Energy Conversion by Semiconductor Devices

Jun-Ho YUM
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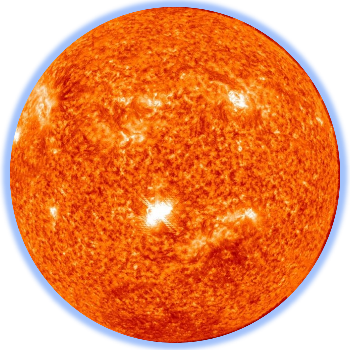
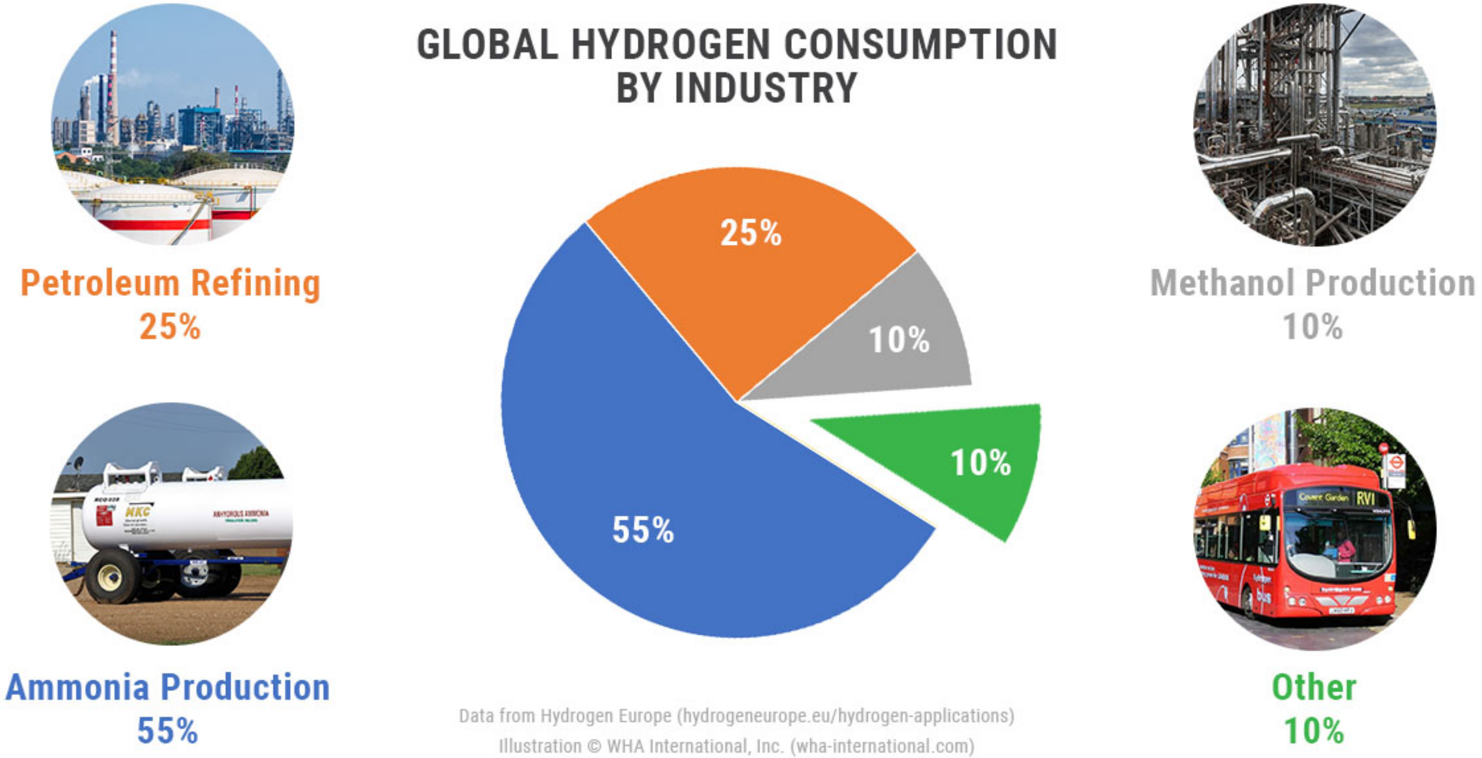
Background



Storable

Intermittency



Data from Hydrogen Europe (hydrogeneurope.eu/hydrogen-applications)
Illustration © WHA International, Inc. (wha-international.com)

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Background

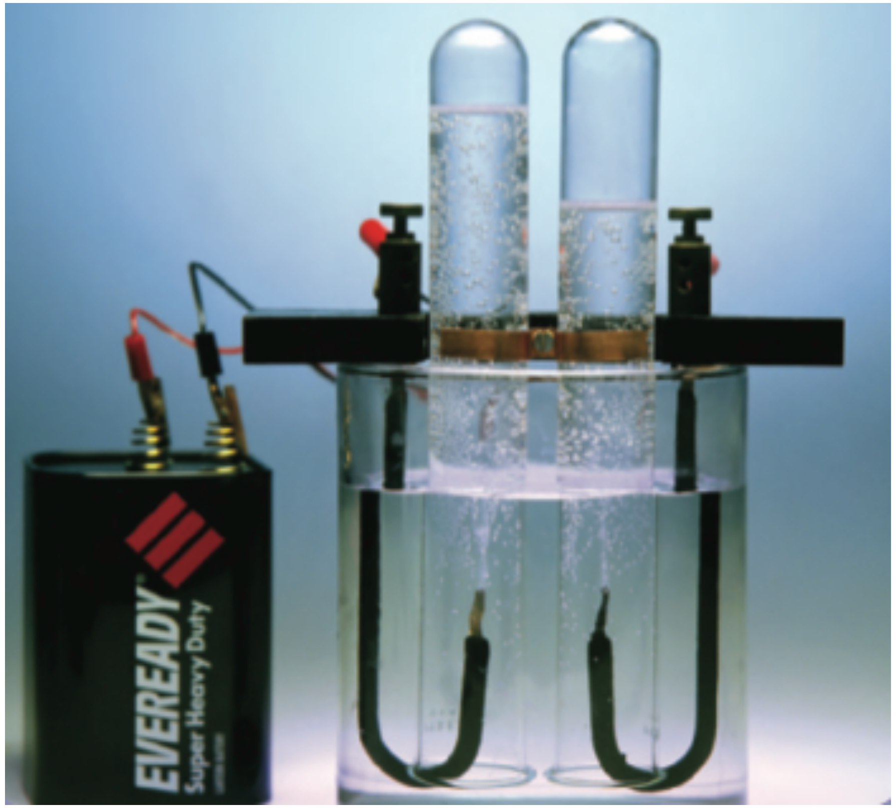
- The most abundant element in the universe, hydrogen, does not exist in the form of H_2 on Earth (0.00005% in the atmosphere), but rather in molecular forms such as water and other organic compounds.

- Hydrogen's highly combustible characteristics enable it to be pursued as a promising energy vector (as a comparison, 3kg of H_2 corresponds to about 100 kWh of chemical energy, whereas a 450 kg lithium ion battery is needed to produce the same quantity of electrical energy).

- Hydrogen is primarily utilized in oil refining and ammonia production for the petroleum and chemical industries, more precisely in the Haber process to synthesize ammonia from atmospheric nitrogen for the production of fertilizer.

- Unfortunately the manufacture of hydrogen from fossil fuels is nonrenewable and furthermore leads to CO_2 as a byproduct, consequently contributing to greenhouse gas production (Steam Methane Reforming).

Background



Ferrero *et al.*, *Energy Procedia*, ***101***, 50-57 (2016)
Hinkley *et al.*, CSIRO Energy (2016)

- **Electrolyzer**

  - This technological concept uses electricity to split water molecules in order to form oxygen and hydrogen gases in a device.

  - First demonstrated in 1789 by Jan Rudolph Deiman and Adriaan Paet van Trootswijk using an electrostatic generator to produce an electrostatic discharge between two Au electrodes.

  - Abundant starting material (H_2O)

  - ***Clean process*** to split water into H_2 and O_2

Cost 5.20 \$ Kg H_2

Mostly due to cost of electricity

Today's >100 Mt (10^9 kg) of Hydrogen (> 95%) is produced at large scale by ***steam reforming of natural gas* vs 4% from *electrolysis.***

Cost approx. 1.50-2.50\$ Kg H_2

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Background

- Amongst the current potential clean hydrogen production methods, the most developed solution is water electrolysis: alkaline electrolyzers (which have been used since the early 20th century), proton exchange membrane electrolyzers (otherwise known as polymer electrolyte membrane electrolyzers which are recently commercially available), and solid oxide electrolyzers (which can work at higher temperatures).

- However, the energy required by the process is roughly four times larger than the energy required for the production of hydrogen from natural gas reforming/gasification processes.

- Electrolysis-based solutions are only beneficial for the environment if the electricity used for the electrolysis is produced from carbon-free fuels.

- Therefore, combining this known water splitting technology with solar energy, a renewable source of electricity, has been adopted within the last few decades.

Background

- **Steam Methane Reforming (SMR)** $CH_4 + H_2O + heat \rightarrow CO + 3H_2$

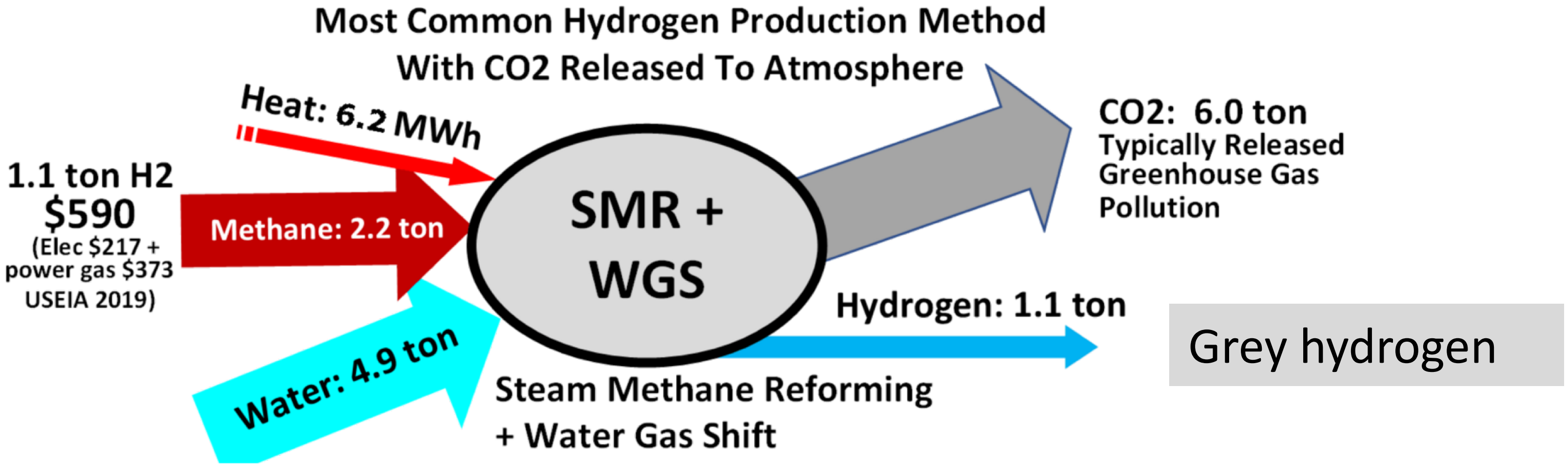
  - Producing syngas (H_2 + CO) through the reaction of hydrocarbons, e.g. methane, with water.
  - Natural gas is the most common feedstock.
  - Highly endothermic reaction (700 – 1,100 °C).

- **Water Gas Shift (WGS)** $CO + H_2O \rightarrow CO_2 + H_2 + small\ amount\ of\ heat$

  - CO and steam are reacted using a catalyst to produce CO_2 and more H_2 (Exothermic).

- **Pressure-swing adsorption**

  - CO_2 and other impurities are removed.



Most Common Hydrogen Production Method
With CO2 Released To Atmosphere

Heat: 6.2 MWh

1.1 ton H2
$590
(Elec $217 + power gas $373 USEIA 2019)

Methane: 2.2 ton

Water: 4.9 ton

SMR + WGS

CO2: 6.0 ton
Typically Released Greenhouse Gas Pollution

Hydrogen: 1.1 ton

Steam Methane Reforming + Water Gas Shift

Grey hydrogen

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Background

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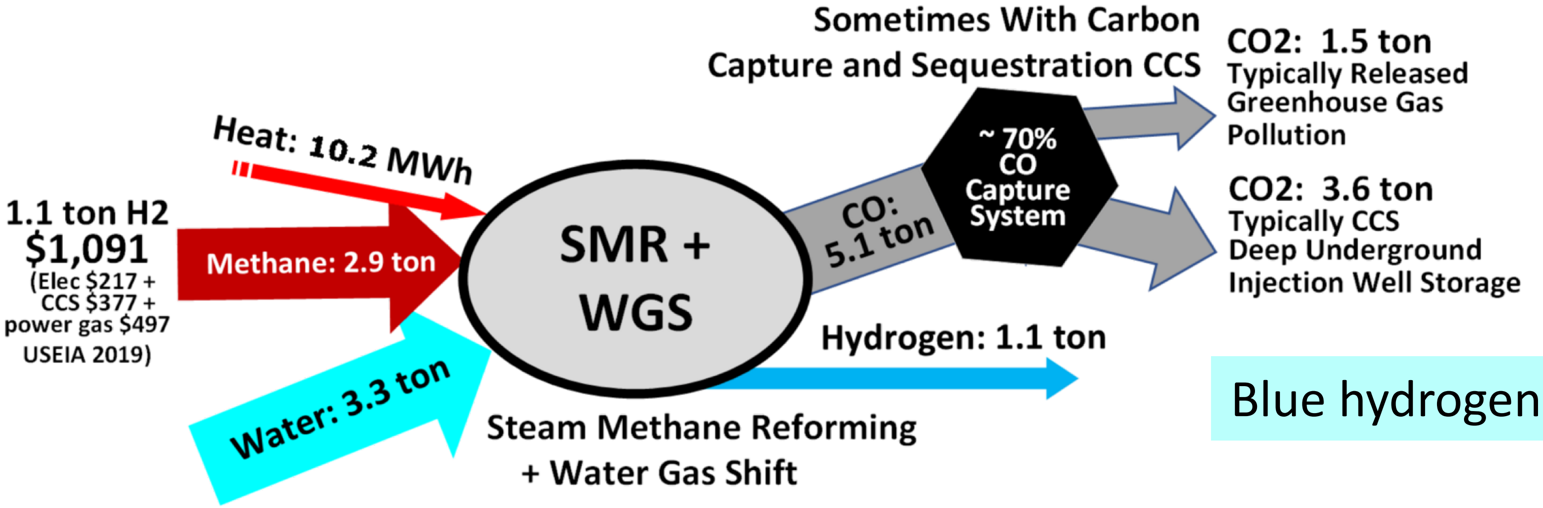

Blue hydrogen

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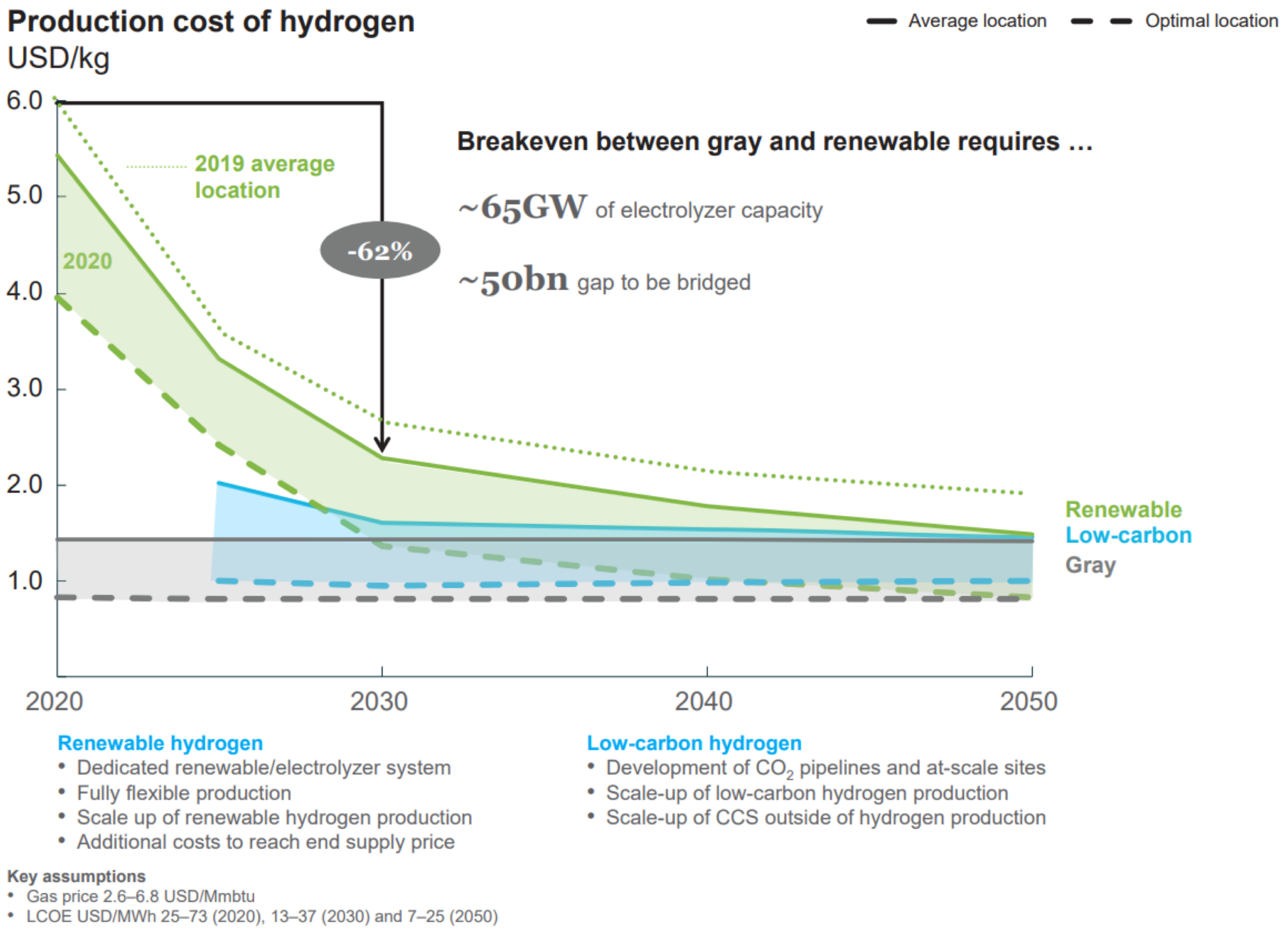
Background



Production cost of hydrogen
USD/kg

Breakeven between gray and renewable requires …

~65GW of electrolyzer capacity

~50bn gap to be bridged

Renewable hydrogen
- Dedicated renewable/electrolyzer system
- Fully flexible production
- Scale up of renewable hydrogen production
- Additional costs to reach end supply price

Low-carbon hydrogen
- Development of CO_2 pipelines and at-scale sites
- Scale-up of low-carbon hydrogen production
- Scale-up of CCS outside of hydrogen production

Key assumptions
- Gas price 2.6–6.8 USD/Mmbtu
- LCOE USD/MWh 25–73 (2020), 13–37 (2030) and 7–25 (2050)

Grey hydrogen

Blue hydrogen

Green hydrogen

Green hydrogen is hydrogen produced by splitting water by electrolysis using renewable energy sources.

https://hydrogencouncil.com/wp-content/uploads/2021/02/Hydrogen-Insights-2021-Report.pdf

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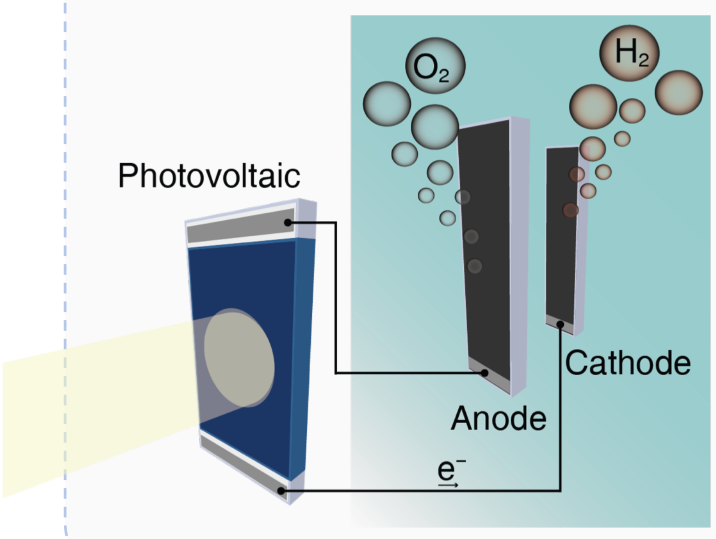
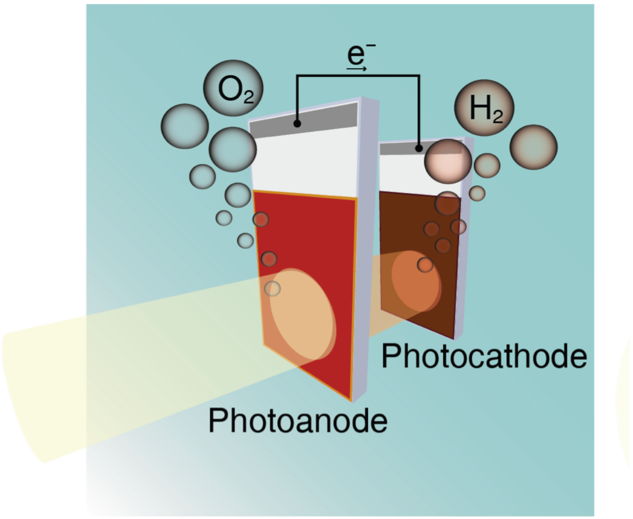
Solar Hydrogen Production

PV-EC



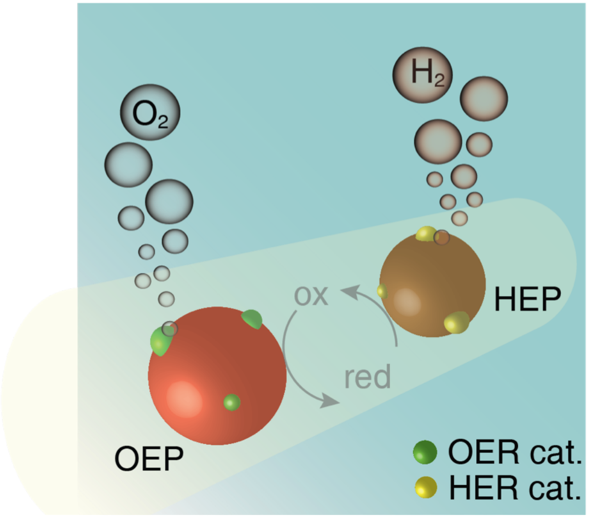
5 – 12 $/Kg H_2 (1)

PEC



3 – 18 $/Kg H_2 (2)

PC



1 – 3 $/Kg H_2 (2)

- 🟩 Higher efficiency
- 🟥 Complexity of the system and higher cost

(1) “DOE Technical Targets for Hydrogen Production from Electrolysis” http://www.energy.gov
(2) B.A. Pinaud, et al. *Energy Environ. Sci.*, **6**, 1983 (2013)

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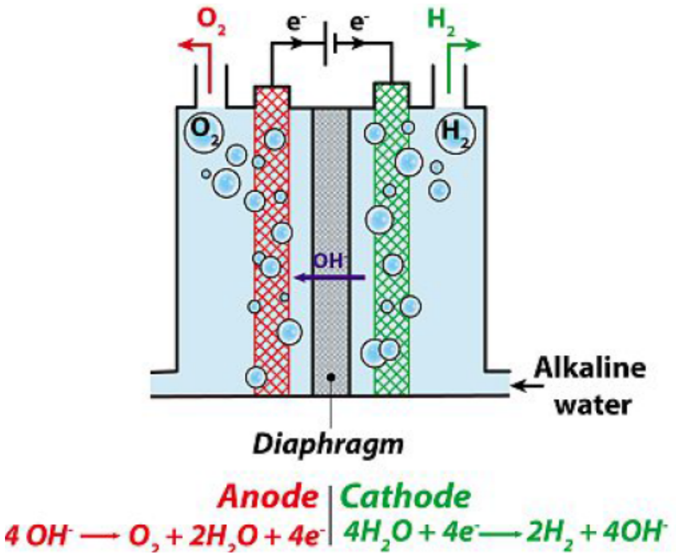
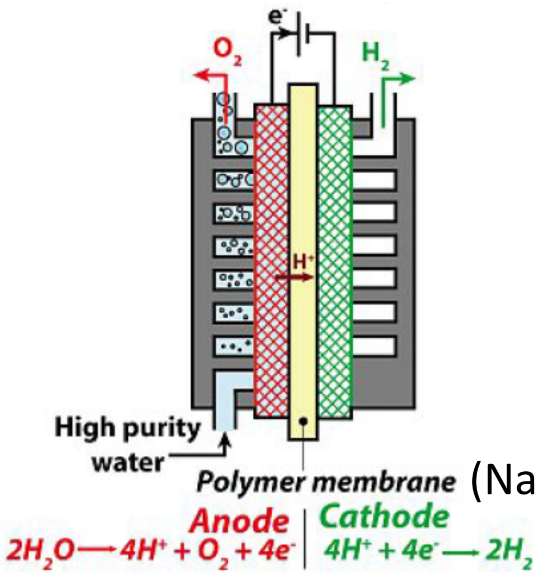
Alkaline or Proton Exchange Membrane (PEM) Electrolysis

Alkaline Electrolyzer



PEM Electrolyzer



(Nafion)

Image taken from F. Le Formal et al., *Chimia*, **69**, 789 (2015)

Redox reactions: Water is broken down at the cathode. Electrodes are mainly nickel alloys, coated onto specialized steel.

Porous diaphragm: The OH^- ions diffuse across the cell to the anode.

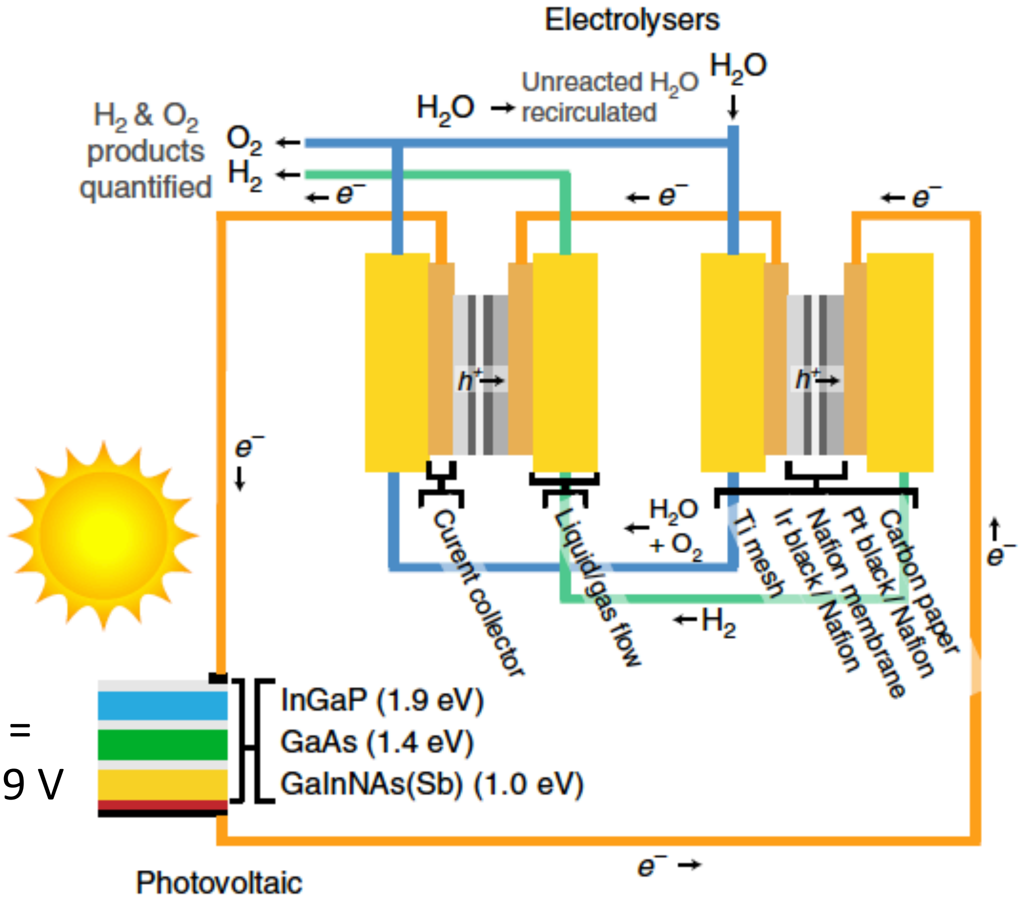
Redox reactions: Water is broken down at the anode, which is coated with Pt. The cathode is Pt and Ir.

Polymer membrane: The H^+ ions diffuse across the cell to the cathode.

https://www.finh2.fi/electrolyser-technologies/
https://thundersaidenergy.com/2023/01/17/green-hydrogen-alkaline-versus-pem-electrolysers/

Solar Hydrogen Production

Solar to Hydrogen Efficiency = 30%



V_{oc} = 2.79 V

Image taken from J. Jia et al., *Nat. Commun.*, **7**:13237 (2016)

Triple-junction solar cell (39%) and two PEM electrolyser in series.

Solar to Hydrogen Efficiency = 12%

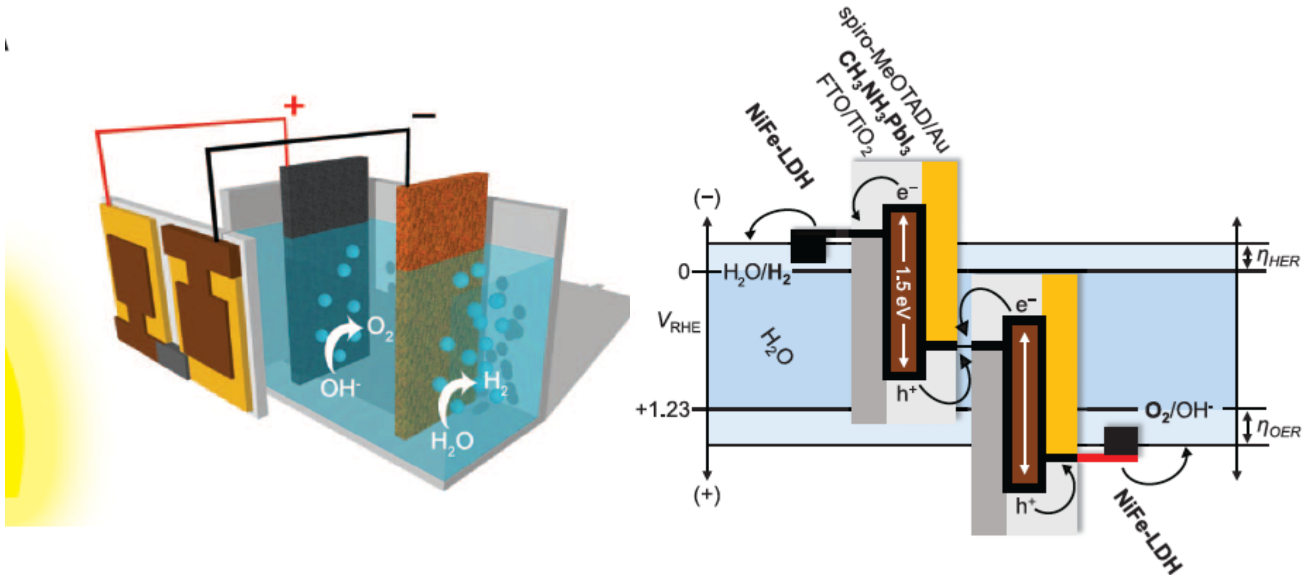


Image taken from J. Luo et al., *Science*, **345**, 1593 (2014)

Two perovskite solar cells (16%) in series and low cost electrocatalysts based on NiFe.

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Water Electrolysis

- The total energy required for electrolytic hydrogen production at standard temperature and pressure (298 K and 1 atm)

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 286\ - (0.163 \times T)\ kJ/mol = 237\ kJ/mol\ H_2$$

- This is equivalent to a standard cell voltage by $\Delta G^0 = -nFE^0$

n = the number of electrons transferred in the reaction,
F = the Faraday constant 96,500 C/mol

E^0 = 1.23 V

The electrochemical decomposition of water is possible when the electromotive force of the cell (EMF) is equal to or larger than 1.23 V (Gibbs free energy, 237 kJ/mol H_2).

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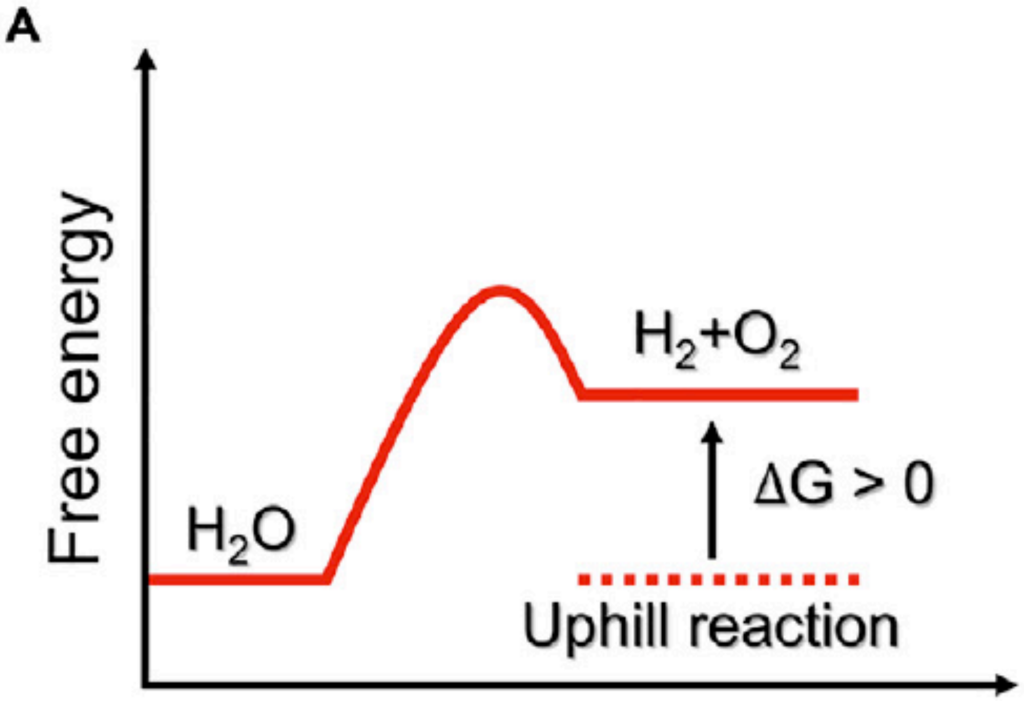
Water Electrolysis



C. Bie et al., *Chem*, **8**, 1-8 (2022)

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Water Electrolysis

- E^0 is the energetic potential at standard temperature and pressure, STP, (25°C and 1bar)

$$2H_2O\ (\text{liquid}) + 4h^+ + 4e^- \leftrightarrow O_2(\text{gas}) + 2H_2(\text{gas})$$

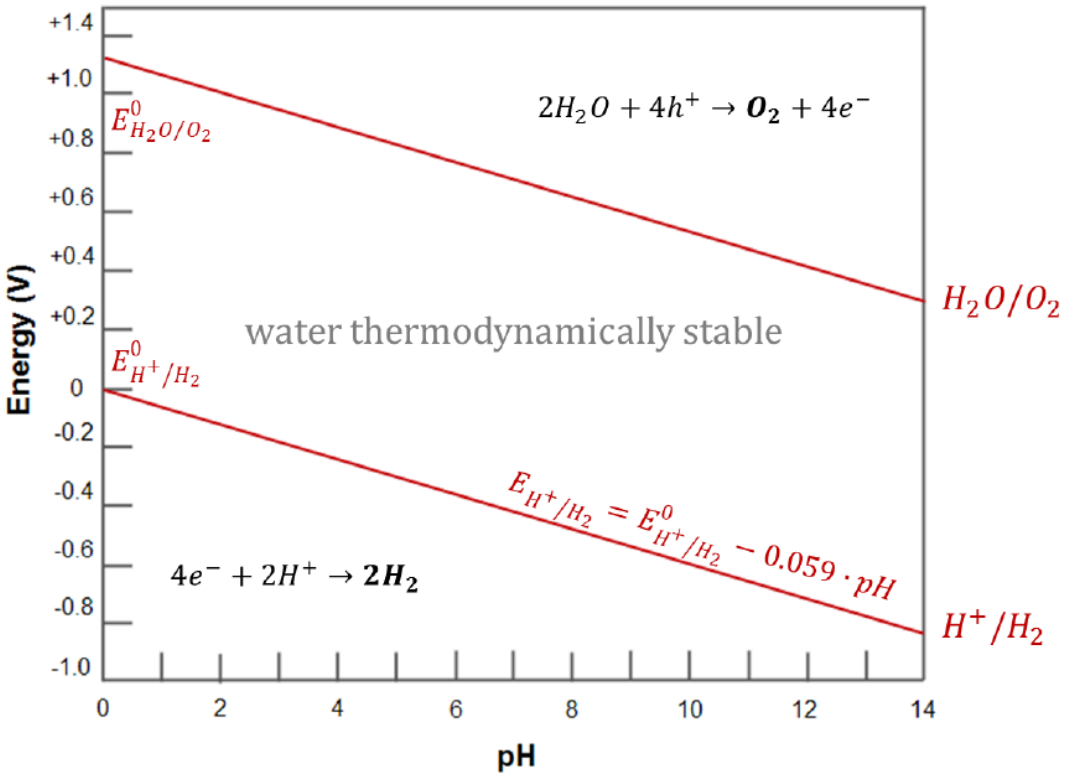
$2H_2O\ (\text{liquid}) + 4h^+ \leftrightarrow O_2(\text{gas}) + 4e^- + 4H^+$ $\quad E^0_{H_2O/O_2} = 1.23\ V\ vs. SHE$ Oxygen Evolution Reaction (OER)

$2H^+ + 2e^- \leftrightarrow H_2(\text{gas})$ $\quad E^0_{H^+/H_2} = 0\ V\ vs. SHE$ Hydrogen Evolution Reaction (HER)

In alkaline environments (pH 14)

$4OH^- + 4h^+ \leftrightarrow 2H_2O + O_2$ $\quad E^0_{H_2O/O_2} = 0.4\ V\ vs. SHE$

$2H_2O + 2e^- \leftrightarrow H_2(\text{gas}) + 2OH^-$ $\quad E^0_{H^+/H_2} = -0.83\ V\ vs. SHE$



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Kinetic Challenges

The thermodynamic potential is 1.23 V at 25 °C and 1 atm. However, due to the kinetic barrier for the reaction, water electrolysis requires a higher potential (called overpotential) than thermodynamic potential (1.23 V) to overcome **the kinetic barrier**.

Electrocatalytic process in micro- to seconds *vs* Photophysical processes in a few femto- to nano-seconds

A catalyst is a material that lowers the energy threshold for both, the hydrogen and oxygen evolution.

- Speeds up reactions.
- Consumes less energy.
- Stabilization of the transition state.
- Determines product selectivity.
- Destabilization of the reactants.

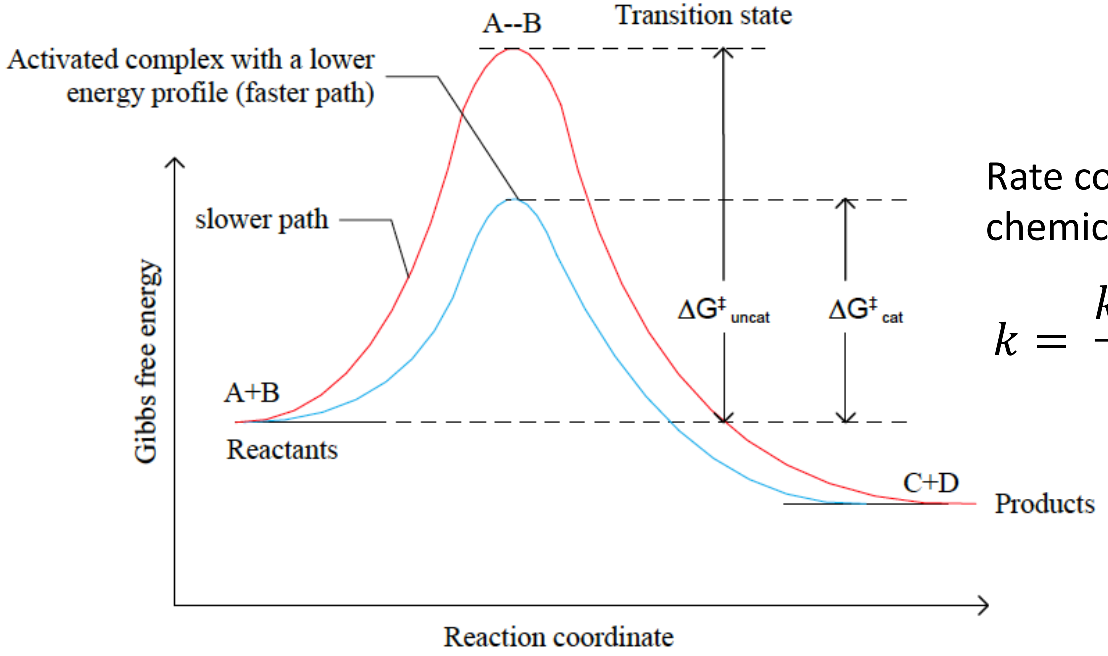

Image taken from the chapter in Alternative Energies by D. Delgado

Rate constant of a chemical reaction

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

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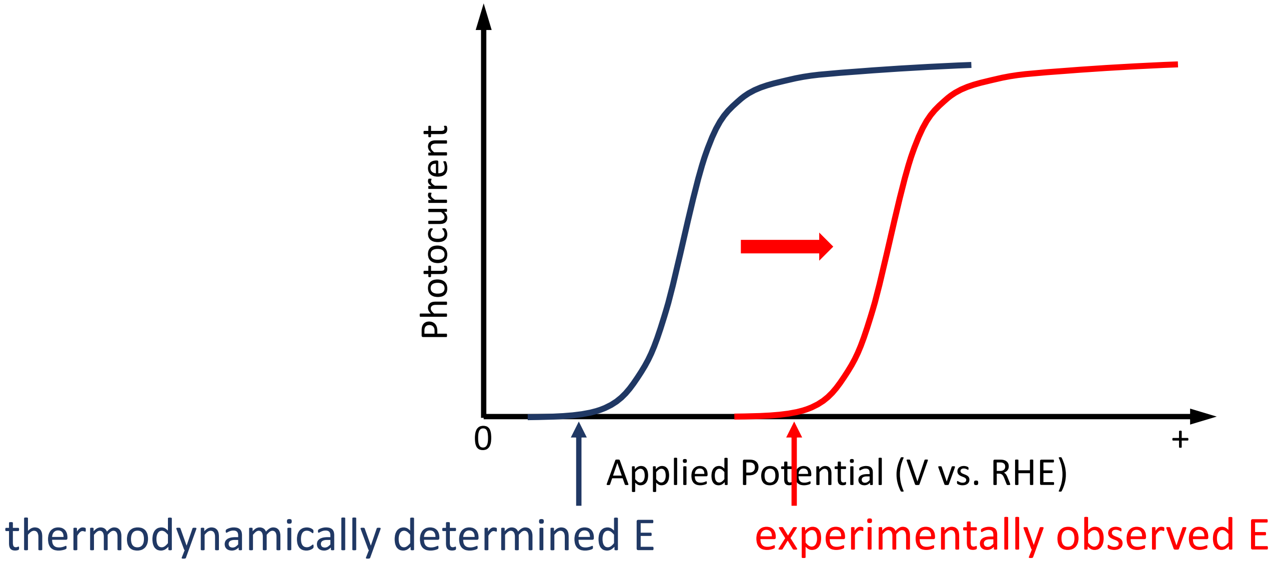
Overpotential

The overpotential is the potential difference between the thermodynamically determined potential and experimentally observed value of a redox reaction.

- **Activation overpotential:** the activation energy necessary to transfer an electron from an electrode to an electrolyte. This can also be called “**charge transfer overpotential**”.
- **Concentration overpotential:** the potential difference caused by a difference in the concentration of charge-carriers between bulk solution and the electrode surface (battery).
- **Resistance overpotential:** this overpotential is caused by the resistance from the electron or ion transport.



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Electrocatalytic process in micro- to seconds *vs* Photophysical processes in a few femto- to nano-seconds

Hydrogen Evolution Reaction (HER)

In Acidic Media		In Alkaline Media
$H^+ + M + e^- = (M - H_{ad})$	Volmer Step	$H_2O + M + e^- = OH^- + (M - H_{ad})$
1. $H^+ + e^- + (M - H_{ad}) = H_2 + M$	Heyrovsky Step	$H_2O + e^- + (M - H_{ad}) = OH^- + H_2 + M$
2. $2(M - H_{ad}) = H_2 + 2M$	Tafel Step	$2(M - H_{ad}) = H_2 + 2M$

M represents the hydrogen adsorption site

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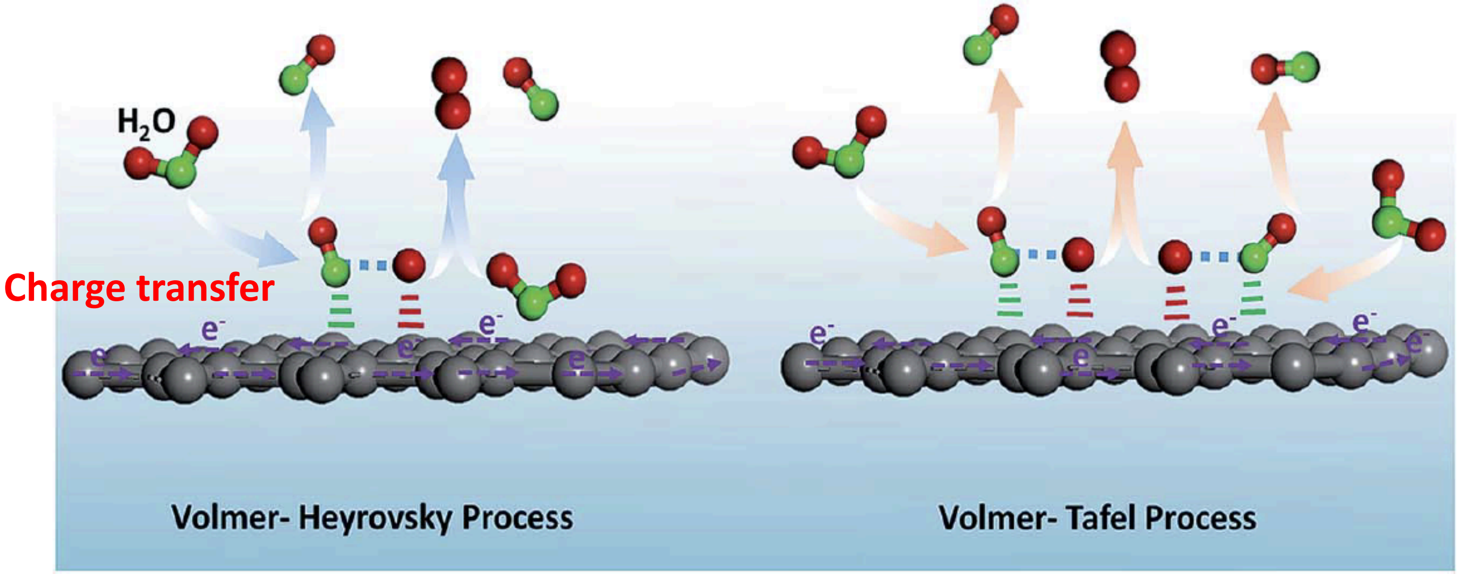
Kinetic Challenges

HER in Alkaline Media

$$H_2O + M + e^- = OH^- + (M - H_{ad})$$

$$H_2O + e^- + (M - H_{ad}) = OH^- + H_2 + M$$

$$2(M - H_{ad}) = H_2 + 2M$$

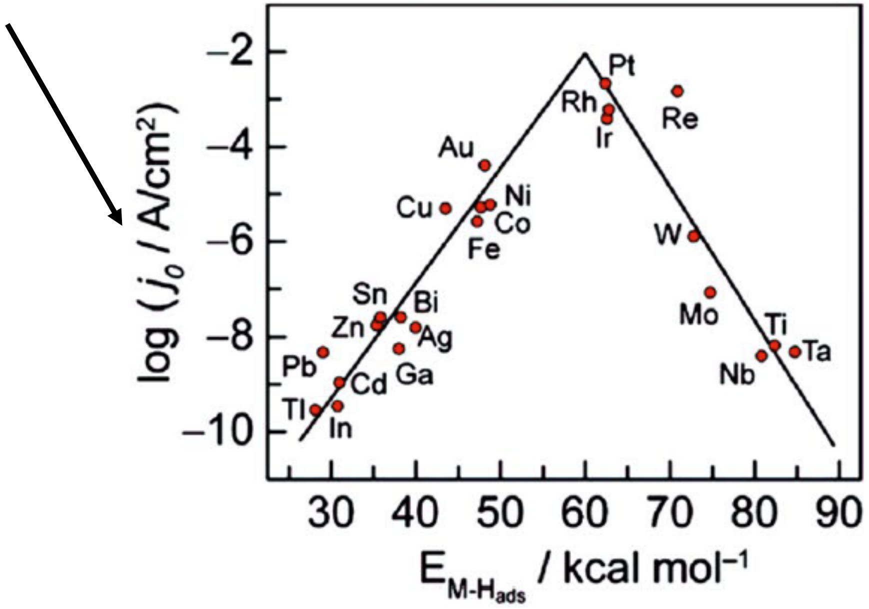


Charge transfer

Image taken from Z. Chen et al., *J. Mater. Chem. A*, ***7***, 14971–15005 (2019)

Volcano plot

Exchange current



- A higher exchange current density means a greater charge transfer rate and a lower reaction barrier.
- A moderate value of hydrogen binding energy will benefit HER process.

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Kinetic Challenges

OER occurs at the anode and involves **a four-electron transfer process, a slow hole transfer** (larger effective mass of hole), **a slow diffusion** (16 times as massive as H atom), and **high oxygen affinity** of (photo-)catalysts (difficult to desorb), which requires a remarkably high overpotential compared to HER. OER is known to be the major bottleneck in improving the overall efficiency of electrochemical water splitting.

Oxygen Evolution Reaction (OER)

acid (blue line)
alkaline (red line)

$$OH^- + M = (M - OH) + e^-$$

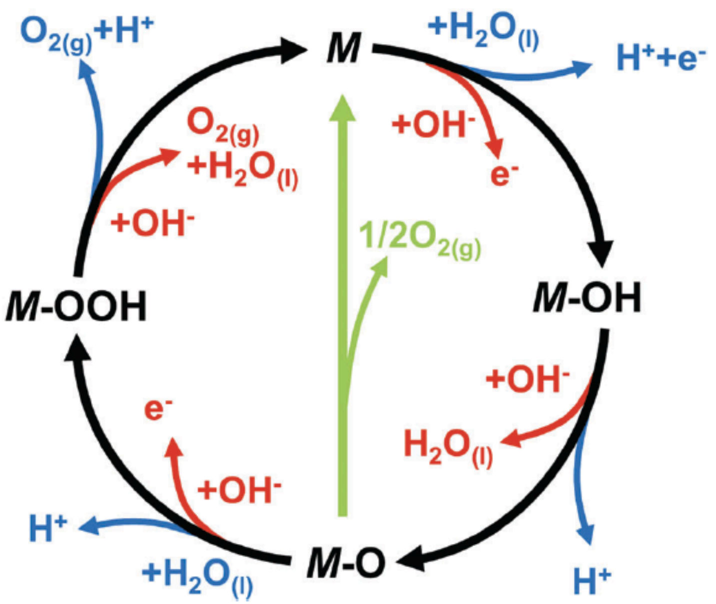
$$(M - OH) + OH^- = (M - O) + H_2O + e^-$$

1. $$(M - O) + OH^- = (M - OOH) + e^-$$

RDS

$$(M - OOH) + OH^- = O_2 + H_2O + e^- + M$$

2. $2(M - O) = 2M + O_2 + 2\,e^-$ (a large activation barrier)



N.-T. Suen et al., *Chem. Soc. Rev.,* 46, 337 – 365 (2017)

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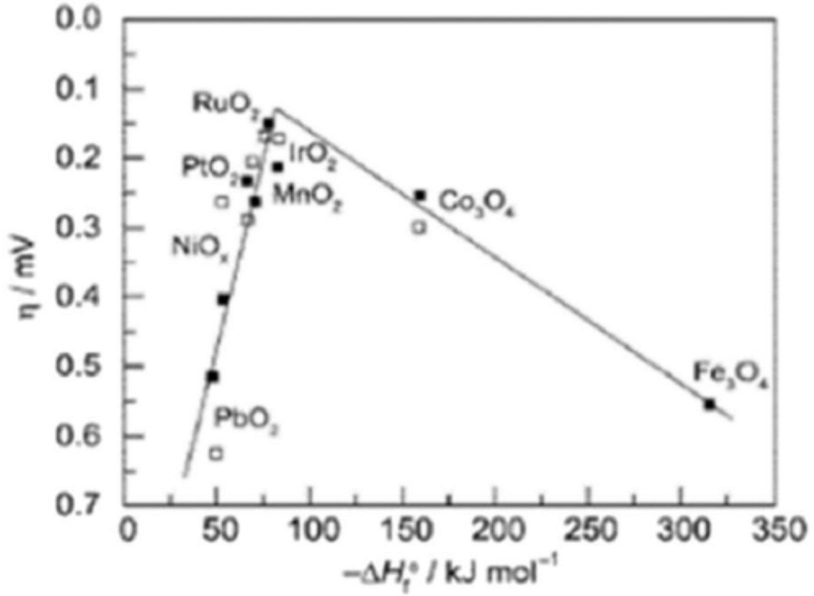
Oxygen Evolution Reaction (OER)

$$OH^- + M = (M-OH) + e^-$$

$$\left.\begin{aligned}&(M-OH) + OH^- = (M-O) + H_2O + e^-\\ \text{1. }\quad &(M-O) + OH^- = (M-OOH) + e^-\end{aligned}\right\}\ \text{RDS}$$

$$(M-OOH) + OH^- = O_2 + H_2O + e^- + M$$

2. $2(M-O) = 2M + O_2 + 2\,e^-$ (a large activation barrier)



Wang et al., *Nano Convergence,* 8:4 (2021)

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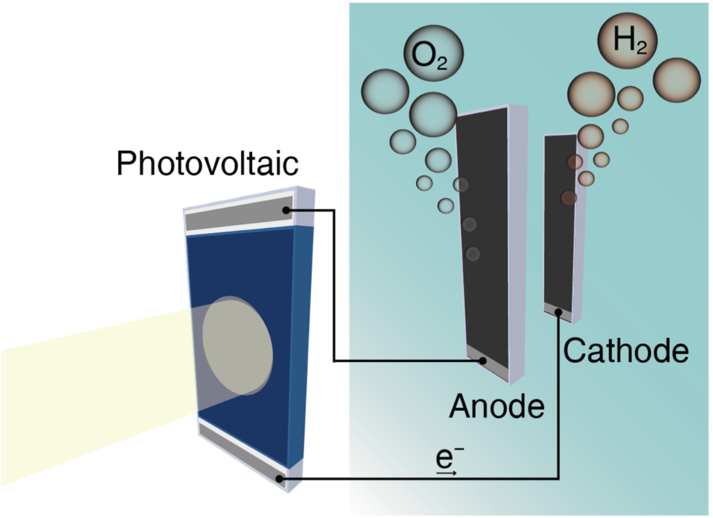
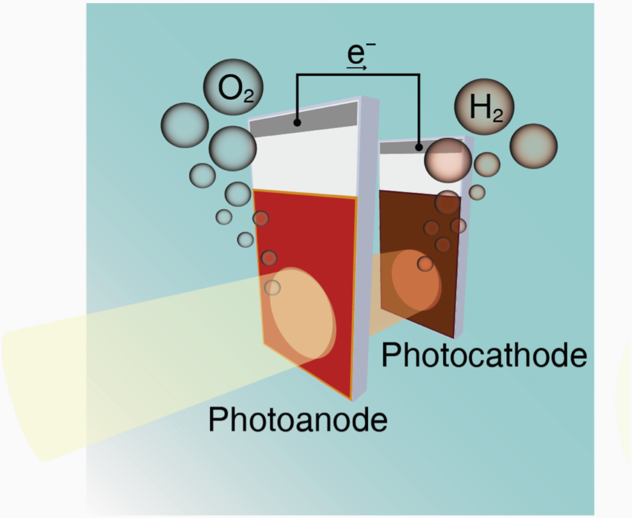
Solar Hydrogen Production

PV-EC



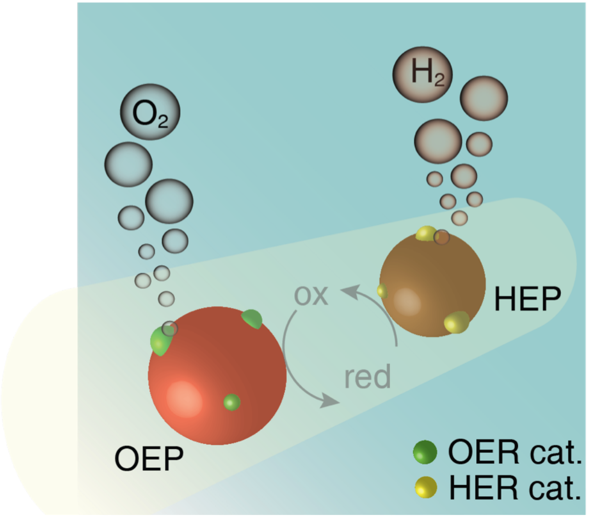
$5 – 12\ \$/\mathrm{Kg}\ \mathrm{H}_2\ ^{(1)}$

PEC



$3 – 18\ \$/\mathrm{Kg}\ \mathrm{H}_2\ ^{(2)}$

PC



$1 – 3\ \$/\mathrm{Kg}\ \mathrm{H}_2\ ^{(2)}$

- 🟩 Higher efficiency
- 🟥 Complexity of the system and higher cost

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(2) B.A. Pinaud, et al. *Energy Environ. Sci.*, **6**, 1983 (2013)

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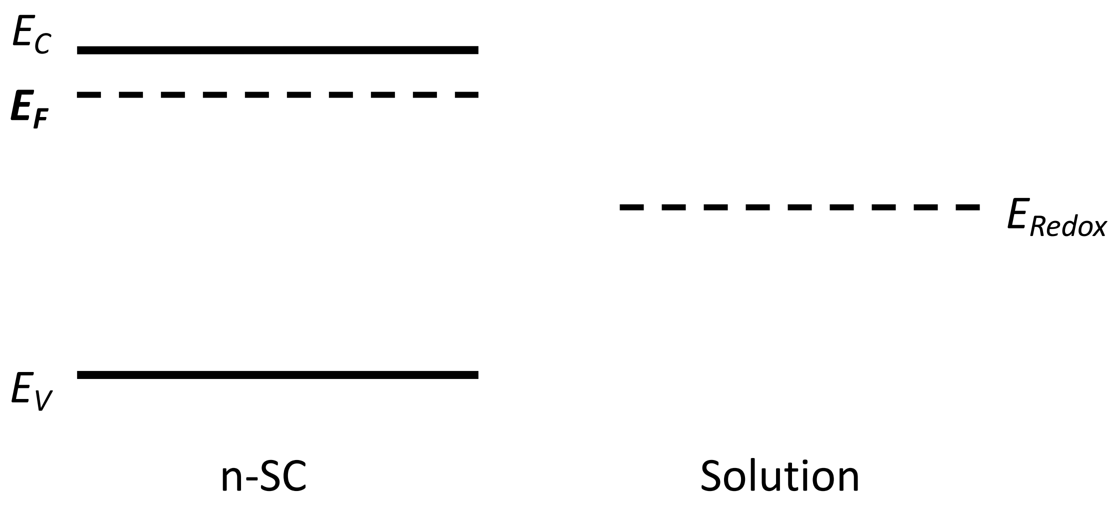
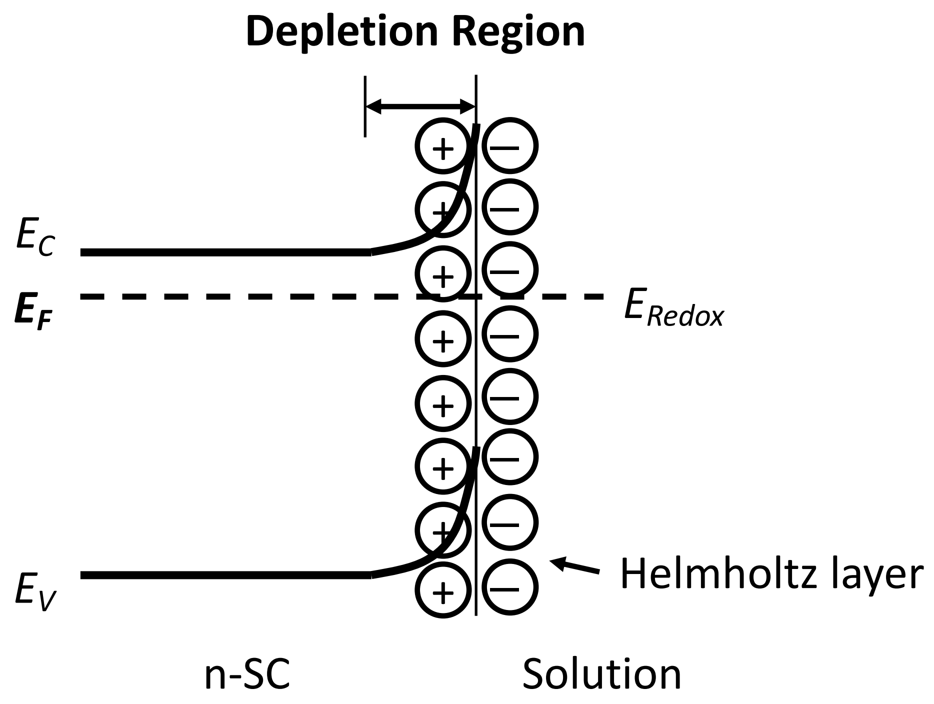
N-type Semiconductor-Liquid Junction

- The Fermi level is typically higher than the redox potential of the electrolyte.
- Electrons will be transferred from the electrode into the solution.
- Positive charge associated with the space charge region, and this is reflected in an upward bending of the band edges.
- The electron of the semiconductor has been removed from this region (depletion layer).

Before contact



In thermal equilibrium



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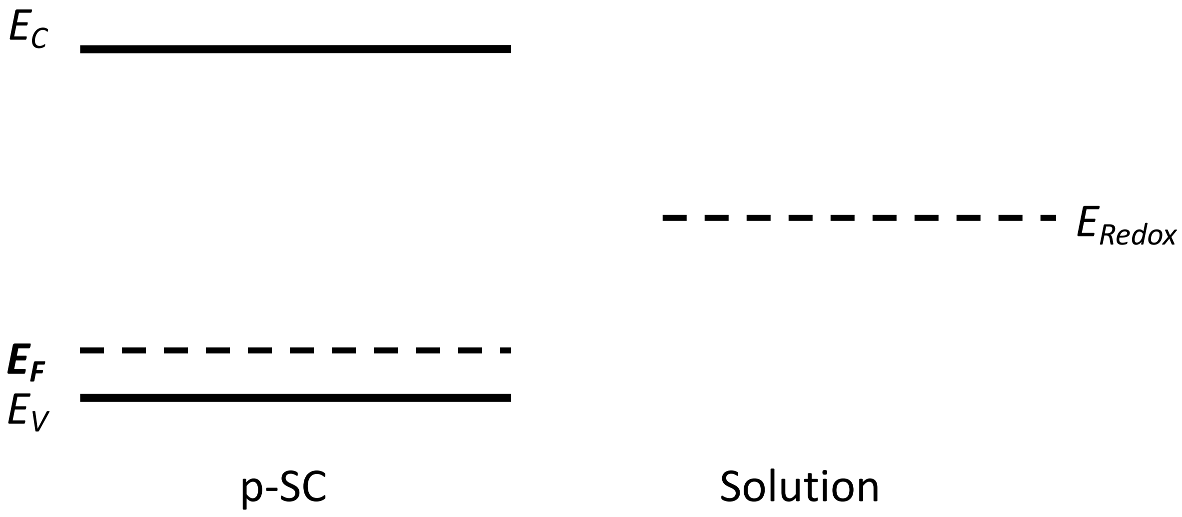
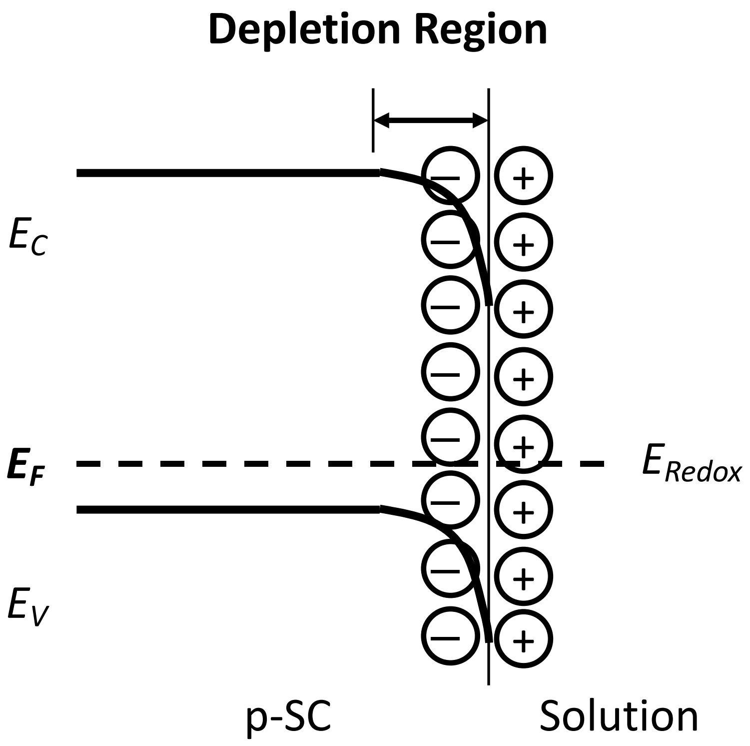
P-type Semiconductor-Liquid Junction

- The Fermi level is typically lower than the redox potential of the electrolyte.
- Electrons will be transferred from the solution into the semiconductor.
- Negative charge associated with the space charge region, and this is reflected in an downward bending of the band edges.
- The holes of the semiconductor has been removed from this region (depletion layer).

Before contact



In thermal equilibrium



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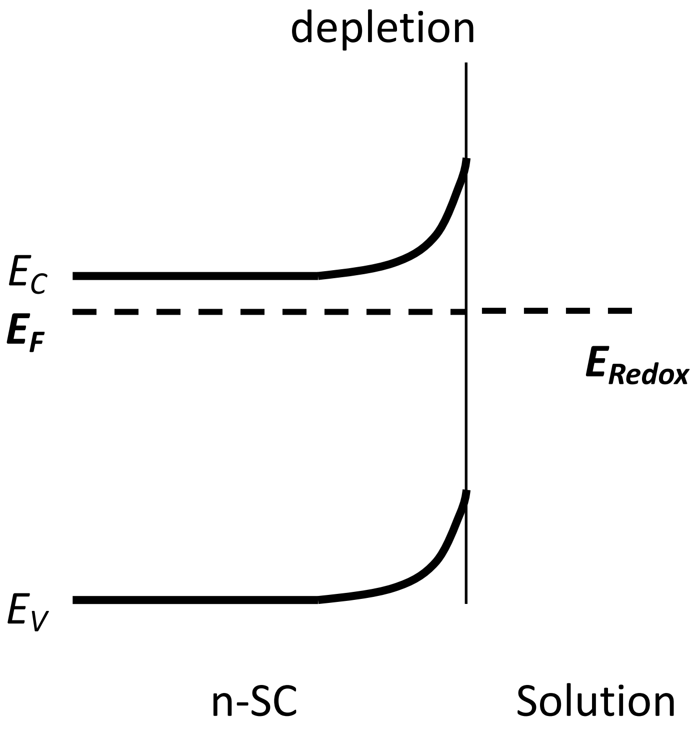
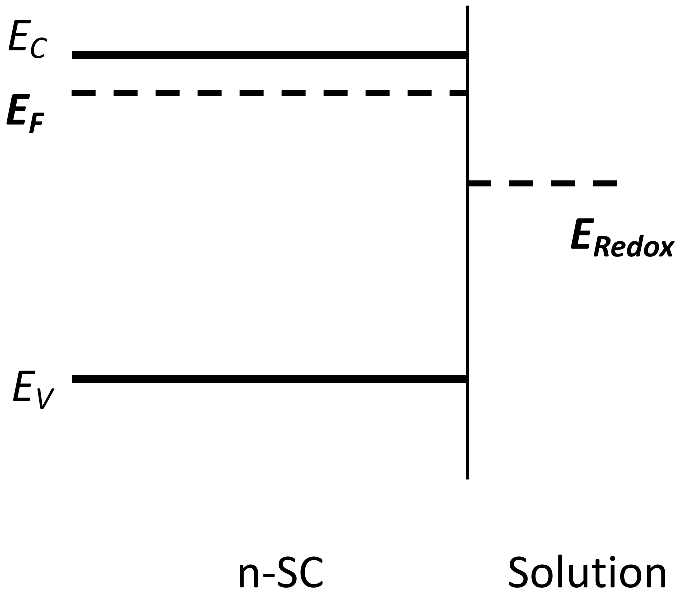
Effect of Applied Potential: n-type SC

- The band edges in the interior of the SC (away from the depletion region), the magnitude and direction of band bending, vary with the applied potential.
- The energies of the band edges at the interface are not affected by changes in the applied potential.
- Flat band potential, **E_{fb}**: Potential where there is no net transfer of charge, and hence there is no band bending.



$E = E_{fb}$



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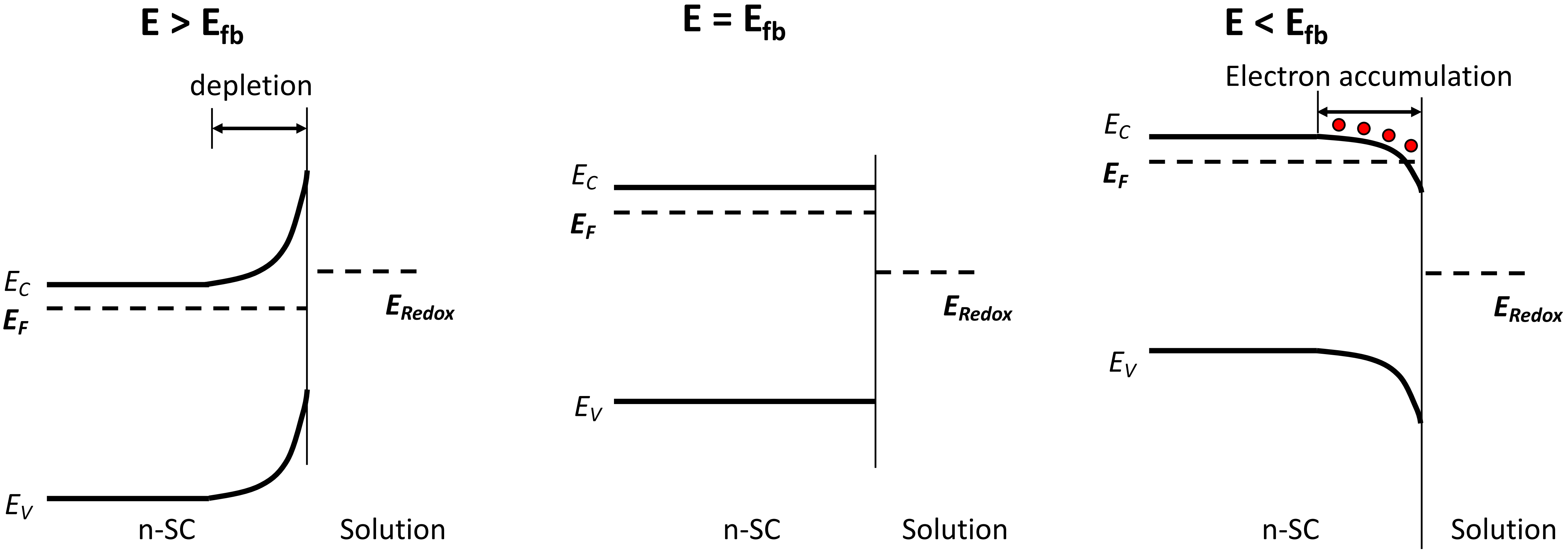

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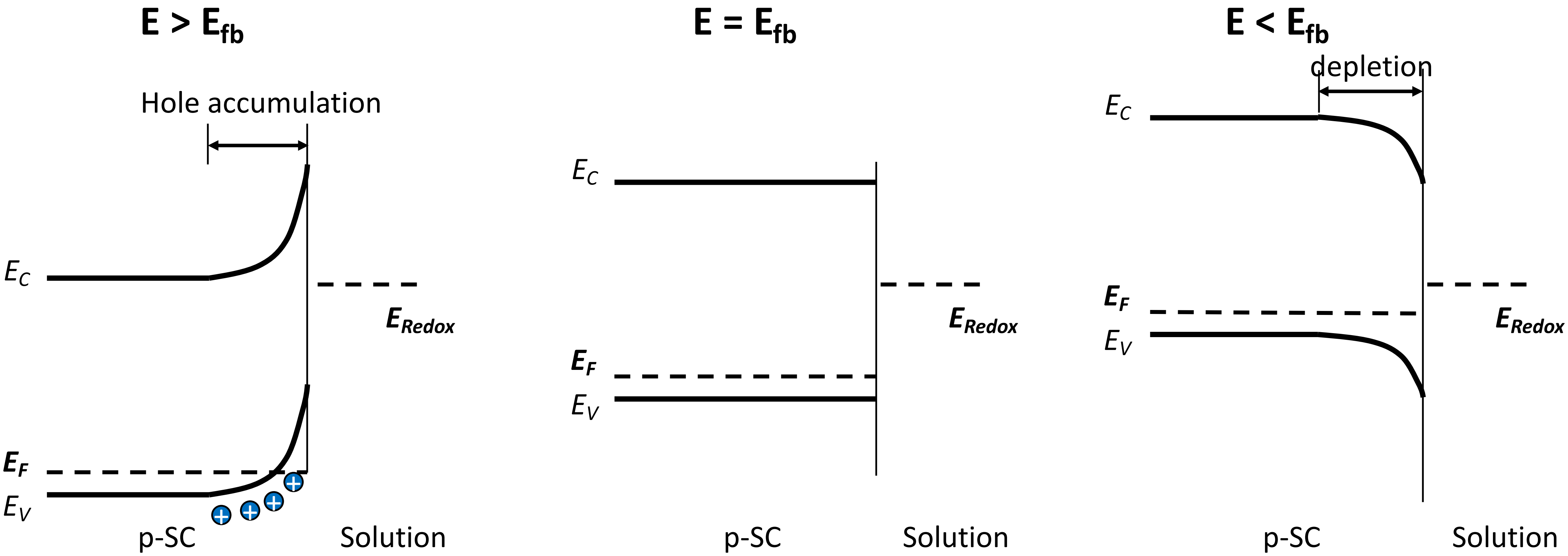
Effect of Applied Potential: p-type SC

- The band edges in the interior of the SC (away from the depletion region), the magnitude and direction of band bending, vary with the applied potential.
- The energies of the band edges at the interface are not affected by changes in the applied potential.
- Flat band potential, $\mathbf{E_{fb}}$: Potential where there is no net transfer of charge, and hence there is no band bending.



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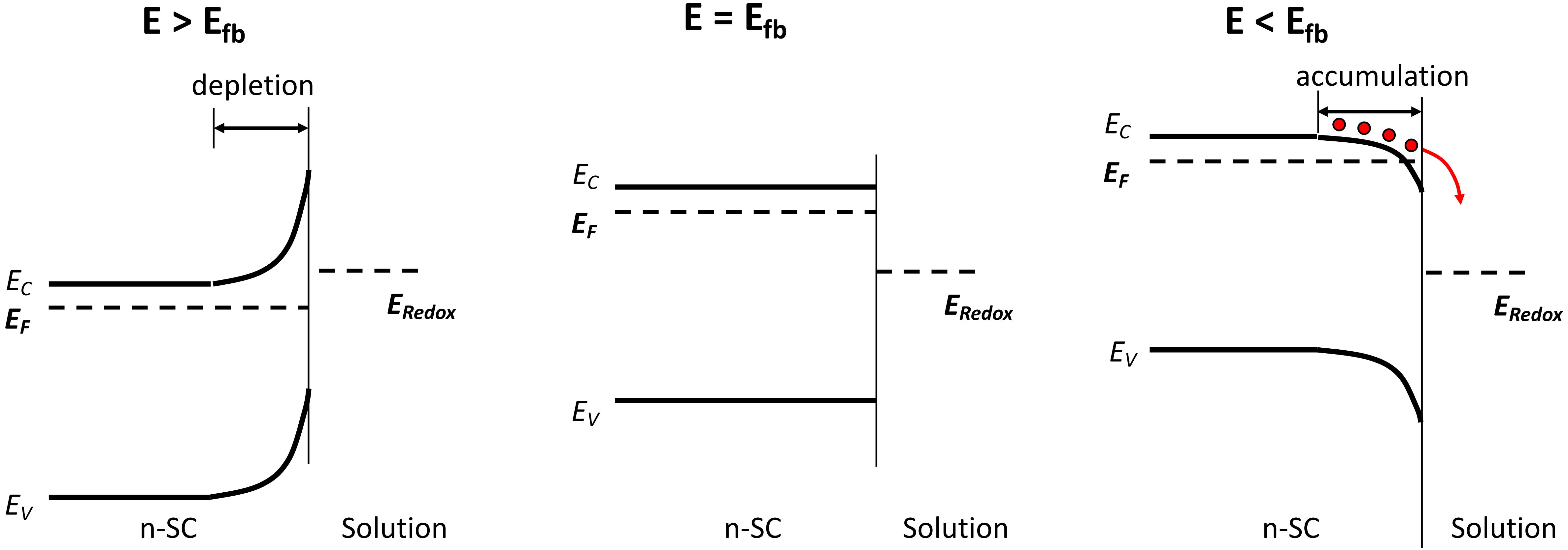
Charge Transfer In Dark

- The behavior of SC electrode is similar to that of a metallic electrode when an accumulation layer is formed: an excess of the majority carrier available for charge transfer.
- In contrast, a depletion layer forms a barrier for the majority carrier.



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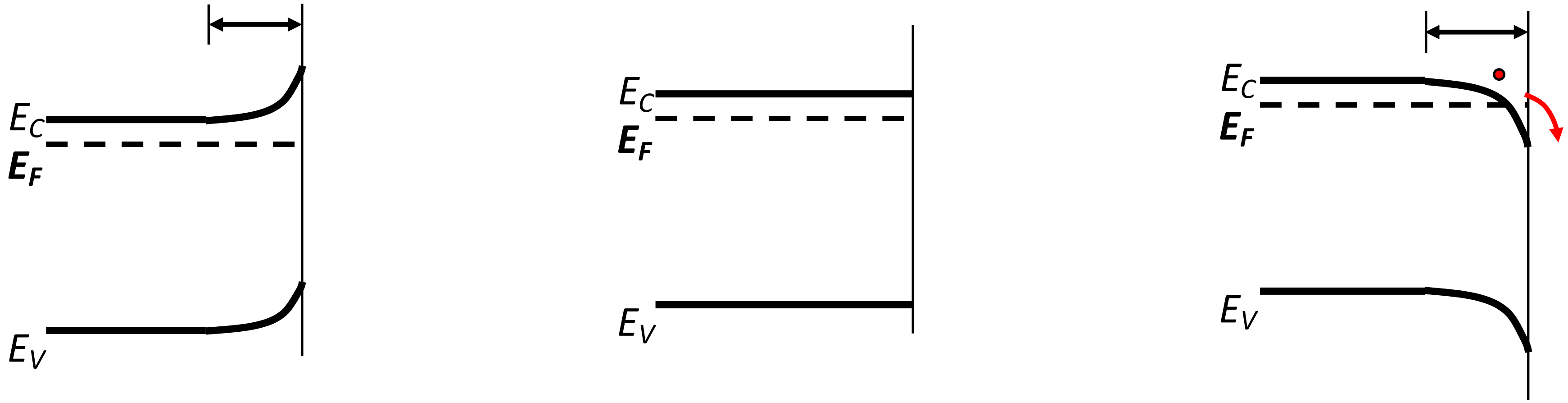
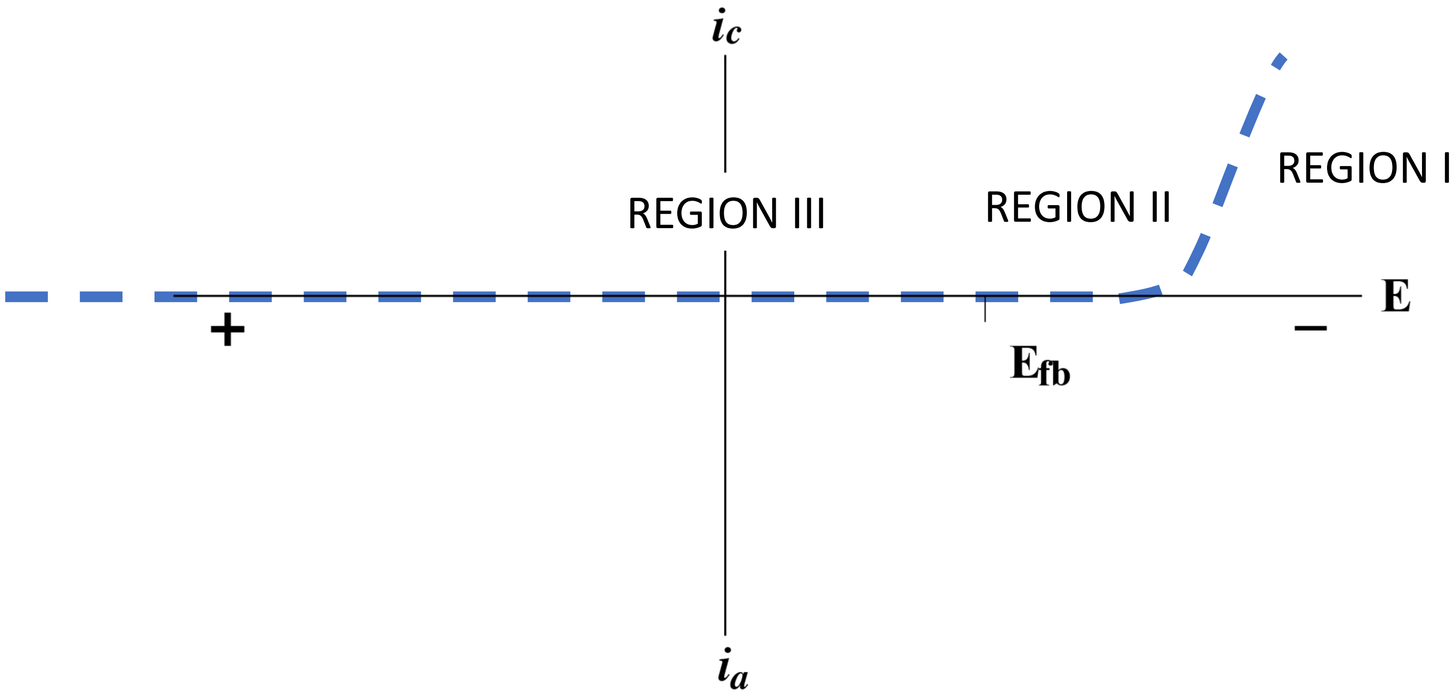
Ideal Behavior for an n-type SC in Dark



Region III ($E > E_{fb}$)

Region II ($E = E_{fb}$)

Region I ($E < E_{fb}$)



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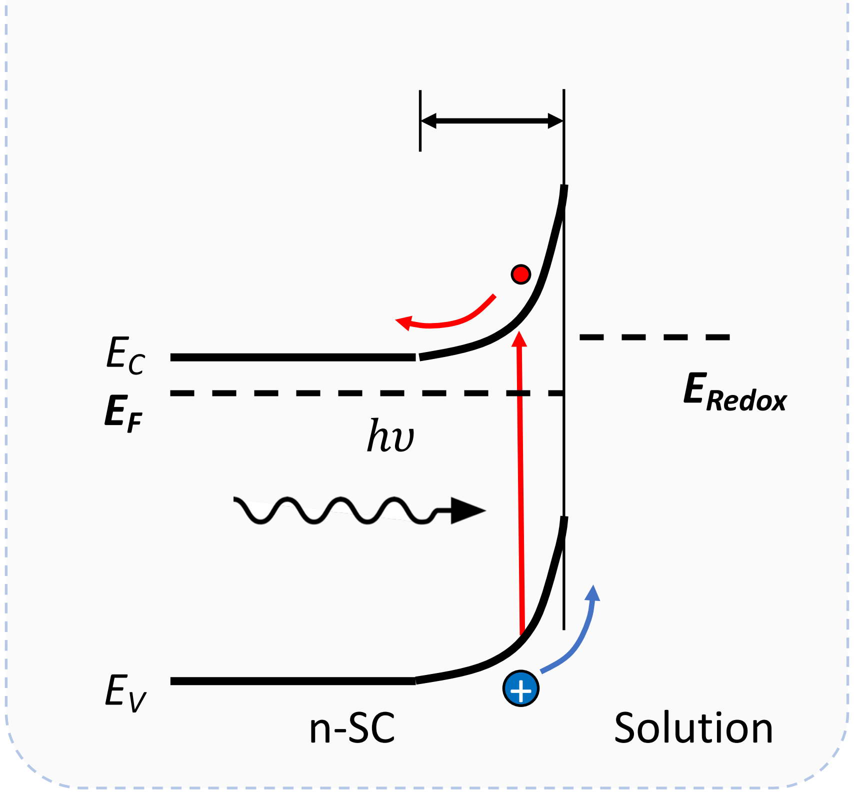
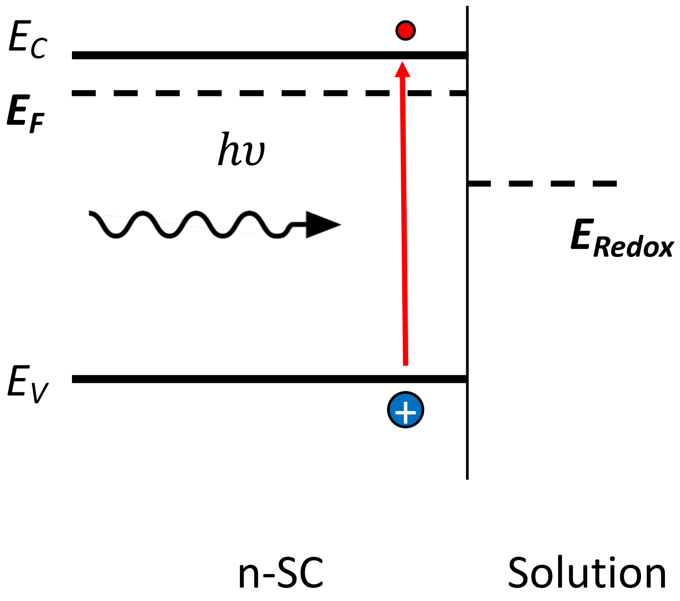
Charge Transfer Under Illumination

- Under illumination, photoexcited electrons and holes are produced: promotion of electrons to C.B.
- If this process occurs in the interior of the semiconductor, recombination of the promoted electron and the resulting hole typically occurs, together with the production of heat.
- However, if it occurs in the space charge region, the electric field in this region will cause the separation of the charge.

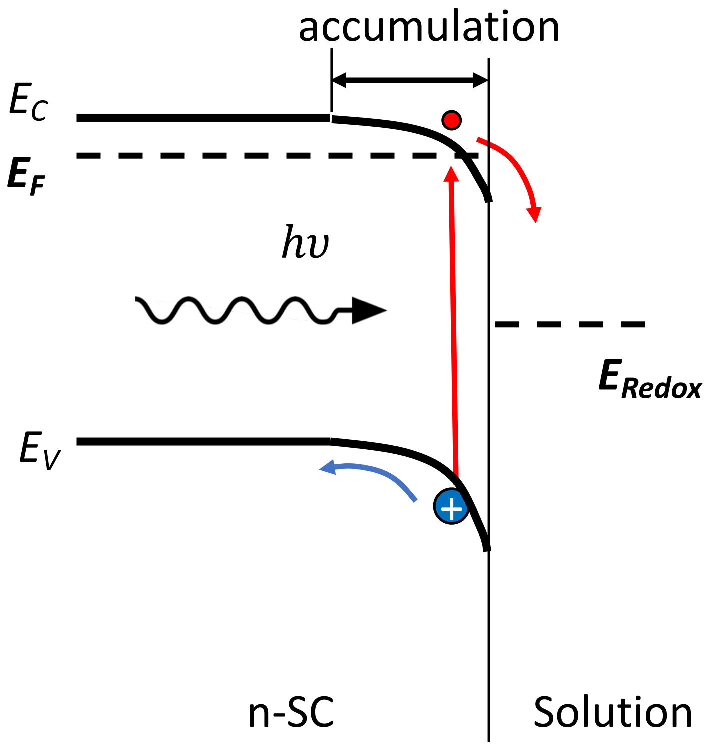
$E > E_{fb}$



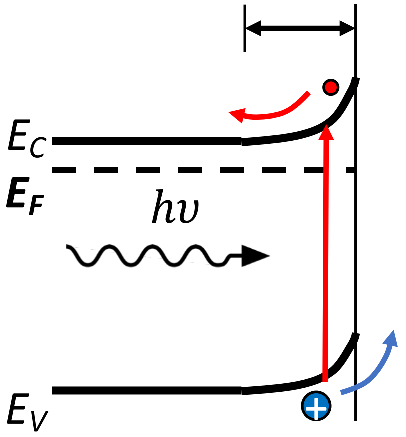
$E = E_{fb}$



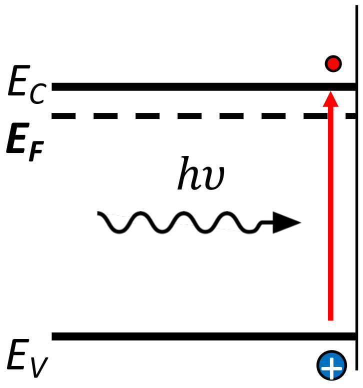
$E < E_{fb}$



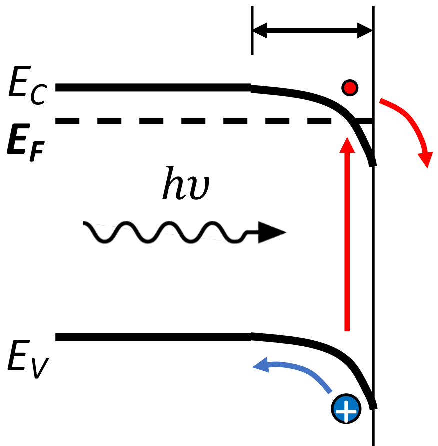
Ideal Behavior for an n-type SC under illumination



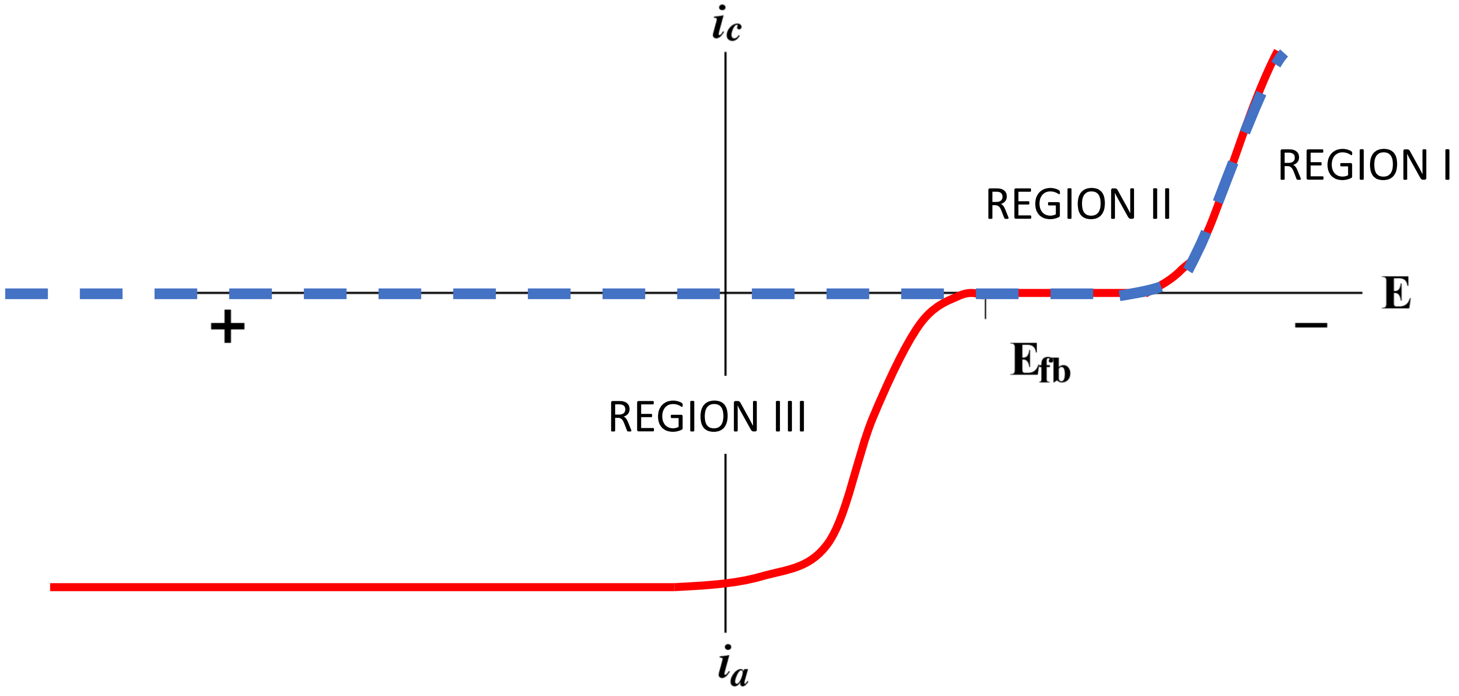
Region III (E > E_{fb})



Region II (E = E_{fb})



Region I (E < E_{fb})



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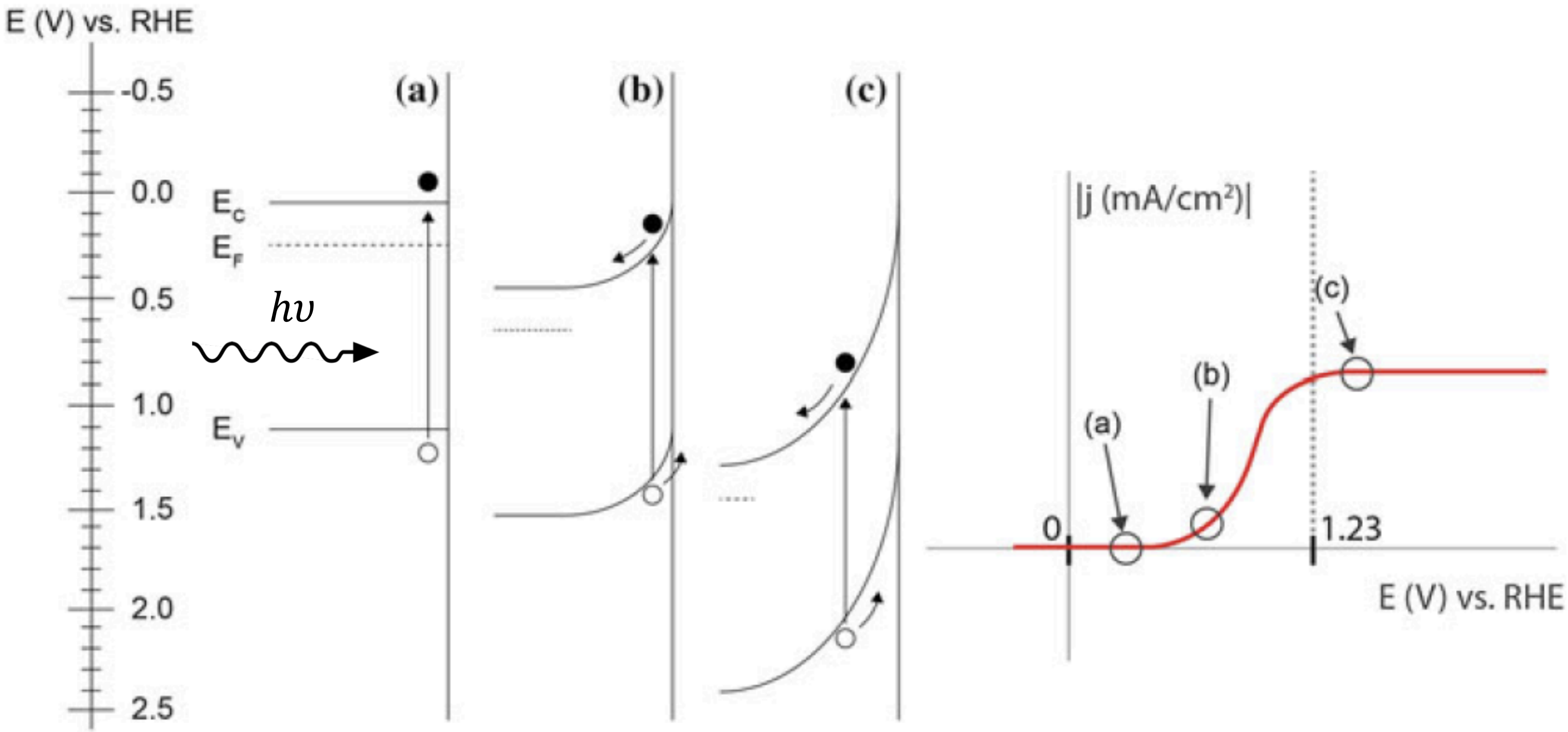
Techniques to Measure The Flat band Potential

- The **photocurrent onset** from *J-V* curve.
- **Open circuit potential (OCP)** of semiconductor electrode under high irradiance.
- Application of the **Mott–Schottky (MS**) equation to the semiconductor capacitance, determined by electrochemical impedance spectroscopy (EIS).

Photocurrent Onset

- The photocurrent onset can be used to estimate the E_{fb}, and can be determined by measuring the photocurrent density (J_{ph}) as a function of the potential versus a reference electrode (E_{ref}).



From a book "Photoelectrochemical Water Splitting" by Z. Chen, H. N. Dinh, et E. Miller

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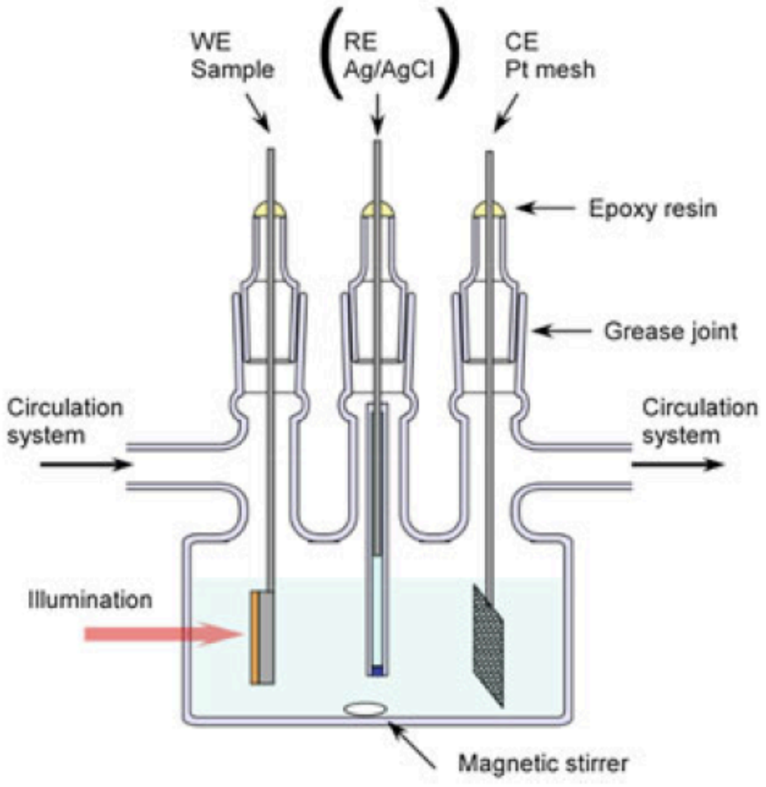
Photocurrent Onset



From a book “Photoelectrochemical Water Splitting” by Z. Chen, H. N. Dinh, et E. Miller

- Overpotential: The onset of photocurrent does not necessarily define the E_{fb} potential because other interfacial effects may delay the onset to a point beyond the transition from accumulation to depletion.
  ex) recombination in the space charge layer, carrier trapping at surface defects, poor charge transfer kinetics.

- Use of catalyst: The modification of electrode surfaces with catalysts may influence the SC/electrolyte junction and surface states.

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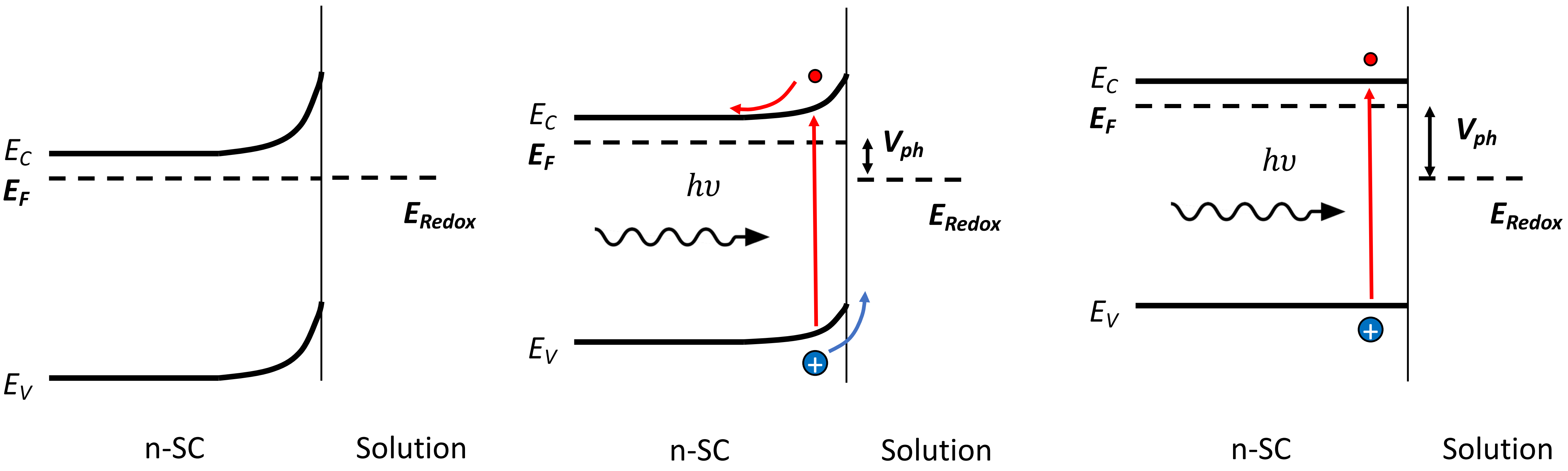
OCP under Illumination

- This method can be used to estimate the E_{fb} if the above-band gap illumination is sufficiently intense to completely remove pre-existing band bending at the surface and carrier recombination rate is not so high.



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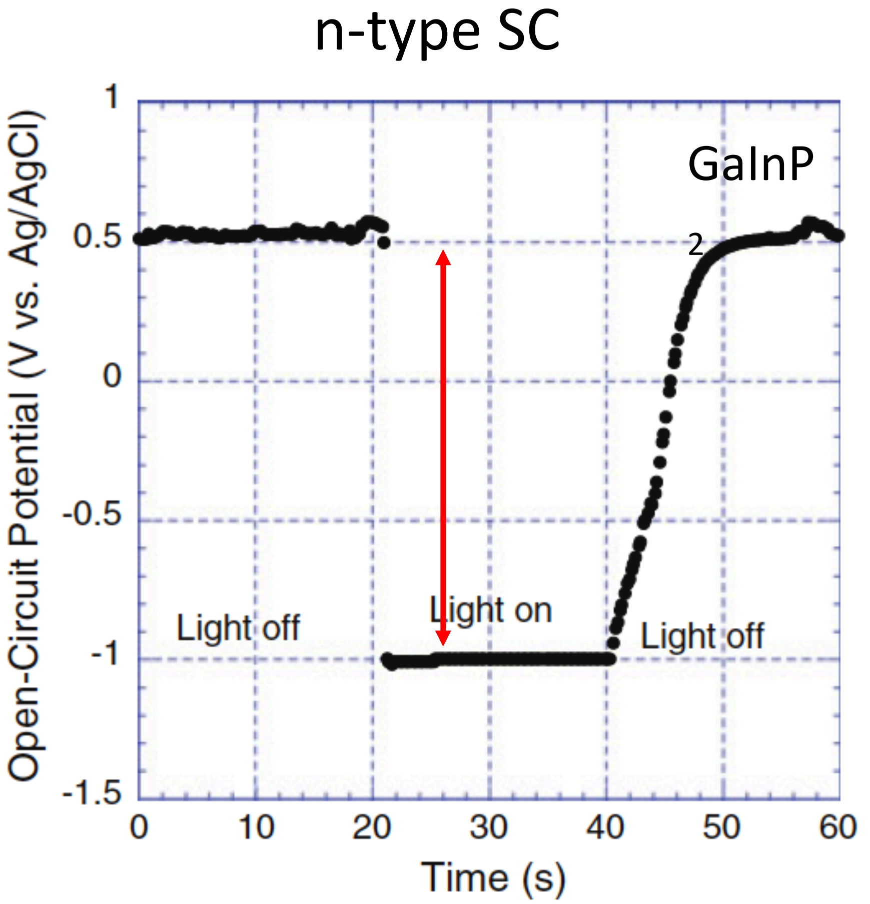
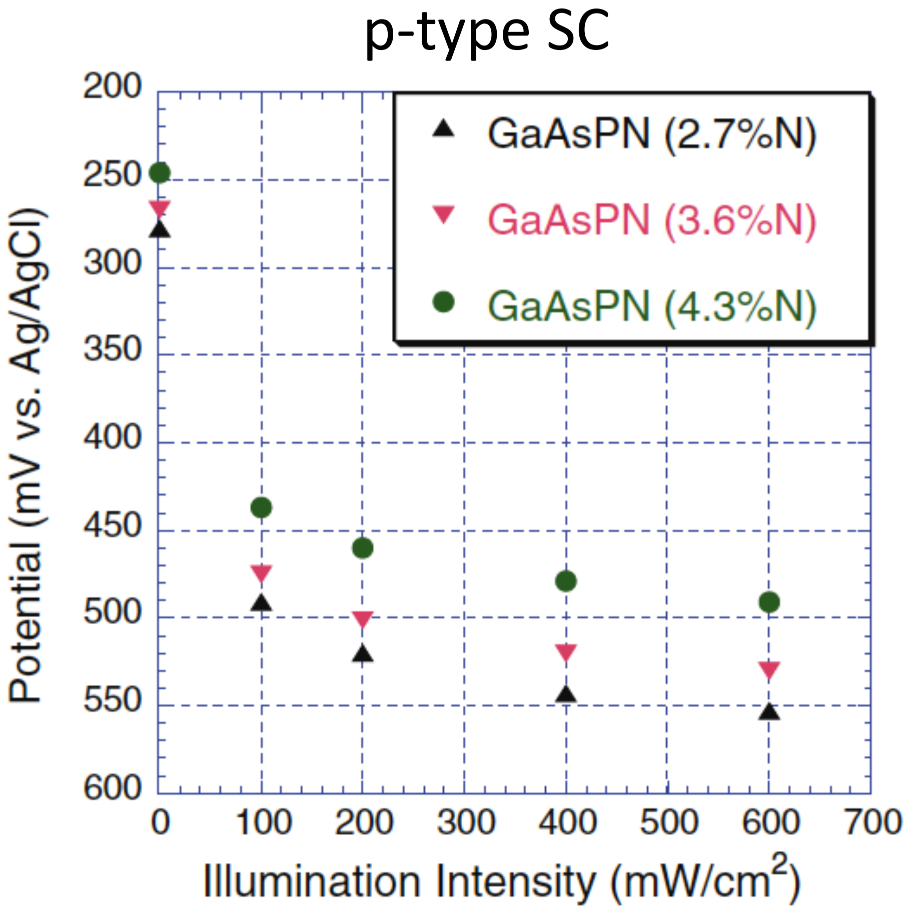
OCP under Illumination





Limit: - Unstable values for the OCP in the dark or under illumination could be due to adsorption of electrolyte species at the surface, and/or corrosion reactions.

- The determination of E_{fb} values by OCP can also be complicated by materials that have a high density of defect sites which can serve as recombination centers: high light intensity is required.

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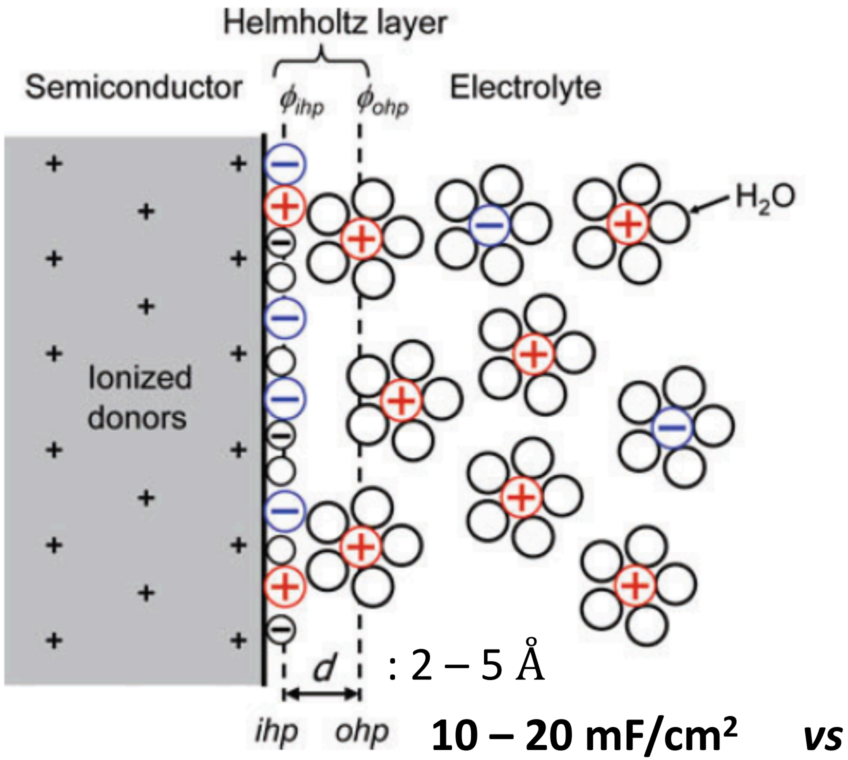
Mott-Schottky Equation

- The measurement of the capacitance to the applied potential across a semiconductor-liquid junction.

$$\frac{1}{C_{Interface}} = \frac{1}{C_{SC}} + \frac{1}{C_H}$$

$C_{interface}$: Total capacitance of the interfacial double layer
C_{SC}: the semiconductor capacitance
$C_{H:}$ the capacitance of the Helmholtz layer in the electrolyte



: 2 – 5 Å

10 – 20 mF/cm² ***vs*** **C_{SC} are 10 – 1,000 nF/cm²**

ihp: inner Helmholtz plane, H^+ and OH^- that are specifically adsorbed at the semiconductor surface.

ohp: outer Helmholtz plane, closest approach for ions still in the solution.

⊕ Proton
⊖ Hydroxide ion
⊖ Electron in surface state

From a book "Photoelectrochemical Hydrogen Production", R. van de Krol and M. Grätzel

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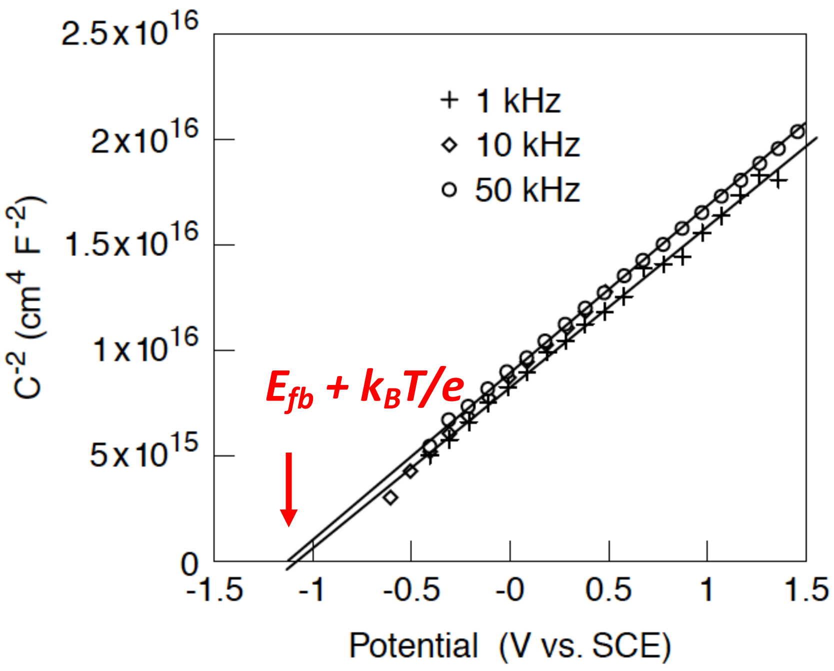
Mott-Schottky Equation

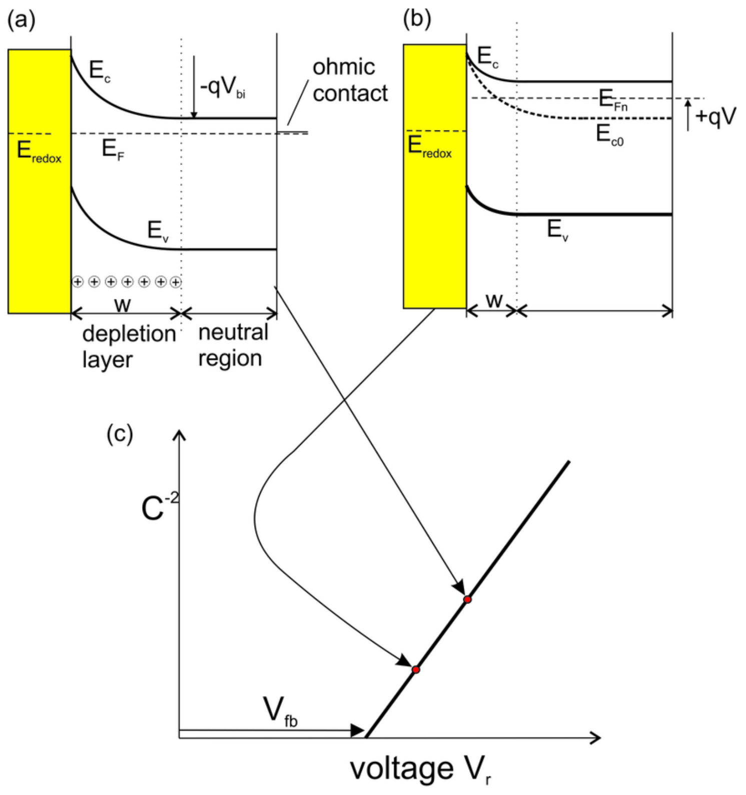
- The semiconductor capacitance is described by the Mott–Schottky equation:

$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon_0 \varepsilon_r e N_D A^2}\left(E_A - E_{fb} - \frac{k_B T}{e}\right)$$

N_D: the concentration of donors
E_A: the applied potential
E_{fb}: the fat band potential

MS plot for an n-type silicon





← From wikipedia

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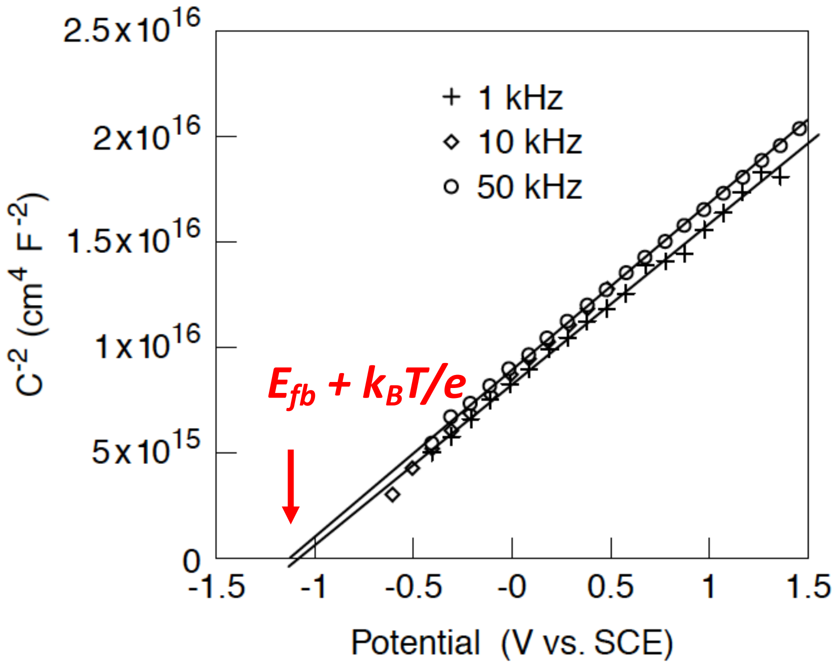
Mott-Schottky Equation

- The semiconductor capacitance is described by the Mott–Schottky equation, which for an n-type material is:

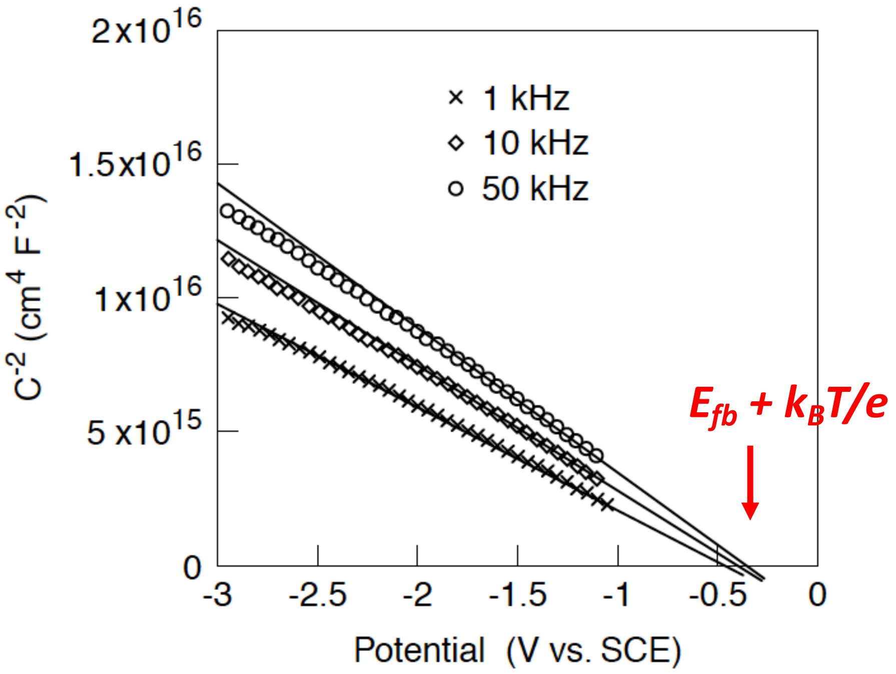
$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon_0 \varepsilon_r e N_D A^2}\left(E_A - E_{fb} - \frac{k_B T}{e}\right)$$

N_D: the concentration of donors
E_A: the applied potential
E_{fb}: the fat band potential

MS plot for an n-type silicon



MS plot for an p-type silicon



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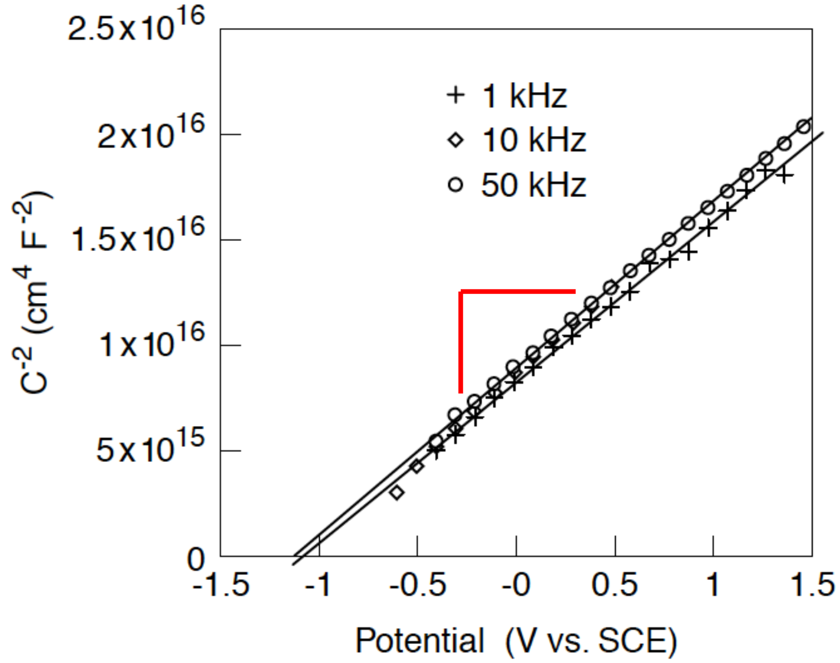
Mott-Schottky Equation

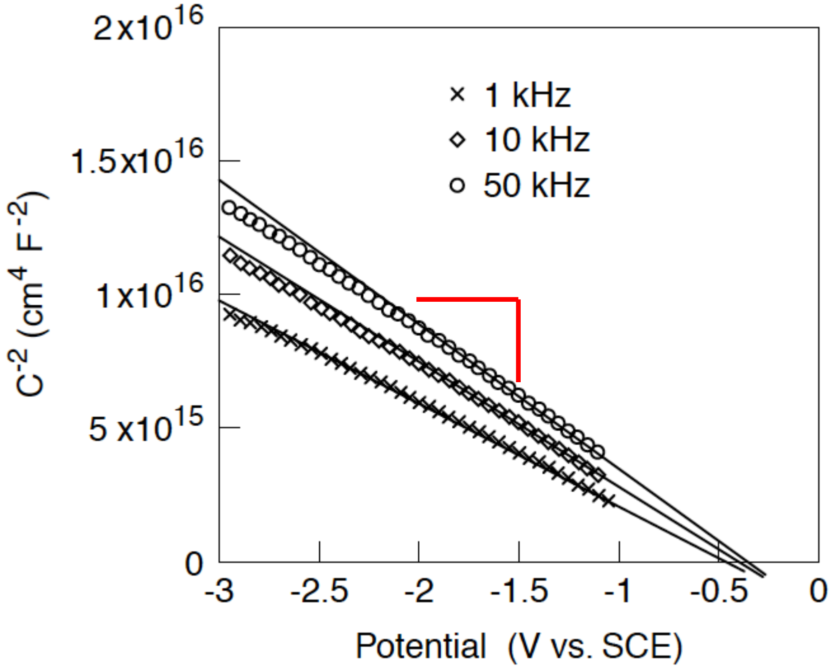
- The slope is proportional to the charge carrier concentration or doping density:

$$N_D(cm^{-3}) = \frac{1.41 \times 10^{32}(cm \times F^{-2} \times V^{-1})}{\varepsilon_r \times A^2(cm^4) \times slope(F^{-2} \times V^{-1})}$$

MS plot for an n-type silicon



MS plot for an p-type silicon



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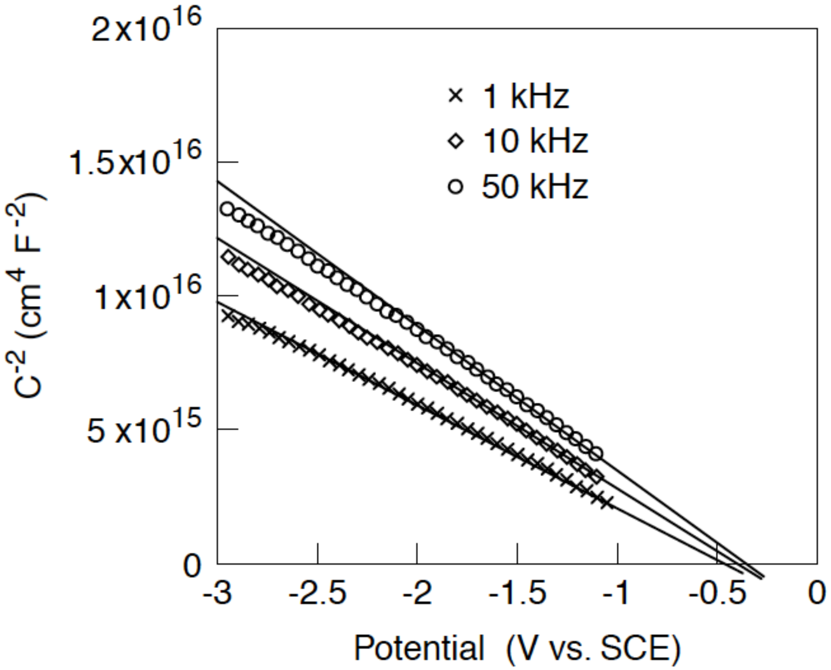
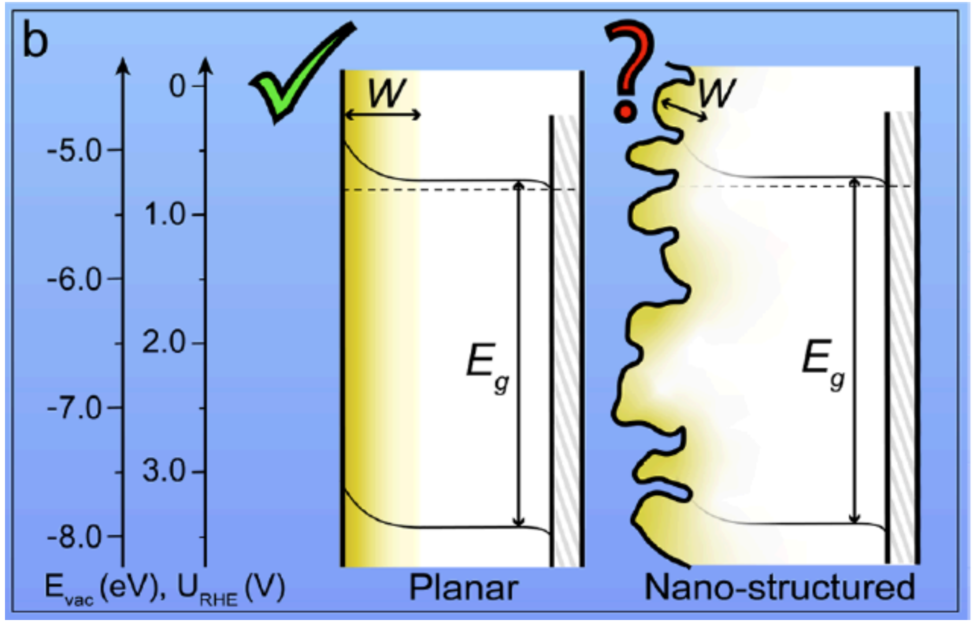
Cautions Needed for M-S Analysis

- The E_{fb} is ideally not dependent on the frequency.
  - Contribution from surface state capacitance and double-layer capacitance, giving a rise to a frequency dependence to M-S results.
  - Typically, a frequency is chosen to be fast enough not to allow for effective filling and unfilling of surface states or for the buildup of a double-layer capacitance (1–20 kHz applicable for highly crystalline materials).
- Nanostructured film.
  - The equation is established based on a planar geometry of the SC-electrolyte junction.





K. Sivula, *ACS Energy Lett.*, **6**, 2549–2551 (2021)

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