms of energy (heat via combustion or electricity via fuel cells)
- Besides to energy, it is handy in ammonia synthesis and petroleum refining
- Reliable abundance

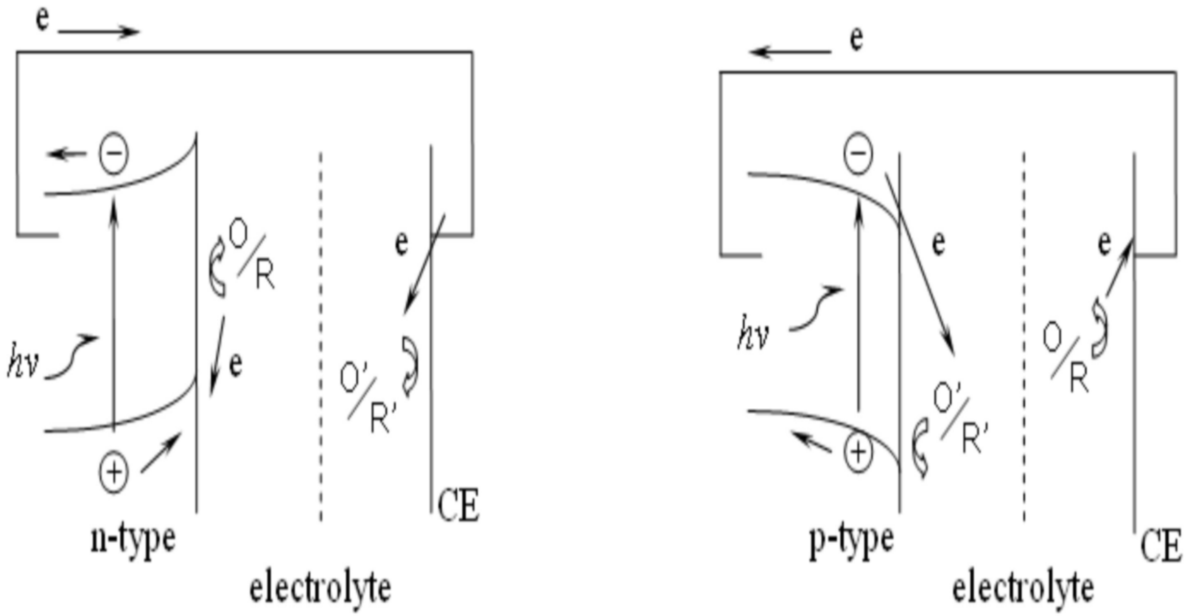
Conti…

b) Photocatalytic PECs;

- $\Delta G < 0$
- Solar energy gives activation energy for the reaction.

$$e.g.\ N_2 + 3H_2 \rightarrow 2NH_3$$

- The reaction is thermodynamically exothermic



Electrochemical photocatalytic cell

Conti…

2) Electrochemical photovoltaic cells

- Also called **Regenerative PECs**
- Have $\Delta G = 0$
- solar energy → electrical energy
- Contains two interfaces at which charge transport to switch from electronic to ionic and vice versa as in battery
- The semiconductor may be n- or p- type

Conti…

When shining the sun light;

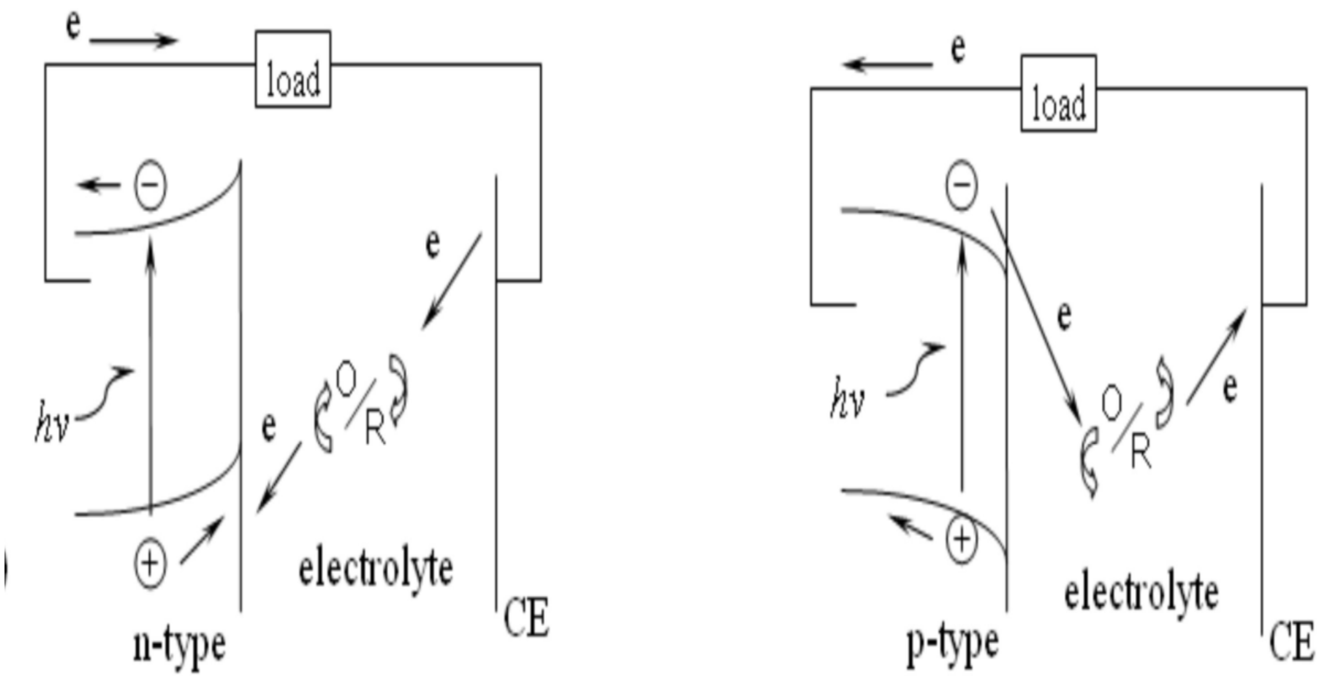
-oxidation reaction will occur on the surface of n-type semiconductors,

-reduction reaction will happen on the surface of p-type semiconductors.

-The electrochemical reaction occurring at the counter electrode (CE) is opposite to the reaction at the semiconductor working electrode.

Conti…

- **Photons of energy exceeding the band gap generate electron–hole pairs, which are separated by the electric field present in the space-charge layer**



Electrochemical photovoltaic cell

Conti…

a) Electrochemical photovoltaic cells without dyes

Also known as wet-type photoelectrochemical cells

- ✓ Both the semiconductor electrode and the counter electrode are immersed in the redox electrolyte,
- ✓ The incident light excites the semiconductor electrode and the photogenerated electrons and holes are separated in the space charge region,

Conti…

- ✓ Specific reactions occur only at the semiconductor and the metal

  $\text{Red} + h^{+} \rightarrow \text{Ox}^{+}$ (anode reaction) and,

  $\text{Ox}^{+} + e^{-} \rightarrow \text{Red}$ (cathode reaction)

- ✓ Charge is balanced due to oxidation and reduction processes in the electrolyte

- ✓ Such cells suffer instability of semiconductor in aqueous media which makes it to be less efficient to replace solid-PV

Conti…

b) Dye sensitized (Gratzel) solar cells (DSSC)

Composed of;

-nanocrystalline semiconductor oxide film electrode,

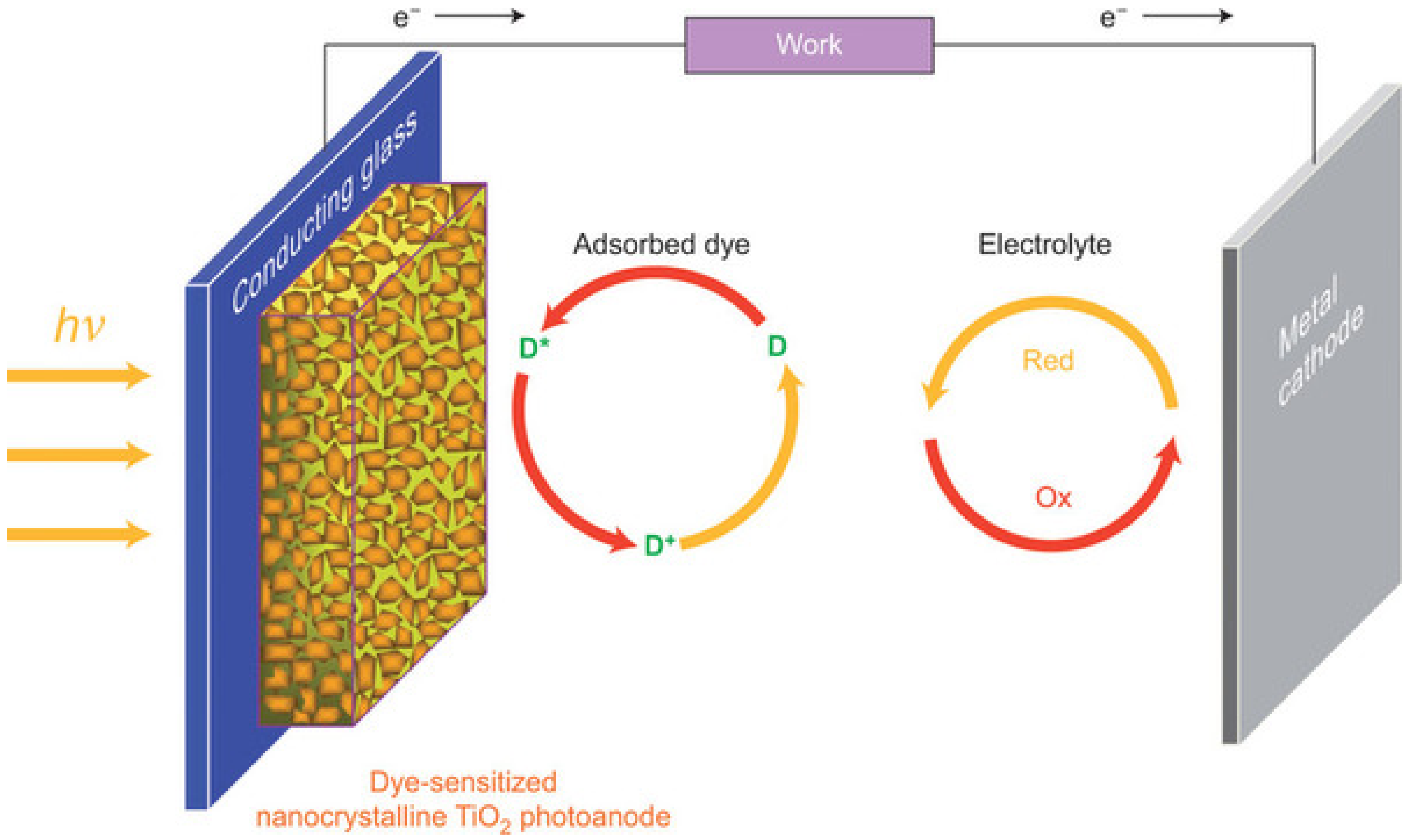
-dye sensitizers (photoactive),

-electrolytes,

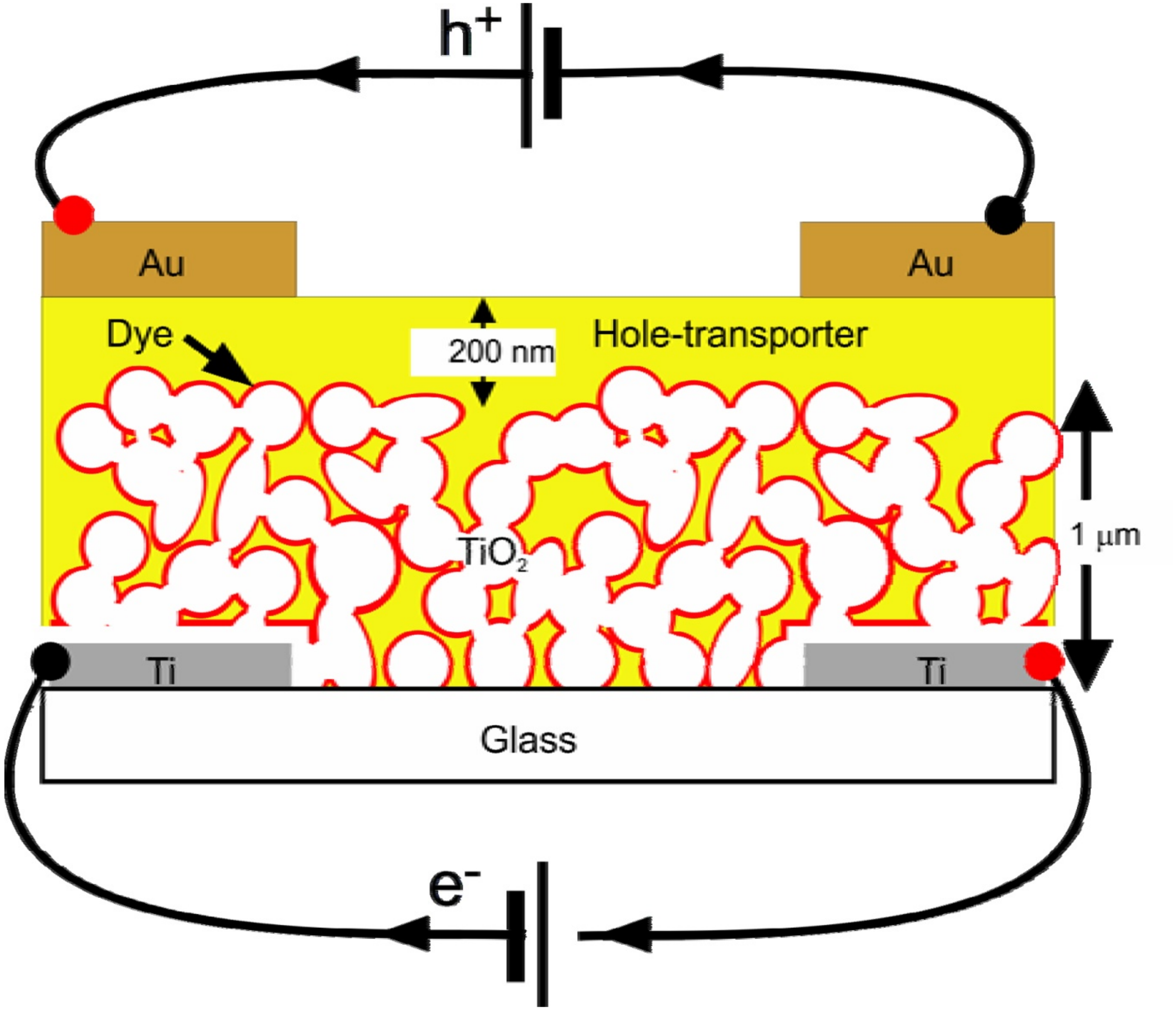
-counter electrode and transparent conducting substrate.

- The first DSSC was reported by Grätzel with PCE 7.1% and currently it reach over 12% though the maximum expected is 30%

Conti…


e⁻
Work
e⁻
Conducting glass
hν
Adsorbed dye
D*
D
D⁺
Electrolyte
Red
Ox
Metal cathode
Dye-sensitized
nanocrystalline TiO₂ photoanode

Conti…



The prototype solid state DSSC

Conti…

- Dye-derived nanocrystalline titania films used as photoanode, platinized counter electrode, filled with electrolyte solution of I_3^-/I^- in organic solvent, then the sandwiched solar cells are formed.

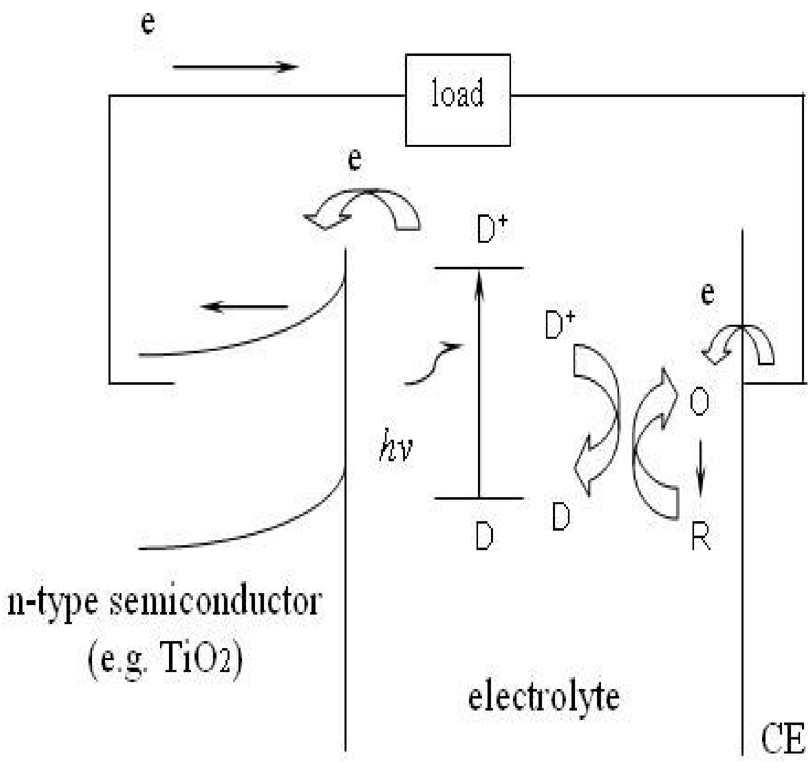
- Unlike electrochemical photovoltaic cells the initial photoexcitation does not occur in the semiconductor working electrode, but occurs in the light absorbing dye.

Conti…

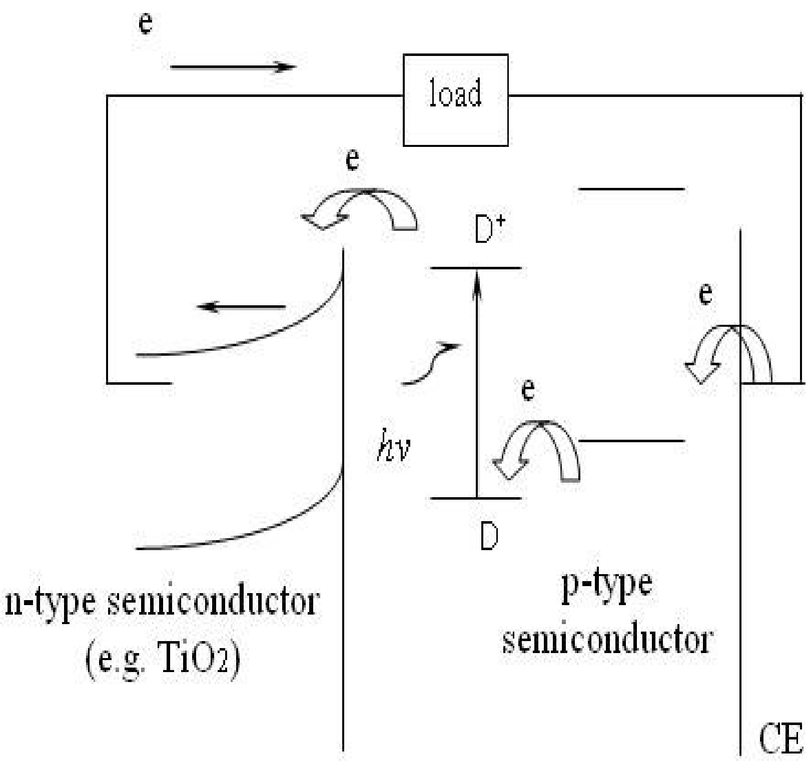
- Subsequent injection of an electron from the photo-excited dye into the conduction band of semiconductors results in the flow of current in the external circuit.

- Sustained conversion of light energy is facilitated by regeneration of the reduced dye (D) either via a reversible redox couple (O/R), which is usually I_3^-/ I^- or via the electron donation from a p-type semiconductor.

Conti…



a)



b)

Wet-type DSSC with redox couple in the electrolyte

Solid state DSSC with p-type semiconductor which replaces the redox couple

Conti…

Traditional wet-type DSSC contains redox couples electrolyte

a) The photoanode, made of a mesoporous dye-sensitized n-type semiconductor (TiO_2, ZnO, SnO_2, Nb_2O_5, etc…), receives electrons from the photo-excited dye (D)

$$D + h\nu \rightarrow D^+ + e-$$

b) The neutral dye (D) is regenerated by the oxidation reaction ($R \rightarrow O$) of the redox couple dissolved in the electrolyte.

$$R + D^+ \rightarrow O + D$$

Conti…

c) The mediator R will then be regenerated by reduction at the cathode (O → R) by the electrons circulated through the external circuit

- Overall, electric power is generated without permanent chemical transformation.
- The major advance in DSSC was made by the use of a high surface area nanoporous TiO_2 layer which gives high photon to electron conversion efficiencies

Conti…

Dyes synthesizers (photoactive Components)

The dyes (Sensitizers) used in DSSC may be organic and inorganic

- ✓ organic dye includes natural organic dye and synthetic organic dyes,
  - o easy to be designed and various in style with molar extinction coefficient and low cost.
- ✓ Inorganic dye includes metal complex, such as polypyridyl complexes of ruthenium and osmium, metal porphyrin, phthalocyanine and inorganic quantum dots,
  - o Have high thermal and chemical stability

Conti…

The requirement for photoactive dye that used for DSSC;

a) Should absorb all light below a threshold wavelength of about 920 nm.

b) Should be tightly attached to the semiconductor oxide surface

c) Its redox potential should be sufficiently high so that it can be regenerated rapidly by electron donation from the electrolyte or a hole conductor.

d) It should be stable enough to sustain at least 10^8 redox turnovers under illumination corresponding to about 20 years of exposure to natural light.

Conti…

❑ Electrolyte

- Is one of the key components for dye-sensitized solar cells and its properties have much effect on the conversion efficiency and stability of the solar cells.

The electrolyte used in DSSC is divided into three types:

a) Liquid electrolyte,

  - Organic solvent electrolyte
  - Ionic liquid electrolyte

b) Quasi-solid state electrolyte,

c) Solid electrolyte

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6. Semiconductor Electrode Stability

- Narrow band-gap semiconductors whose photo-response matches the solar spectrum are in general unstable in contact with electrolytes.

- When a hole reaches the interface the most likely object of an oxidation reaction is the material of the semiconductor itself! e.g. $CdS + 2h^+ \rightarrow Cd^{2+} + S$.

  This is an example of photocorrosion.

  Wide band-gap semiconductors have stronger chemical bonding, and are therefore more stable.

  One of the earlier application of conducting polymers were photocorrosion prevention.

- Wide band-gap semiconductors are more stable but absorb only the small portion of the solar radiation.

Conti…

- h^+ or e^- instead of being injected into electrolyte cause decomposition
- Causes inoperability or short electrode life times
- Typical decomposition reactions

  Anodic

  - $CdS + 2h^+ \rightarrow Cd^{2+}(aq) + S$
  - $ZnO + 2h^+ \rightarrow Zn^{2+} + 1/2O_2$

  Cathodic

  - $CdS + 2e^- \rightarrow Cd + S^{2-}(aq)$
  - $ZnO + H_2O + 2e^- \rightarrow Zn + 2OH^-$

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7. Semiconductor Electrode Stabilization Techniques

- Degradative corrosion: e.g. n-GaAs, n-CdS
- Inactive film formation: e.g. n-Si

a) Conducting polymer Coating

- Demonstrated for n-type Si, GaAs, CdS, GaP, CdTe with polypyrrole, polyaniline, polythiophene, etc

b) Use of redox couples

For electorchemical photovoltaic cell

- Demonstrated for n-CdS electrode with sulfide/polysulfide (S^{2-}/S_n^{2-})

Conti…

c) Overcoating with wide band gap semiconductors or metal films

- Demonstrated for TiO_2 on n-type Si, GaAs, CdS, GaP, InP

d) Chemical derivatization of semiconductors

$$h^+ + [A]_{surf} \rightarrow [A^+]_{surf} + S$$

$$[A^+]_{surf} + B \rightarrow [A]_{surf} + B^+$$

- Demonstrated for n-Si, with ferrocene based polymer to oxidize $Fe(CN)_6^{4-}$ in aqueous solution

e) Use of polymer electrolytes (ion conducting polymers) to produce all-solid-state PECs

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Conclusions

- Photoelectrochemistry has vivid future to answer our globe energy demand and envirnomental issues.
- To realize this semiconductors which are stable, cost-effective and efficiently absorb in the intense solar flux region (600-1100 nm) to get better output is required
- Photoelectrochemical solar energy to chemical fuel compete with photosynthesis
- Photoelectrochemical solar energy to electricity compete with solid state photovoltaic device

Thank You!!!