Energy Conversion by Semiconductor Devices

Jun-Ho YUM
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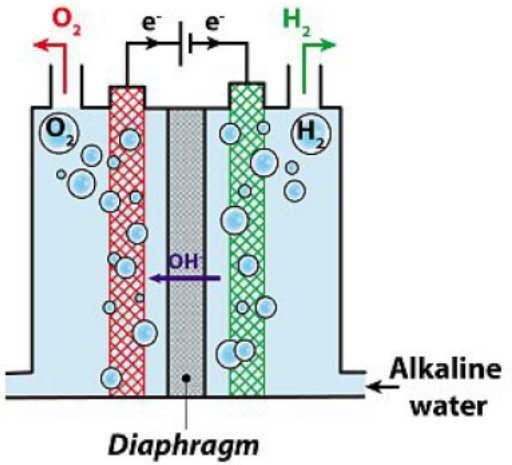
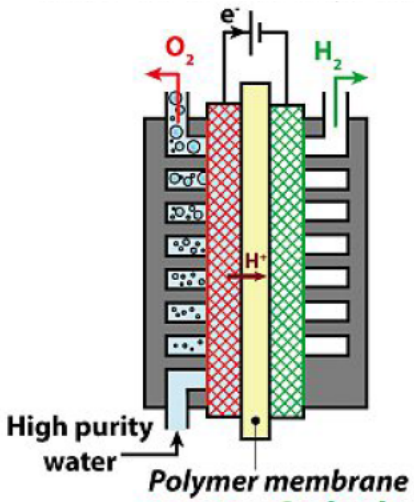
Alkaline or Proton Exchange Membrane (PEM) Electrolysis

Alkaline Electrolyzer



PEM Electrolyzer



(Nafion)

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

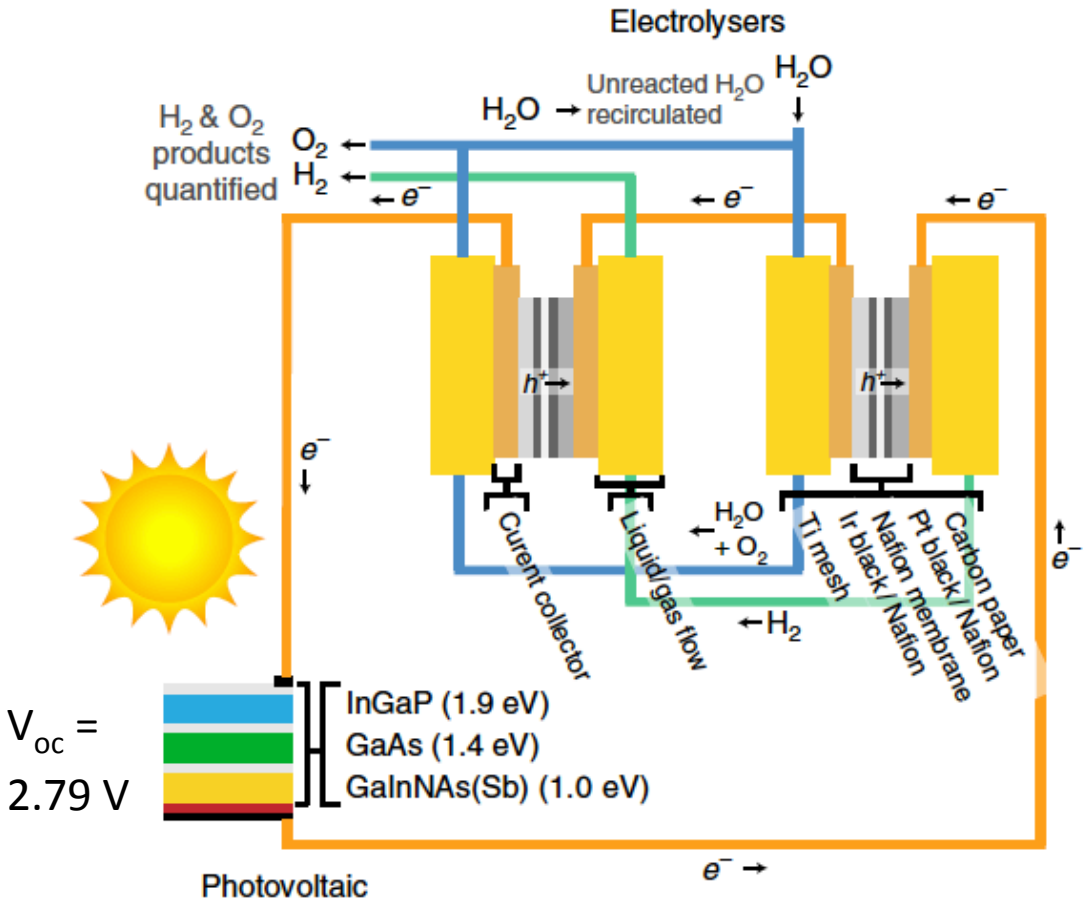
Redox reactions: Water is broken down at the cathode. Electrodes are mainly nickel alloys, coated onto specialised steel.
Porous diaphragm: The OH^- ions diffuse across the cell to the anode.

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%

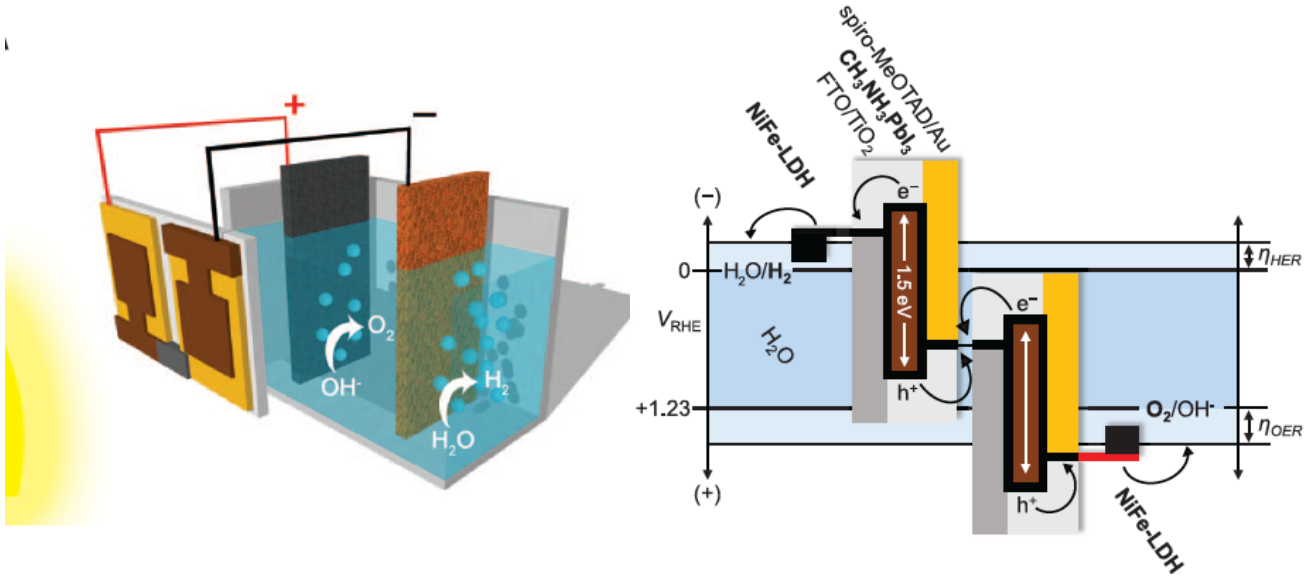


Image taken from J. Luo et al., *Science*, **345**, 1593 (2014)

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

Water Electrolysis

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

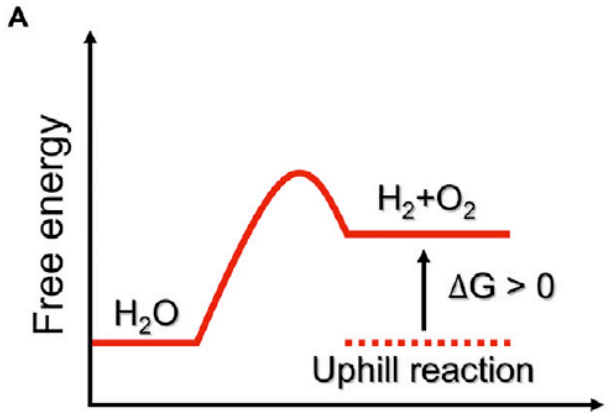
$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 286\ - (0.163 \times T)\ kJ/mol = 237\ kJ/mol\ H_2$$

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

E⁰ = 1.23 V

n = the number of electrons transferred in the reaction,

F = the Faraday constant 96,500 C/mol



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).

Water Electrolysis

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

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

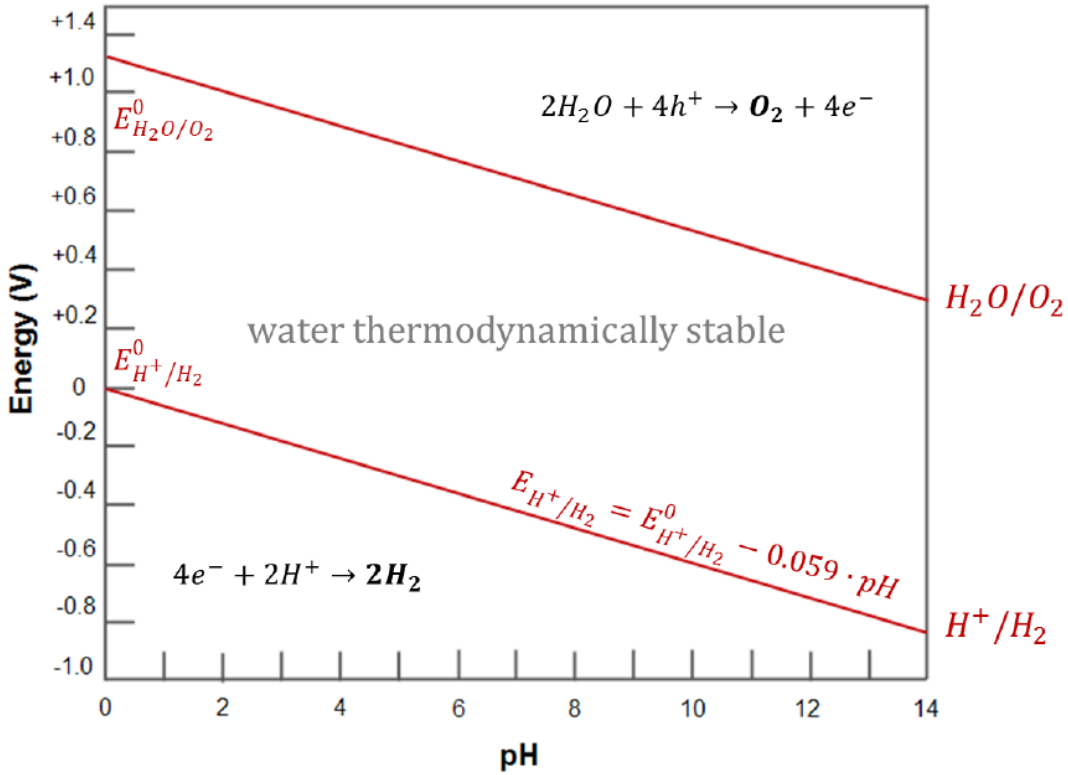
$2H_2O\ (liquid) + 4h^+ \leftrightarrow O_2(gas) + 4e^- + 4H^+$ $\quad E^0_{H_2O/O_2} = 1.23\ V\ vs.SHE$ Oxygen Evolution Reaction (OER)

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

In alkaline environments (pH 14)

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

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



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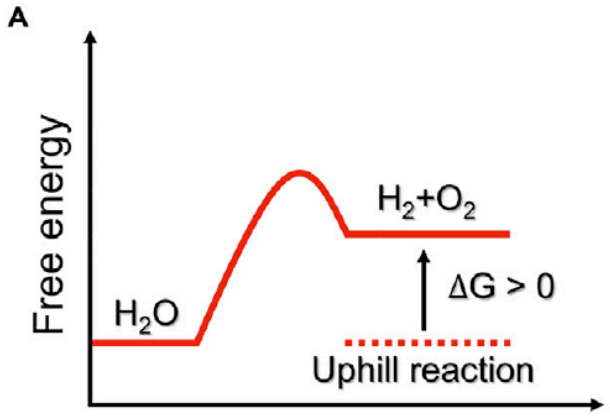

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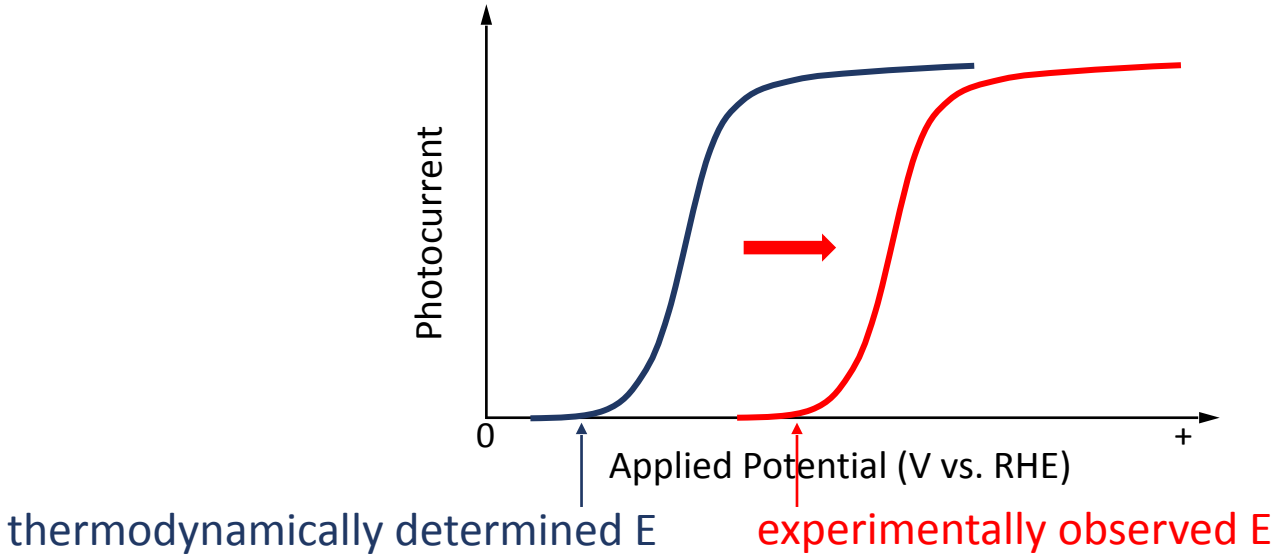
Kinetic Challenges

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

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**".

Other reasons: Concentration
Resistance

Kinetic Challenges

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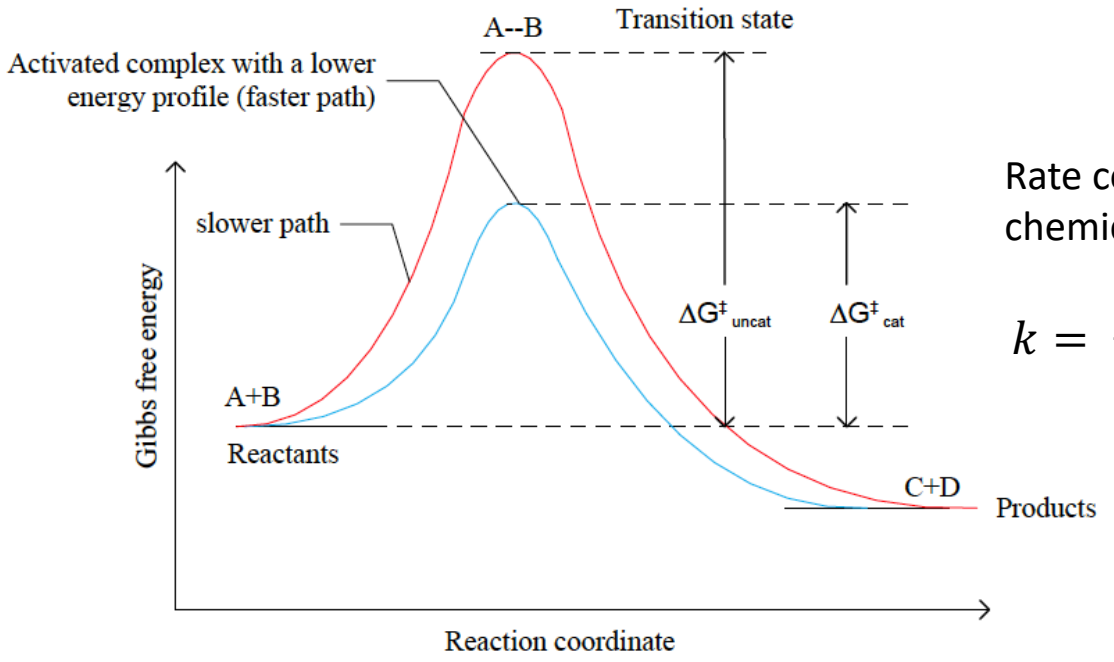
Electrocatalytic process in micro- to seconds *vs* Photophysical processes in a few femto- to nano-seconds

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.



Rate constant of a chemical reaction

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

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

Kinetic Challenges

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	$H_2O + e^- + (M - H_{ad}) = OH^- + H_2 + M$
OR			
2.	$2(M - H_{ad}) = H_2 + 2M$	Tafel Step	$2(M - H_{ad}) = H_2 + 2M$

M represents the hydrogen adsorption site

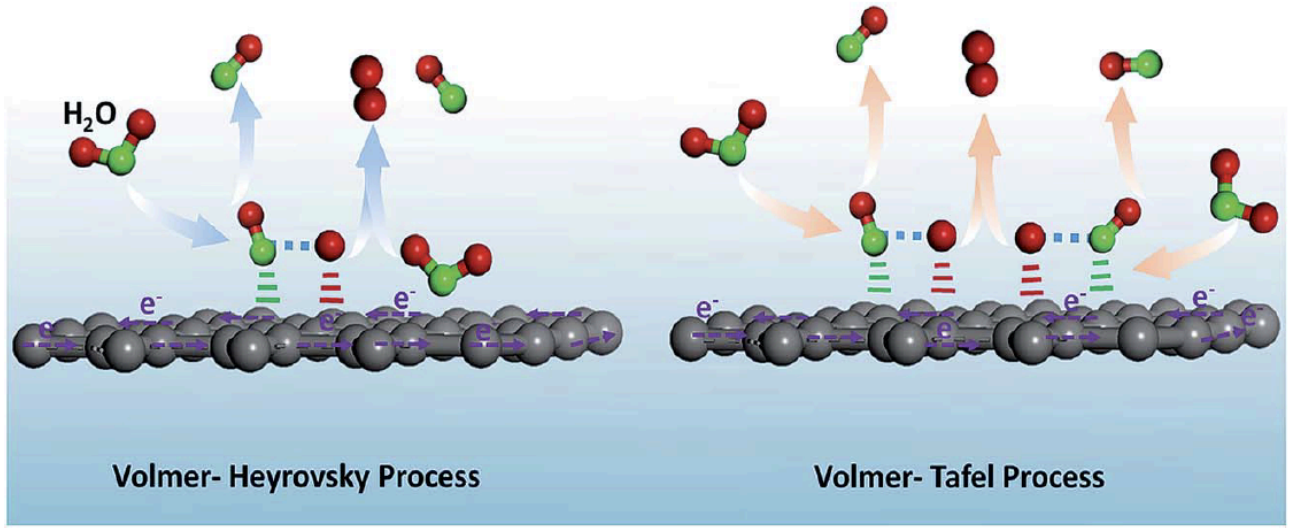


Image taken from Z. Chen et al., *J. Mater. Chem. A*, ***7***, 14971–15005 (2019)

Kinetic Challenges

Hydrogen Evolution Reaction (HER)

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In Alkaline Media

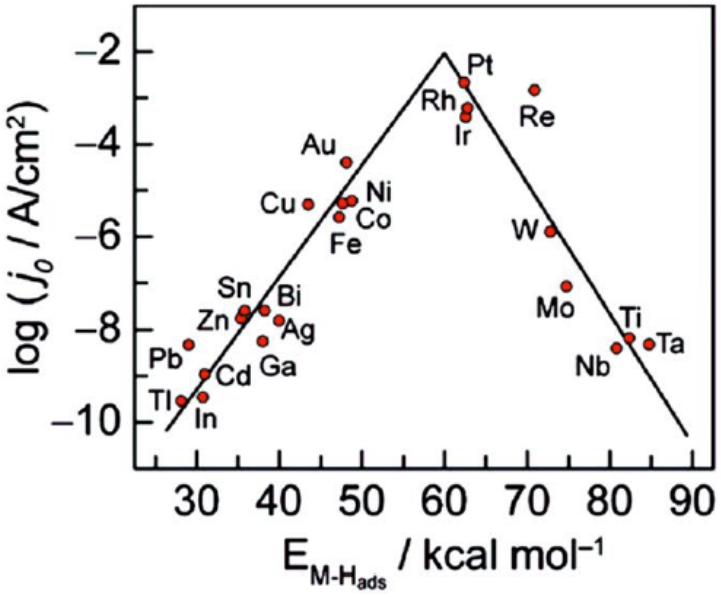
$$H_2O + M + e^- = OH^- + (M - H_{ad})$$

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

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

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.

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 of oxygen** (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)

In Alkaline Media

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

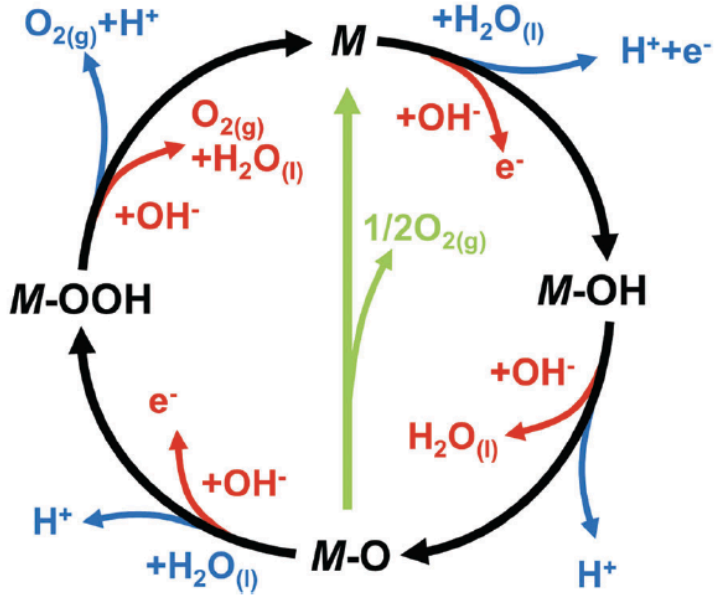
$$(M - OH) + OH^- = (M - O) + H_2O + e^-$$

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

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

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

RDS: Rate-Determining Step



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

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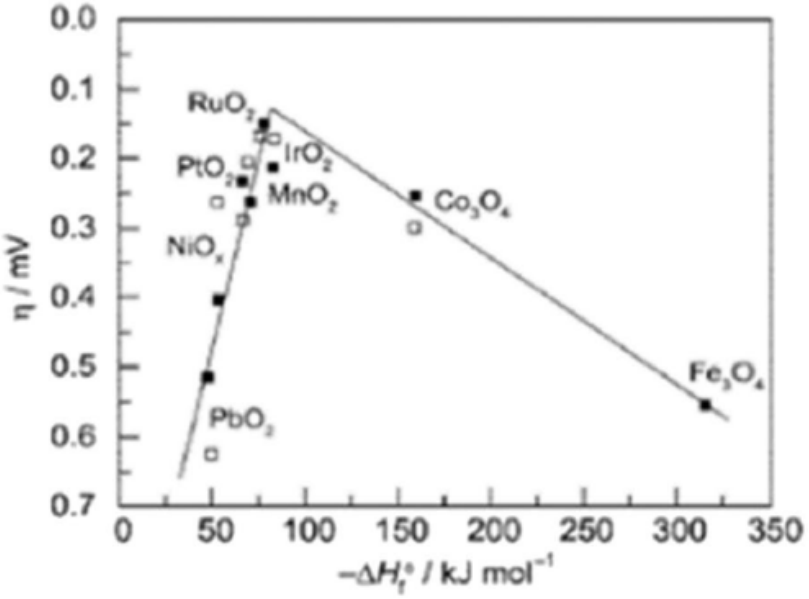
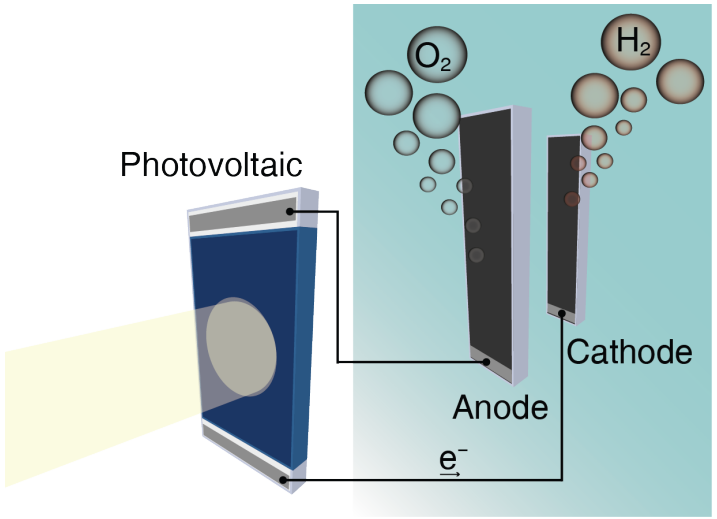


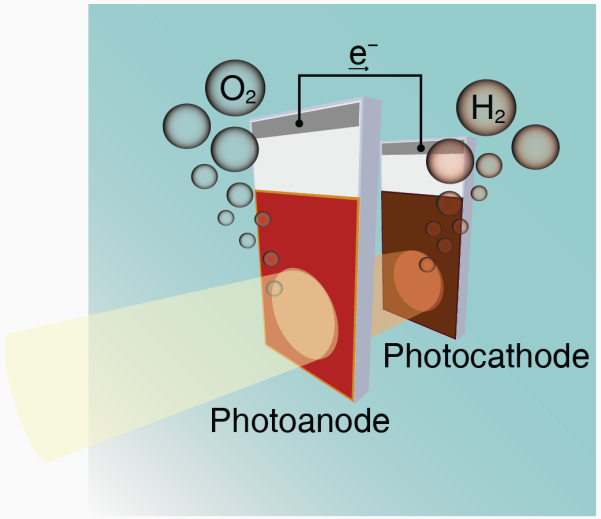
Wang et al., *Nano Convergence,* 8:4 (2021)

Solar Hydrogen Production

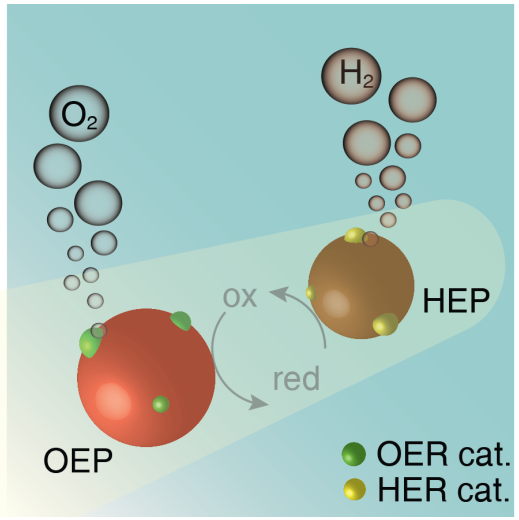
PV-EC



PEC



PC



5 – 12 \$/Kg H_2 (1)

3 – 18 \$/Kg H_2 (2)

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

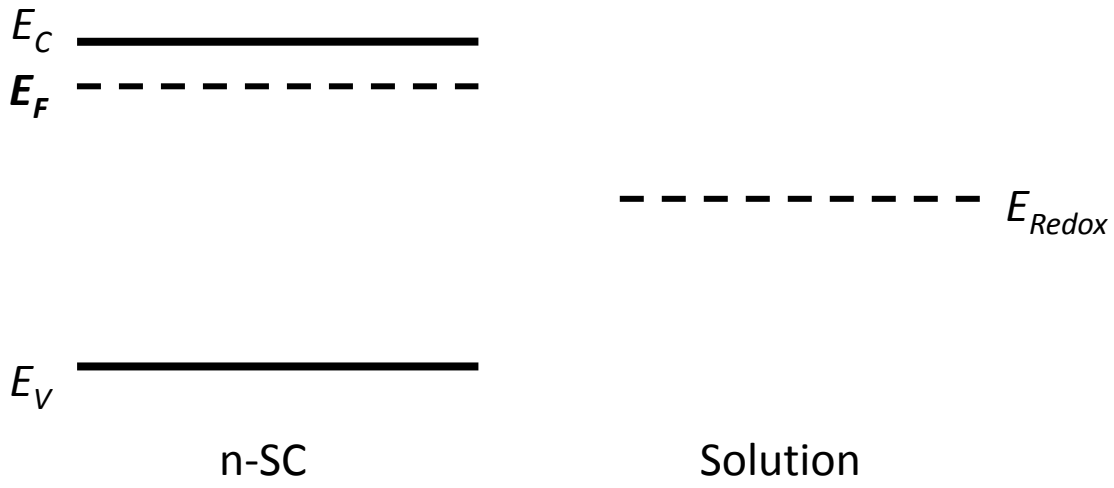
(2) B.A. Pinaud, et al. *Energy Environ. Sci.*, **6**, 1983 (2013)

- Jun-Ho YUM, junho.yum@epfl.ch

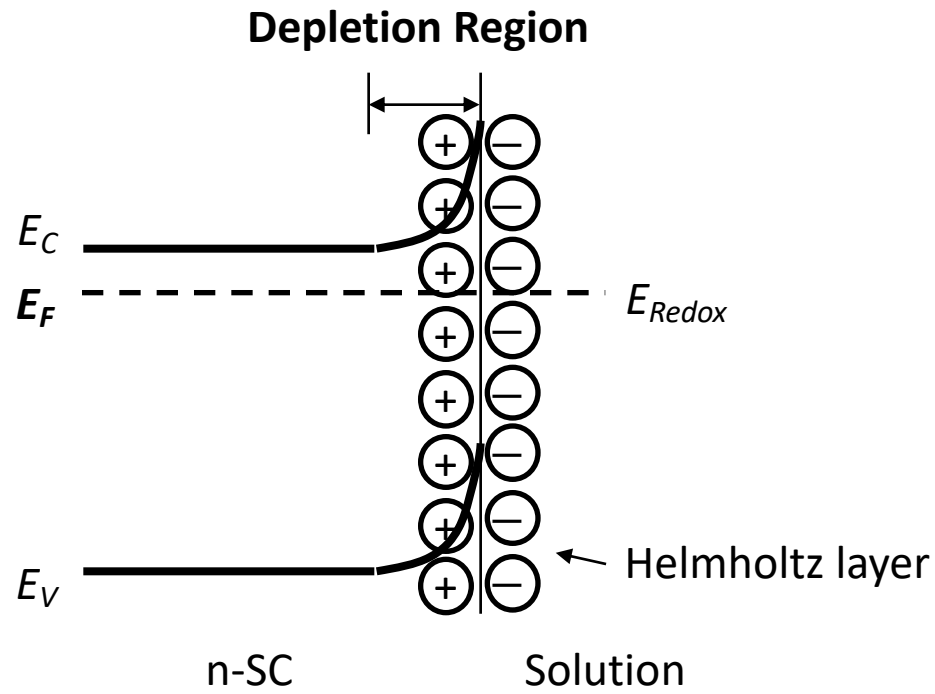
N-type Semiconductor-Liquid Junction

- 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



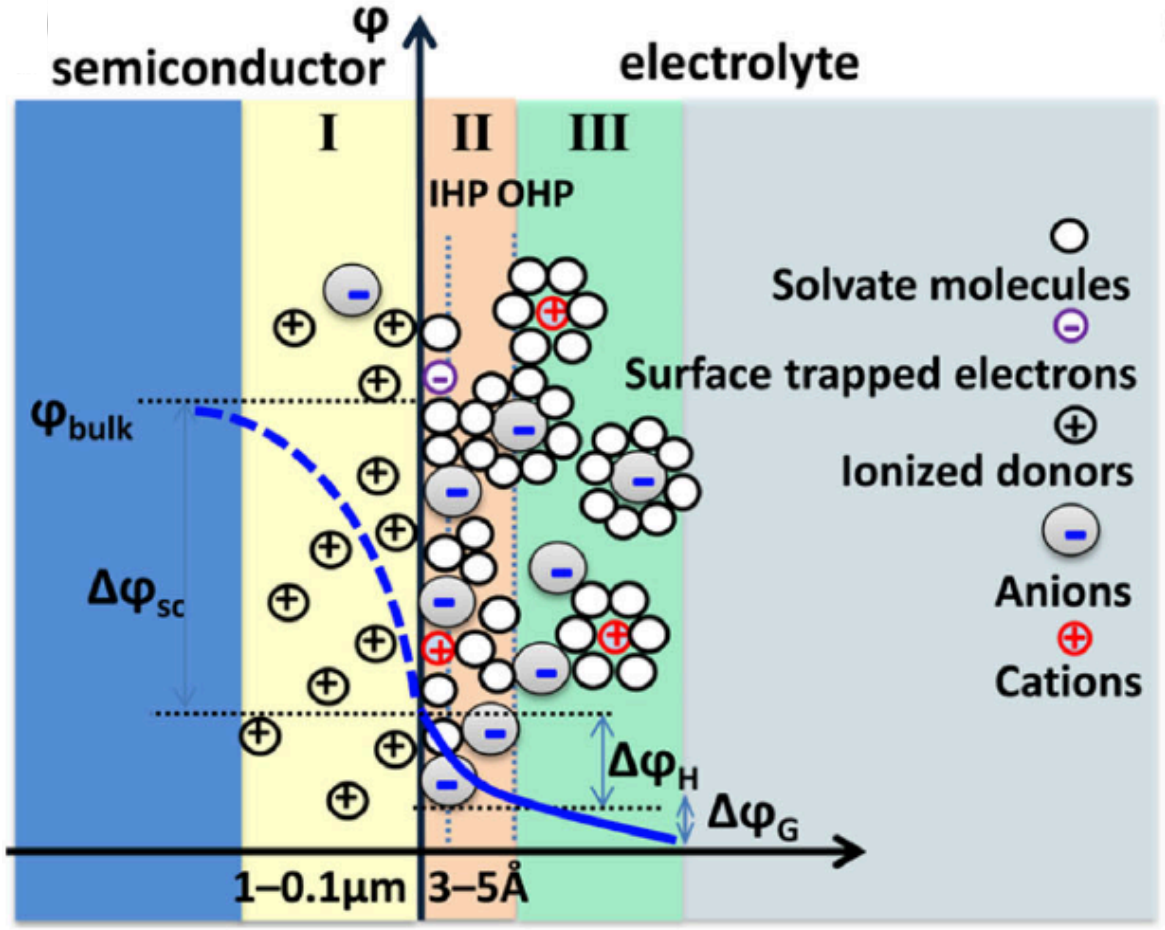
In thermal equilibrium



No band bending in an electrolyte:
High ionic concentration
Electrochemical double layer neutralises the E-field

N-type Semiconductor-Liquid Junction

In thermal equilibrium



$\Delta\varphi_H$ and $\Delta\varphi_G$ are the potential drops in the Helmholtz layer (II) and Gouy layer (III)

IHP: inner Helmholtz plane, electrons in trapped states, solvate molecules, adsorbed ions H^+ and OH^- that are specifically adsorbed at the semiconductor surface.
OHP: outer Helmholtz plane, closest approach for solvated ions to an electrode surface.

the width of the space charge layer

$$W_{SC} = \left(\frac{2\Delta\phi_{SC}\varepsilon\varepsilon_0}{qN_d}\right)^{1/2}$$

$\Delta\varphi_{sc}$ = *the difference between the* E_F *of the SC in a vacuum and the redox potential of the electrolyte*

ε = *the relative permittivity,*

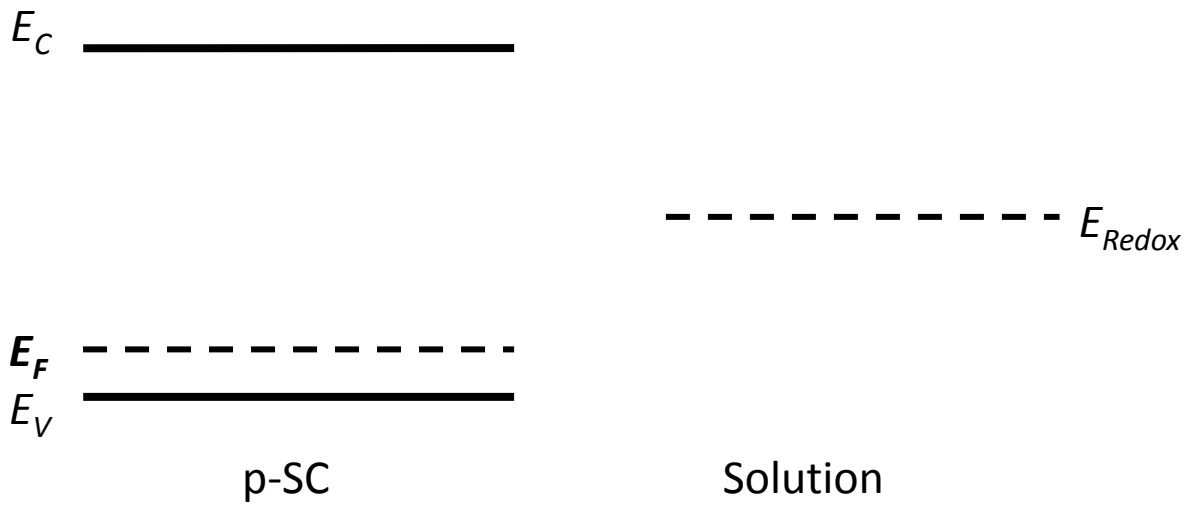
ε_0 = *the permittivity of free space*

N_d = *the donor density*

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



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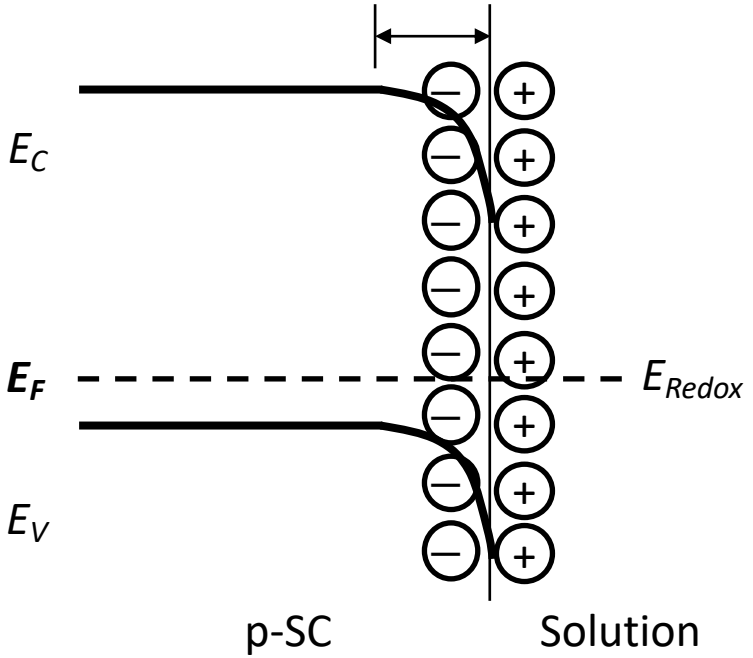
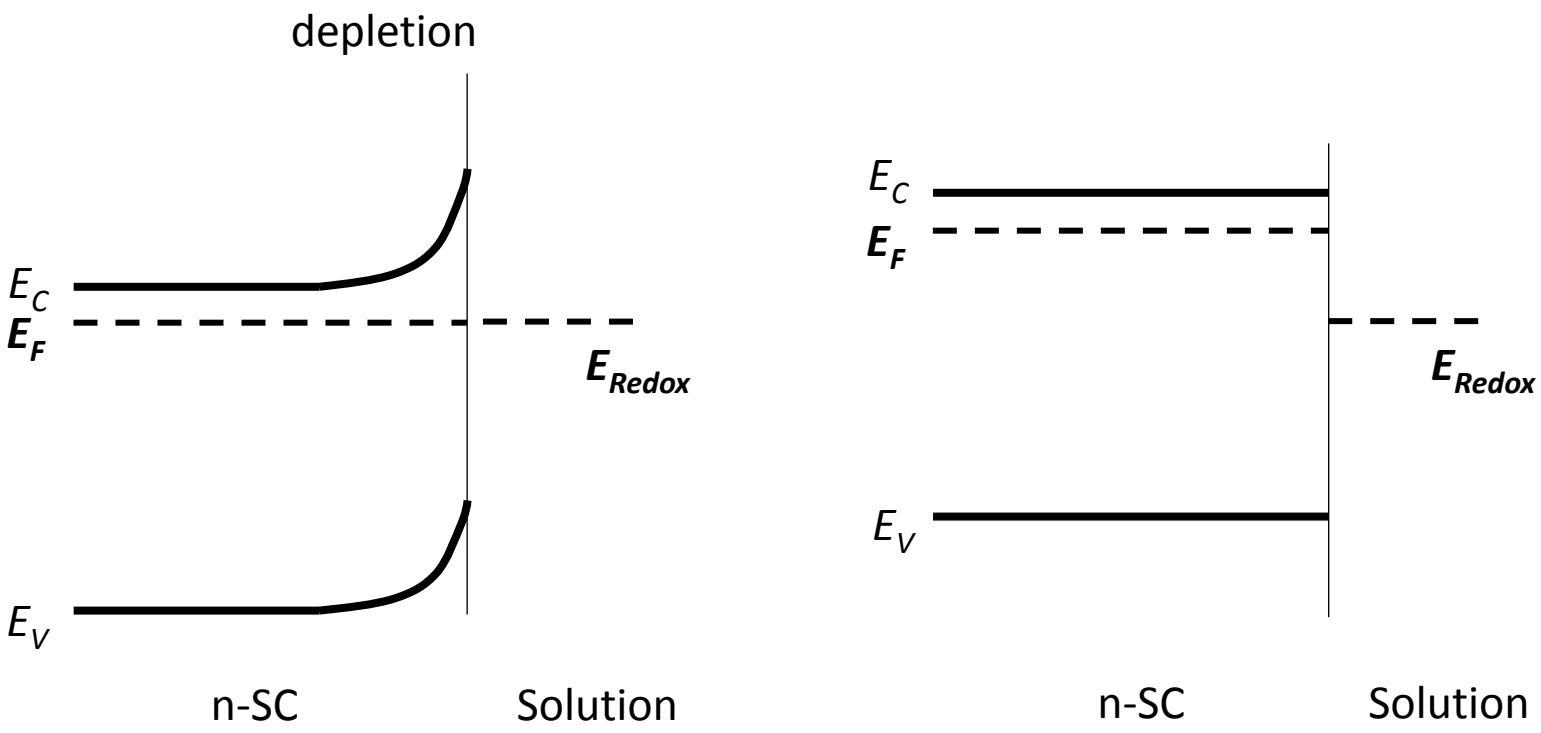


Effect of Applied Potential: n-type SC

- 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, $\mathbf{E_{fb}}$: Potential where there is no net transfer of charge, and hence there is no band bending.

$E = E_{fb}$



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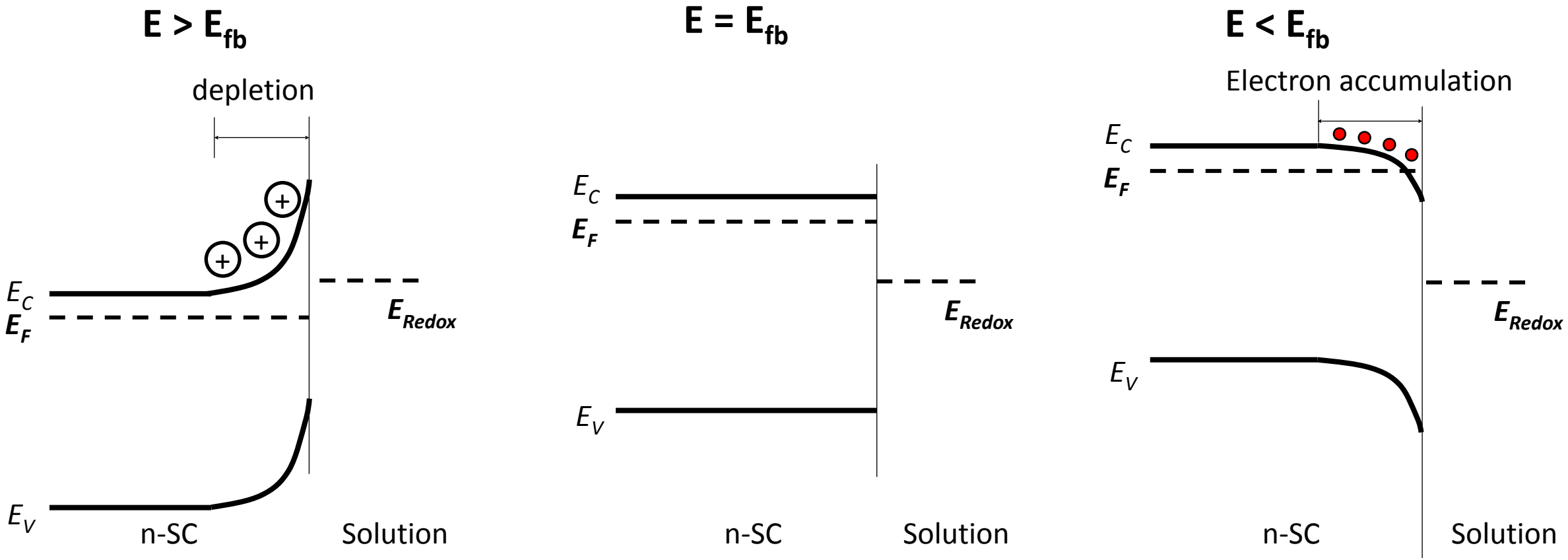

Effect of Applied Potential: p-type SC

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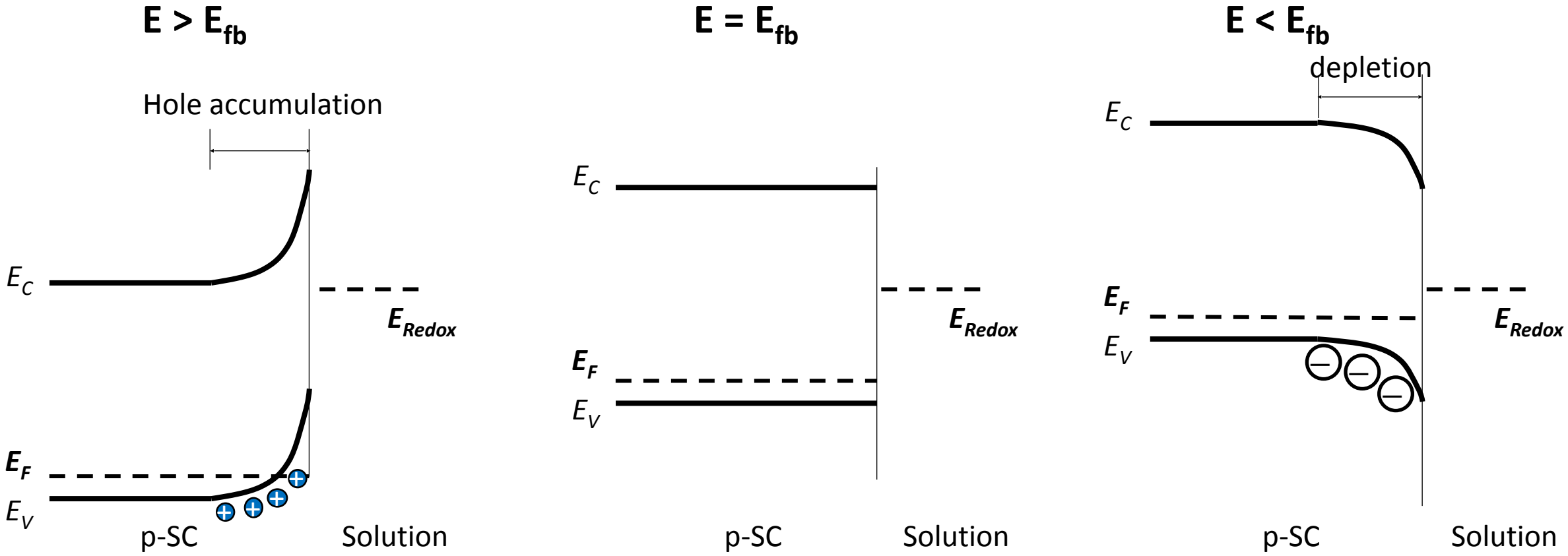
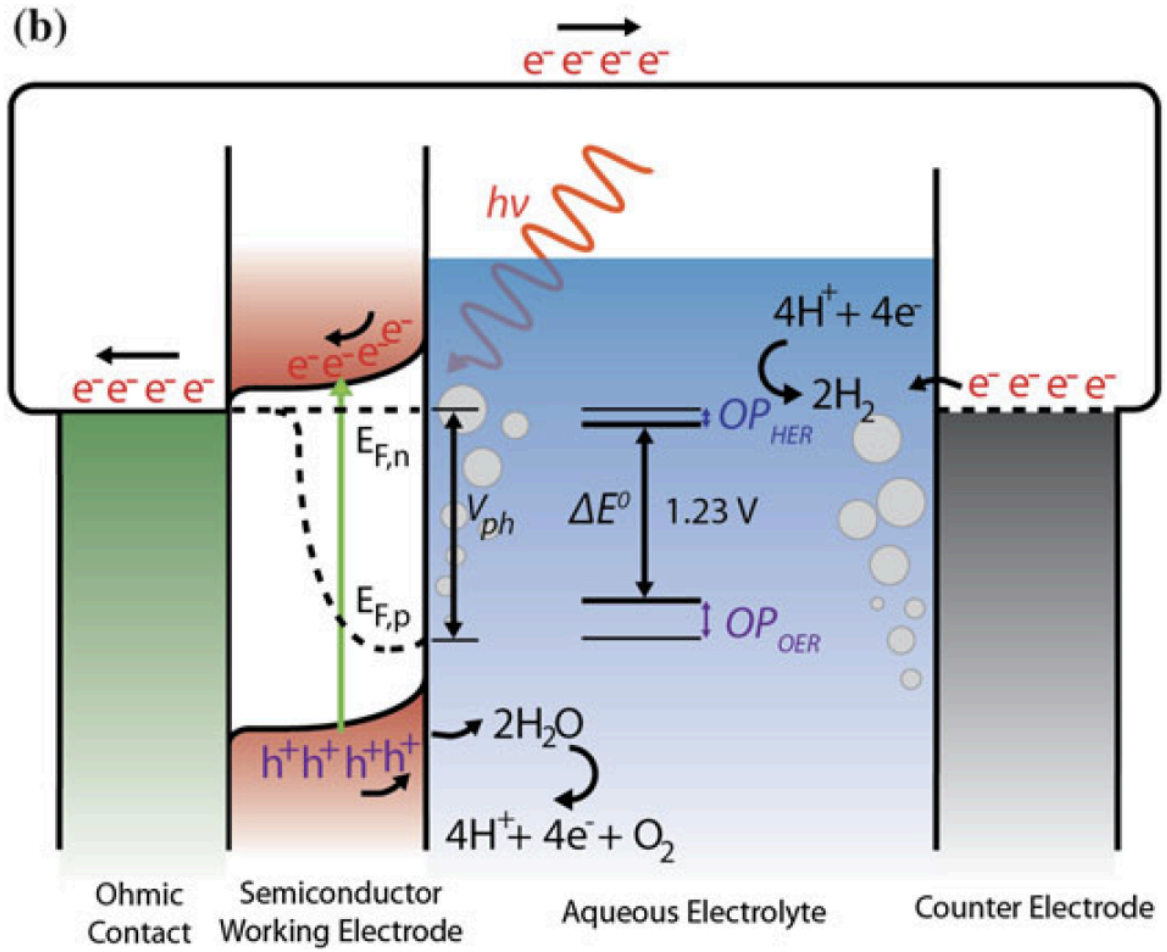


Thermodynamic Energy to Split Water

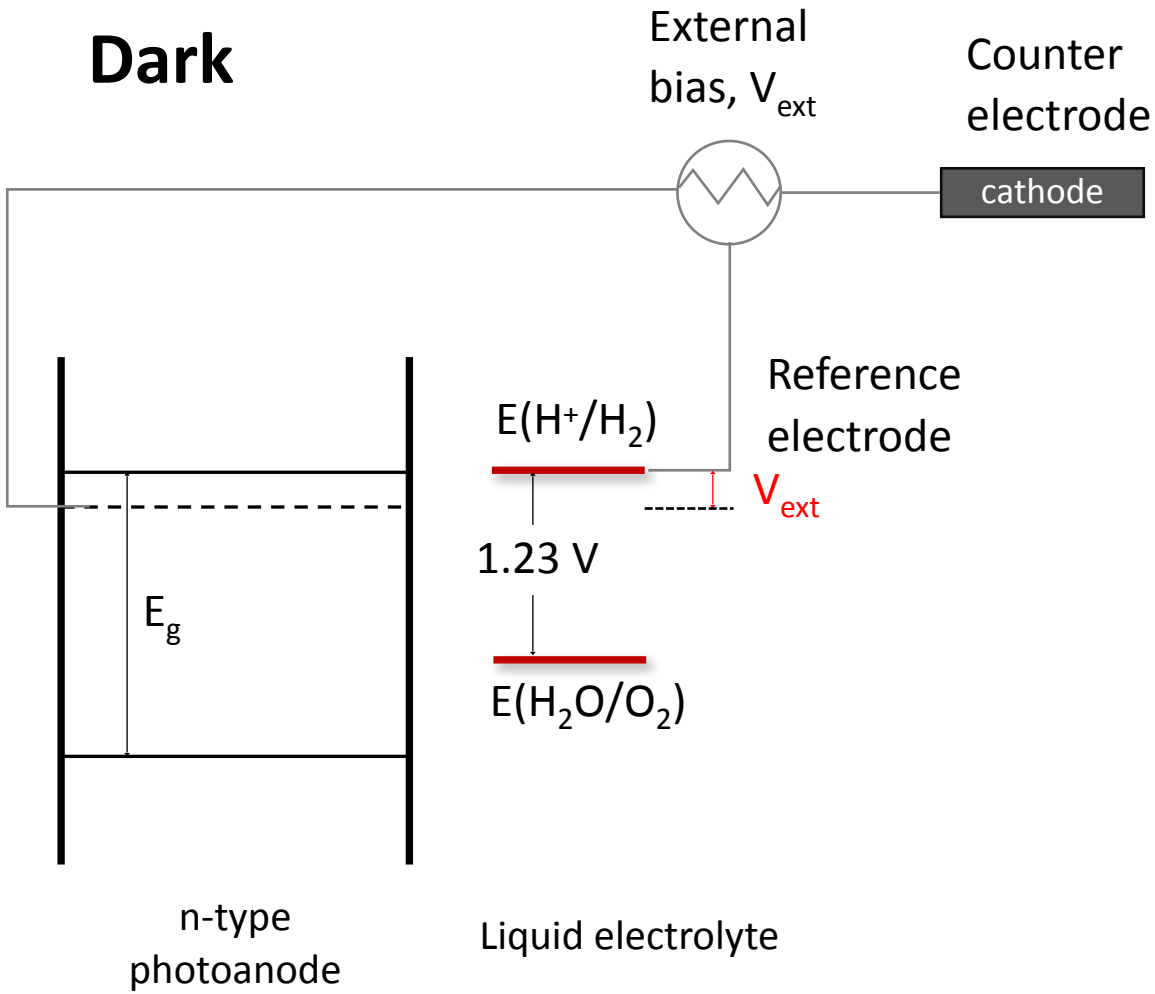


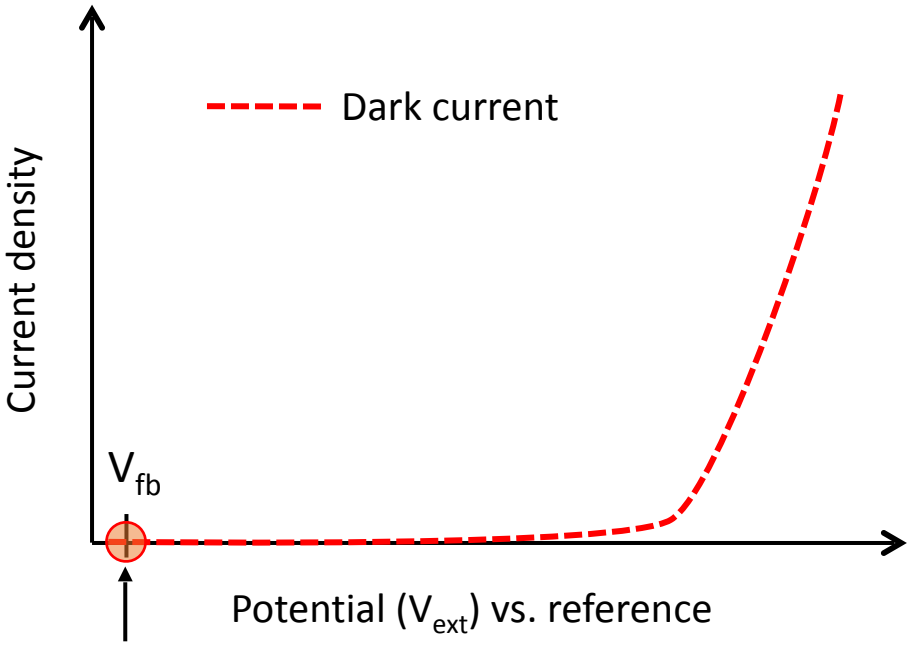
$$E_{Fn} = E_i + k_B T ln(\frac{n}{n_i}) \qquad n = n_0 + \Delta n \approx n_0$$

$$E_{Fp} = E_i - k_B T ln(\frac{p}{n_i}) \qquad p = p_0 + \Delta p \approx \Delta p$$

- The photovoltage in the semiconductor is **the potential difference between the quasi-Fermi levels of electrons ($E_{F,n}$) and holes ($E_{F,p}$) under illumination**.
- **V_{ph} < E_g of the SC**
  due to losses (arising from factors such as radiative recombination, incomplete light trapping, and non-radiative recombination).
- In addition to the thermodynamic requirement, there are **overpotentials associated with driving the kinetics of the HER and OER** at the solid–liquid interface.

Metrics in Photoelectrode Development

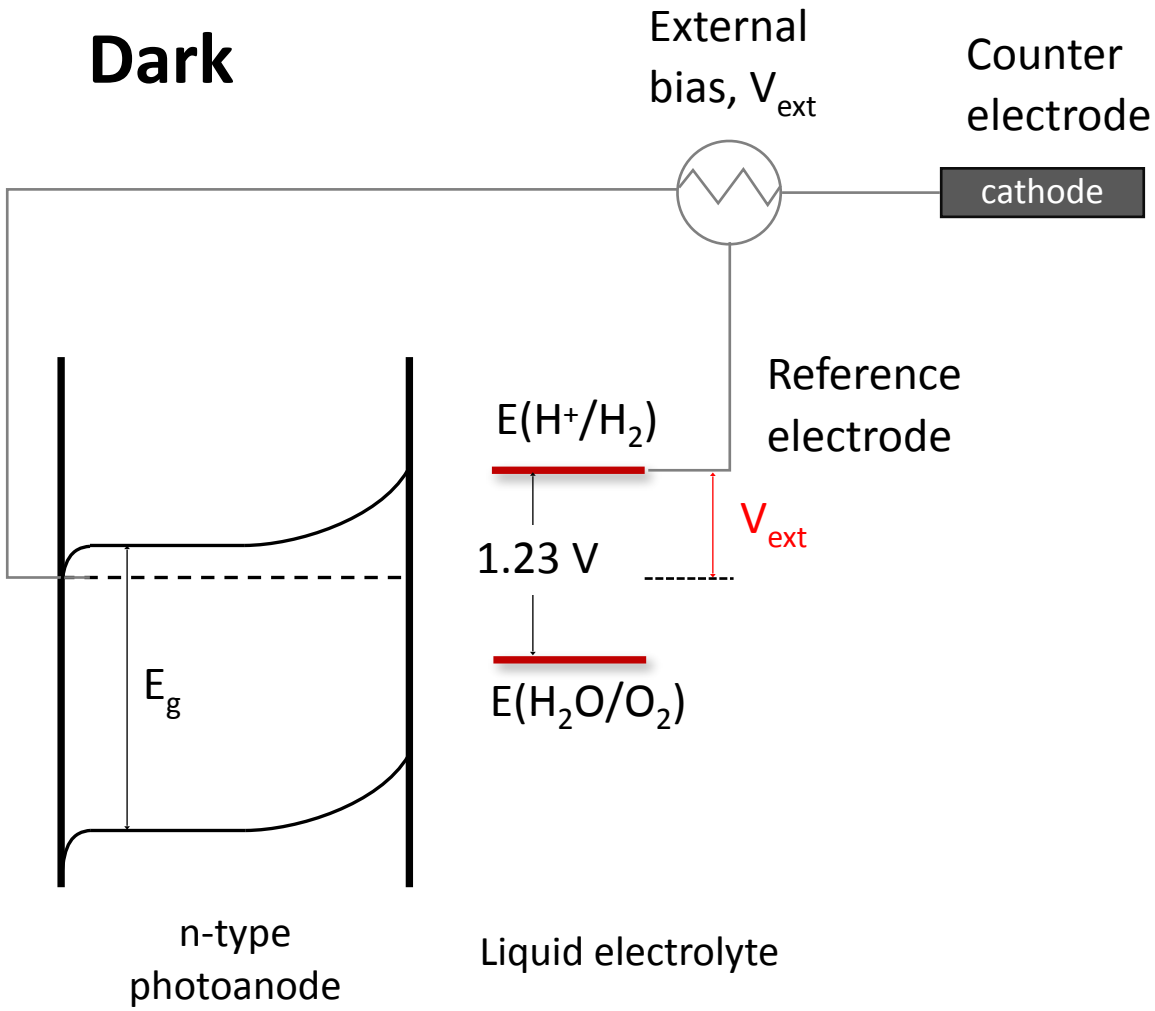


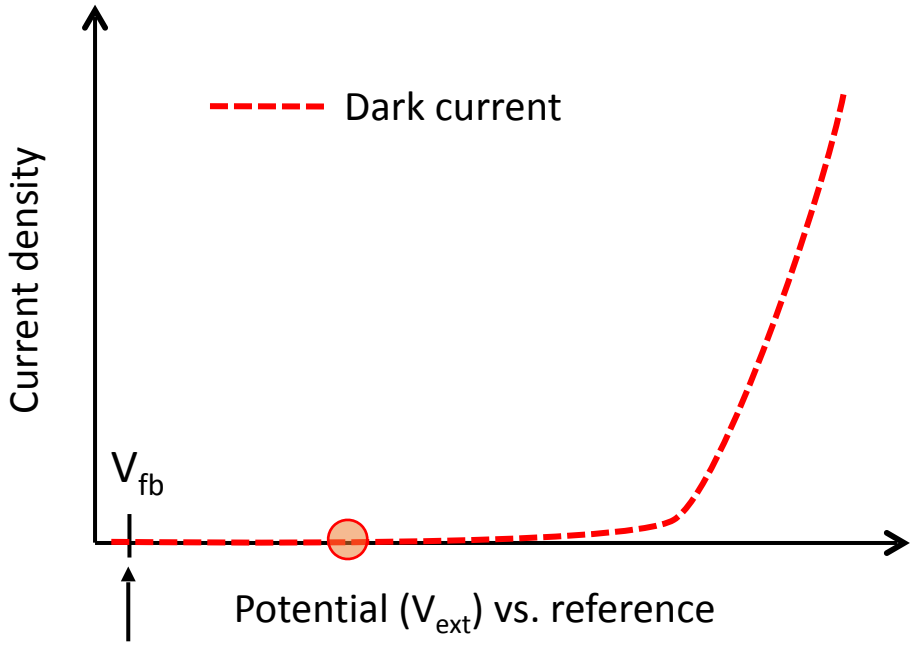


Flat band potential

Dark current before onset should be small, indicating no irreversible processes

Metrics in Photoelectrode Development





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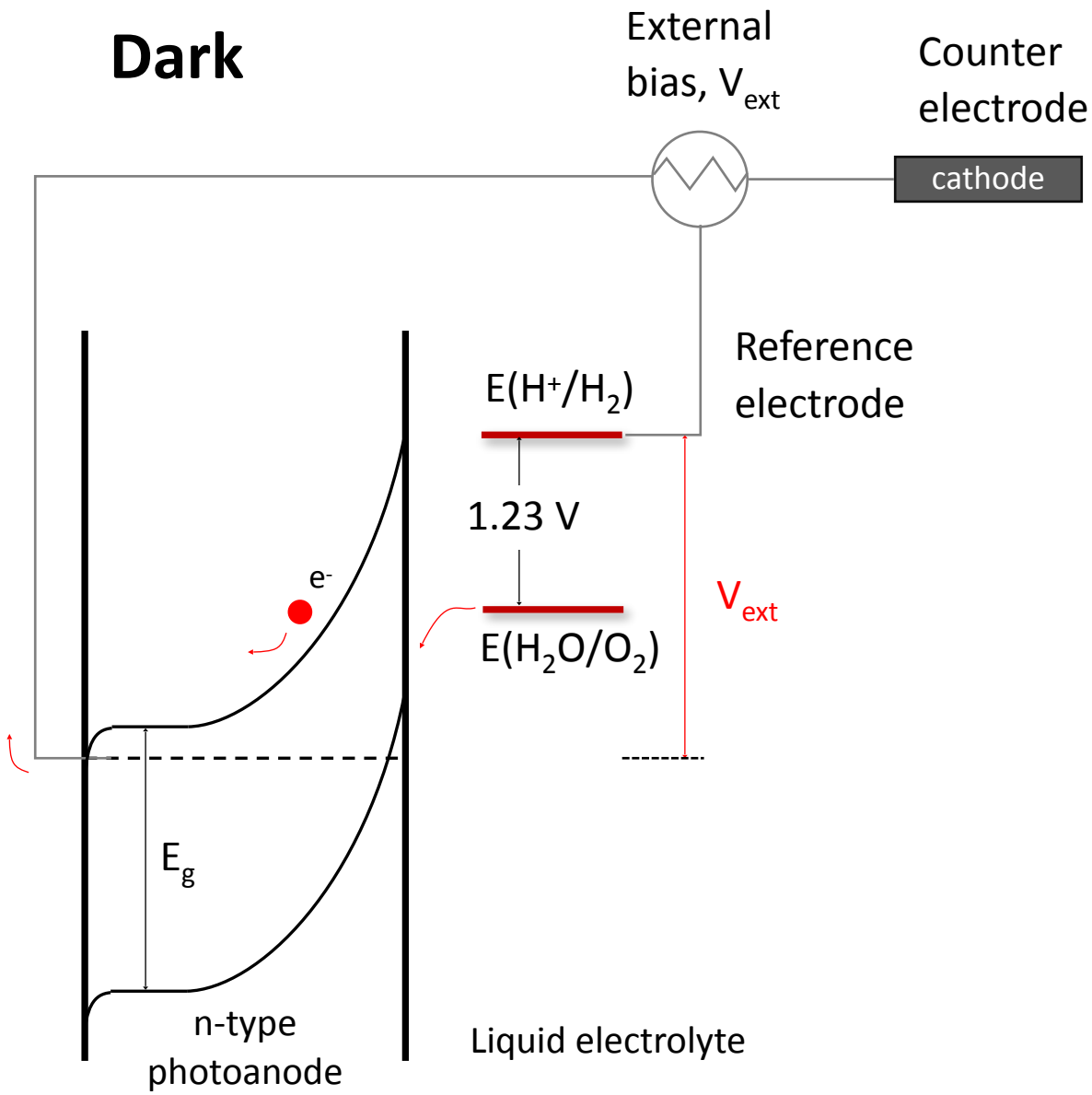
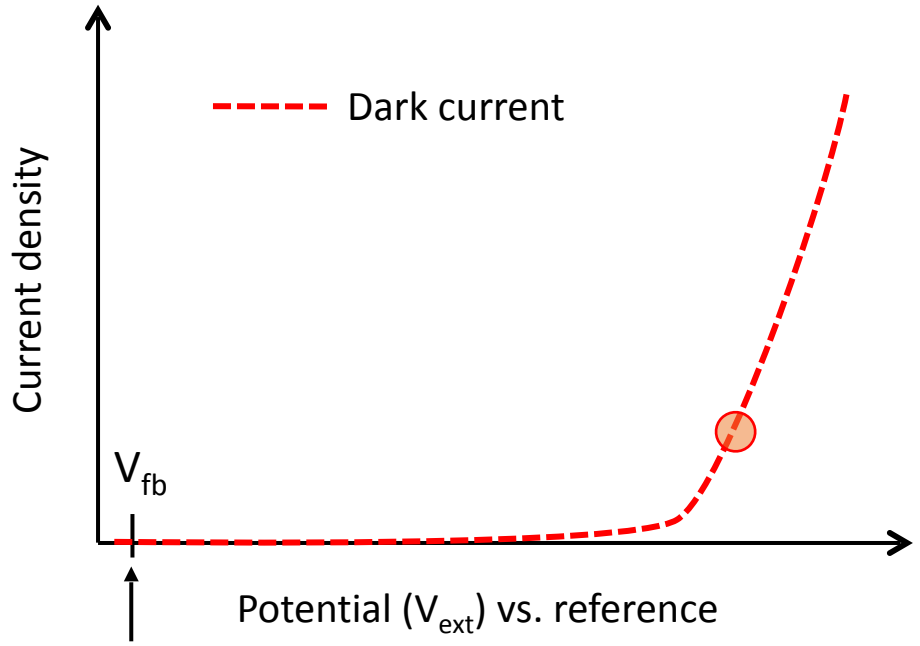
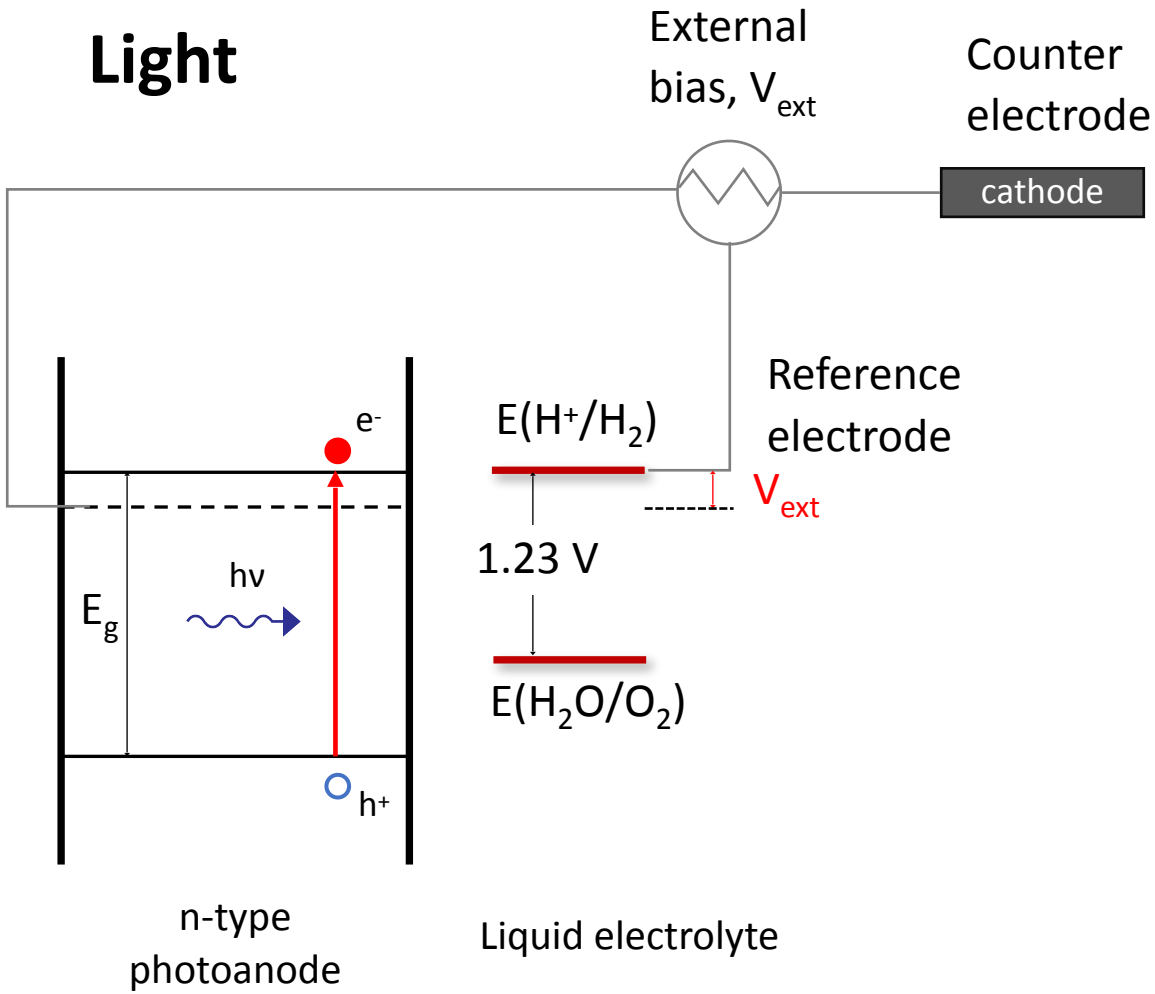


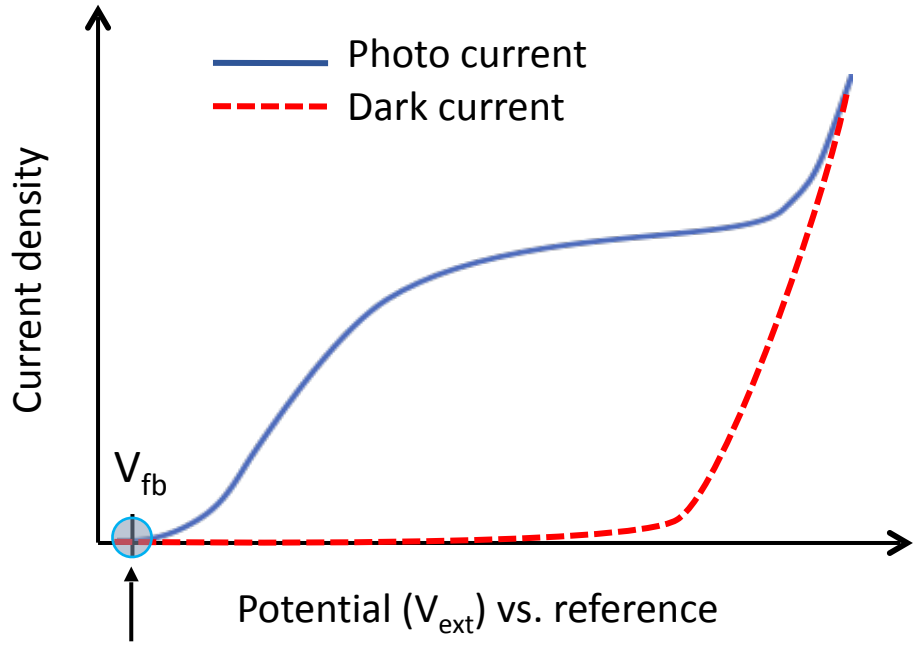


Flat band potential

Dark current increases when energy states become available in conduction band.

Metrics in Photoelectrode Development

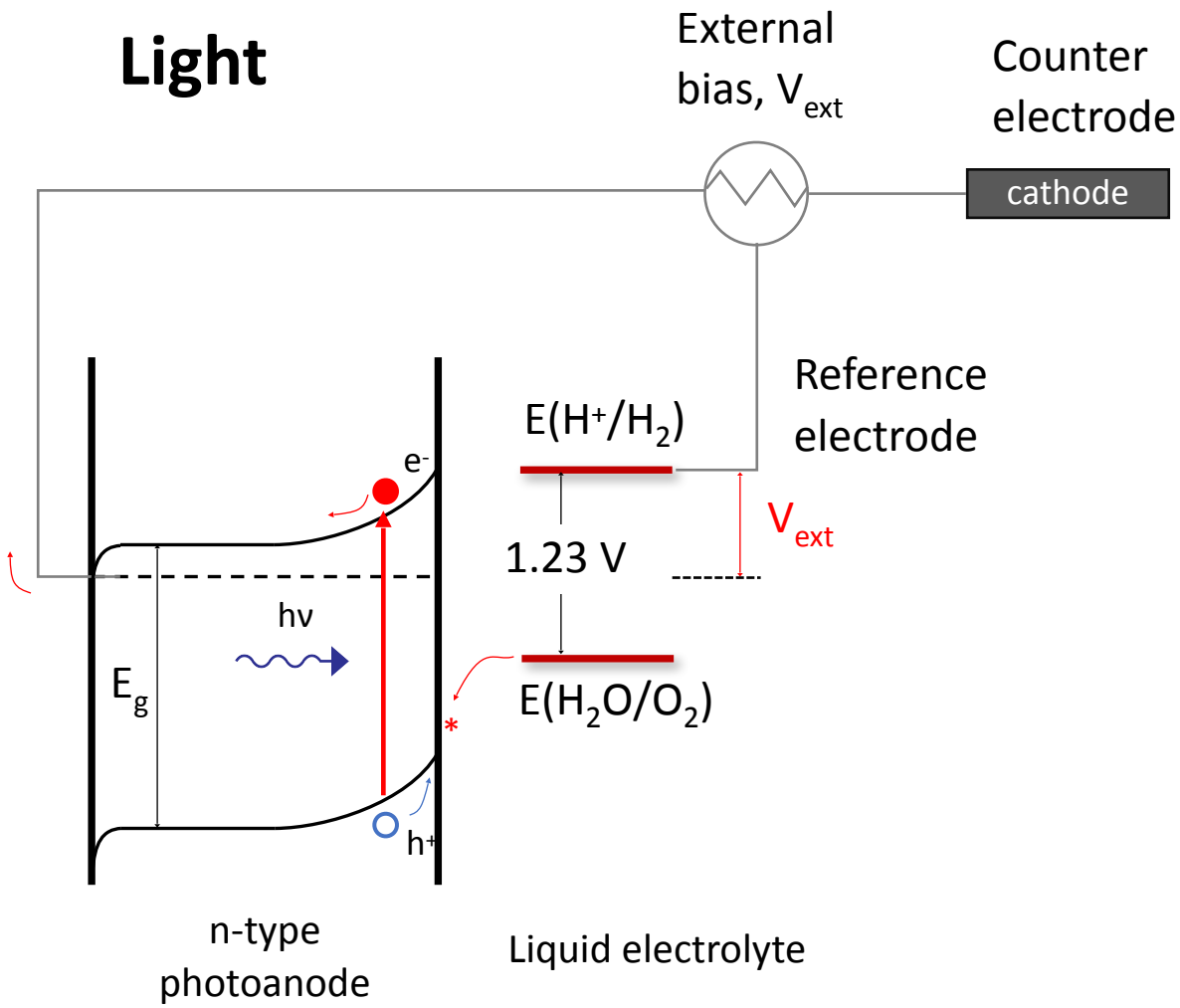


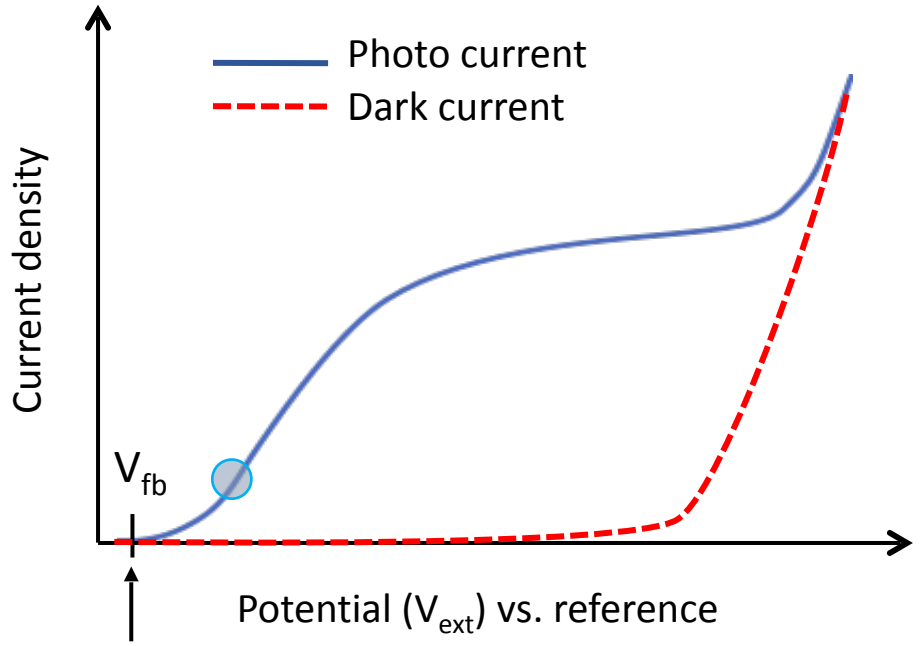


Flat band potential

At the V_{fb}, there is no electric field to separate the photoexcited electron-hole pairs.

Metrics in Photoelectrode Development

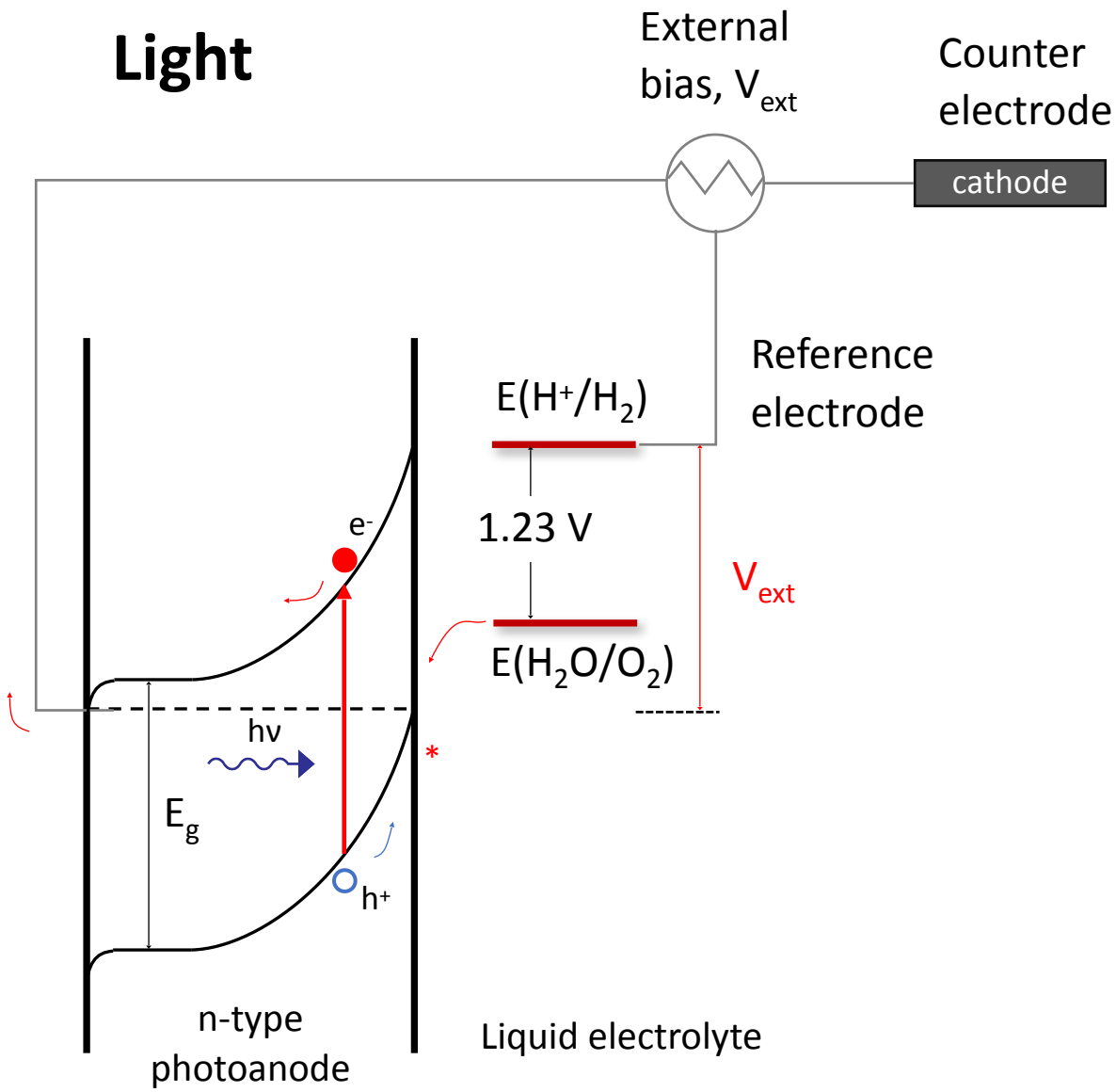


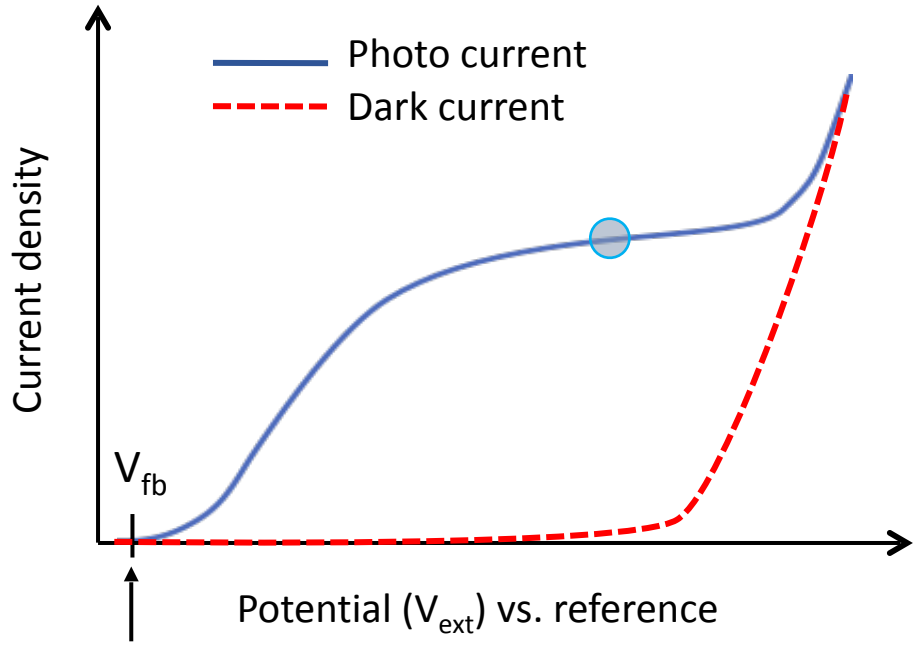


Flat band potential

Under illumination ($hv>E_g$) a photocurrent is observed due to the presence of holes at the interface between the semiconductor and the electrolyte

Metrics in Photoelectrode Development

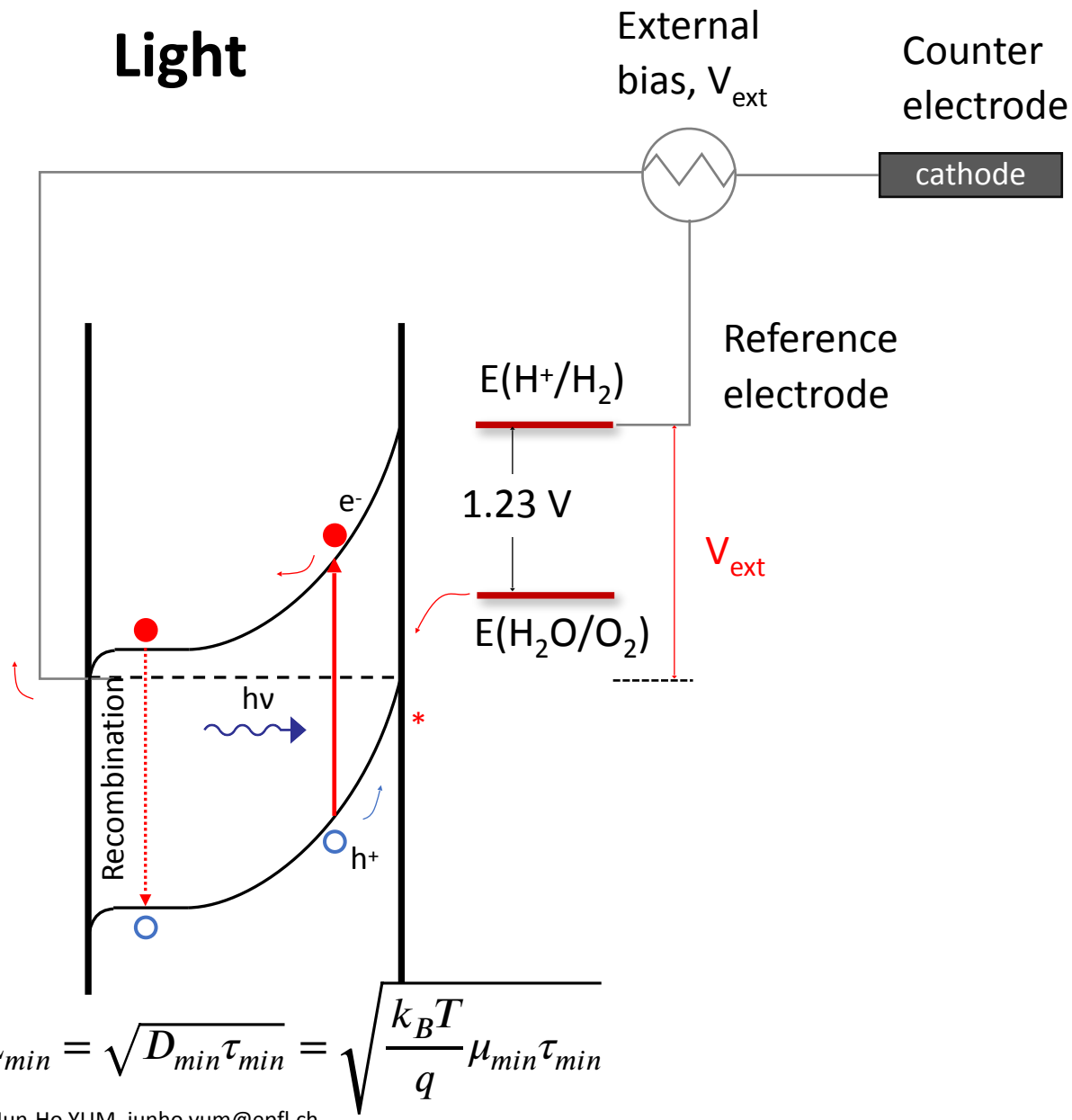




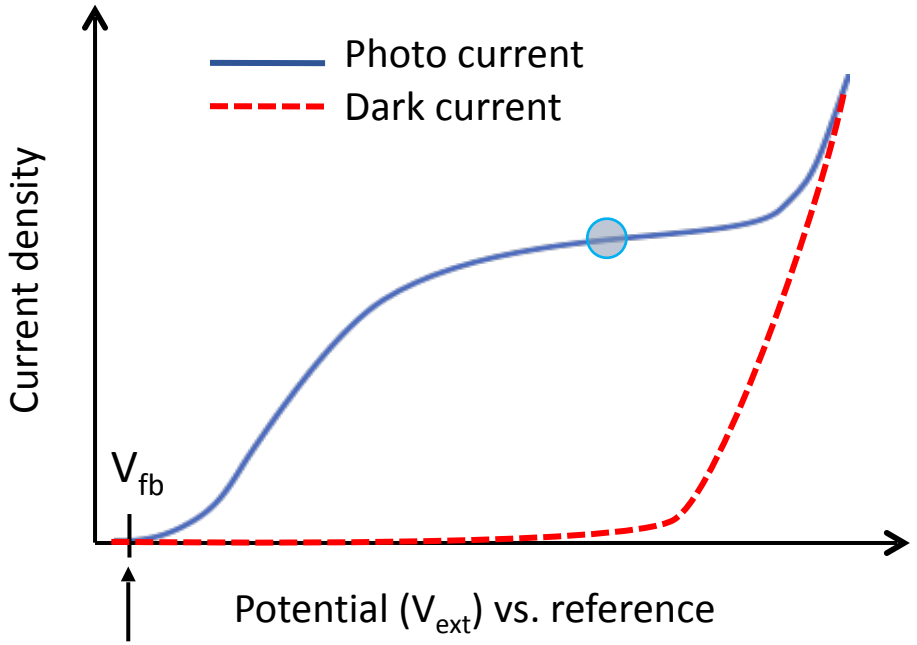
Flat band potential

The photocurrent increases and eventually plateaus due to limitations of light absorption, surface kinetics, carrier transport, etc. Eventually, the dark current sets in.

Metrics in Photoelectrode Development



$$L_{min} = \sqrt{D_{min}\tau_{min}} = \sqrt{\frac{k_B T}{q}\mu_{min}\tau_{min}}$$



Flat band potential

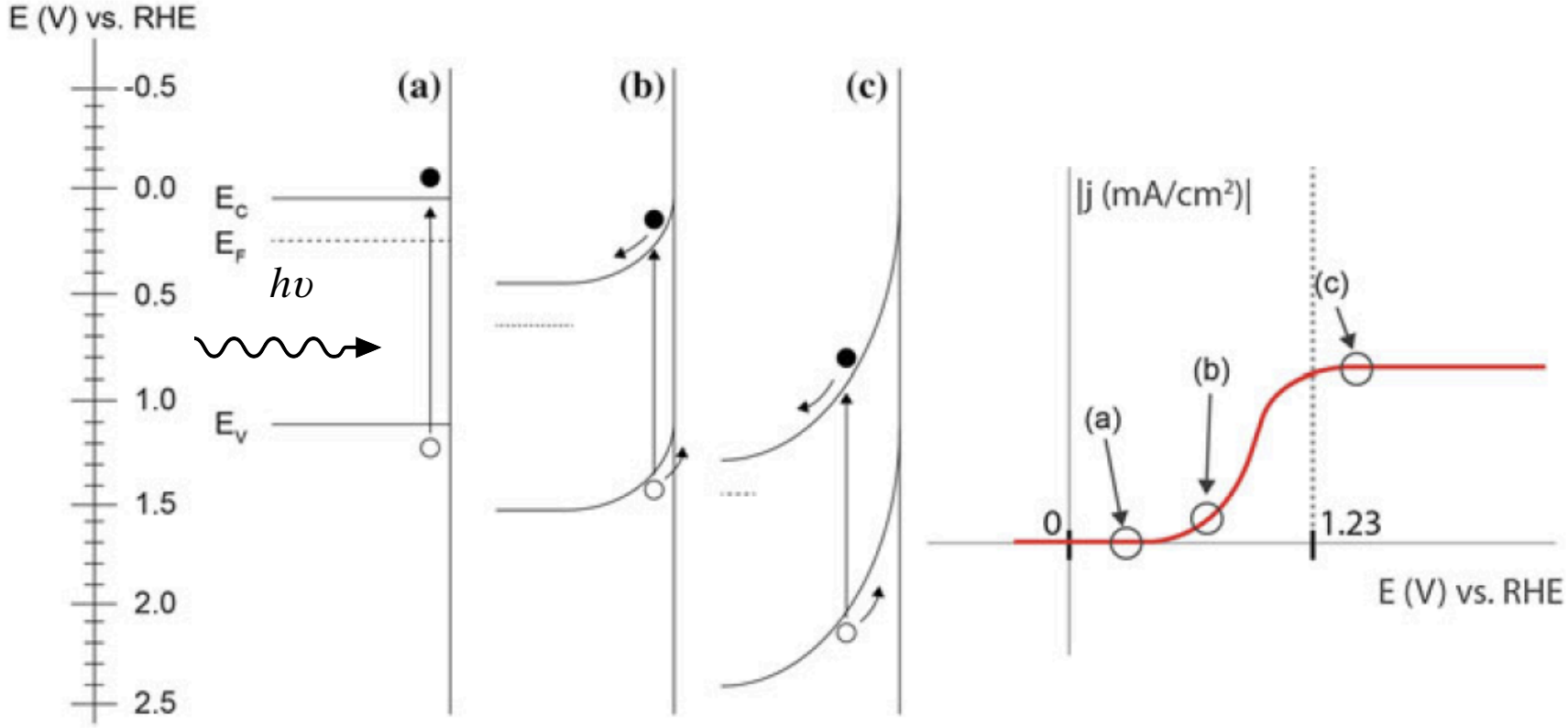
The photocurrent increases and eventually plateaus due to limitations of light absorption, surface kinetics, carrier transport, etc. Eventually, the dark current sets in.

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

Photocurrent Onset

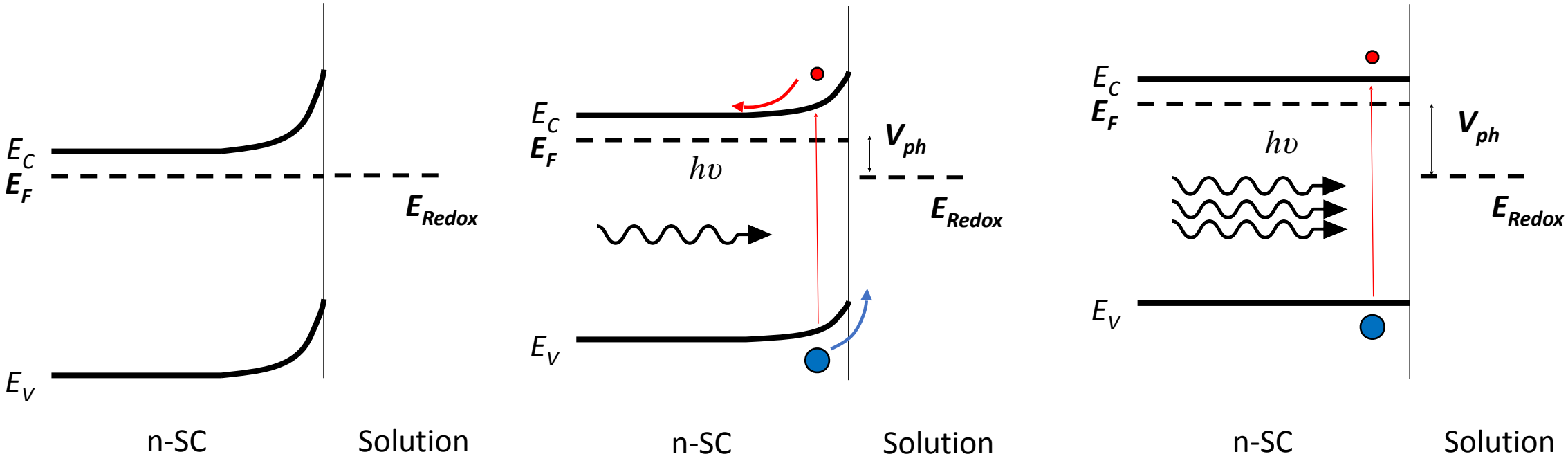
- The photocurrent onset can be used to estimate the E_{fb}, and can be determined by measuring the photocurrent density (J_{ph}) as a function of the potential versus a reference electrode (E_{ref}).

- 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.

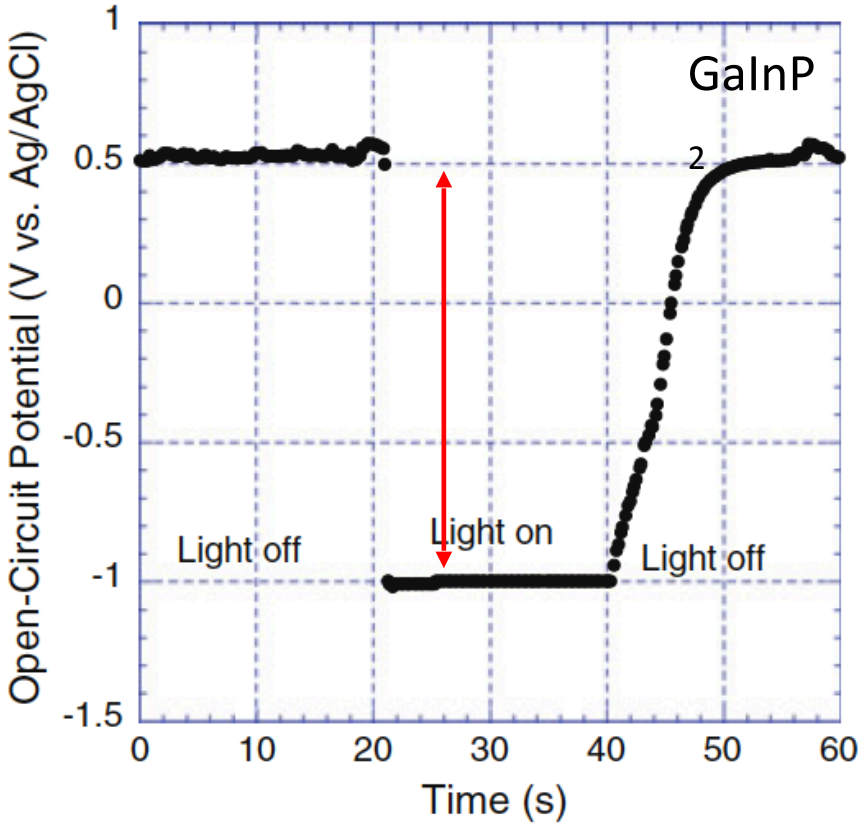
OCP under Illumination

- 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.

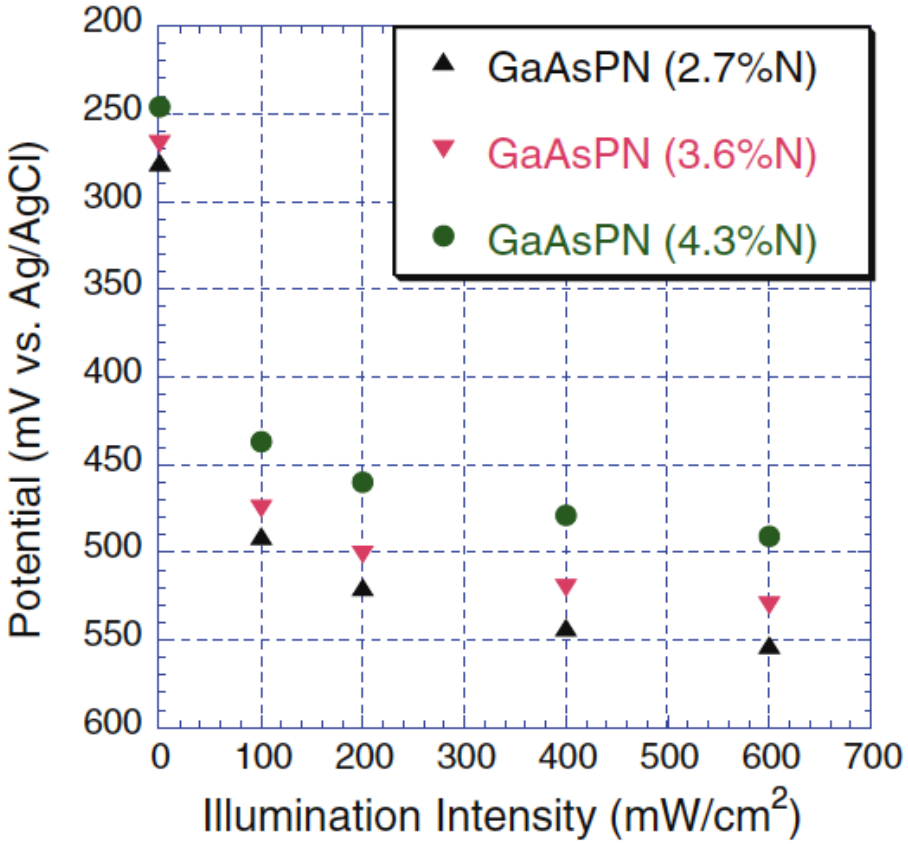


OCP under Illumination

n-type SC



p-type SC

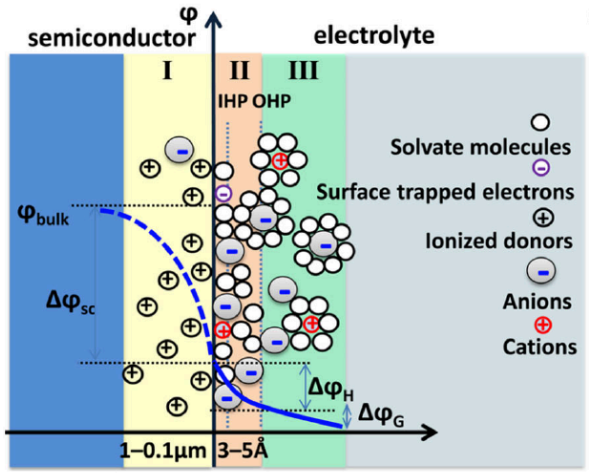


Limit: - The determination of E_{fb} values by OCP can also be complicated by materials that have a high density of defect sites which can serve as recombination centers: high light intensity is required.

- 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.

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

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

- 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

Mott-Schottky Equation

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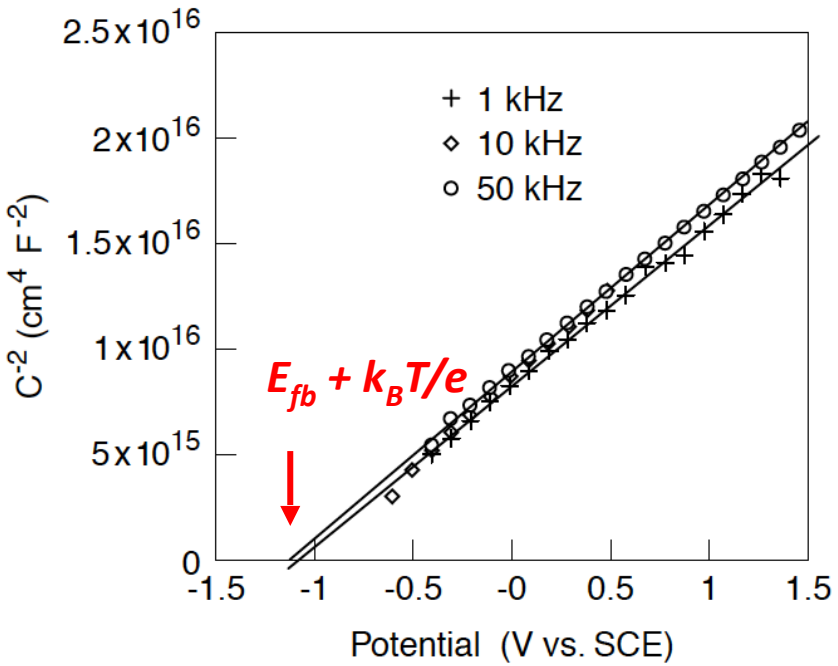
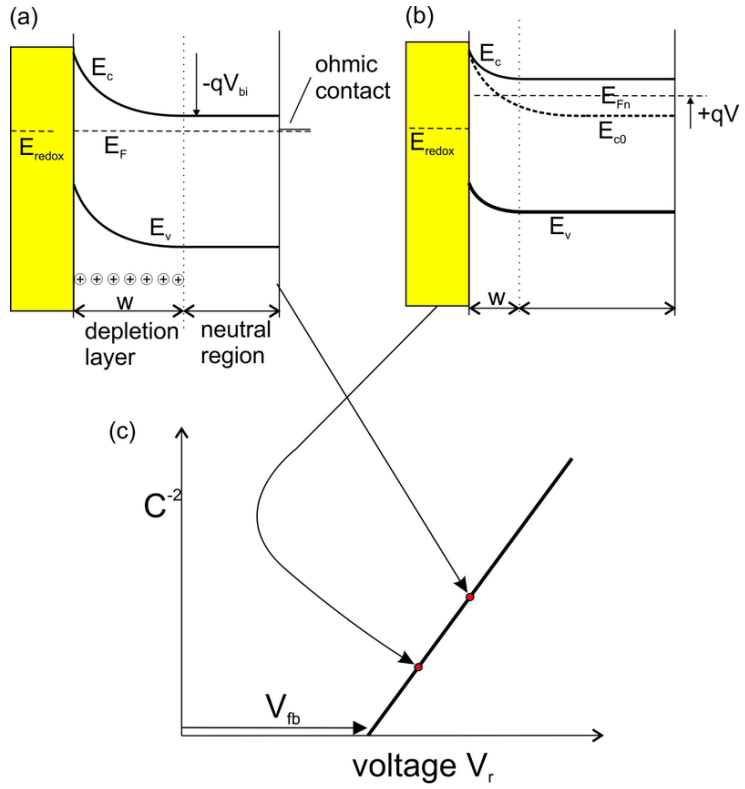
MS plot for an n-type silicon





$C = \varepsilon A / d$

← From wikipedia

Mott-Schottky Equation

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

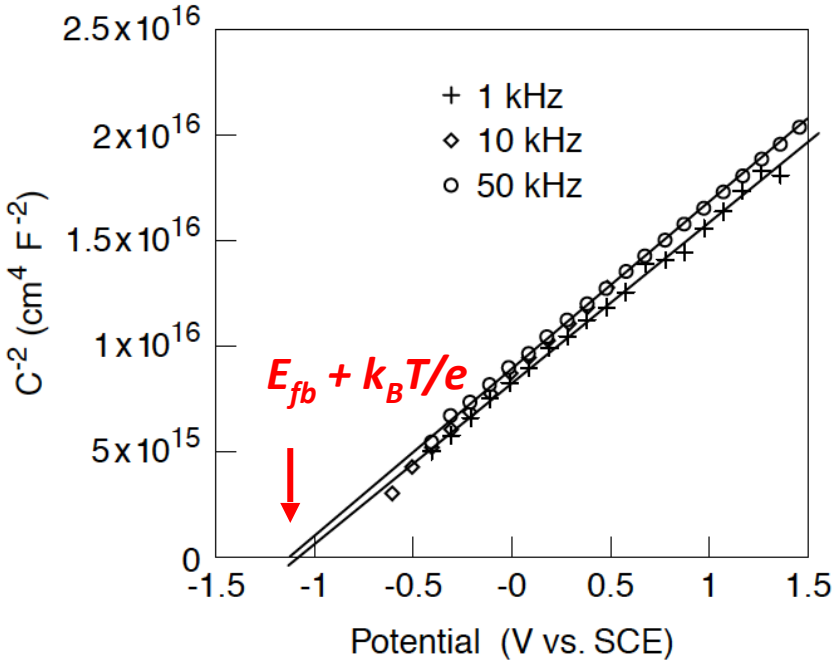
$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon_0 \varepsilon_r e N_A A^2}\left(E_A - E_{fb} - \frac{k_B T}{e}\right)$$

N_A: the concentration of acceptors

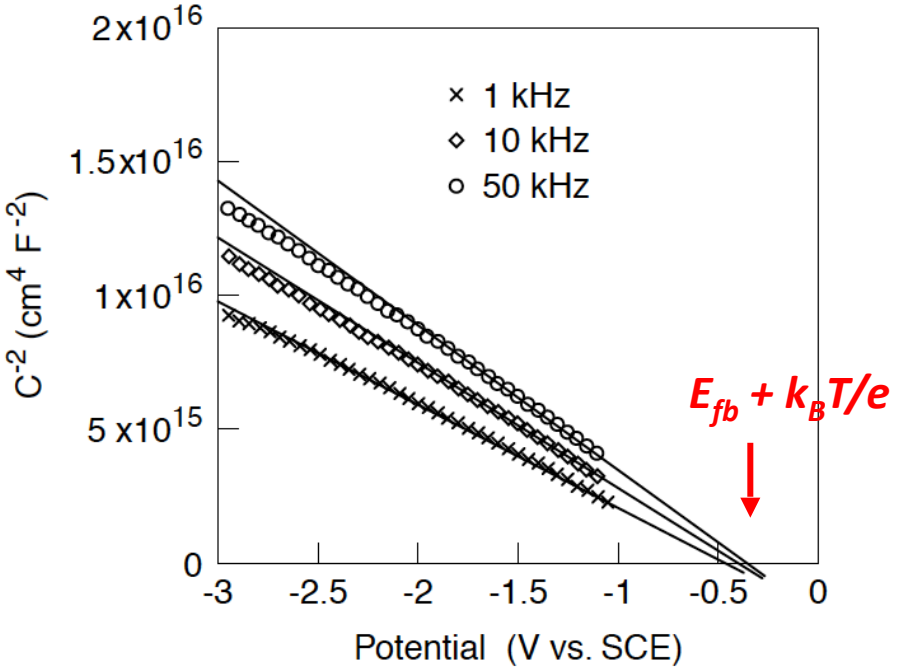
E_A: the applied potential

E_{fb}: the fat band potential

MS plot for an n-type silicon



MS plot for an p-type silicon

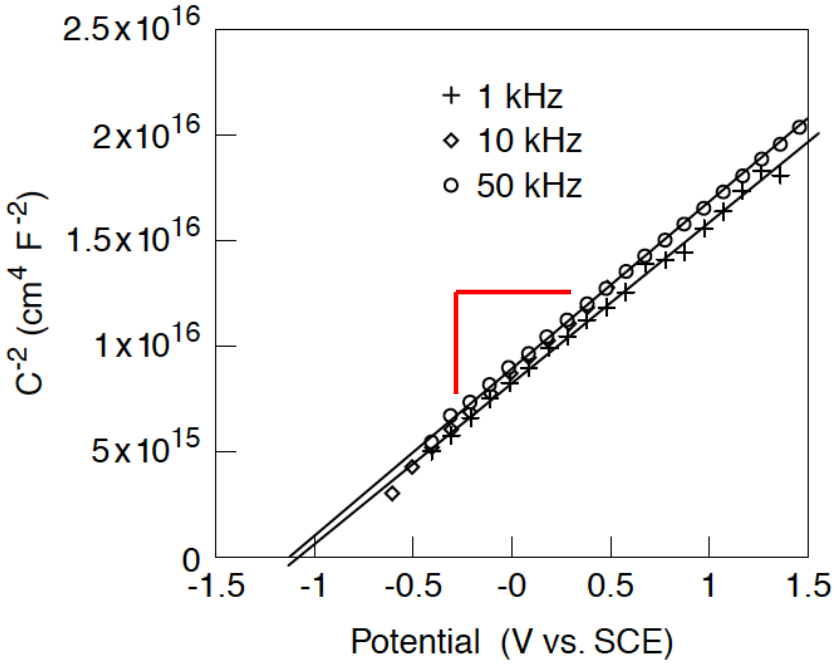


Mott-Schottky Equation

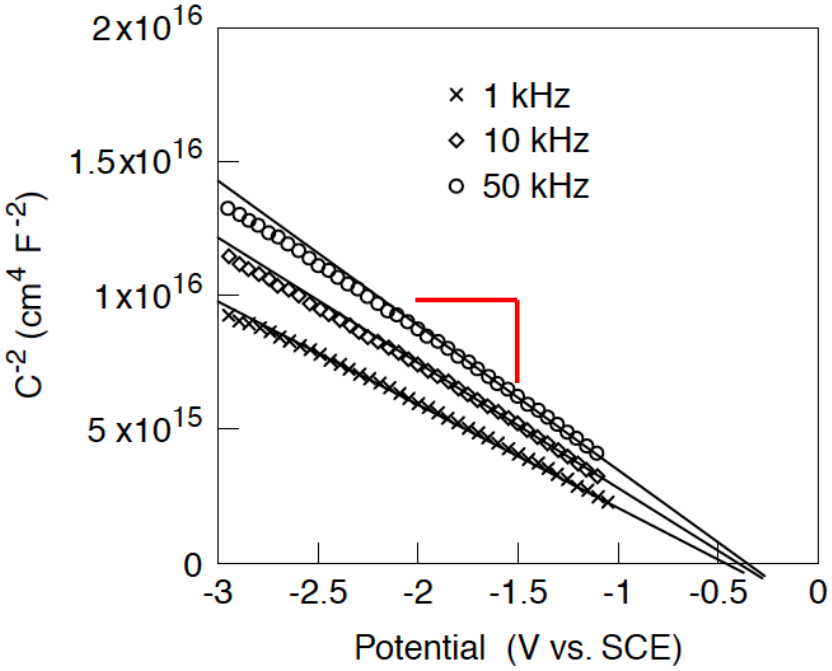
- The slope is proportional to the charge carrier concentration or doping density:

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

MS plot for an n-type silicon

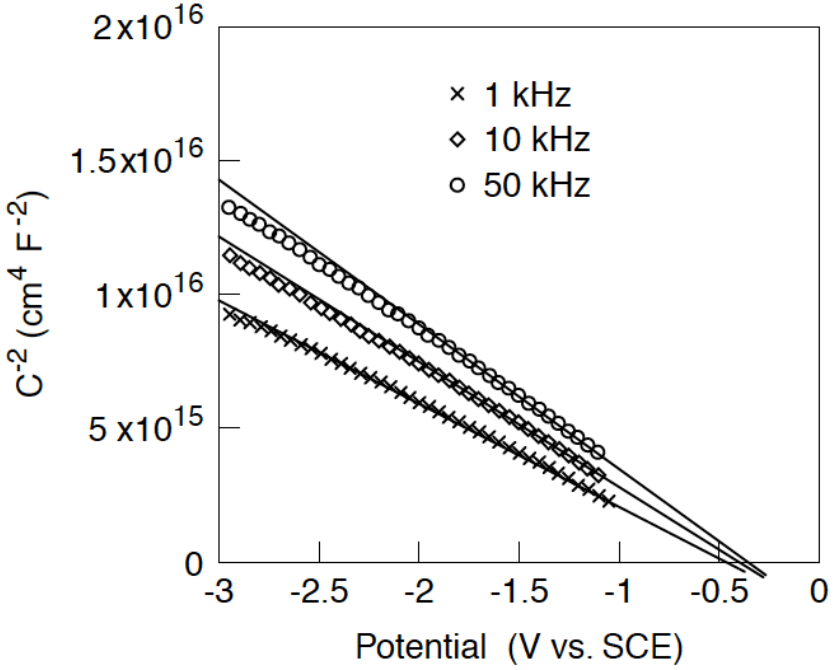


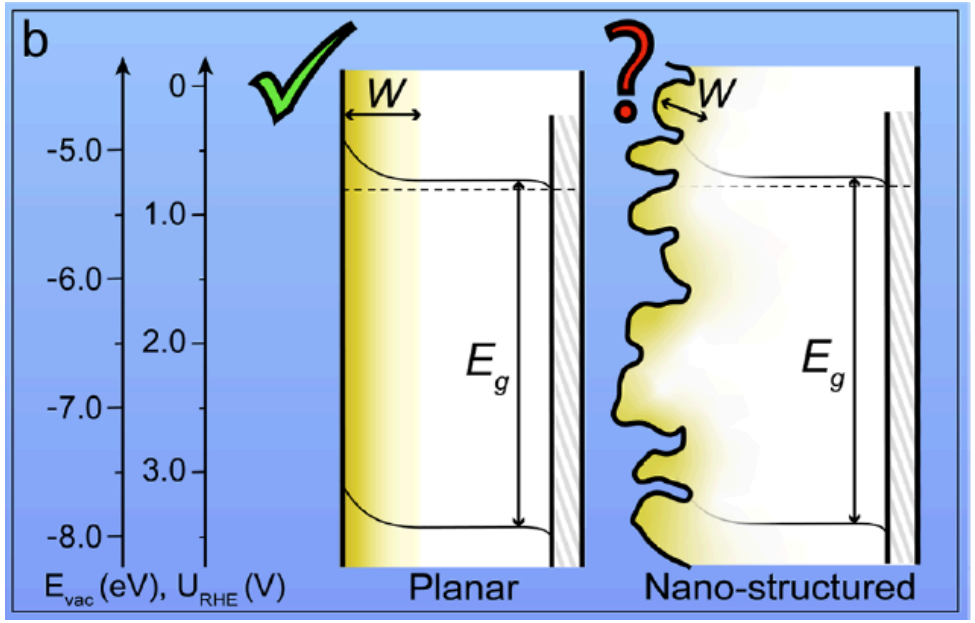
MS plot for an p-type silicon



Cautions Needed for M-S Analysis

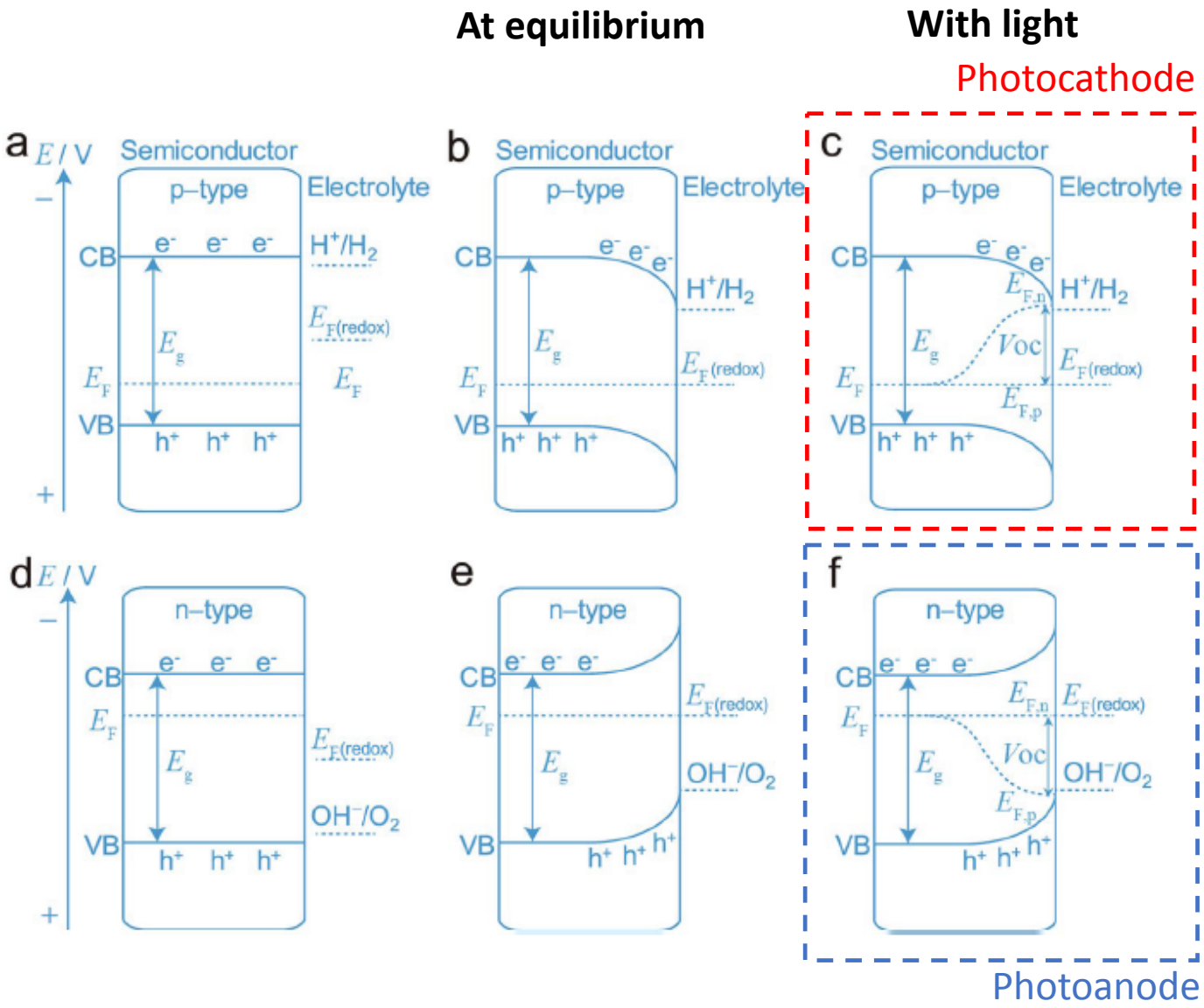
- The E_{fb} is ideally not dependent on the frequency.
  - Contribution from surface state capacitance and double-layer capacitance, giving a rise to a frequency dependence to M-S results.
  - Typically, a frequency is chosen to be fast enough not to allow for effective filling and unfilling of surface 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.

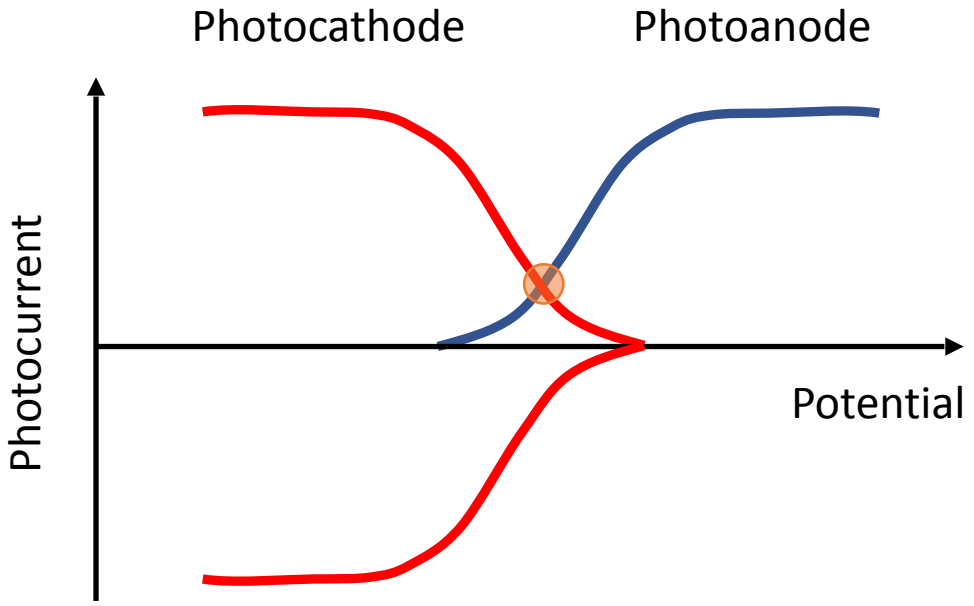




K. Sivula, *ACS Energy Lett.*, **6**, 2549–2551 (2021)

Photoanode and Photocathode





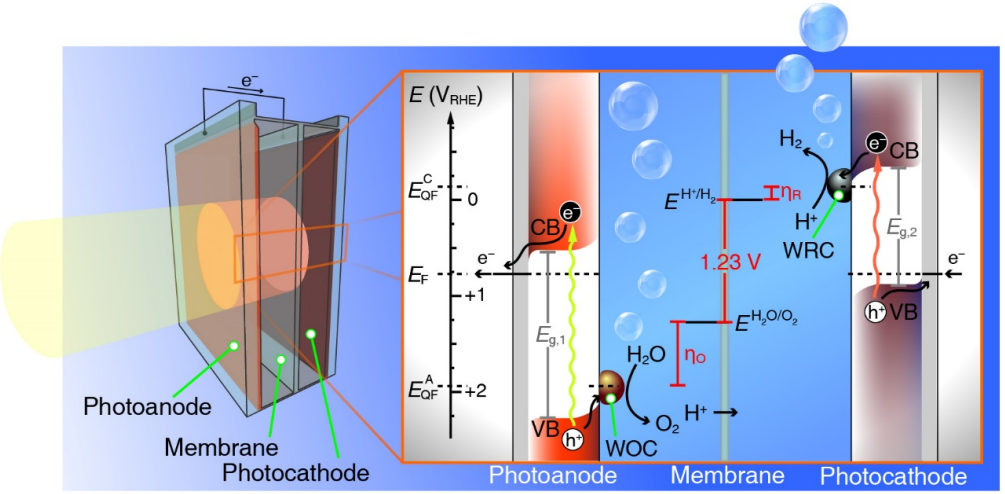
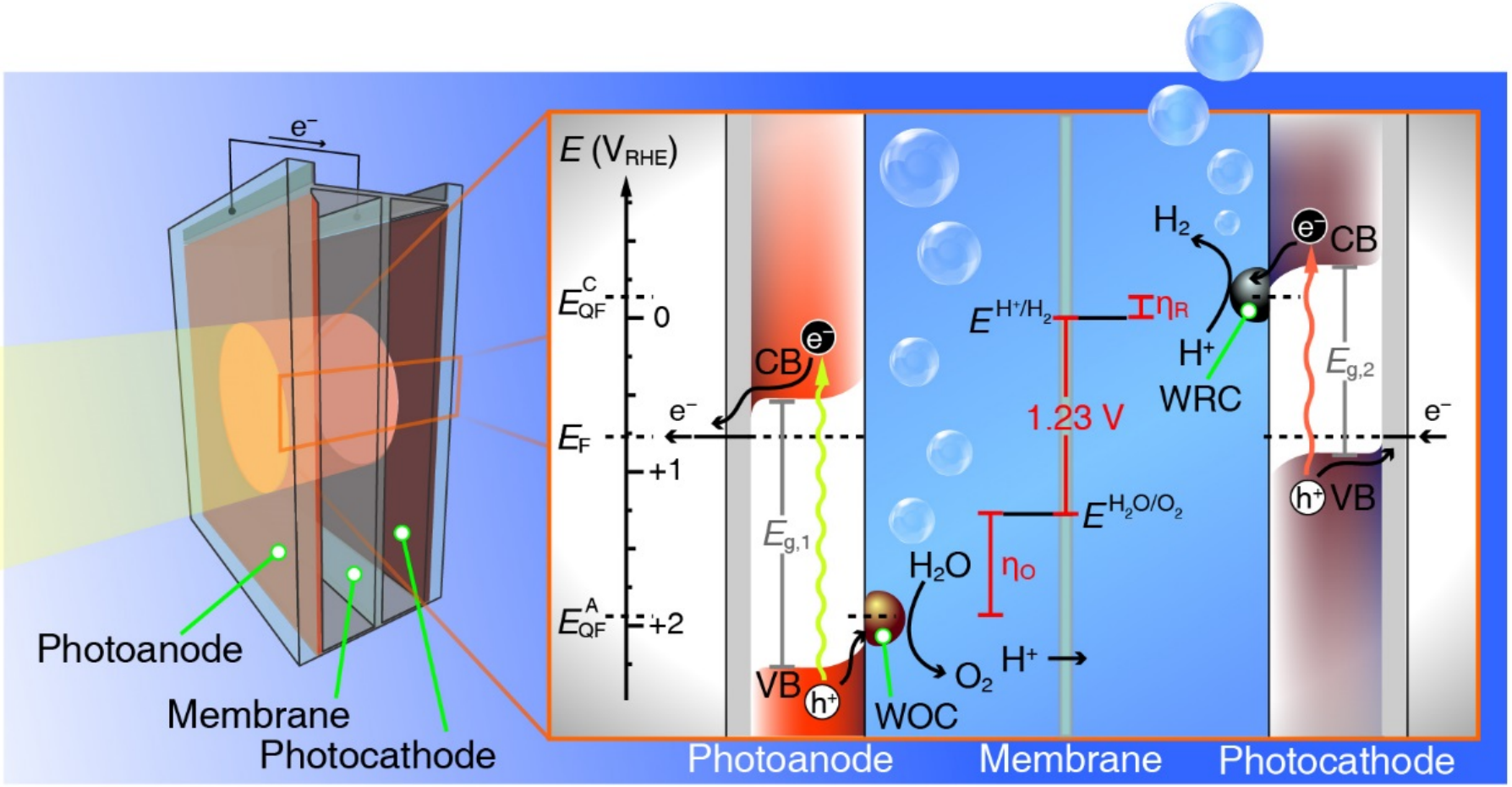


Image taken from Y- Zhao et al., Electrochem. Energy Rev., 6:14 (2023)

Tandem PEC Cell

CB (rigorously $E_{F,n}$) of photocathode higher than $E^{H+/H2} + \eta_{HER}$



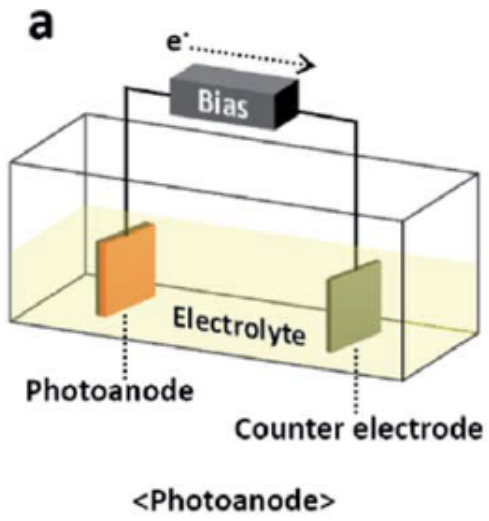
$E_{g,1} > E_{g,2}$

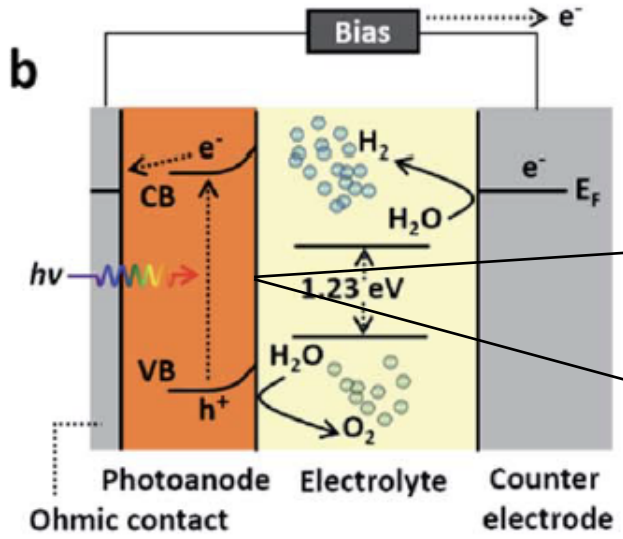
STH 22% with 1.8 eV $E_{g,1}$ and 1.15 eV $E_{g,2}$

VB (rigorously $E_{F,p}$) of photoanode lower than $E^{H2O/O2} + \eta_{OER}$

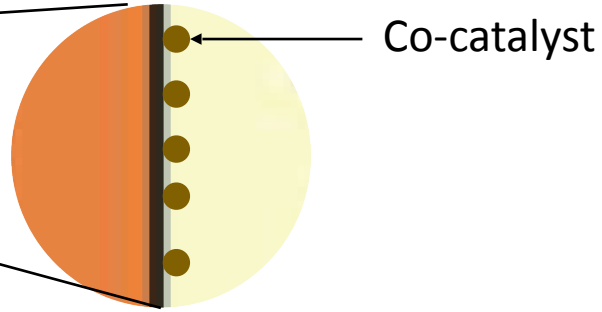
WRC: water reduction catalyst
WOC: water oxidation catalyst

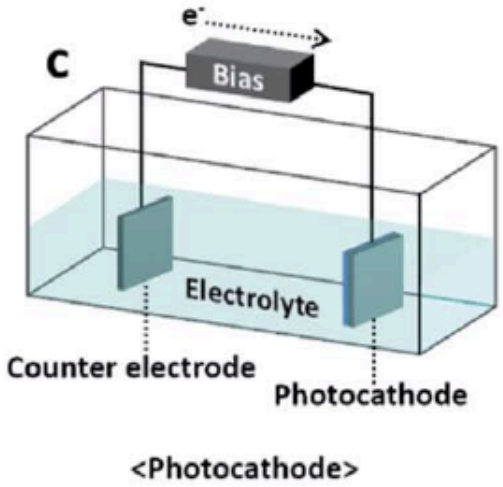
Photoanode and Photocathode

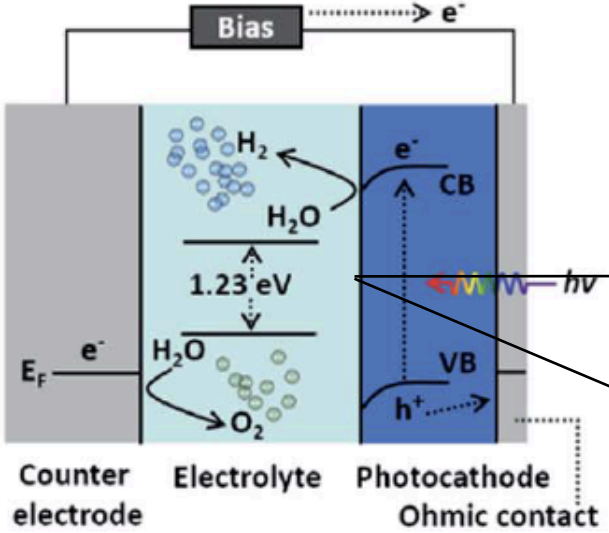




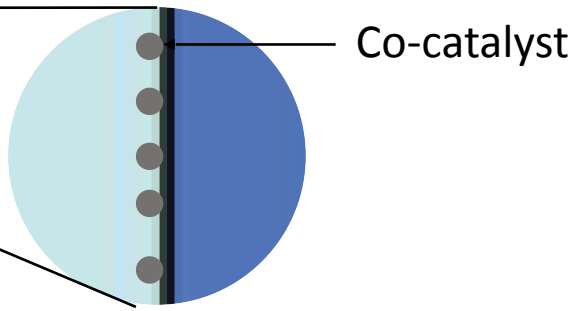
n-type SC: Photoanode





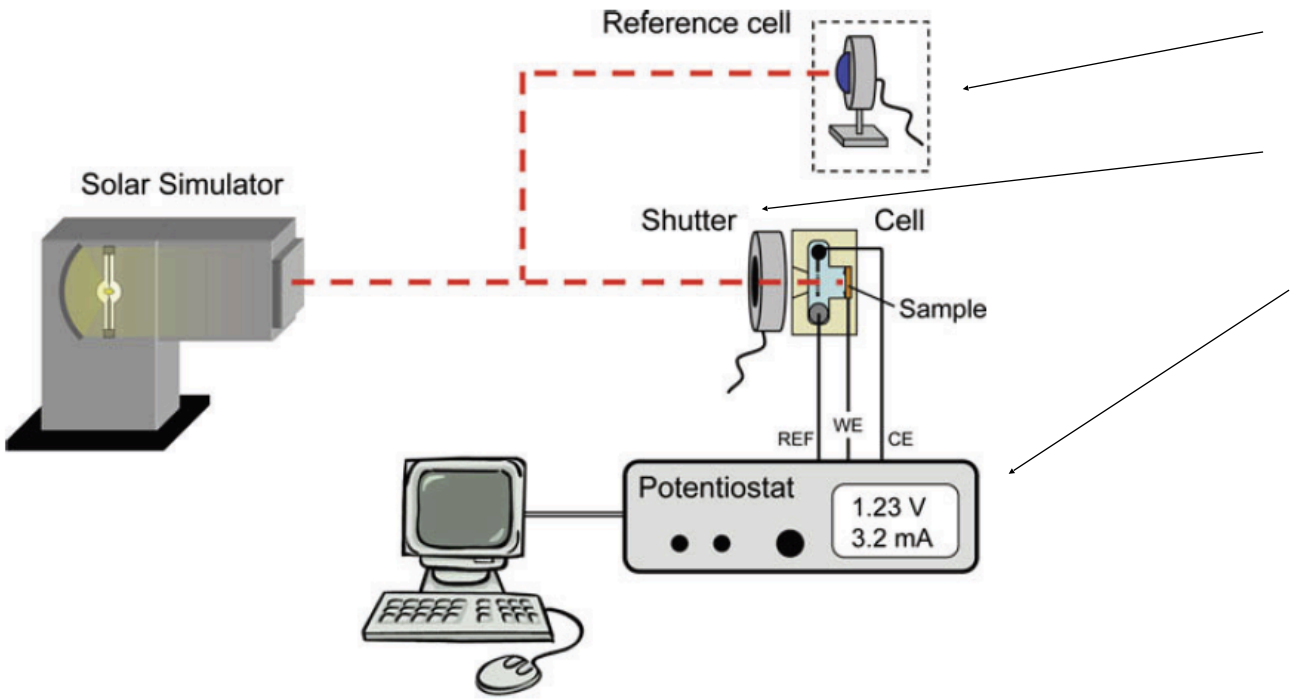


p-type SC: Photocathode



Park et al., *RSC Adv.*, **9**, 30112 (2019)

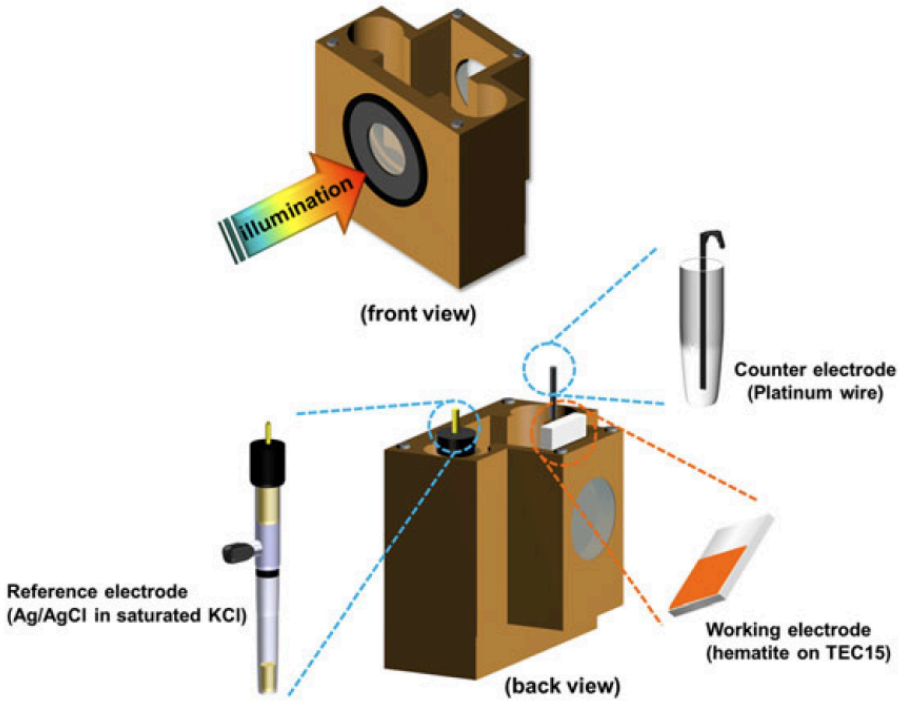
Photoelectrochemical Test Setup



Verify the intensity of the solar simulator

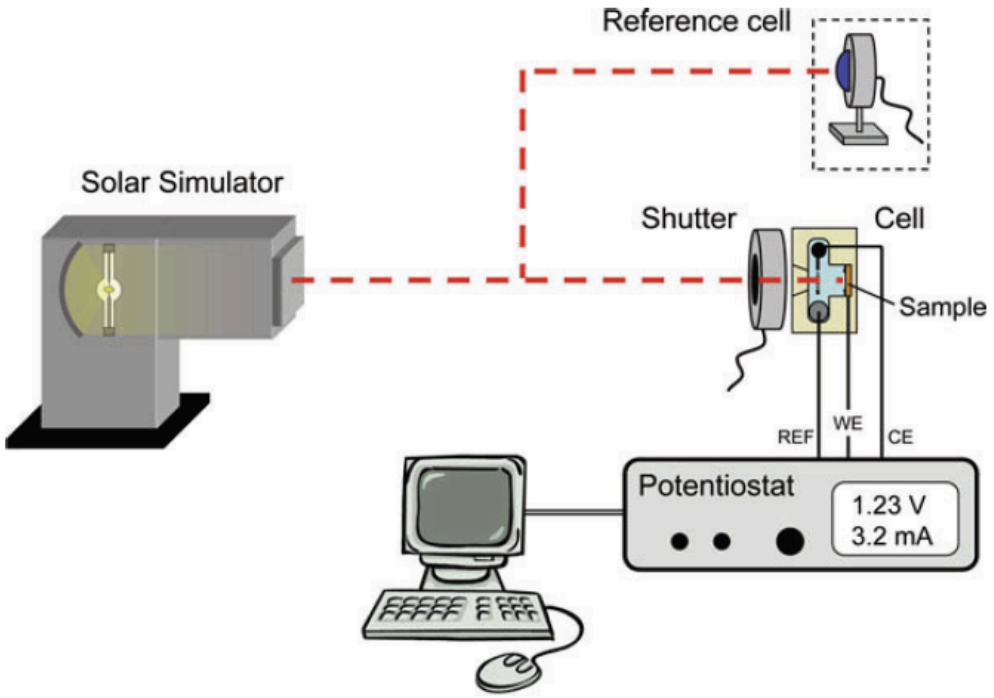
Block the light, e.g. chopped light experiments

Control the sample's potential
Measure the current



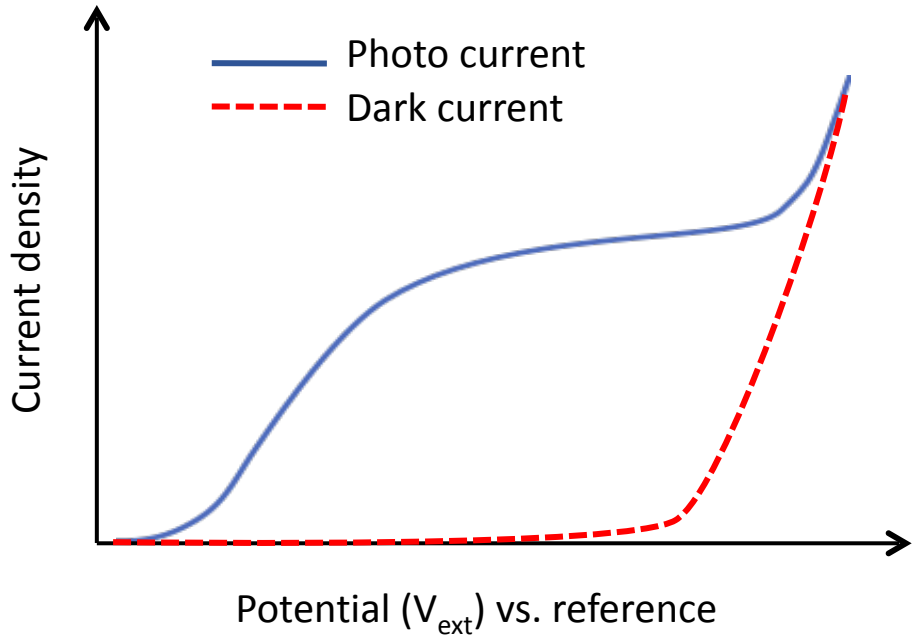
Experimental setup for measuring the performance of a photoelectrode under irradiation with simulated sunlight.

Photoelectrochemical Test Setup



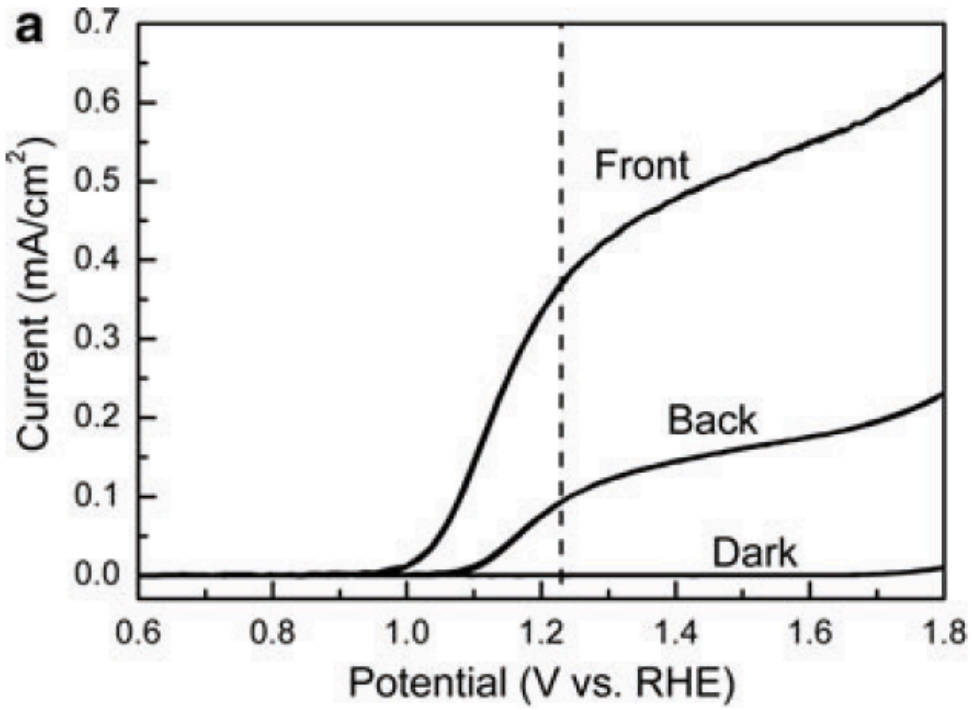
Experimental setup for measuring the performance of a photoelectrode under irradiation with simulated sunlight.

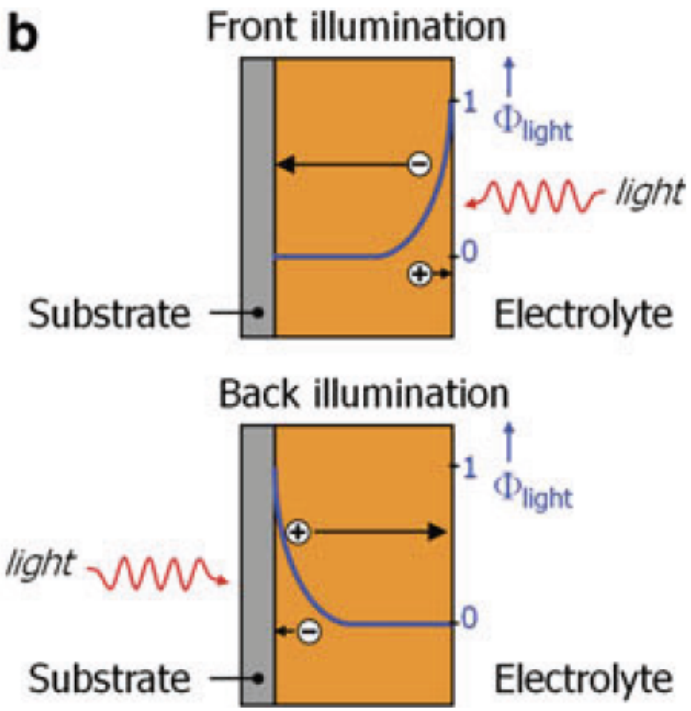
Current-Voltage Curve



Photoelectrochemical Measurements

Front- and Back-side Illumination





The blue curved line represents the exponentially decaying light intensity in the film.

h^+ transport is more difficult than e- transport in Fe_2O_3!

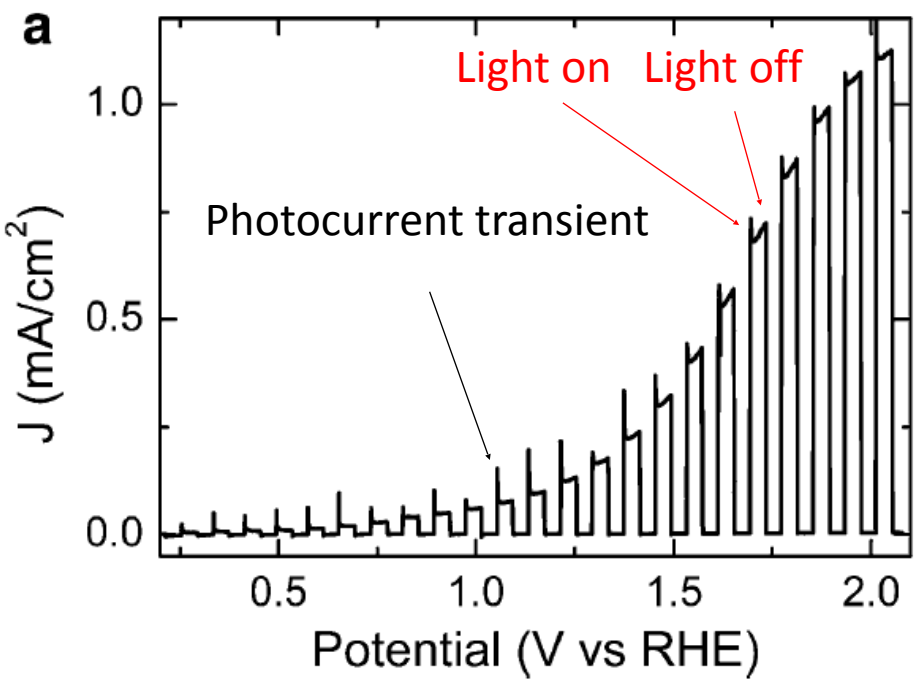
Current–voltage curve of a spray-deposited film of 0.2% Si-doped a-Fe_2O_3 in the dark and under continuous front- or back-side illumination with 80 mW/cm² simulated sunlight.

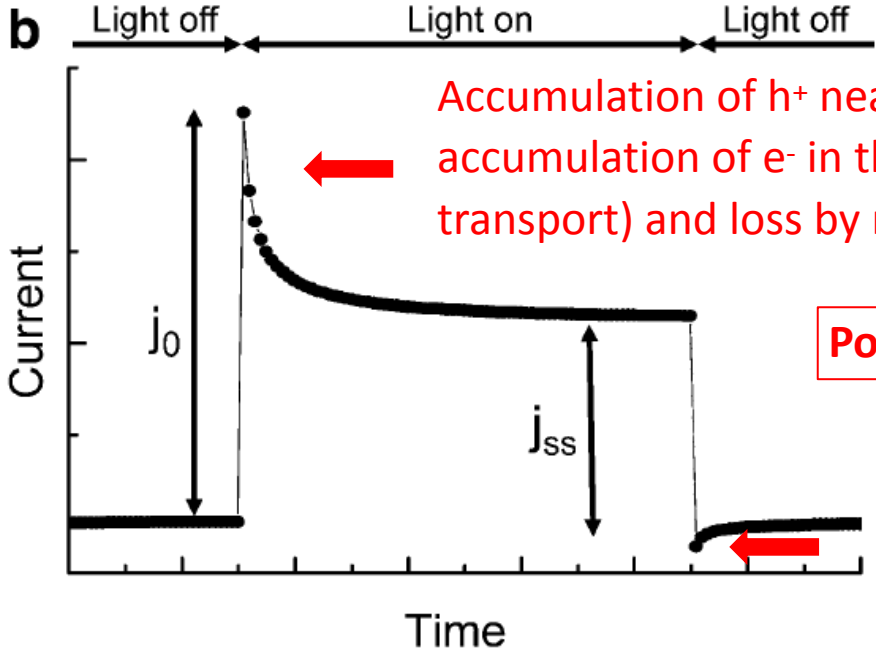
Y. Liang et al., Int. J. Photoenergy, Article ID 739864 (2008).

Under front-side illumination, most light is absorbed near the semiconductor/electrolyte interface.
This means that the photogenerated electrons have to travel a larger distance before reaching the interface than the photogenerated holes.
For backside illumination, the situation is reversed.

Photoelectrochemical Measurements

Chopped Voltammogram





Accumulation of h^+ near the interface, accumulation of e^- in the bulk (i.e., slow e^- transport) and loss by recombination.

Poor e^- transport

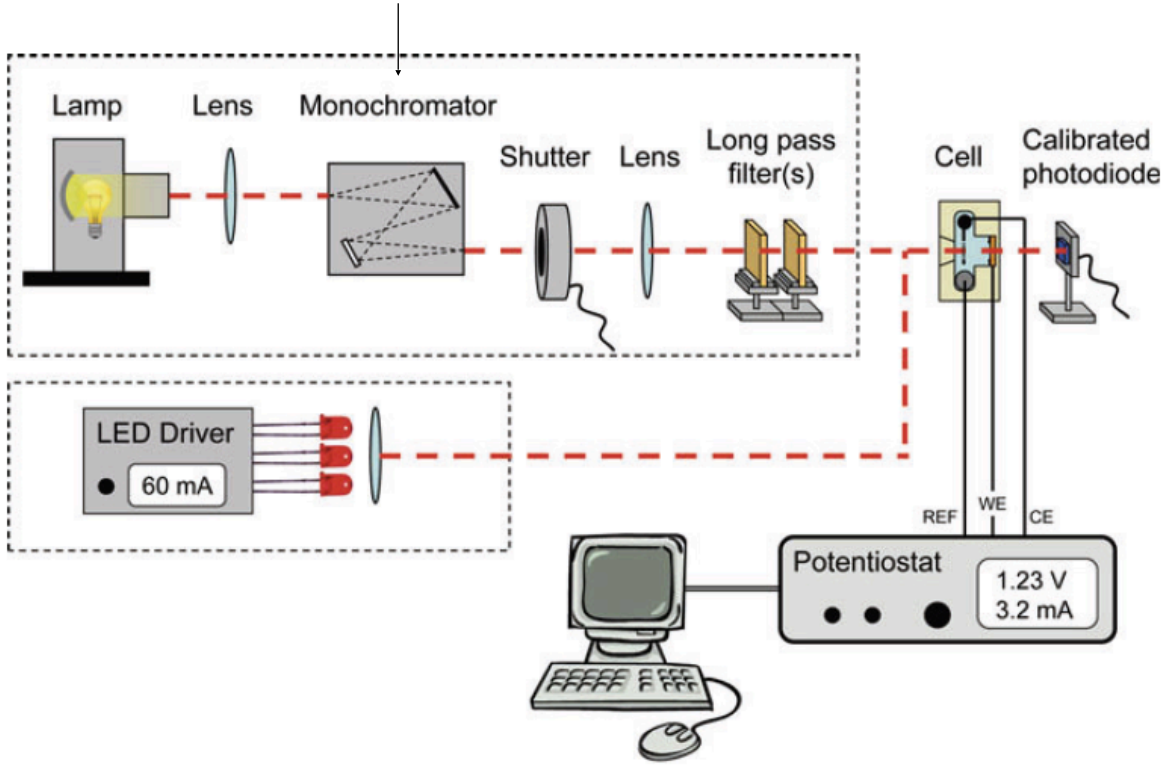
Accumulation of h^+ can be ruled out as the main recombination mechanism.

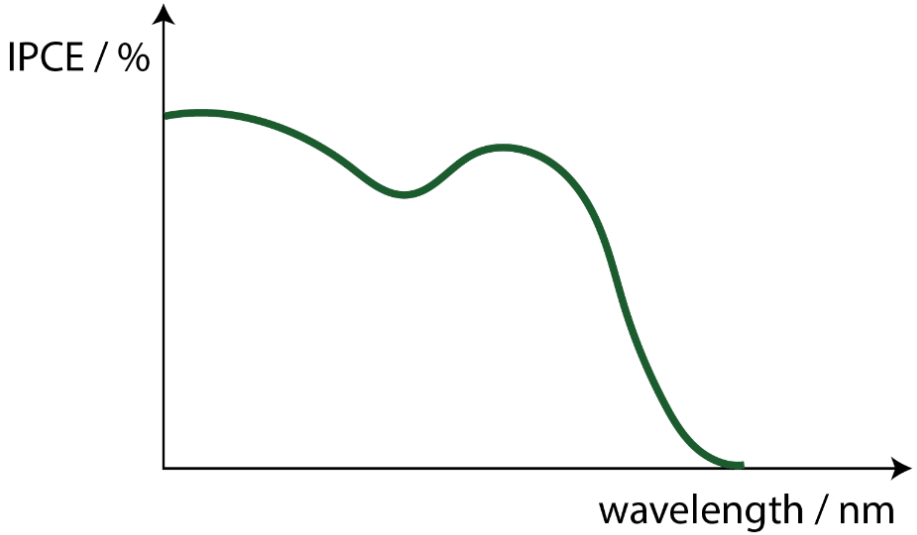
(a) Voltammogram for a spray-deposited $BiVO_4$ **photoanode** on FTO glass under chopped AM1.5 illumination.

(b) Current vs. time curve for $BiVO_4$ under high-intensity illumination with 364 nm light from a continuous-wave Ar^+ laser at a potential of 1.23 V_{RHE}. In both cases, a 0.15 M K_2SO_4 aqueous electrolyte solution was used.

Photoelectrochemical Test Setup: EQE

A monochromator is used to filter out a narrow part of the spectrum centered around the wavelength of interest.





Experimental setup for measuring the photocurrent and/ or quantum efficiency as a function of wavelength.

IPCE, APCE and ABPE

Incident Photon-to-Current (Conversion) Efficiency (IPCE) or External Quantum Efficiency (EQE) =

$$\frac{Collected\ electrons\ at\ a\ given\ wavelength}{Photons\ in\ at\ a\ given\ wavelength} = \frac{J_{SC}/q}{P_{in}/h\upsilon} = \frac{J_{SC}(A/cm^2)}{P_{in}(W/cm^2)} \times \frac{1240}{\lambda(nm)} \times 100$$

Absorbed Photon-to-Current (Conversion) Efficiency (APCE) or Internal Quantum Efficiency (IQE) =

$$\frac{electrons/sec}{absorbed\ photons/sec} = \frac{EQE}{1-R-T} = \frac{EQE}{LHE}$$

Applied Bias Photon-to-Current (Conversion) Efficiency (ABPE or ABPC) =

$$\frac{(Total\ power\ output\ -Electrical\ input\ power)}{Light\ power\ input} = \frac{J_{bias} \times (1.23 - |V_a|) \times \eta_F}{P_{in}}$$

ABPE accounts for the power required from the external electrical bias!

Faraday Efficiency

Faraday efficiency (also called faradaic efficiency, faradaic yield, coulombic efficiency or current efficiency) **describes the efficiency with which charge (electrons) is transferred in a system facilitating a desired electrochemical reaction**. In other words, the faraday efficiency is the ratio of experimentally measured moles of gas divided by the theoretical number of moles of product gas.

$$\eta_F = \frac{n_{prod}}{Q/nF}$$

n_{prod} is the gas measured experimentally in mole.
Q is the charge in coulombs corresponding to the photocurrent at time (s) (C = A x s)
F is faraday's constant (96485.33 C/mol)
n is the number of charges needed to drive the reaction

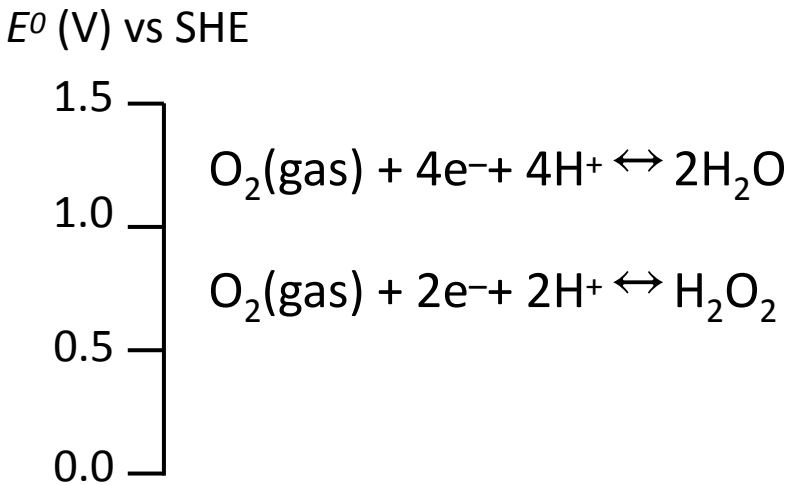
For H_2 production: $\eta_F = \frac{n_{H_2}}{Q/2F}$

For O_2 production: $\eta_F = \frac{n_{O_2}}{Q/4F}$

Faradaic Losses

Faradaic losses are experienced when electrons or ions participate in unwanted side reactions.
These losses appear as chemical byproducts and/or heat.

Example 1) In the oxidation of water to oxygen at the positive electrode in electrolysis, some electrons are diverted to the production of hydrogen peroxide. The fraction of electrons so diverted represent a faradaic loss.



$$E^{0}_{H_2O_2/O_2} = 0.682\ V\ vs.\ SHE$$

Solar-To-Hydrogen Efficiency

- Solar-To-Hydrogen (STH) efficiency is defined as ***chemical energy of the hydrogen produced*** divided by ***solar energy input from sunlight incident on the process***.

- The ***chemical energy of the hydrogen produced*** = The rate of hydrogen production (mmol H_2/s) multiplied by the change in Gibbs free energy per mole of H_2 ($\Delta G^0 =$ 237.2 kJ/mol at 25 °C).

$$\boldsymbol{STH} = \left[\frac{(mmol\ H_2/s) \times (237{,}200\ J/mol)}{P_{total}\left(\frac{mW}{cm^2}\right) \times Area\ (cm^2)}\right]_{AM1.5G}$$

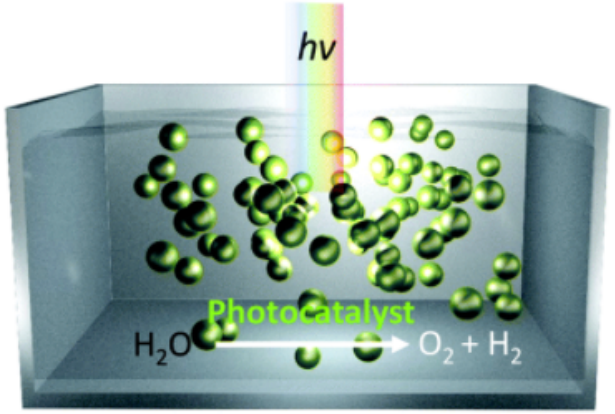
⬅ This equation calculates the power output (numerator) based on the direct measurement of the true H_2 production rate by an analytical method such as gas chromatography or mass spectrometry.

$$\boldsymbol{STH} = \left[\frac{(J_{sc}\ (mA/cm^2) \times (1.23\ V) \times \eta_F}{P_{total}\left(\frac{mW}{cm^2}\right)}\right]_{AM1.5G}$$

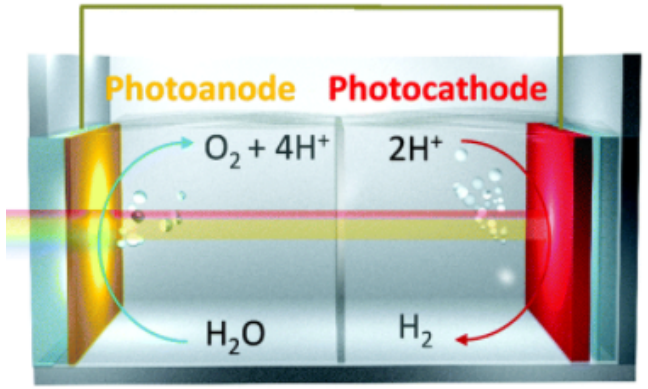
⬅ Alternatively, this equation uses the relation that power is the product of the minimum energy to split water, current, and the Faradaic efficiency for hydrogen evolution

Solar-To-Hydrogen Efficiency

PC



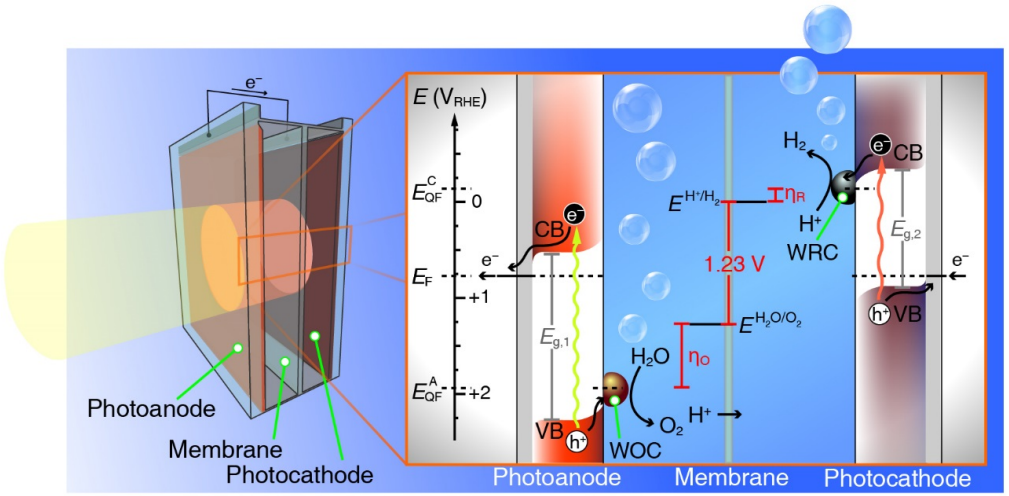
PEC

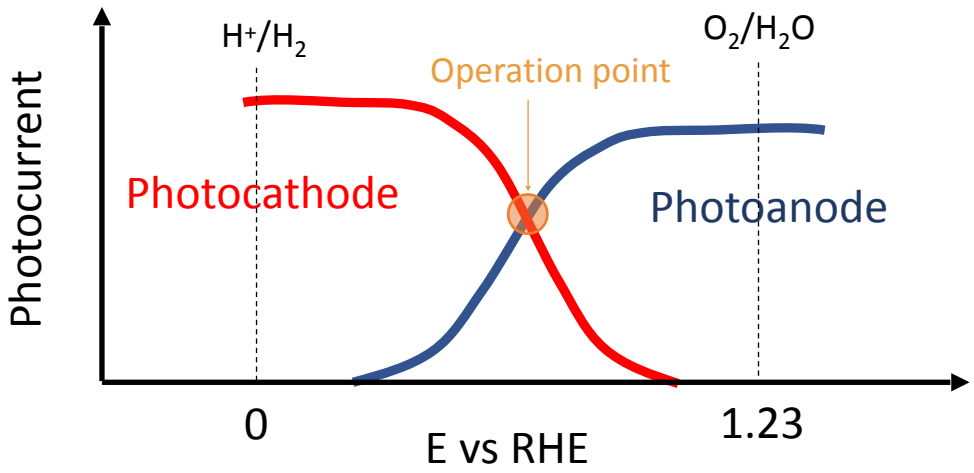


$$\boldsymbol{STH} = \left[\frac{(mmol\ H_2/s) \times (237{,}200\ J/mol)}{P_{total}\left(\frac{mW}{cm^2}\right) \times Area\ (cm^2)}\right]_{AM1.5G}$$

$$\boldsymbol{STH} = \left[\frac{(J_{sc}\ (mA/cm^2) \times (1.23\ V) \times \eta_F}{P_{total}\left(\frac{mW}{cm^2}\right)}\right]_{AM1.5G}$$

Assessment of a Dual Tandem PEC Cell

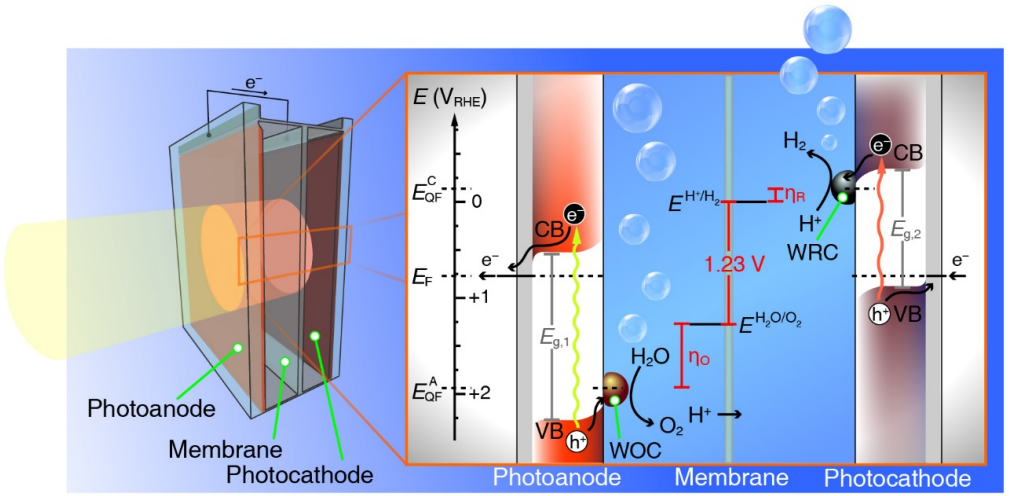


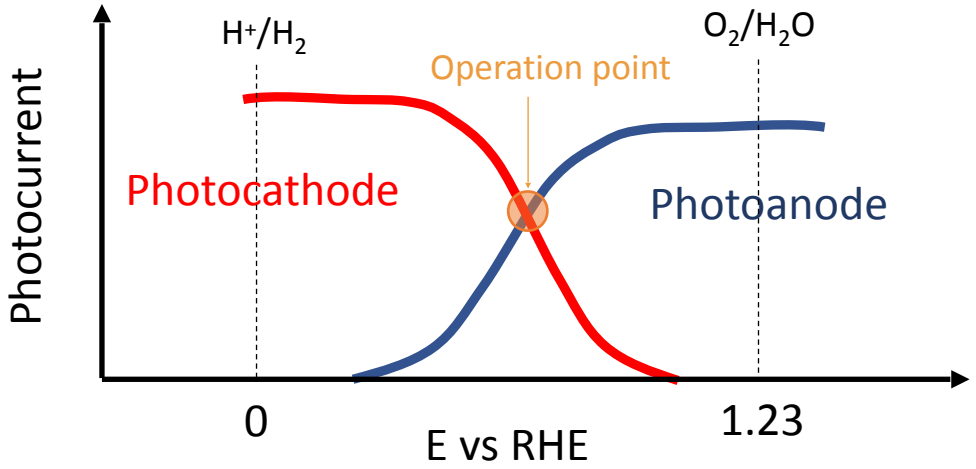


Examine separately photoelectrodes.

Predict 'best' performance (*overlapping of JV curves*)

Assessment of a Dual Tandem PEC Cell

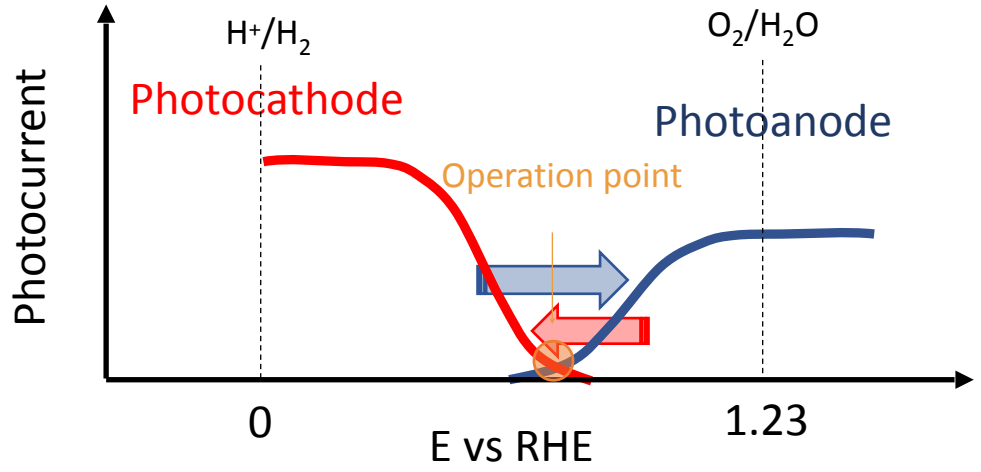




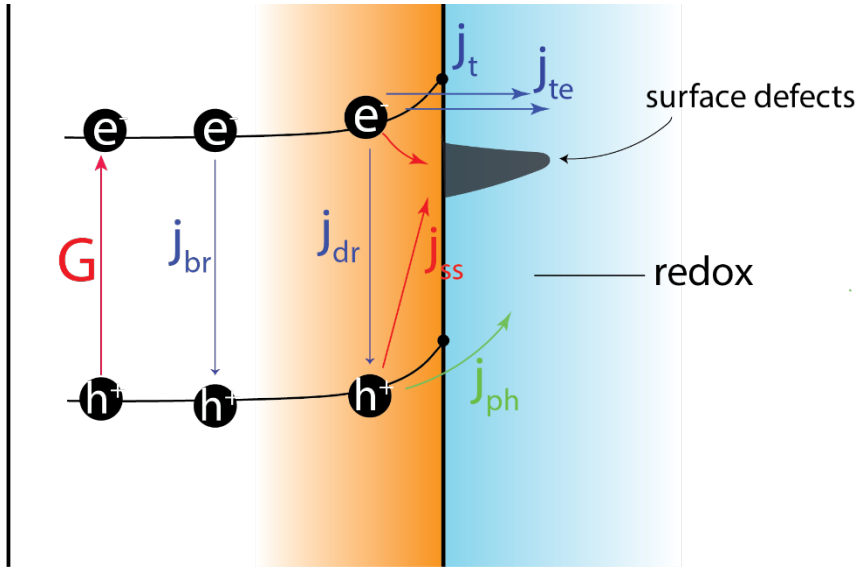
Today's low-cost PEC cells suffer from poor STH

- Poor performance of photoelectrodes
- Non-optimized combination of photoelectrodes (band gaps)

Real



Challenges to Address



$$J_{ph} = G - J_{br} - J_{dr} - J_{ss} - J_t - J_{te}$$

- Charge recombination in the bulk (br), in the depletion layer (dr) and via surface states (ss).
- Electron losses by reaction with redox through tunneling (t) across the potential barrier or at the surface (te)

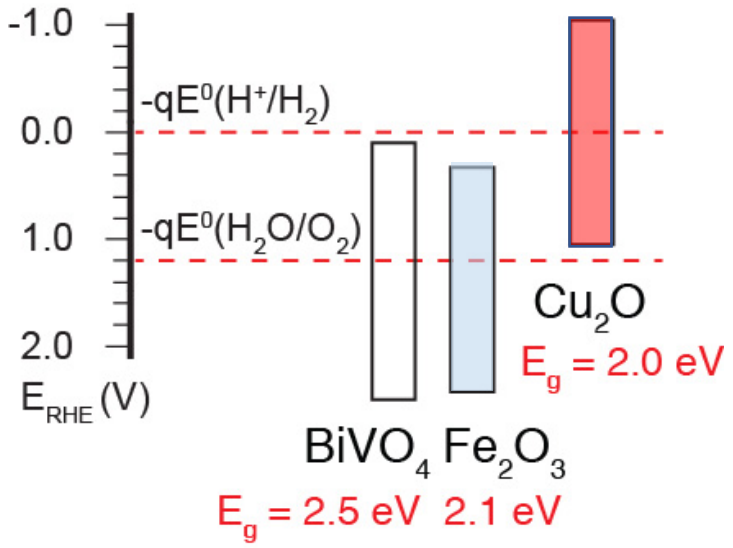
BULK PROPERTIES

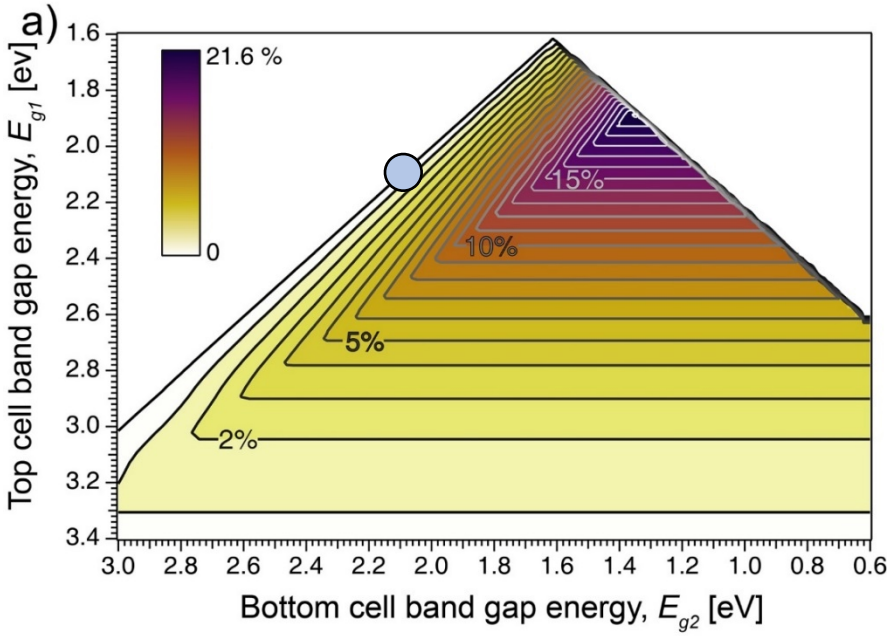
- Bulk defects (recombination)
- Carrier transport
- Doping density (conductivity, depletion depth)
- Morphology (charge collection)

SURFACE PROPERTIES (Semiconductor-liquid junction)

- Surface defects (recombination)
- Catalytic properties
- Stability

Assessment of a Dual Tandem PEC Cell

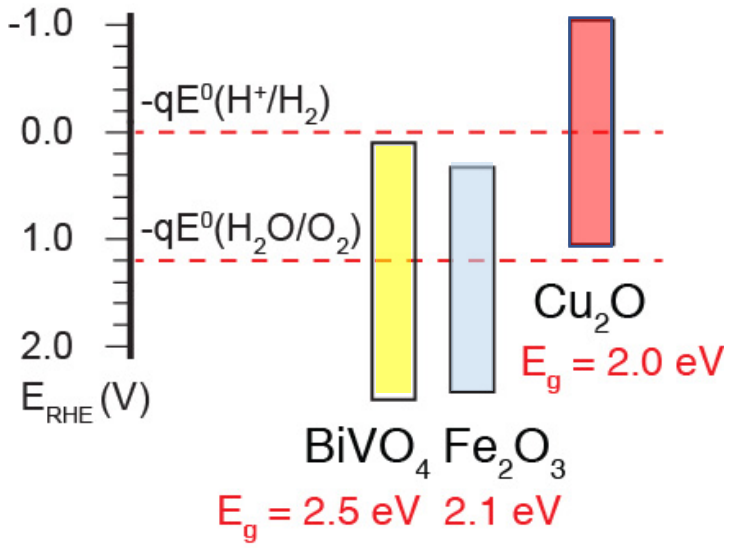


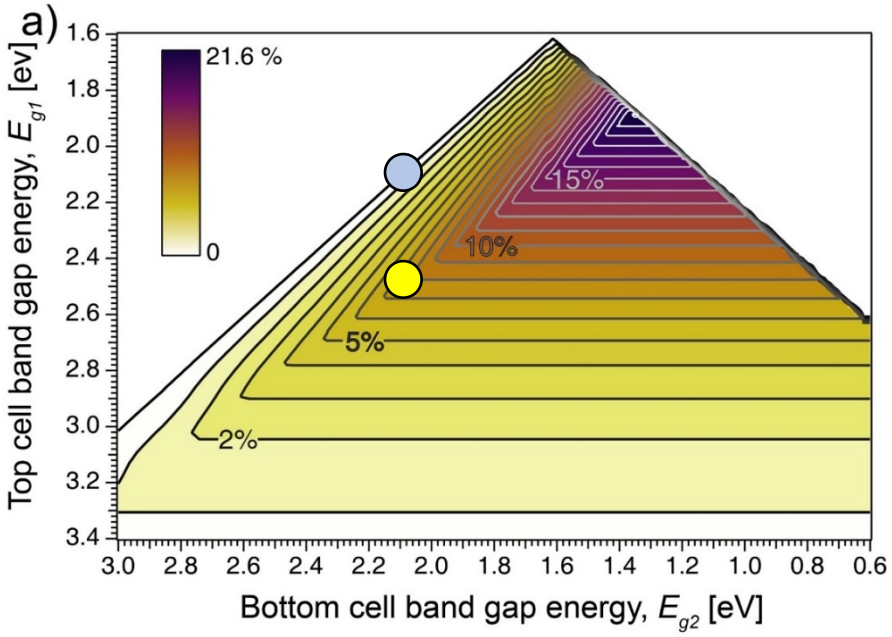


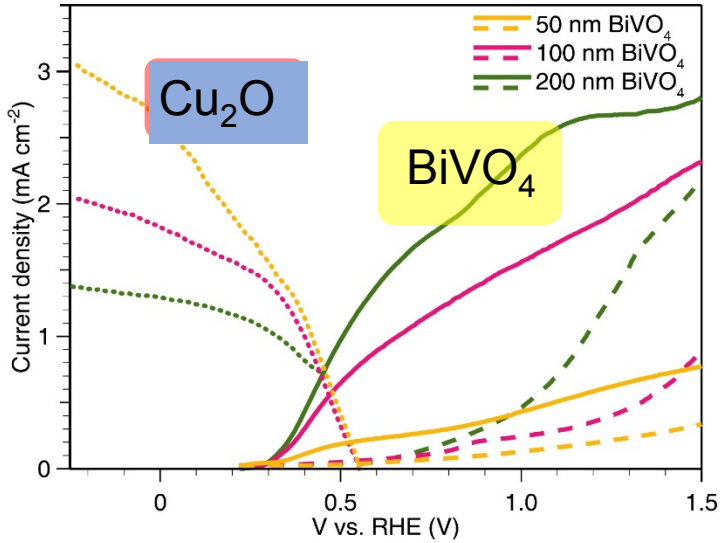
Low performance (non-complementary light absorption).

Hematite filters useful light for Cu_2O

Assessment of a Dual Tandem PEC Cell







Optimized combination of photoelectrodes (band gaps and thickness) are needed!

Bornoz *et al. J.Phys. Chem. C.* **118**, 16959-16966 (2014).