ELCOREL Workshop, Oud Poelgeest Castle, Oegstgeest

Electrode Processes
at
Illuminated Semiconductors

Laurie Peter
University of Bath

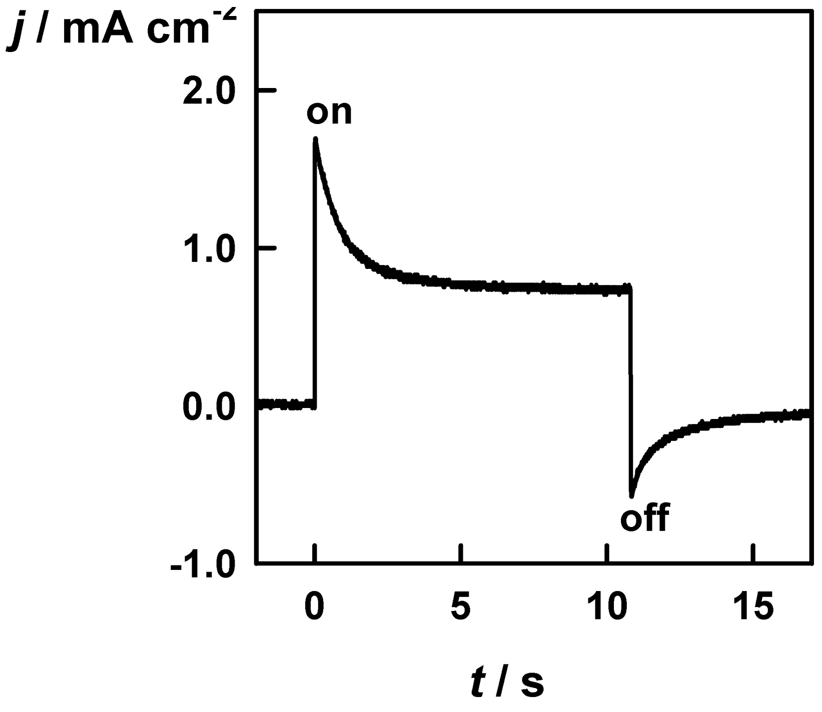
Experimental Methods to Study Electrode Kinetics

Electrode processes at metal electrodes are studies by **perturbing the potential**. This changes the potential drop across the double layer and hence the rate constant for electron transfer.

Electrode processes at illuminated semiconductor can be studied by **perturbing the illumination**. This changes the supply of minority carriers (e.g. holes for an n-type electrode) to the interface.

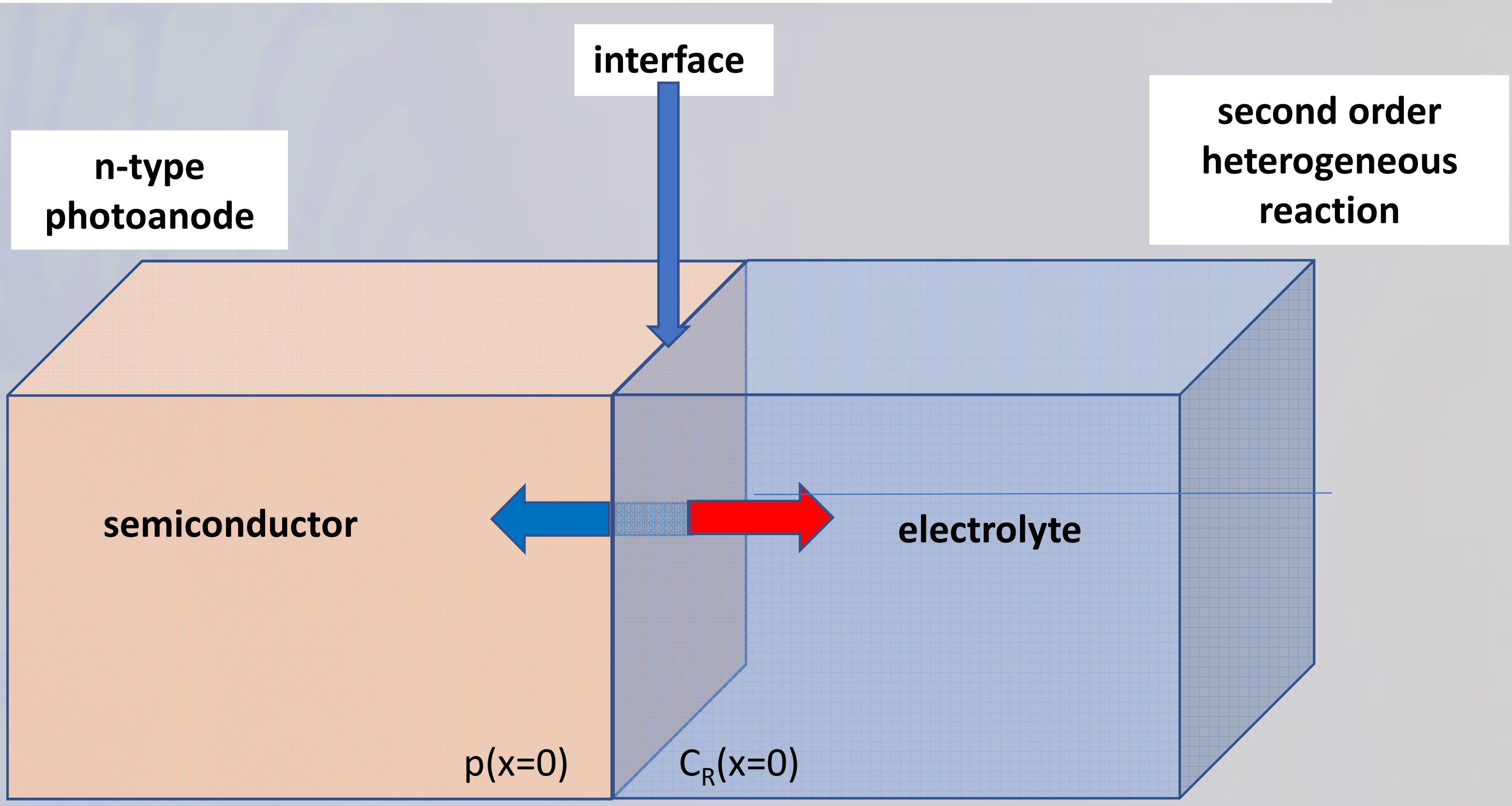
The simplest experiment involves **switching the light on and off** at a fixed potential.

Typical Photocurrent Transient for Hematite Photoanode



Transient photocurrent response of α-Fe_2O_3 electrode at 0 V vs. Ag|AgCl showing the decay and overshoot characteristic of surface electron-hole recombination. Electrolyte 1.0 M NaOH.

Rate of electron transfer reaction at a semiconductor surface



interface

n-type photoanode

second order heterogeneous reaction

semiconductor

electrolyte

$p(x=0)$

$C_R(x=0)$

$$\upsilon = k_{2,het}\, p_{x=0}\, C_{R,x=0}$$

$\mathrm{cm^{-2}\,s^{-1}}$ $\mathrm{cm^{4}\,s^{-1}}$ $\mathrm{cm^{-3}}$ $\mathrm{cm^{-3}}$

Note units of rate constant : $\mathrm{cm^{4}\,s^{-1}}$

Simplifying things…

1) Assume large excess of reactant in electrolyte: $[H_2O] = 55\ M = 3.3 \times 10^{22}\ cm^{-3}$

Reaction becomes *pseudo first order heterogeneous.*

$$k_{1,het} = k_{2,het} C_R$$

$cm\ s^{-1} = cm^4\ s^{-1} \times cm^{-3}$

2) Replace $p_{x=0}$ by *surface concentration* in terms of *tunnelling distance* δ

$$p_{surf} = \delta p_{x=0}$$

cm^{-2}

3) Define simple **first order rate constant**

$$k_{trans} = \frac{k_{1,het}}{\delta} = \frac{k_{2,het} C_R}{\delta}$$

4) Rate equation becomes

$$\upsilon = k_{trans} p_{surf}$$

s^{-1}

Note that units of k_{trans} are s^{-1}

Rate Constants and Time Constants: $\tau = 1/k_{trans}$

maximum rate constant for outer sphere reactions at semiconductor electrodes lie in the range

$k_{2,het} = 10^{-17} - 10^{-16}$ cm^4 s^{-1} Royea et al., *J. Phys. Chem. B* **1997,** *101,* 11152

Let's calculate the corresponding k_{trans}

Let R = 10^{20} cm^{-3} (0.17 M)

Let $\delta = 10^{-7}$ cm

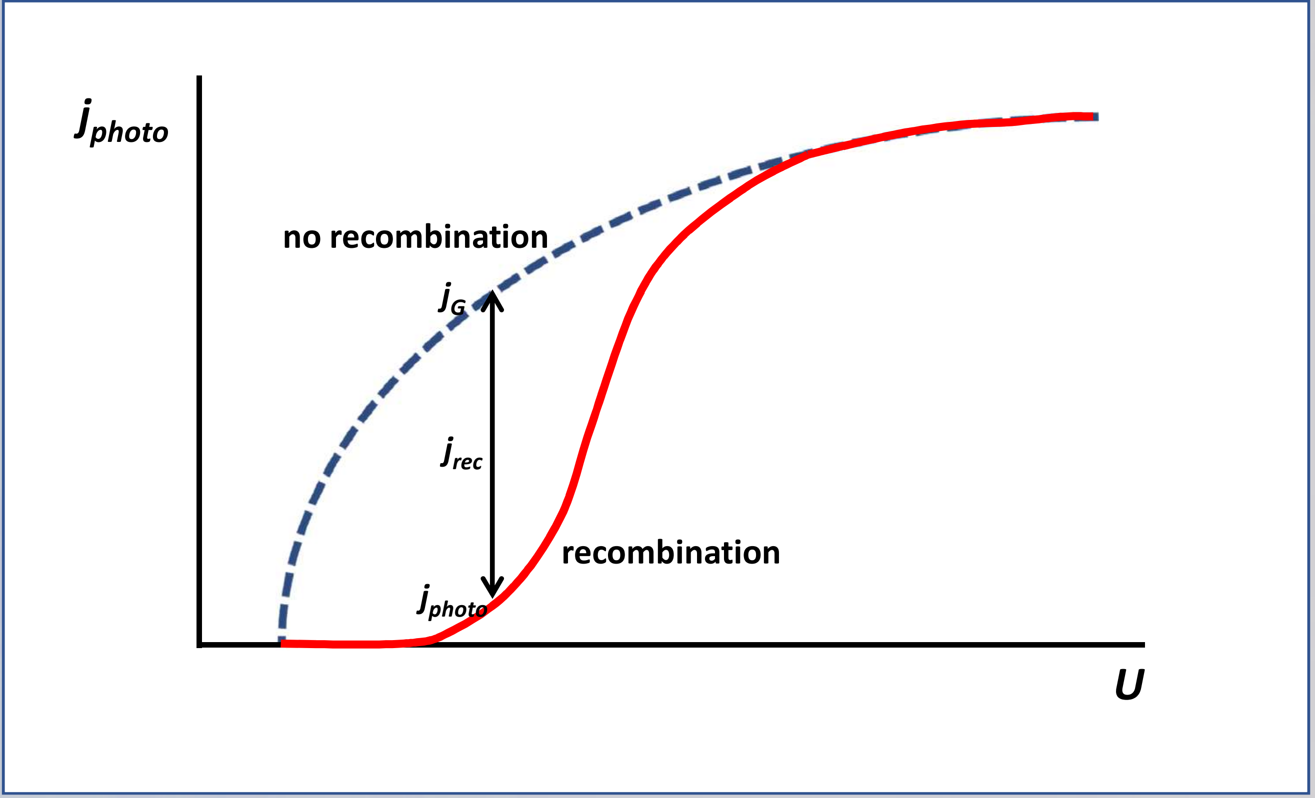
$$k_{trans} = \frac{k_{2,het} \times R}{\delta} = \frac{10^{-17} \times 10^{20}}{10^{-7}} = 10^{10} \ \text{s}^{-1}$$

Maximum first order rate constant in range **10^{10} - 10^{11} s^{-1}**

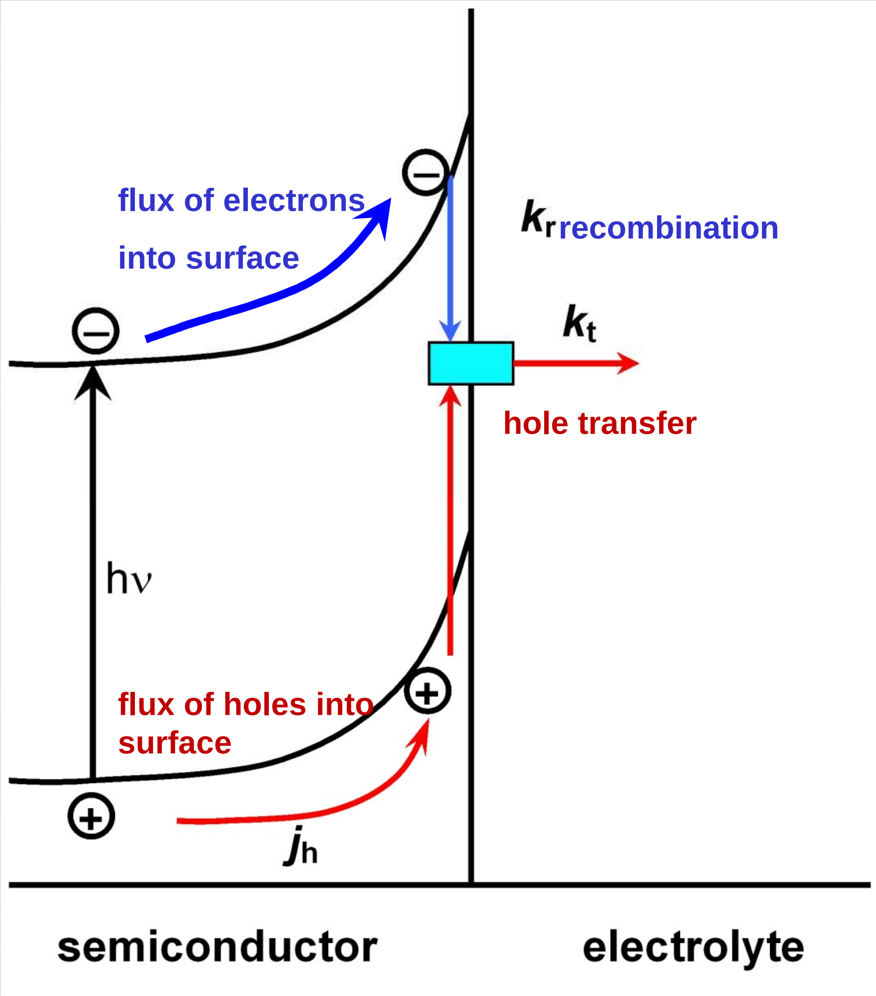
1st order lifetime = $1/k_{trans}$ = 10 - 100 ps! Very fast….

Contrast this with time constants for water splitting - milliseconds to seconds!

Delayed Photocurrent Onset Due to Surface Recombination



Simplified Model for Competition between Electron Transfer and Surface Recombination



flux of electrons

into surface

k_r recombination

k_t

hole transfer

hν

flux of holes into surface

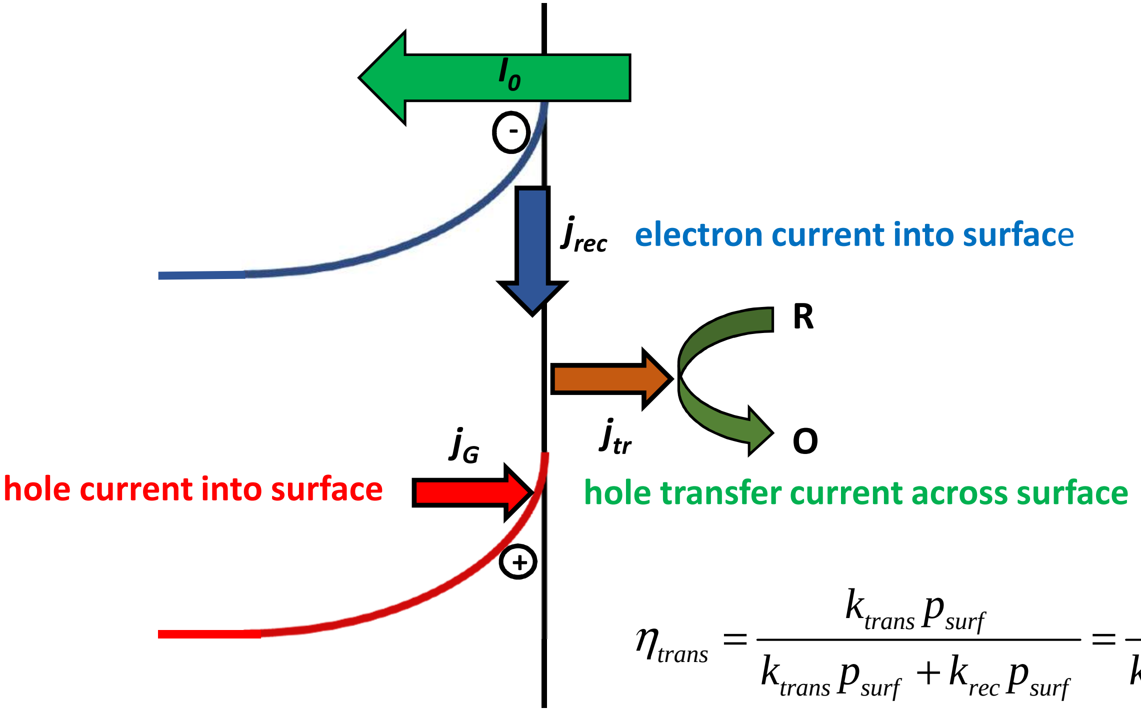
j_h

semiconductor

electrolyte

Competion between Electron Transfer and Surface Recombination determines Transfer Efficiency

$$j_{tr} = qk_{tr}\,p_{surf} \qquad j_{rec} = k_{rec}\,p_{surf} = \sigma \upsilon_{th} n_{x=0}\,p_{surf}$$



electron current into surface

hole current into surface

hole transfer current across surface

$$\eta_{trans} = \frac{k_{trans}\,p_{surf}}{k_{trans}\,p_{surf} + k_{rec}\,p_{surf}} = \frac{k_{trans}}{k_{trans} + k_{rec}}$$

hole transfer efficiency

How can we *measure* k_{trans} and k_{rec}?

Measuring the ***rate*** of any photoelectrochemical reaction is easy. Just measure the current.

But this doesn't give us the ***rate constant***.

For that we need to know the **concentration of reacting minority carriers** e.g. $p_{x=0}$ or p_{surf}

So what determines p_{surf}?

Under **steady state conditions** the rate of change of p_{surf} with time is zero

$$\frac{dp}{dt} = 0 = \text{flux of holes into surface - flux of holes out of surface}$$

$$\frac{dp}{dt} = \frac{1}{q} j_{hole} - k_{trans} p - k_{rec} p$$

holes can either oxidize water or recombine with electrons

charge transfer - recombination

Non steady state conditions

If we switch on the light, holes will begin to flow to the surface and p_{surf} will begin to increase.

As p_{surf} increases, so too will the rates of electrons transfer (hole consumption) and recombination

The steady state surface hole concentration will be approached with a time constant given by

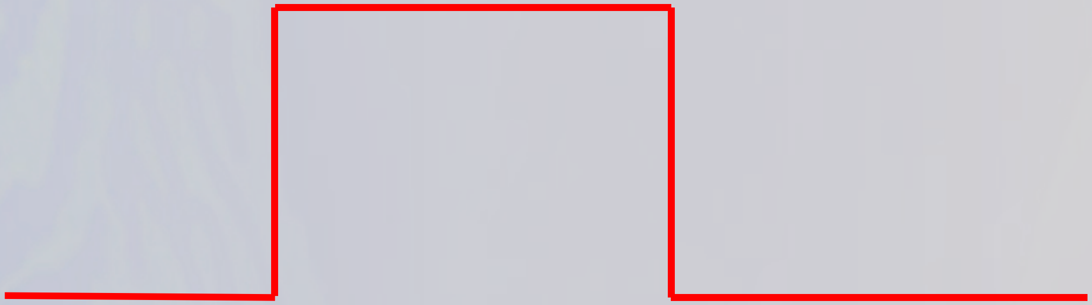
$$\tau = \frac{1}{\left(k_{trans} + k_{rec}\right)}$$

When the light is switched off again, p_{surf} will decay exponentially with the same time constant

But how can we detect the rise and decay of surface hole concentration?

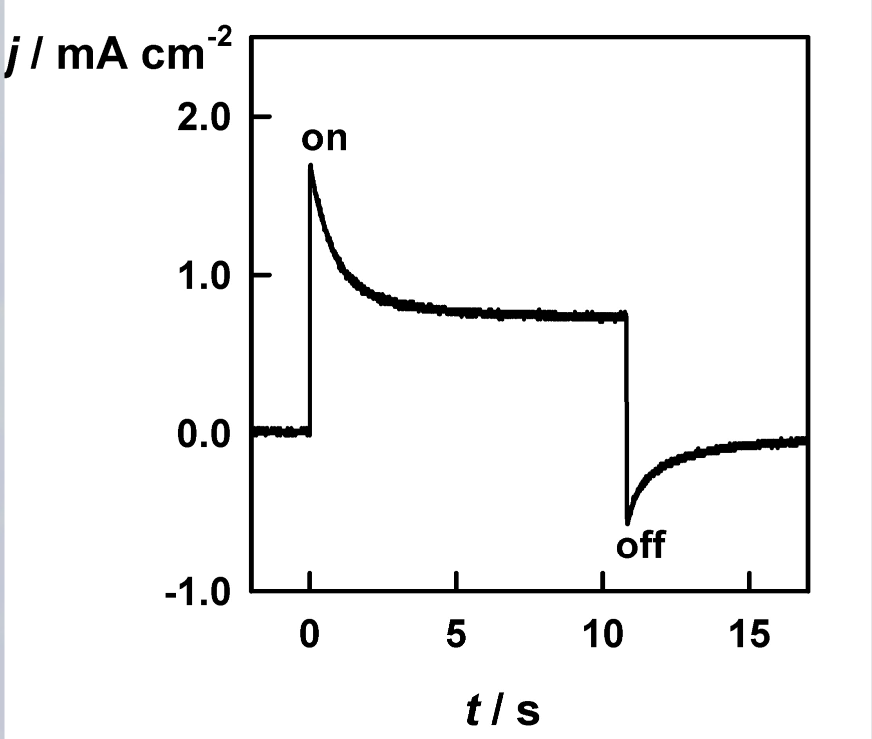
By looking at Photocurrent Transients

Competition between Charge Transfer and Recombination

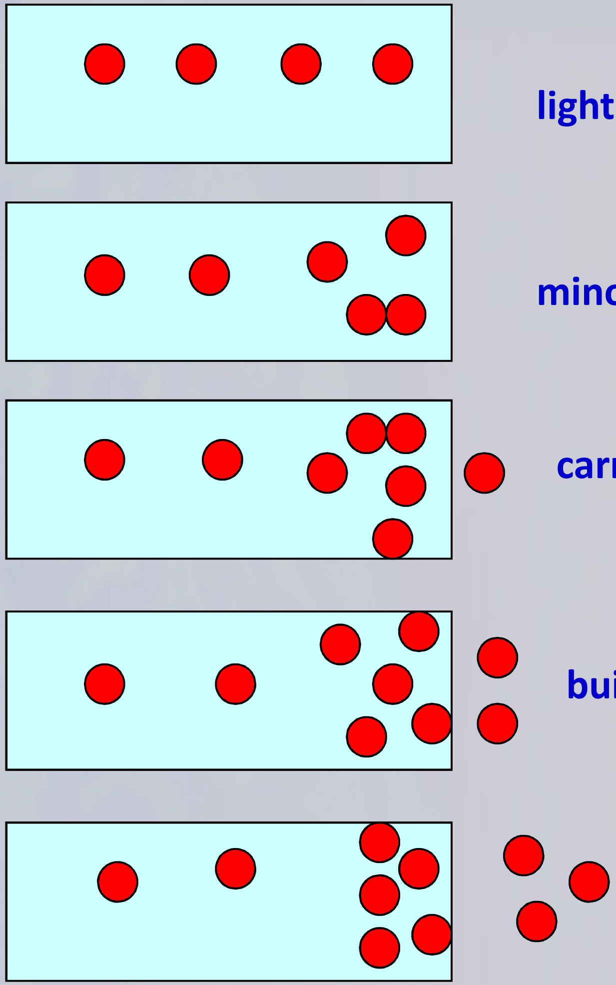


square light pulse

Transient Photocurrent Response



Transient photocurrent response of α-Fe_2O_3 electrode at 0 V vs. Ag|AgCl showing the decay and overshoot characteristic of surface electron-hole recombination. Electrolyte 1.0 M NaOH.



light switched on

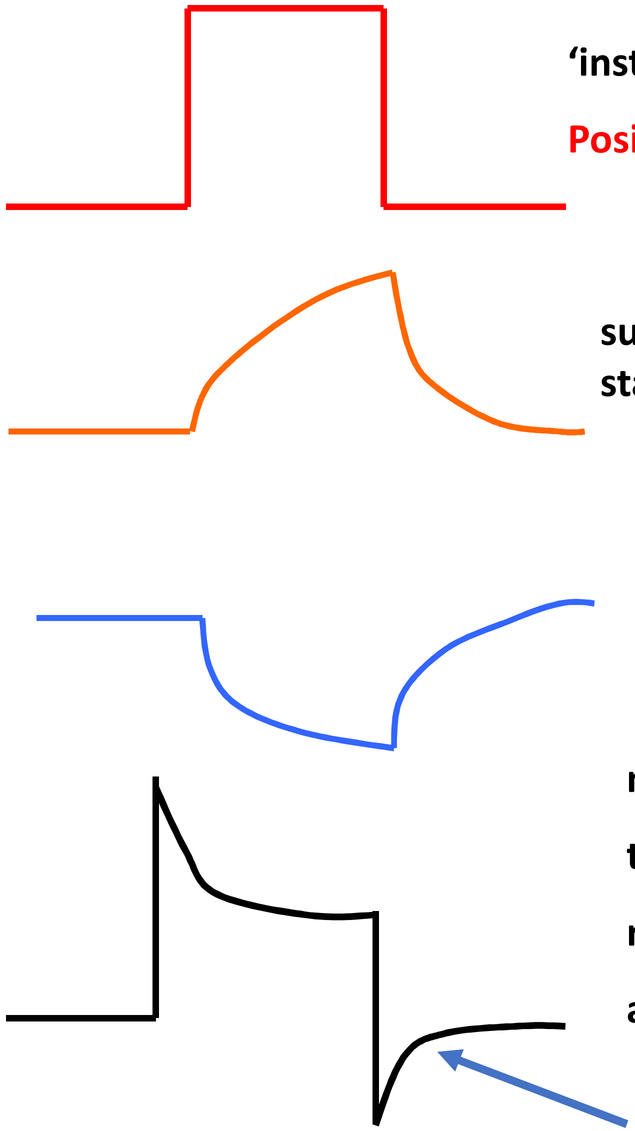
minority carriers move towards surface

carriers queue and leak across

build-up of carriers approaches steady state

steady state reached when

rate of arrival = rate of crossing



'instantaneous' (displacement) hole current into surface.

Positive current

surface concentration of trapped holes builds up towards steady state and then decays when light is switched off

electron current due to surface recombination

mirrors surface hole concentration profile. Negative current

net photocurrent decays from 'instantaneous spike

to steady state and then 'overshoots' as the

remaining surface holes continue to recombine with electrons

after the light is switched off

sum of positive + negative

Example calculation for case where $k_{trans} = k_{rec}$

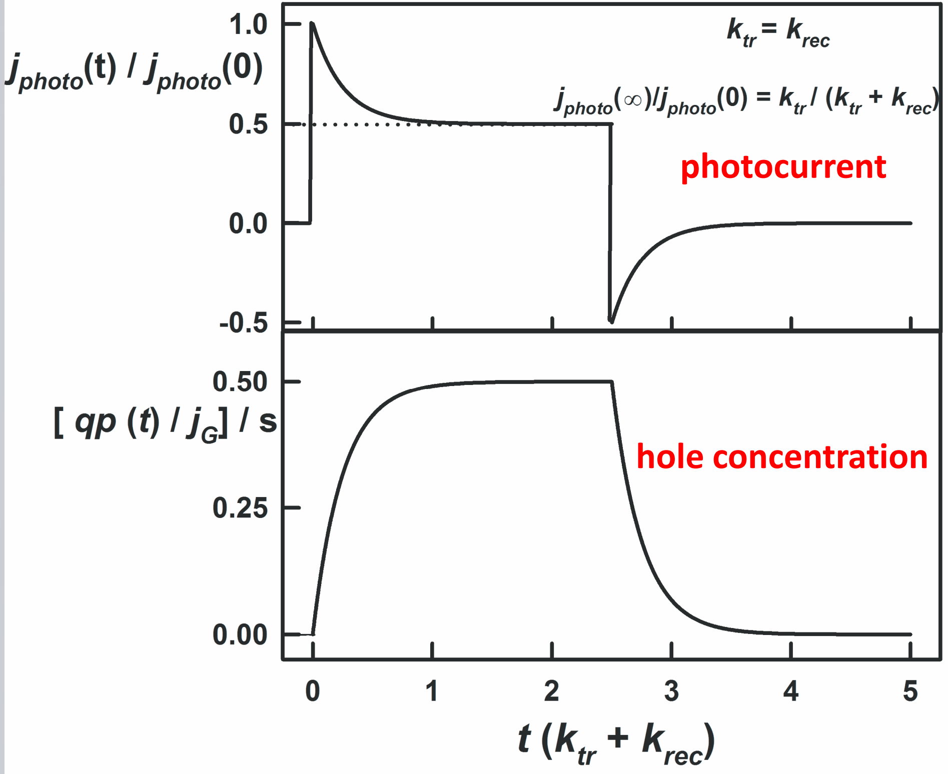
Time constant for the decay and overshoot

$$\tau = \frac{1}{\left(k_{trans} + k_{rec}\right)}$$

Ratio of steady state photocurrent to ‘instantaneous’ photocurrent

$$\frac{j^{\infty}_{photo}}{j^{0}_{photo}} = \frac{k_{trans}}{\left(k_{trans} + k_{rec}\right)} = \eta_{trans}$$

hole transfer efficiency



2 equations – two unknowns, so we can get k_{trans} and k_{rec}

How instantaneous is ‘instantaneous’?

The time constant for separation of electrons and holes in the space charge region is determined by the product of the series (contact) resistance and the space charge capacitance.

This means that there is a **finite rise time** for the current ‘spike’ that we see in a transient experiment

$$R_{ser}C_{sc}$$

A closer look at the recombination rate and k_{rec}

Recombination rate depends on concentration of majority carriers (electrons for n-type) at x=0 (surface)

$$\underset{\text{cm}^{-2}\,\text{s}^{-1}}{\text{rate}} = \overset{\text{cm}^{3}\text{s}^{-1}}{k}\,\underset{\text{cm}^{-3}}{n_{x=0}}\,\underset{\text{cm}^{-2}}{p_{surf}}$$

$n_{x=0}$ depends on band bending

$$n_{x=0} = n_{bulk} \exp\left(-\frac{q\Delta\phi_{sc}}{k_B T}\right)$$

k depends on thermal velocity υ_{th} and recombination cross section σ:

$$k = \upsilon_{th}\sigma$$

For *constant band* ***bending*** $k_{rec} = k \times n_{x=0} = k \times n_{bulk} \exp\left(-\frac{q\Delta\phi_{sc}}{k_B T}\right)$

units of k_{rec} are s^{-1}

Recombination slows down as band bending increases

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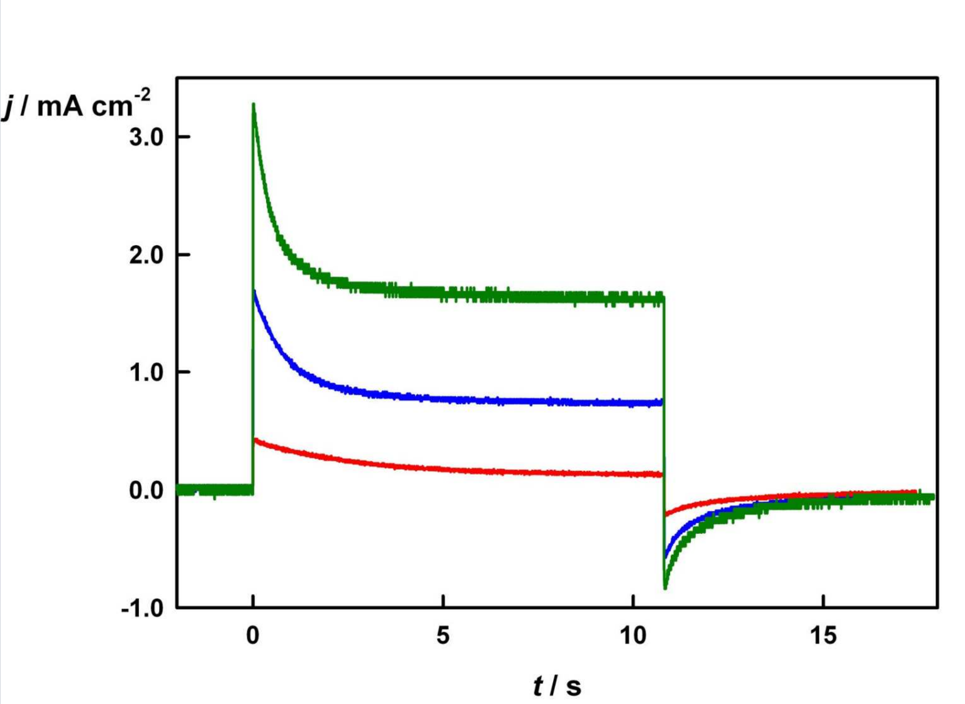
Asymmetric Photocurrent Transients



Transient photocurrent responses of α-Fe_2O_3 electrode at 0 V vs. Ag|AgCl showing the decay and overshoot characteristic of surface electron-hole recombination. Electrolyte 1.0 M NaOH.

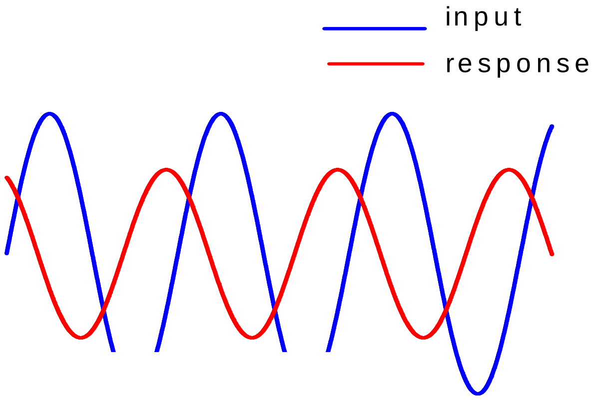
Note **asymmetry at high light intensities** – evidence of **photo-induced band edge unpinning** due to build up of holes at surface

Small amplitude methods

Avoid non-linearity problems with “light on – light off” methods

Intensity Modulated Photocurrent Spectroscopy IMPS

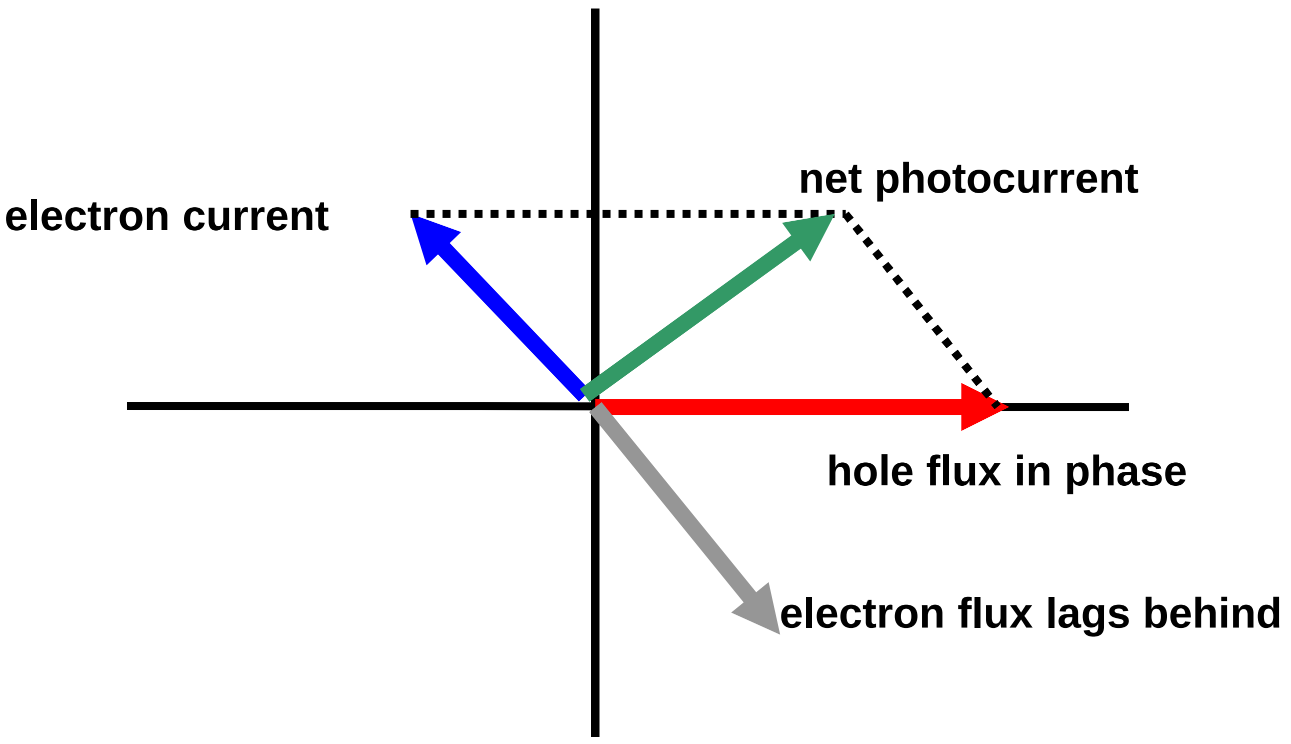
- **Constant voltage**
-
- **Modulate intensity of illumination by a few %**
- **Modulates Hole Flux**



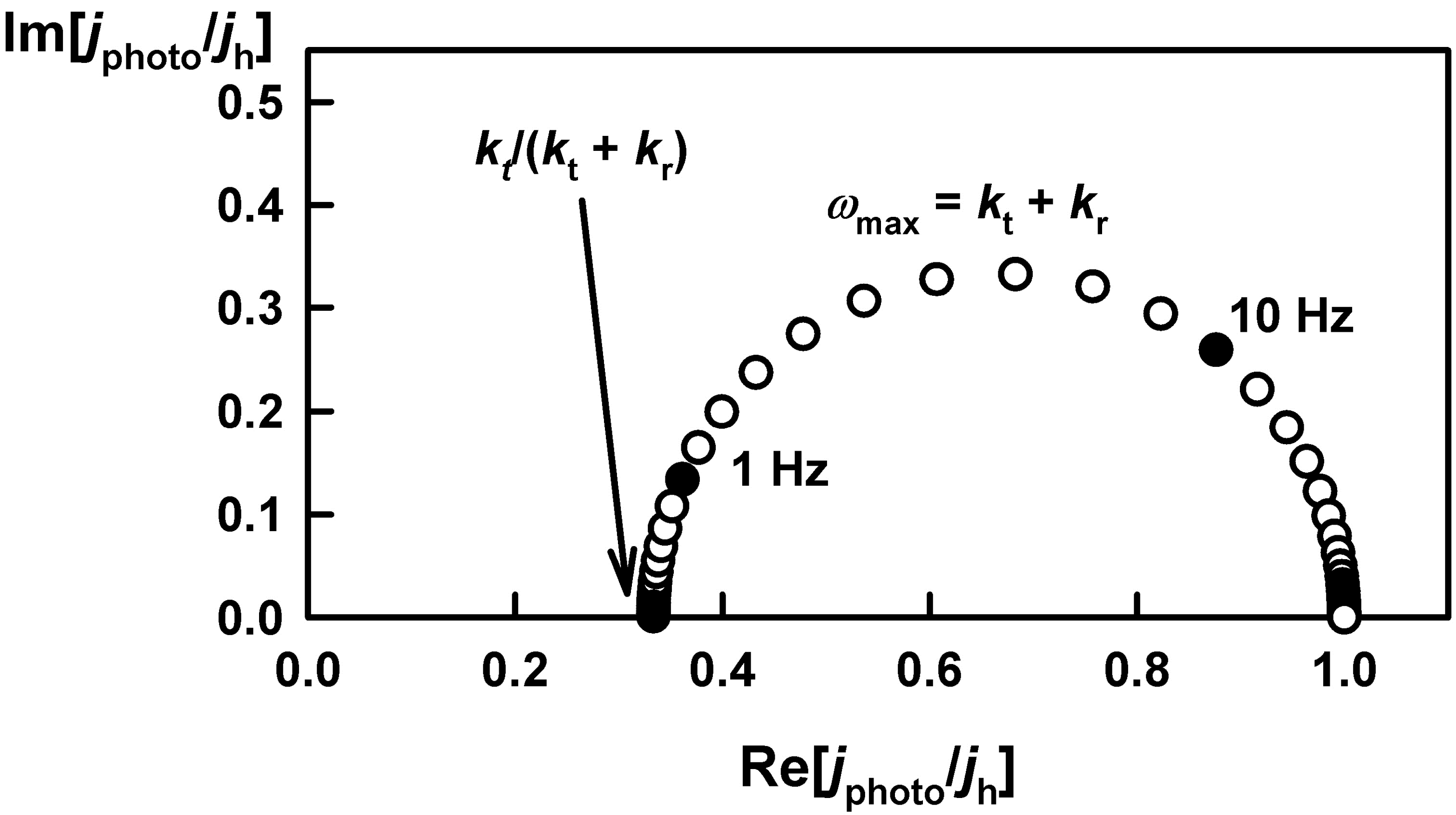
Photoelectrochemical Impedance Spectroscopy PEIS

- **Constant illumination intensity**
- **Modulate potential by a few %**
- **Modulates recombination**

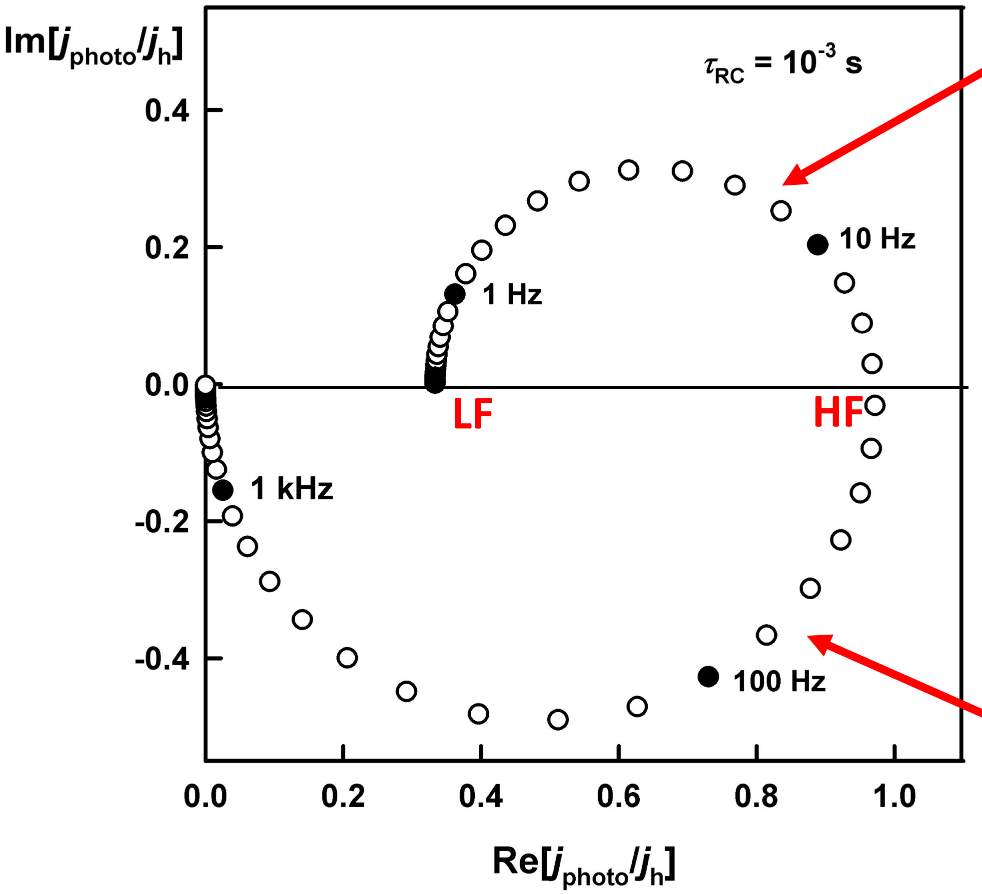
Vector Diagram showing phase relationships for hole and electron fluxes and currents



IMPS response gives k_{trans} and k_{rec}



Effect of $R_{ser}C_{sc}$ on IMPS response

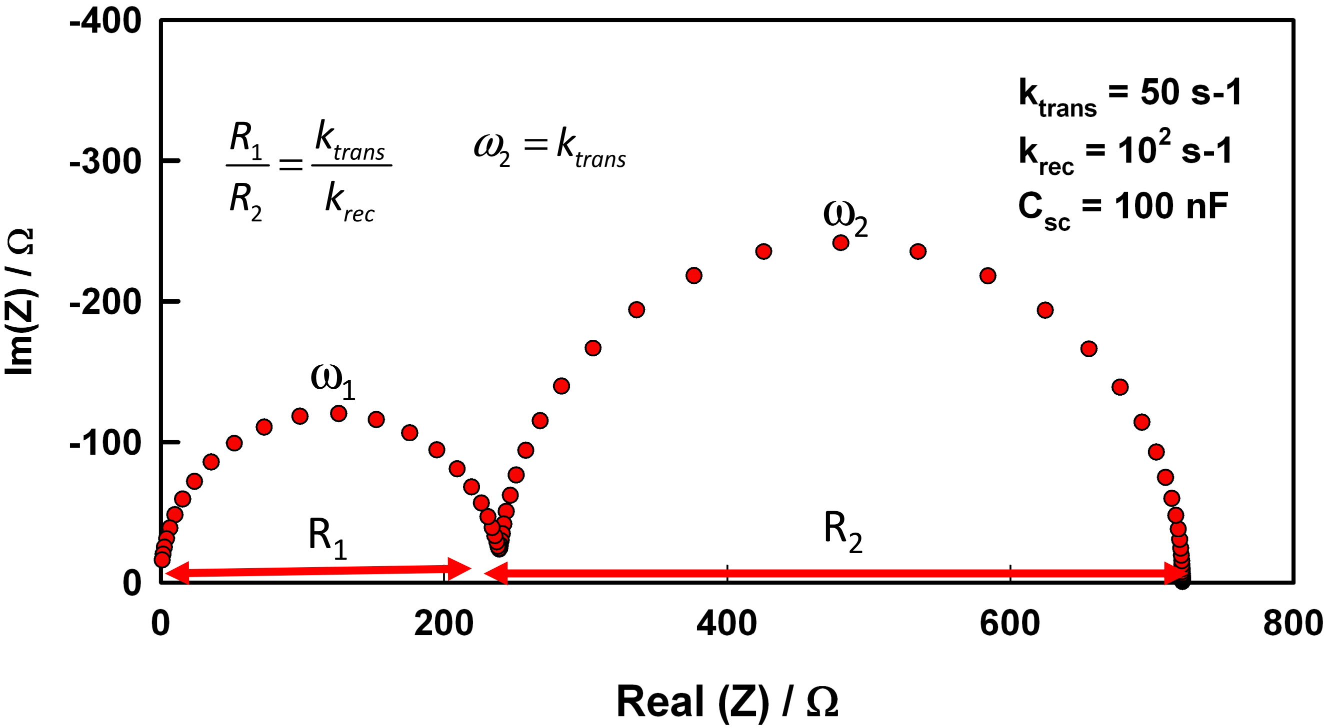


upper semicircle due to recombination

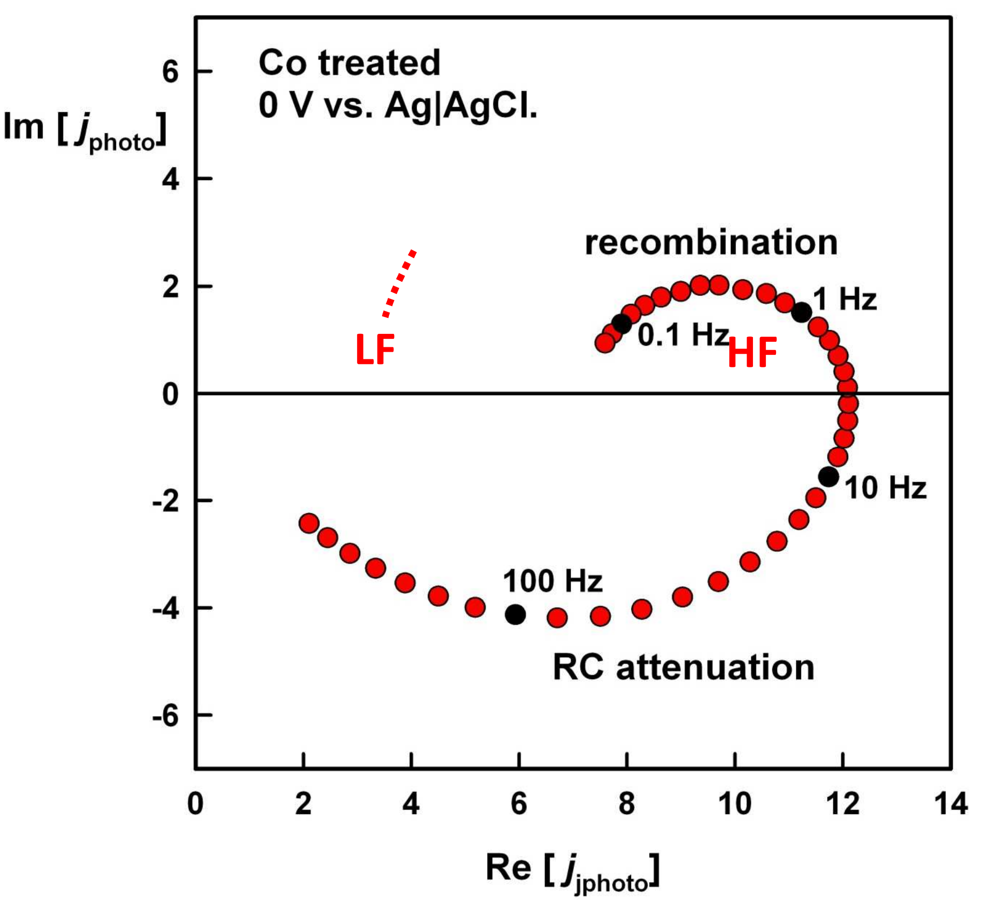
LF intercept and HF crossing point

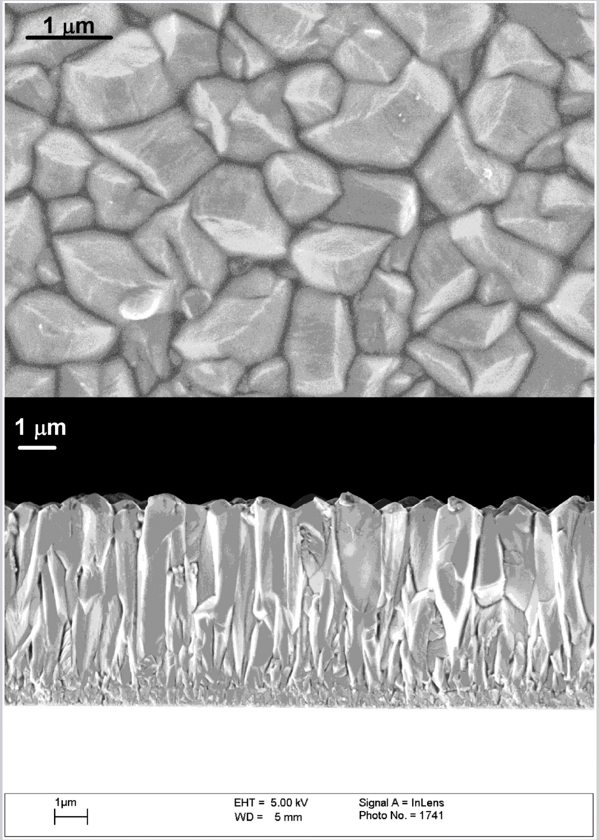
lower semicircle due to RC attenuation

Theoretical PEIS Response – *Two* Semicircles



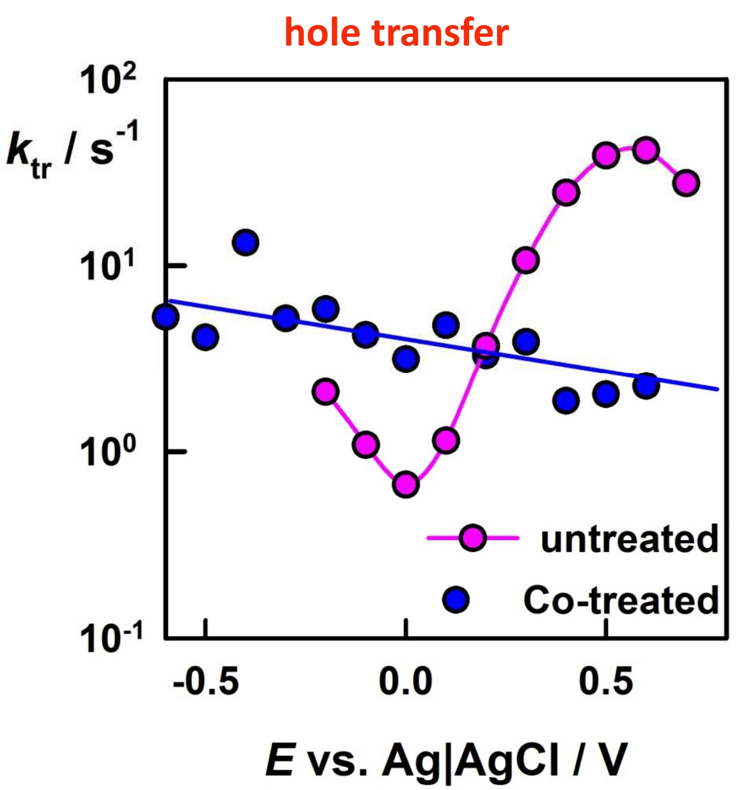
Experimental IMPS response for Fe_2O_3 photoanode

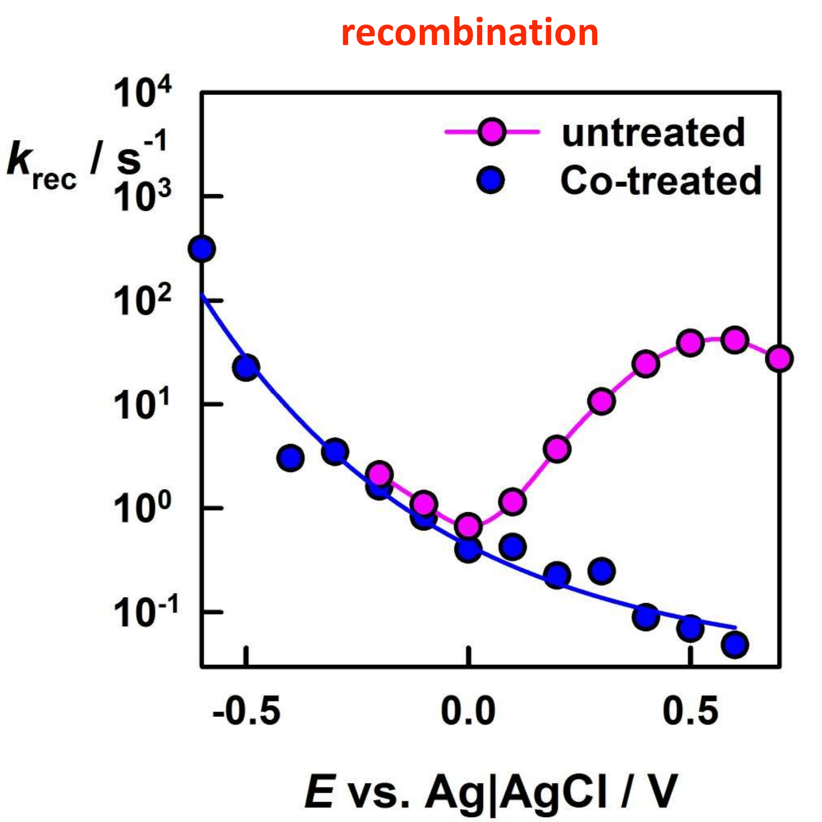




Kinetics of light-driven oxygen evolution at α-Fe_2O_3 electrodes. LM Peter, KGU Wijayantha, AA Tahir. *Faraday Discussions* (*Artificial Photosynthesis*) **155**, 309-322 (20912). (2012).

Kinetics of Recombination and Charge Transfer at Hematite Electrodes

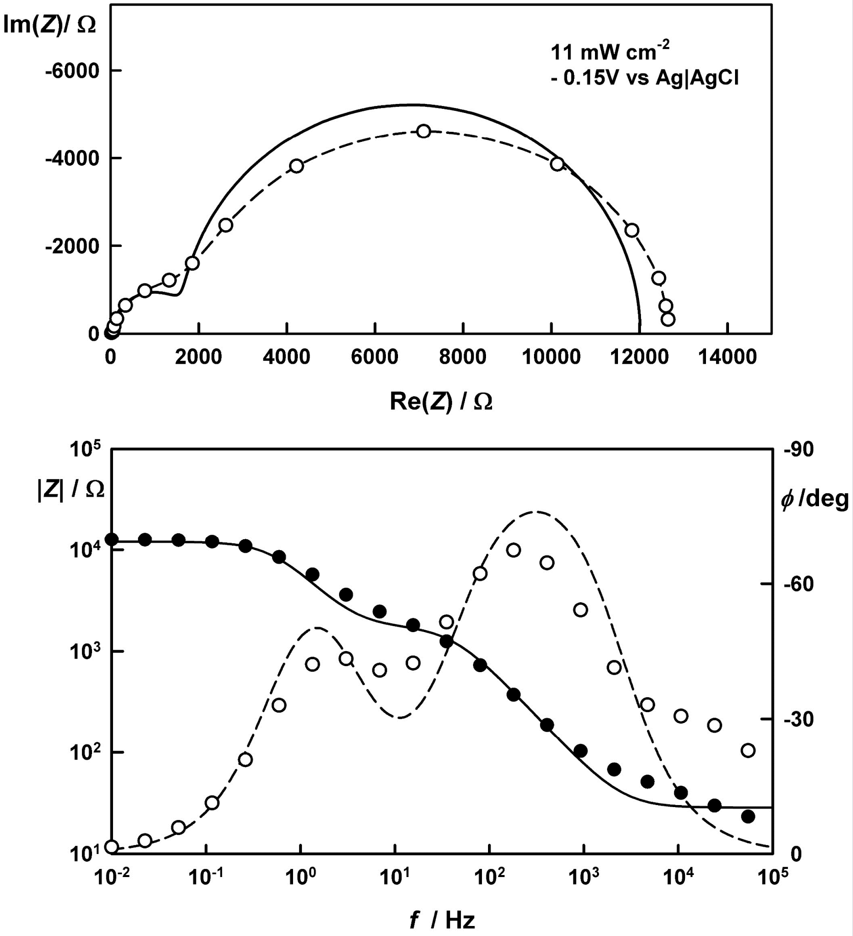




Charge Transfer NOT accelerated – k_{tr} less than 10 s^{-1}

BUT almost complete suppression of surface recombination by Co-treatment

PEIS of Fe_2O_3 photoanode



Note two semicircles

How slow is “slow”?

$$k_{tr} \approx 10\ s^{-1}$$

Translating back to k_{het} gives around 10^{-30} $cm^4\ s^{-1}$

13 orders of magnitude less than fastest outer sphere reaction!

Conclusions

We have a range of experimental methods to measure rate constants of photoelectrochemical reactions

Light-driven OER is remarkably slow – at least one step has a high activation energy

Slow electron transfer leads to efficiency losses due to

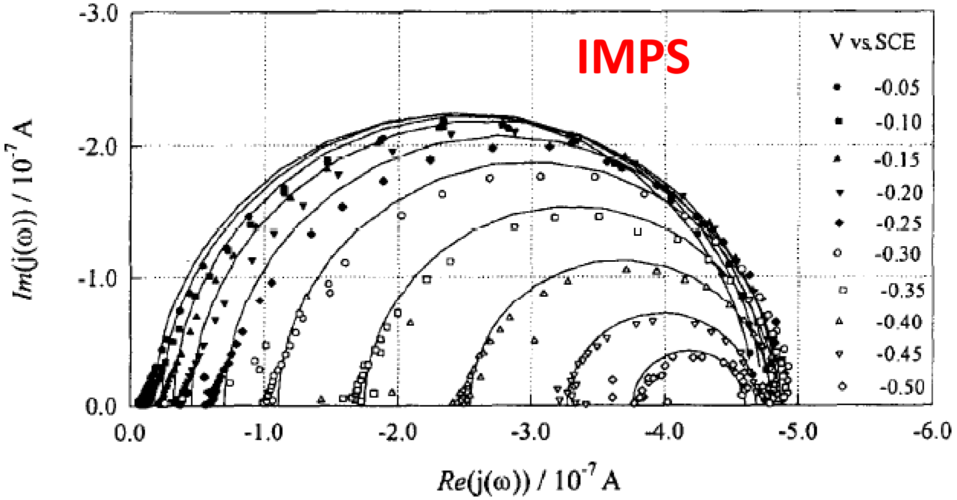
- Competition from **surface recombination**
- Photo-induced **band edge unpinning** increases recombination rate constant

Improving efficiencies requires

- **Catalysis** of multistep electron transfer processes
- **Inhibition** of surface recombination

Some history….

Kinetics of hydrogen evolution on p-InP studied by IMPS

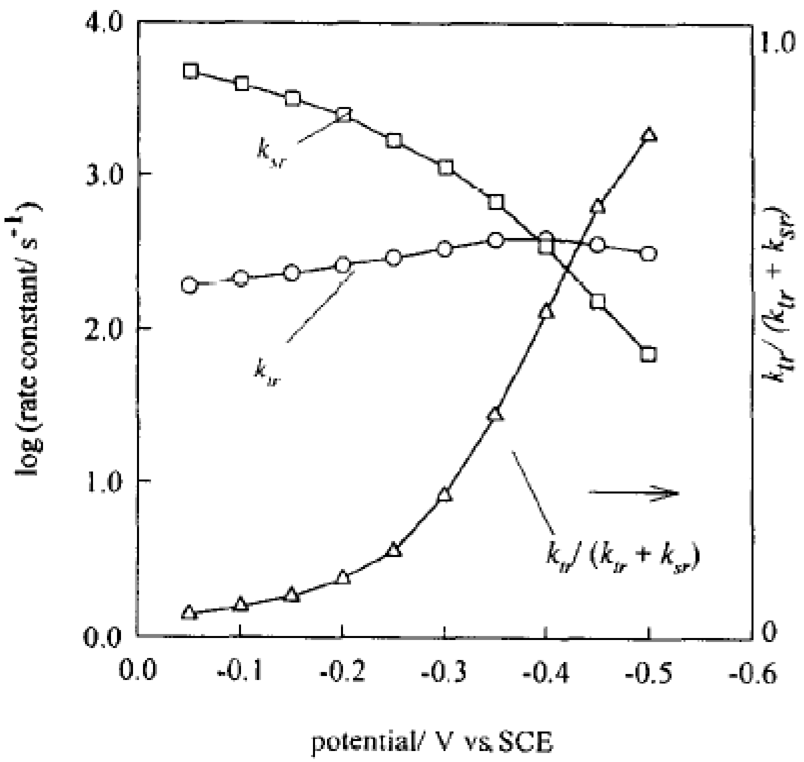


Rate constants for charge transfer and recombination

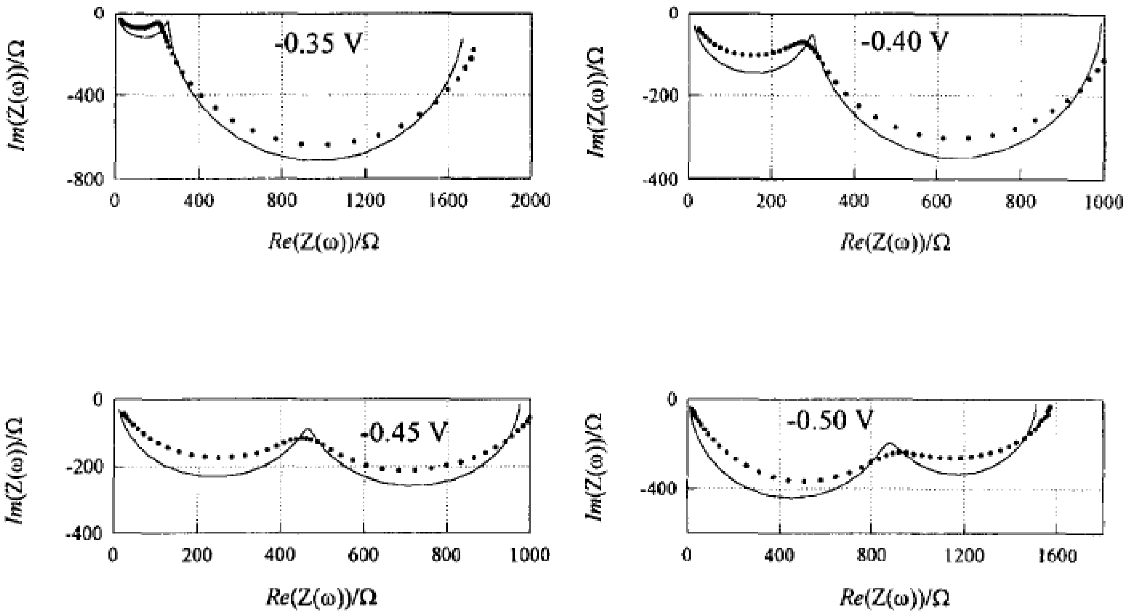
Note that k_{tr} is LOW – a few hundred s^{-1}

E.A. Ponomarev [1], L.M. Peter

Journal of Electroanalytical Chemistry 397 (1995) 45–52



PEIS on the p-InP



Rate constants for recombination and charge transfer derived from IMPS measurements with bias light and with PEIS after they reached steady-state values (saturation photocurrent ~0.8 mA cm^{-2}). The values of C_{sc} derived from PEIS are also given

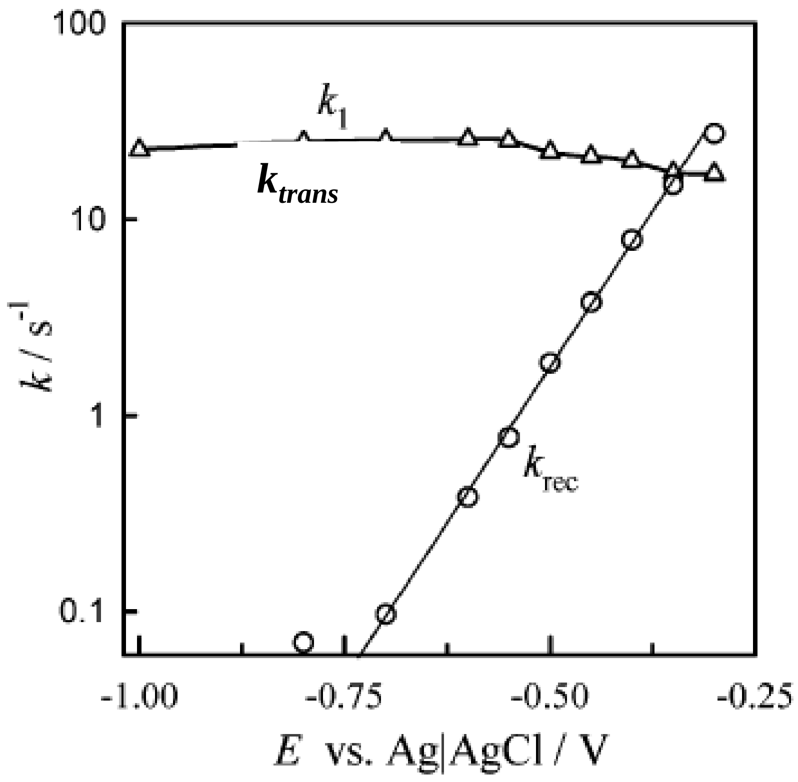
E/V vs. SCE	k_{tr} /s^{-1}		k_{sr} /s^{-1}		$k_{tr}/(k_{tr}+k_{sr})$		C_{sc} / nF
	IMPS	PEIS	IMPS	PEIS	IMPS	PEIS	PEIS
−0.35	45	70	452	404	0.09	0.14	82
−0.40	125	177	435	414	0.22	0.30	74
−0.45	246	236	278	256	0.47	0.48	79
−0.50	297	243	119	168	0.71	0.59	88

Same results from IMPS and PEIS

Rate Constants for Hydrogen Evolution and Recombination on p-Si

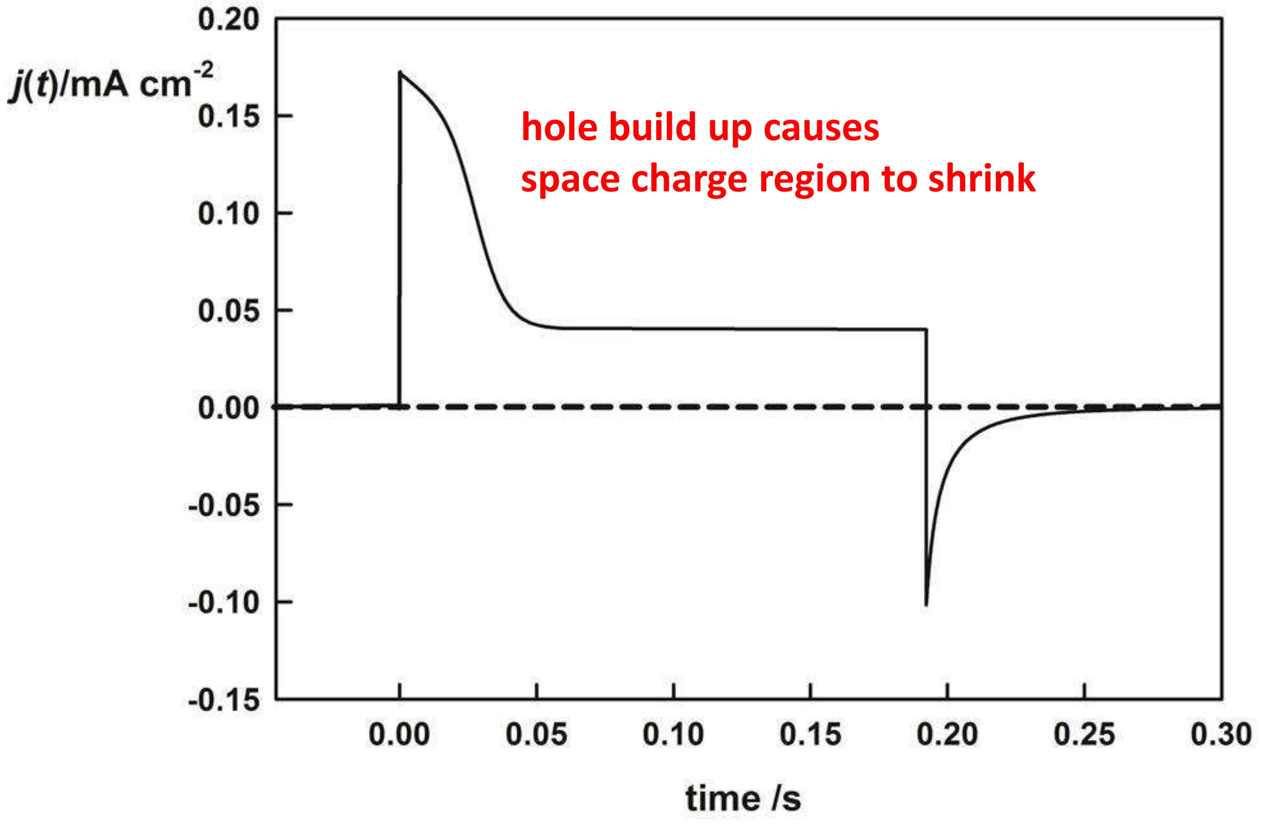
Again hydrogen evolution is SLOW

H-terminated p-Si(111)



Calculated Transient Showing Band Edge Unpinning

Transient calculated for $I_0 = 7.47 \times 10^{15}$ cm^{-2} and an applied voltage of 0.4 V vs flatband



hole build up causes
space charge region to shrink

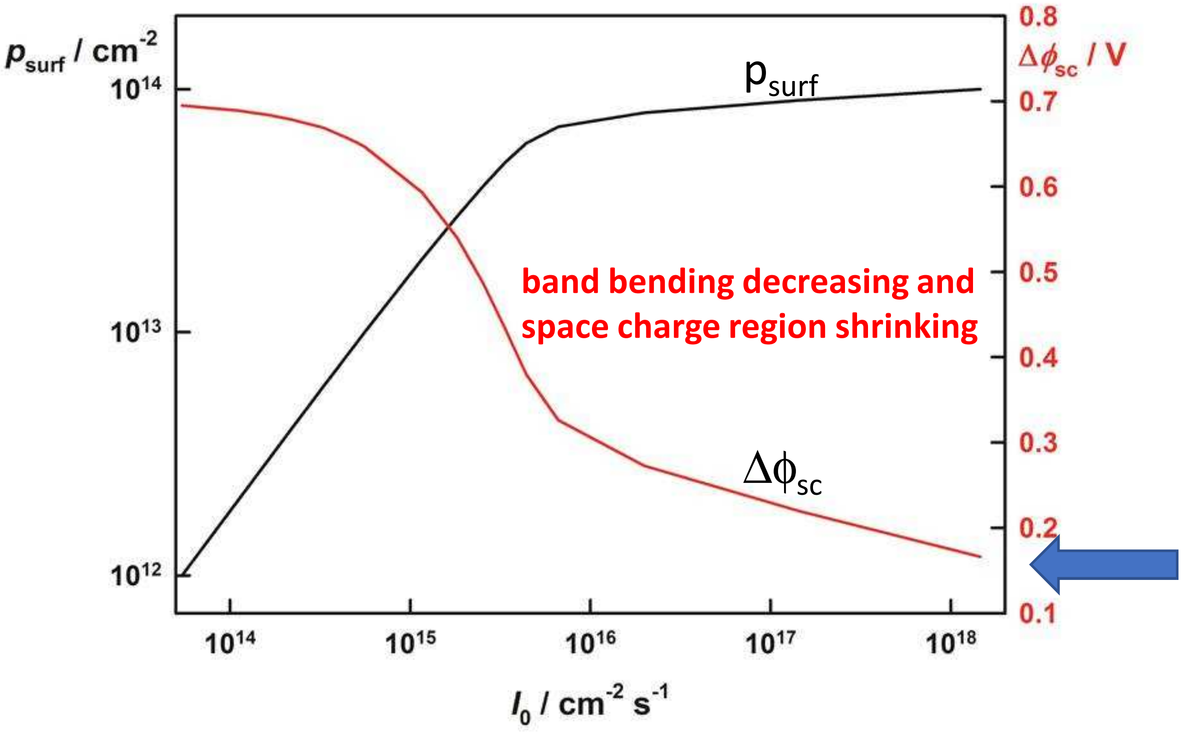
Potential drop across the Helmho
increases by an amount Q_{surf}/C_H a
drop across space charge region *a*
since the total potential drop is cc
The width of the space charge reg
becomes smaller

$\alpha = 1.5 \times 10^5$ cm^{-1} $N_d = 10^{19}$ cm^{-3} $\varepsilon = 25$ $L_p = 1$ nm

$\sigma\nu = 10^{-13}$ cm^{-3} s^{-1} $k_{tr} = 10$ s^{-1} $C_H = 30$ μF cm^{-2}

Photo-induced Band Edge Unpinning - An Extreme Example

Plots showing effects of hole build up as a function of light intensity. Applied Voltage 0.7 V vs flatband



band bending decreasing and space charge region shrinking

bands almost flat!

$\alpha = 1.5 \times 10^5$ cm^{-1} $N_d = 10^{19}$ cm^{-3} $\varepsilon = 25$ $L_p = 1$ nm

$\sigma\nu = 10^{-13}$ cm^{-3} s^{-1} $k_{tr} = 10$ s^{-1} $C_H = 30$ μF cm^{-2}

Photocatalysis or Photosynthesis?

We are interested in converting photon energy into chemical free energy

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

KEEP CALM AND USE PROPER ENGLISH

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$\Delta H^o = 2.86\times10^5 \text{ J mol}^{-1}$

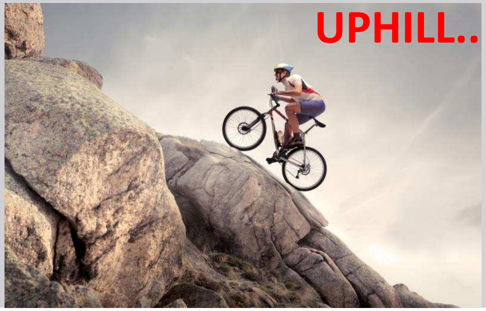
$\Delta G^o = 2.37\times10^5 \text{ J mol}^{-1}$

$\Delta S^o = 189 \text{ J K}^{-1} \text{ mol}^{-1}$

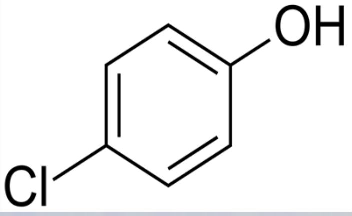
Stored free energy per molecule of H_2 = 2.46 eV

Stored free energy per electron = **1.23 eV**

Free energy IN - Photosynthesis



Use of semiconductor powders such as TiO_2 for environmental remediation



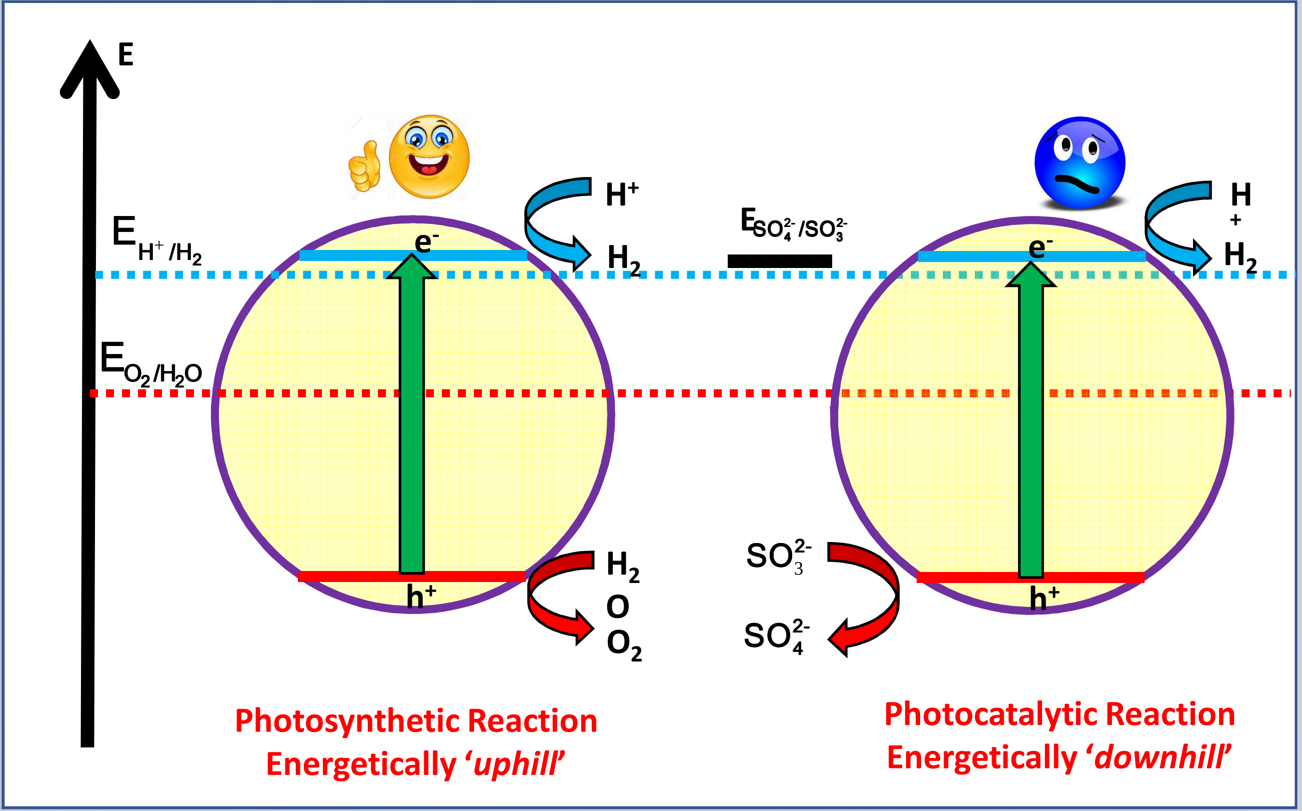
$$+\,6\,\frac{1}{2}O_2 \xrightarrow{h\nu} 6\,CO_2 + 2\,H_2O + HCl$$

“light catalysed combustion” **free energy OUT**

i.e. spontaneous but negligibly slow at room temperature in the absence of a **(photo)catalyst**

Energy out - Photo<u>catalysis</u>

Photosynthetic vs. Photocatalytic Reactions



Photosynthetic Reaction
Energetically *'uphill'*

Photocatalytic Reaction
Energetically *'downhill'*

Right. Light is used to 'catalyze' **reduction of protons to H_2** by **strongly reducing** electron donor species SO_3^{2-}.

Reaction **is already thermodynamically feasible (exo-energetic) in the dark**, but takes place at a negligible rate.

Left. Light energy is used to generate hydrogen and oxygen (**endo-energetic** process).

What do we mean by 'efficiency'

$$STH = \frac{mol\ H_2\ m^{-2} s^{-1} \times\ 237\ kJ\ mol^{-1}}{P_{solar\ AM1.5G}\left(W\ m^{-2}\right)}$$

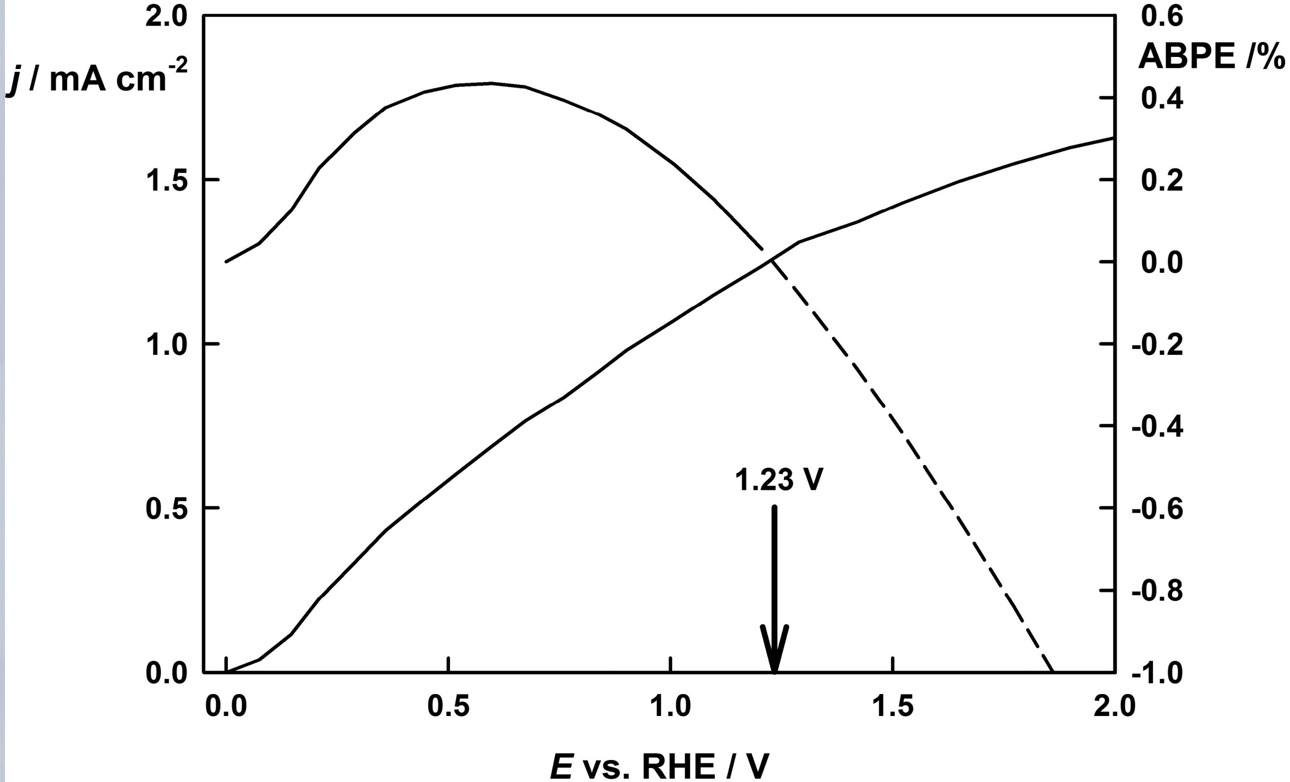
Solar to **H**ydrogen Efficiency

$$STH = \frac{j_{sc}\left(A\ m^{-2}\right)\times\ 1.23V \times \eta_F}{P_{solar\ AM1.5G}\left(W\ m^{-2}\right)}$$

$$ABPE = \frac{j_{photo} \times \left(1.23 - V_{bias}\right)}{P_{solar,\ AM1.5}}$$

Applied
Bias **P**hoton to Current
Efficiency

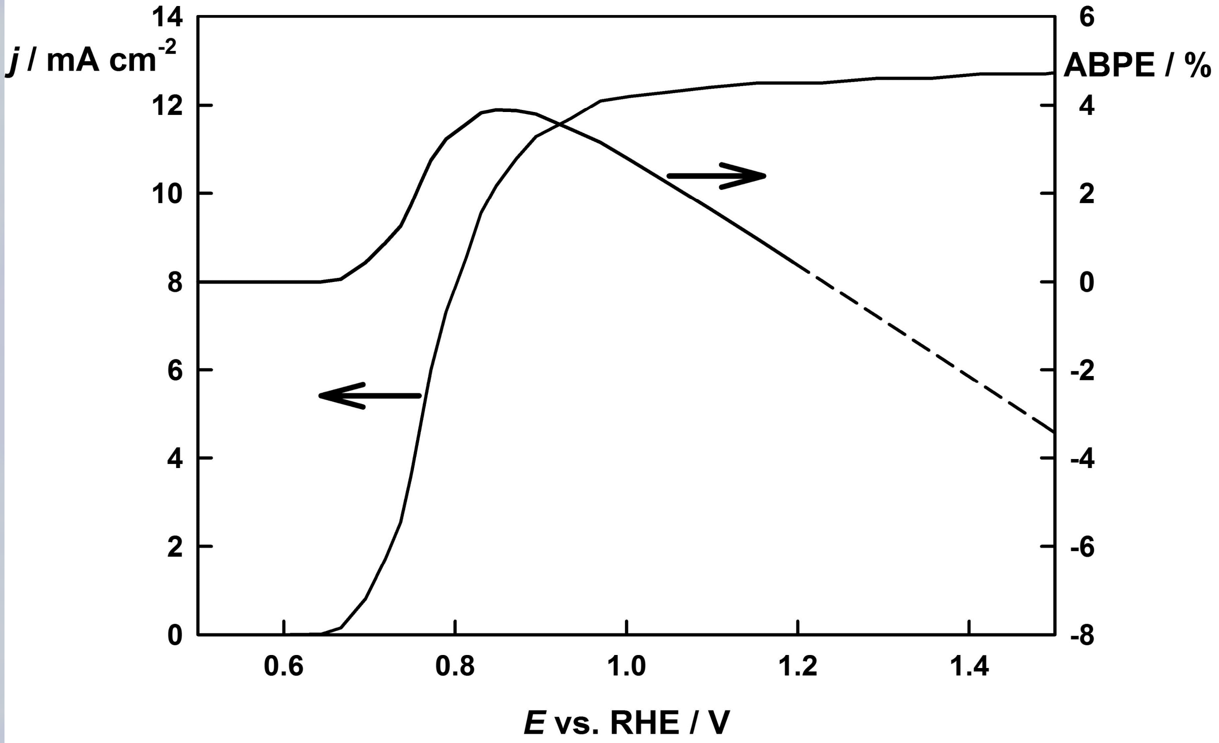
Example of ABPE Calculation



Plot showing calculation of the applied bias photon to current efficiency (ABPE) of a W-doped $BiVO_4$ electrode coated with Co-Pi catalyst. Data from Zhong et al. The broken line shows that the ABPE becomes negative at potentials more positive than 1.23 V.

D. K. Zhong, S. Choi, D. R. Gamelin, *J. Am. Chem. Soc.* **2011**, *133*, 18370-18377.

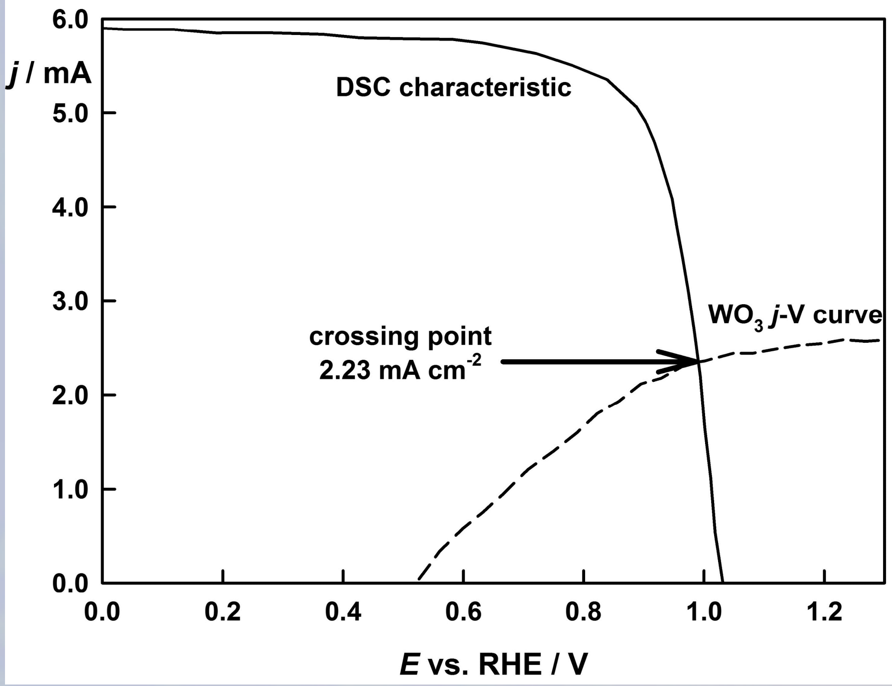
ABPE calculation for buried junction

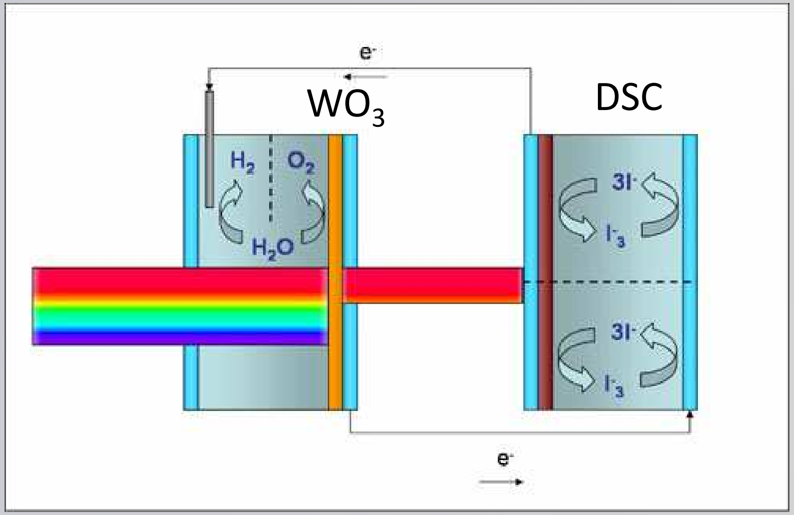


Plot showing calculation of applied bias photon to current efficiency (ABPE) for a single buried GaAs junction coated with a protective amorphous TiO_2 layer. Data from Hu et al. The broken line shows that the ABPE efficiency becomes negative for potentials more positive than 1.23 V. The peak ABPE efficiency is around 4%.

S. Hu, M. R. Shaner, J. A. Beardslee, M. Lichterman, B. S. Brunschwig, N. S. Lewis, *Science* **2014**, *344*, 1005-1009

STH efficiency calculation for photoanode biased by a solar cell



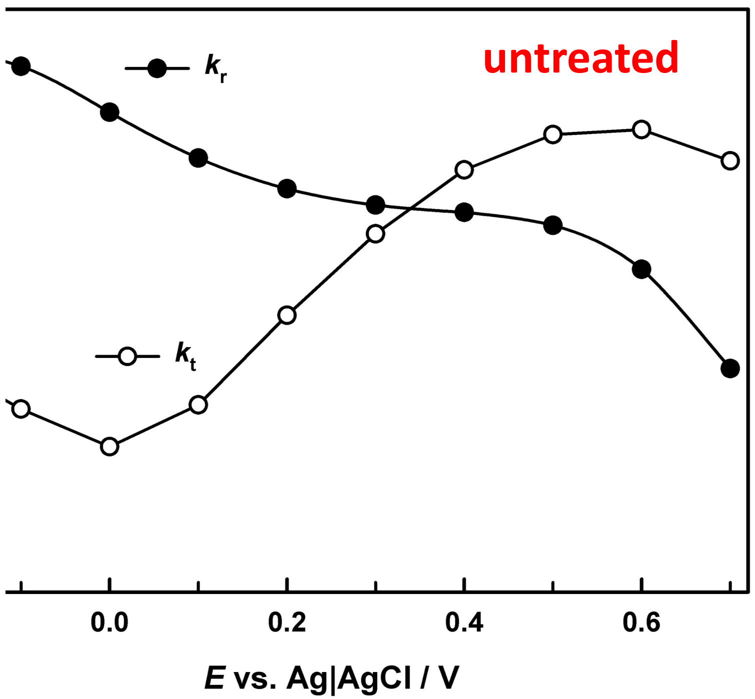


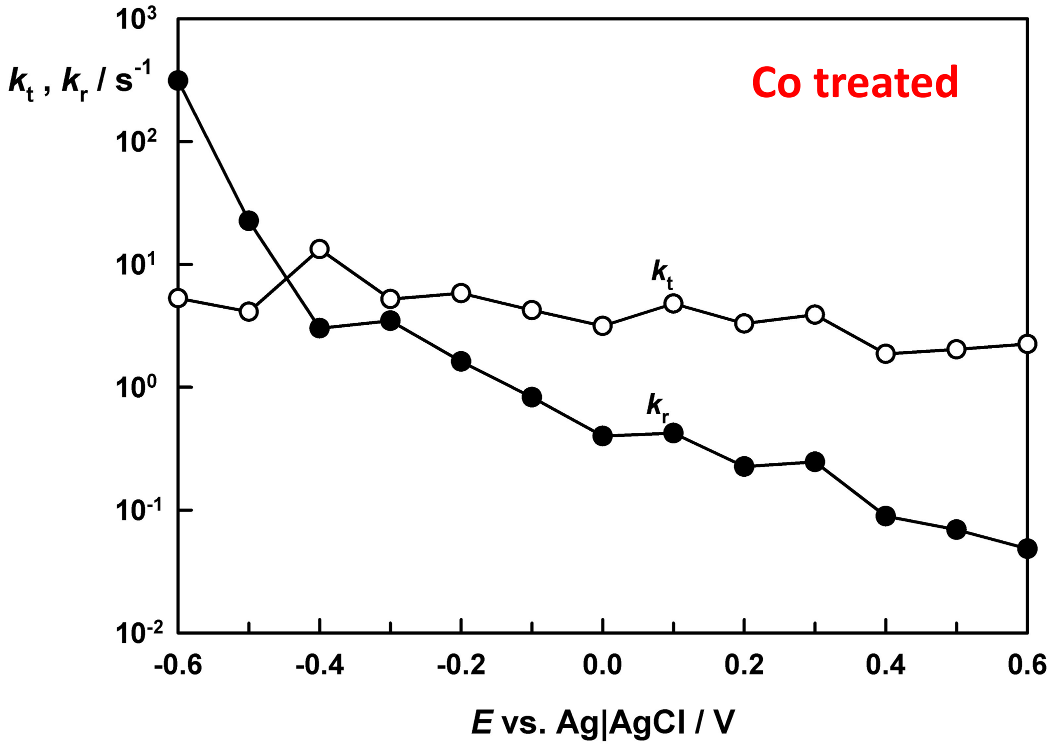
$$STH = \frac{2.23\ mA\ cm^{-2} \times 1.23V}{100\ mW\ cm^{-2}} = 2.7\%$$

Current voltage plots for DSC-biased WO$_3$ photoelectrode. Data taken form Brillet at al.The operating point of the tandem configuration is determined by the crossing point between the dye-cell and photoanode current voltage curves. The solar to hydrogen efficiency (STH) efficiency (neglecting cathode and ohmic overpotential losses) is 2.7%.

J. Brillet, J.-H. Yum, M. Cornuz, T. Hisatomi, R. Solarska, J. Augustynski, M. Graetzel, K. Sivula, *Nat Photon* **2012**, *6*, 824-828.

Rate constants derived from analysis of PEIS for Fe_2O_3





Note $k_t = k_{trans}$

Light-Driven Water Splitting

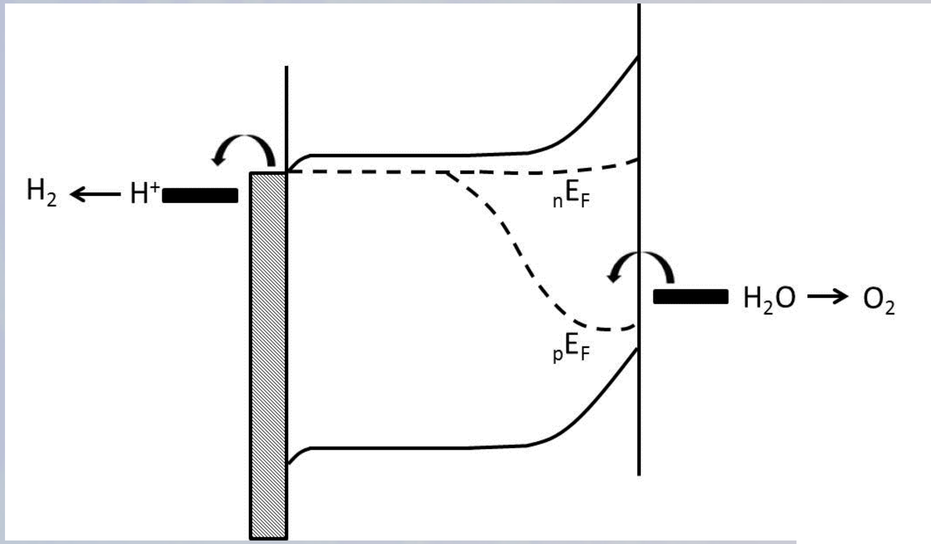
The Role of Interfacial Kinetics

A Huge Challenge!

Multistep Coupled Electron Proton Transfer Reactions at Surfaces

surface-bound intermediates

Water Splitting: Device types



Single junction device

Buried n-p junction device