Materials for a Sustainable Energy Future

IPAM – Tutorials

Sept 10-12, 2013

Continuum Models of Dye-Sensitized Solar Cells

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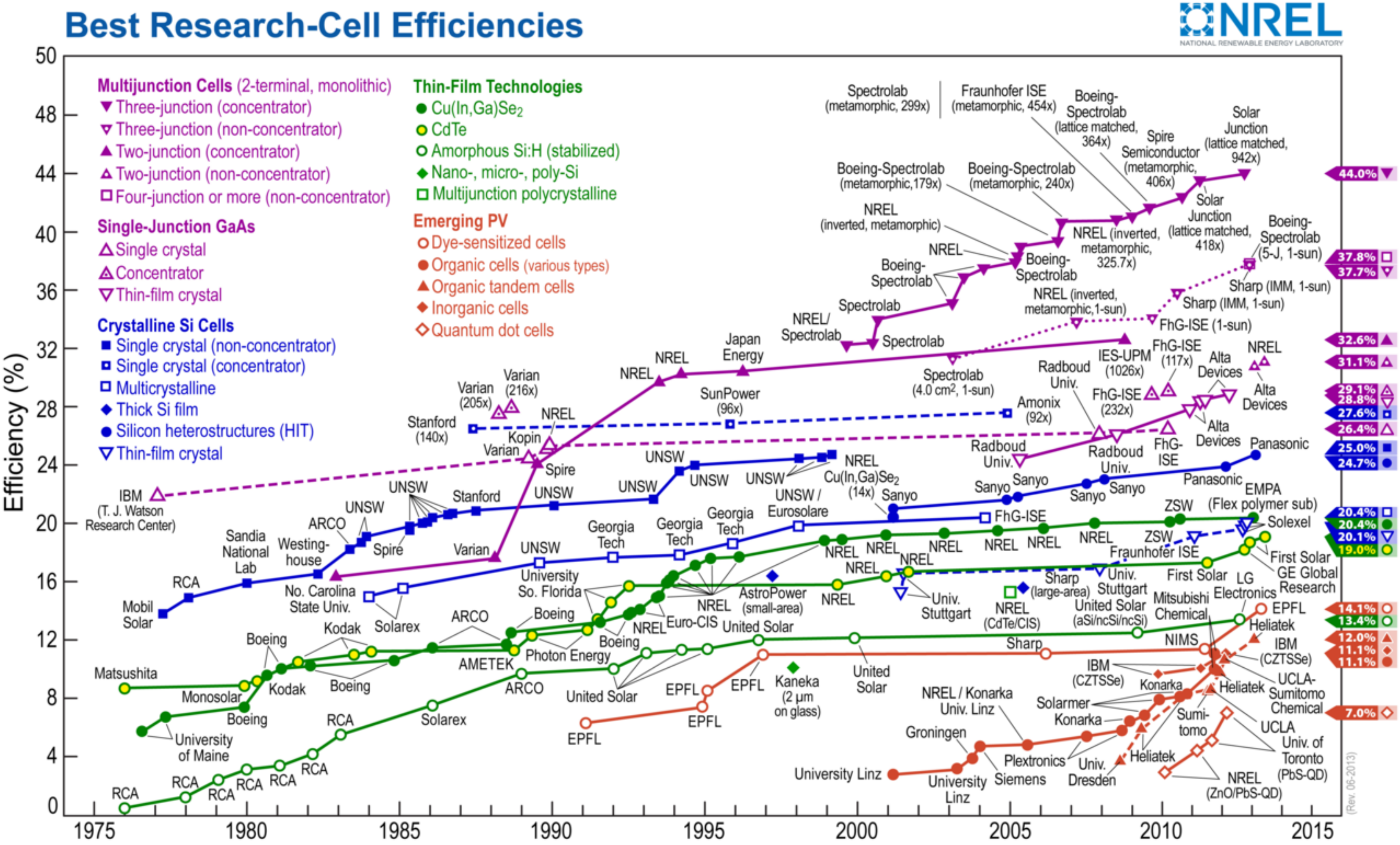
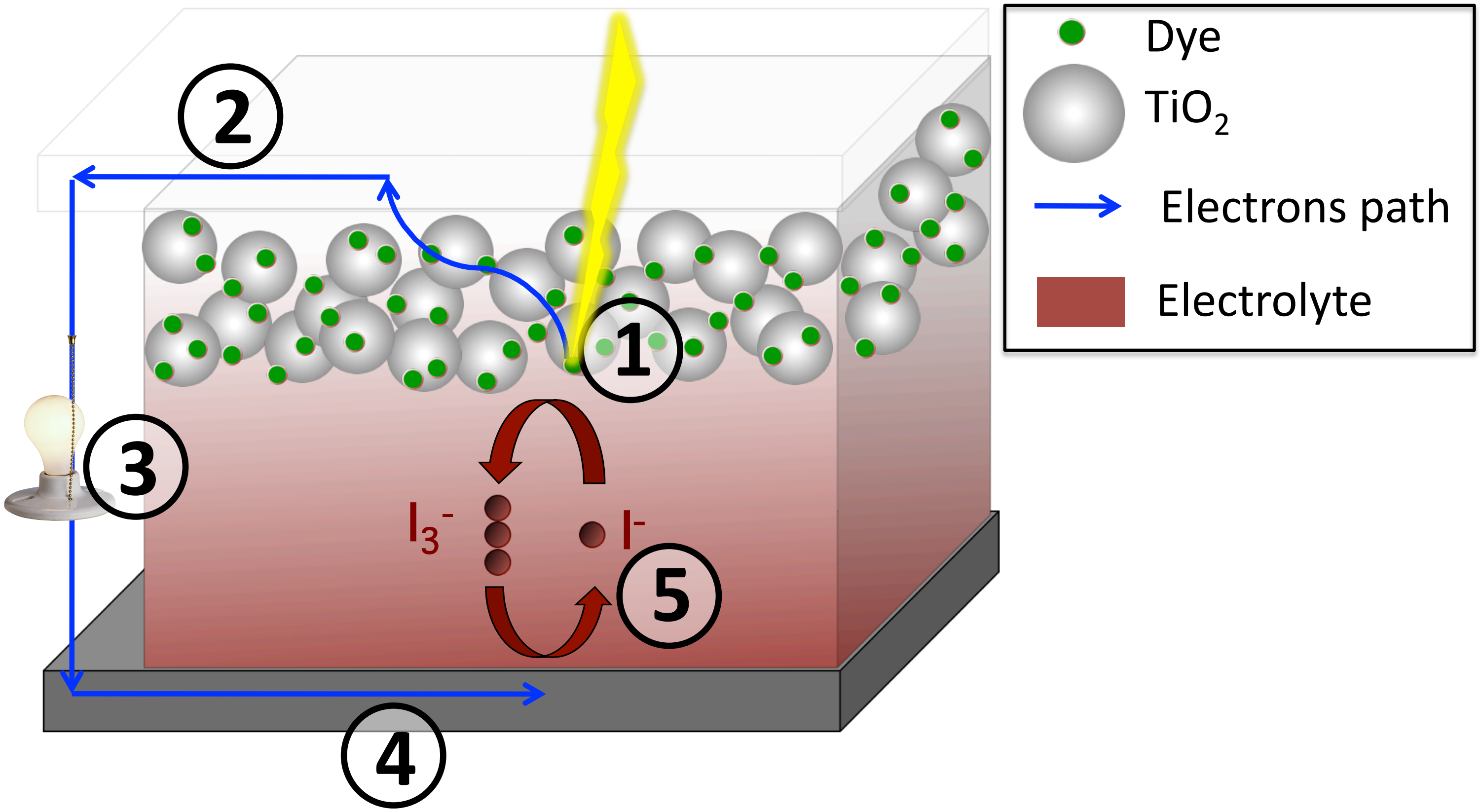
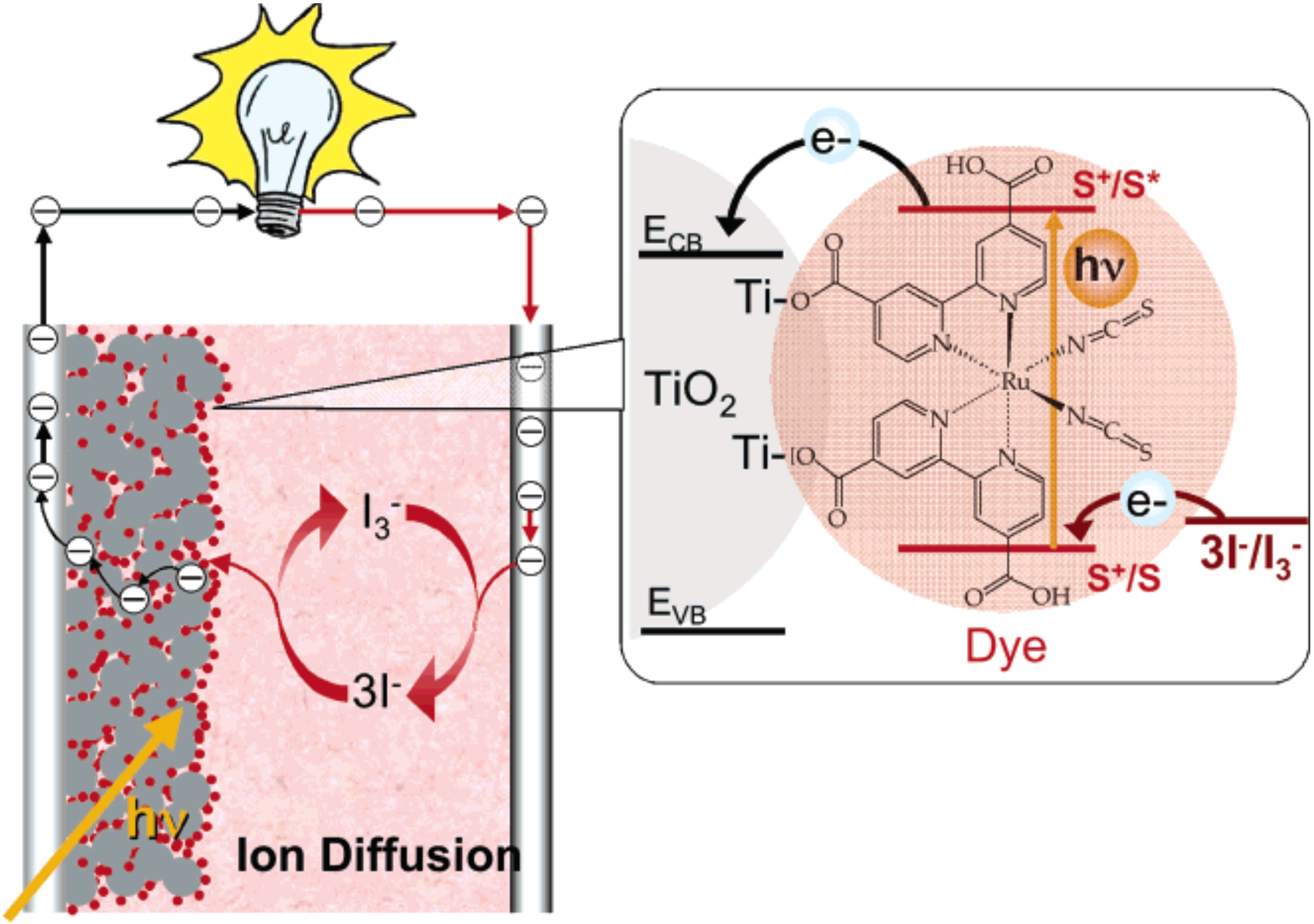

Best Research-Cell Efficiencies
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
Efficiency (%)
50
48
44
40
36
32
28
24
20
16
12
8
4
0
1975
1980
1985
1990
1995
2000
2005
2010
2015
Multijunction Cells (2-terminal, monolithic)
▼ Three-junction (concentrator)
▽ Three-junction (non-concentrator)
▲ Two-junction (concentrator)
△ Two-junction (non-concentrator)
☐ Four-junction or more (non-concentrator)
Single-Junction GaAs
△ Single crystal
△ Concentrator
▽ Thin-film crystal
Crystalline Si Cells
■ Single crystal (non-concentrator)
▣ Single crystal (concentrator)
☐ Multicrystalline
◆ Thick Si film
● Silicon heterostructures (HIT)
▽ Thin-film crystal
Thin-Film Technologies
● Cu(In,Ga)Se2
● CdTe
○ Amorphous Si:H (stabilized)
◆ Nano-, micro-, poly-Si
☐ Multijunction polycrystalline
Emerging PV
○ Dye-sensitized cells
● Organic cells (various types)
▲ Organic tandem cells
◆ Inorganic cells
◇ Quantum dot cells
Spectrolab (metamorphic, 299x)
Fraunhofer ISE (metamorphic, 454x)
Boeing-Spectrolab (lattice matched, 364x)
Spire Semiconductor (metamorphic, 406x)
Solar Junction (lattice matched, 942x)
Boeing-Spectrolab (metamorphic,179x)
Boeing-Spectrolab (metamorphic, 240x)
NREL (inverted, metamorphic)
NREL (inverted, metamorphic, 325.7x)
Solar Junction (lattice matched, 418x)
Boeing-Spectrolab (5-J, 1-sun)
NREL
Boeing-Spectrolab
Boeing-Spectrolab
Spectrolab
NREL (inverted, metamorphic,1-sun)
Sharp (IMM, 1-sun)
Sharp (IMM, 1-sun)
NREL/ Spectrolab
Spectrolab
FhG-ISE (1-sun)
Japan Energy
NREL
NREL
Spectrolab (4.0 cm2, 1-sun)
Radboud Univ.
IES-UPM (1026x)
FhG-ISE (117x)
Alta Devices
NREL
Alta Devices
SunPower (96x)
Amonix (92x)
FhG-ISE (232x)
Varian (205x)
Varian (216x)
NREL
Stanford (140x)
Kopin
Varian
Spire
Radboud Univ.
Radboud Univ.
FhG-ISE
Alta Devices
Panasonic
IBM (T. J. Watson Research Center)
UNSW
UNSW
UNSW
UNSW
UNSW
NREL
Cu(In,Ga)Se2 (14x)
Sanyo
Sanyo
Sanyo
Sanyo
Sanyo
Panasonic
EMPA (Flex polymer sub)
UNSW
Stanford
UNSW
UNSW / Eurosolare
FhG-ISE
ZSW
Solexel
ARCO
Georgia Tech
Georgia Tech
Georgia Tech
ZSW
Fraunhofer ISE
First Solar
GE Global Research
Sandia National Lab
Westing-house
Spire
Varian
UNSW
NREL
NREL
NREL
NREL
NREL
NREL
NREL
RCA
No. Carolina State Univ.
University So. Florida
AstroPower (small-area)
NREL
Univ. Stuttgart
Sharp (large-area)
Univ. Stuttgart
First Solar
LG Electronics
Mobil Solar
Kodak
Solarex
ARCO
Boeing
NREL
Euro-CIS
United Solar
NREL (CdTe/CIS)
United Solar (aSi/ncSi/ncSi)
Mitsubishi Chemical
EPFL
Heliatek
Boeing
Boeing
Photon Energy
Sharp
NIMS
IBM (CZTSSe)
Matsushita
AMETEK
Kodak
Boeing
ARCO
United Solar
EPFL
EPFL
Kaneka (2 μm on glass)
United Solar
IBM (CZTSSe)
Konarka
Heliatek
UCLA-Sumitomo Chemical
Monosolar
NREL / Konarka Univ. Linz
Solarmer
Konarka
Sumi-tomo
UCLA
Boeing
RCA
Solarex
EPFL
University of Maine
Groningen
Univ. of Toronto (PbS-QD)
Plextronics
Univ. Dresden
Heliatek
University Linz
University Linz
Siemens
NREL (ZnO/PbS-QD)
RCA
RCA
RCA
RCA
RCA
RCA
44.0%
37.8%
37.7%
32.6%
31.1%
29.1%
28.8%
27.6%
26.4%
25.0%
24.7%
20.4%
20.4%
20.1%
19.0%
14.1%
13.4%
12.0%
11.1%
11.1%
7.0%
(Rev. 06-2013)

Dye-sensitized (Grätzel) Solar Cells



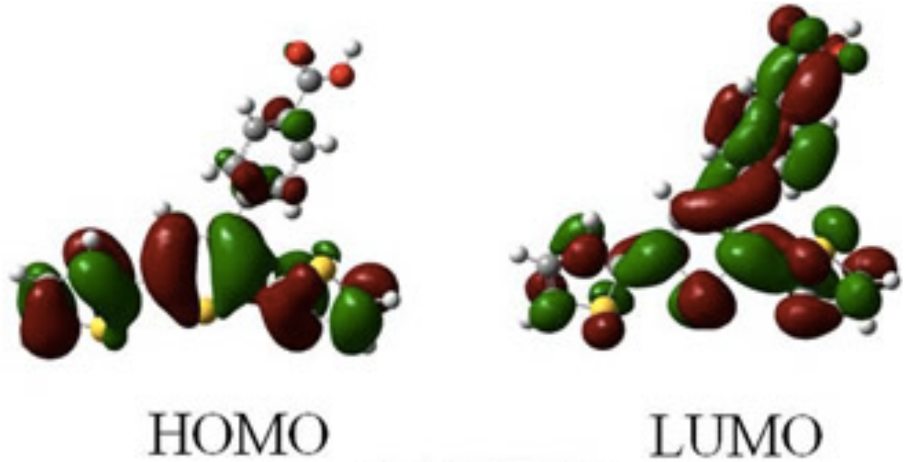
DSSC schematic showing the electrolyte filled TiO_2 film attached to the transparent electrode. The Iodine redox shuttle is in an electrolyte mixture of a Li-Iodine salt and a solvent.

The Dye molecule

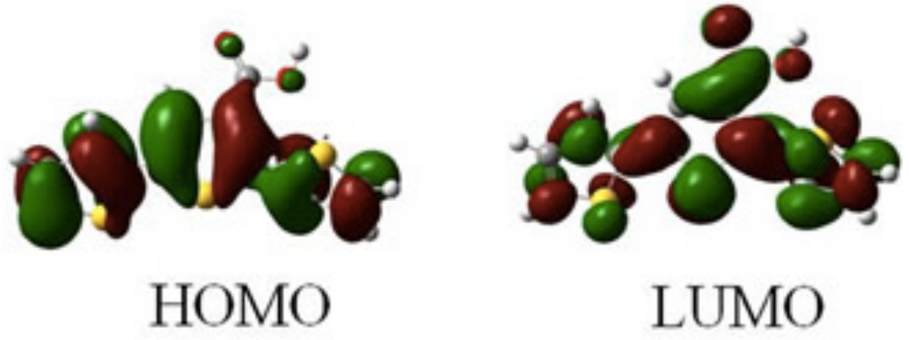


LUMO - HOMO = energy harvest/photon

LUMO verses HOMO



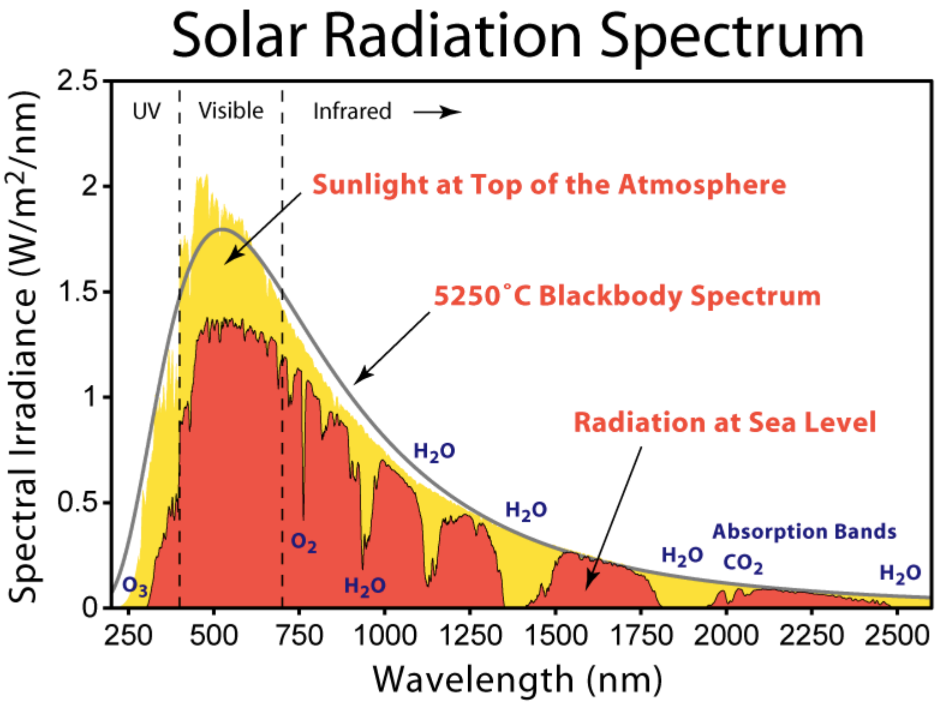
(a) TTBA

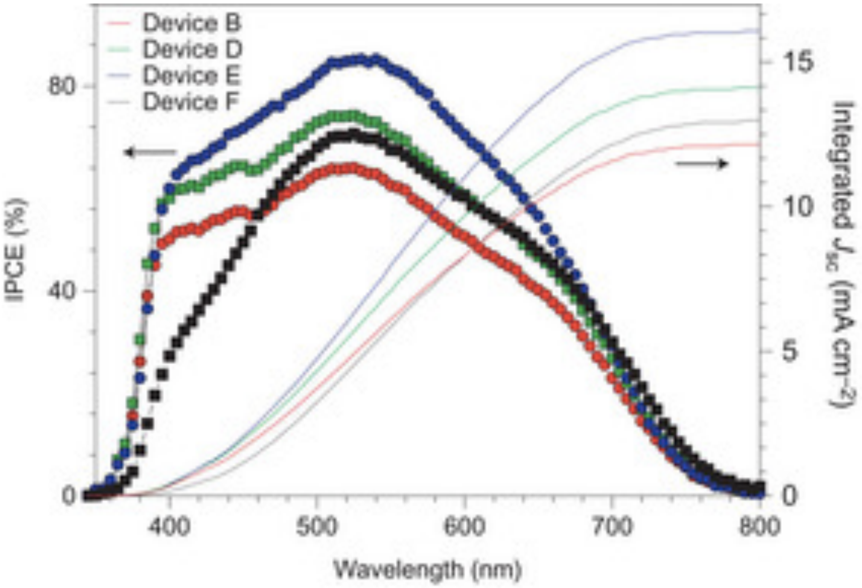


(b) TTCA

Yoon-Bo Shim, Pusan National University, South Korea

Spectrum and IPCE





IPCE = Incident Photon to Collected Electron (ratio) is a standard measurement of dye efficiency and overall electron loss.

First Step: Back of Envelope Calculation

Incident solar light is typically 1000 Watts$/m^2$ and a reference wave-length of $\lambda = 500$nm. From the photonic energy relation

$$E_{\text{photon}} = \frac{hc}{\lambda},$$

where Planck's constant is $h = 6.626 \times 10^{-34}$J-s, and the speed of light in a vacuum is $c = 3 \times 10^{8}$m/s, we find

$$E_{\text{photon}} = 3.98 \times 10^{-19} J.$$

The incident photon flux is thus

$$N_{\text{inc}} = \frac{1000 \frac{J}{m^2 s}}{E_{\text{photon}}} = 2 \times 10^{21} \frac{\text{photon}}{m^2 s},$$

Using Avagadro's number = 6.02×10^{23}/mole, yields the photonic molar flux

$$\boxed{N_{\text{inc}} = 4 \times 10^{-3} \frac{\text{moles}}{m^2 s}.}$$

Dancing in the Dark

If every photon is converted to an electron the incident current is

$$\boxed{I_{\rm inc} = \frac{N_{\rm inc}}{F} = 4 \times 10^{-2}\frac{\rm A}{\rm cm^2}.}$$

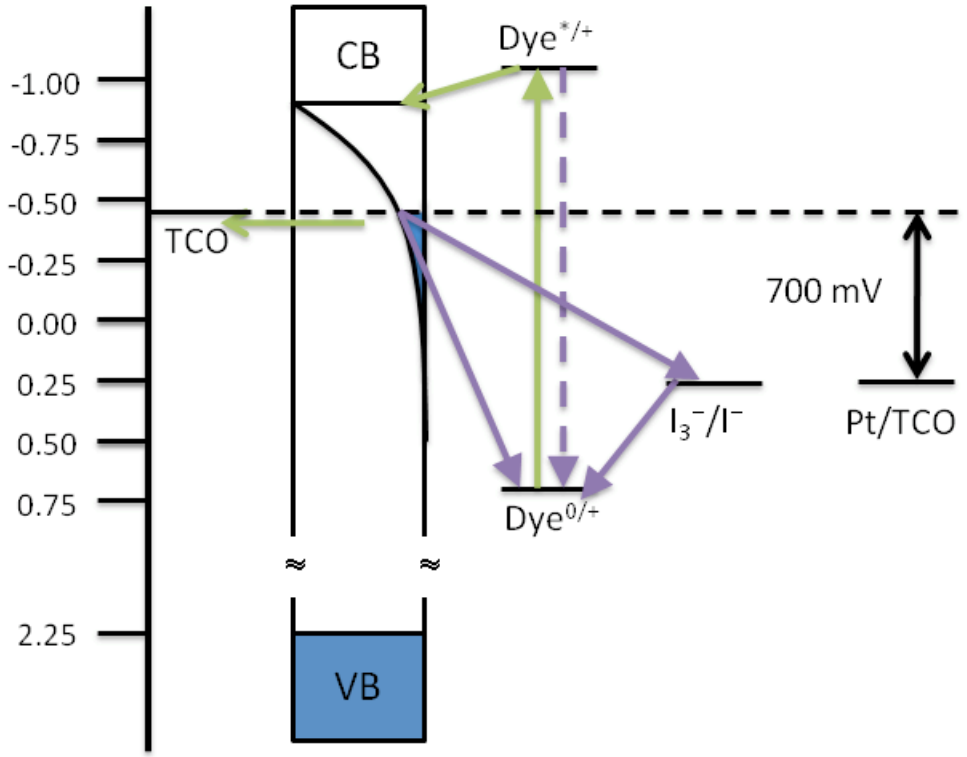
The dye density is roughly, 1 molar = 10^3moles/m^3.

The dye-photon “hit-rate” for perfect absorption in a cell of depth of $l_d = 5\mu$m is

$$\boxed{{\rm Hits} < \frac{N_{\rm inc}}{l_d \times {\rm Dye\,density}} = \frac{4 \times 10^{-3}\frac{\rm moles}{m^2 s}}{5 \times 10^{-6} m \times 10^3 \frac{\rm moles}{m^3}} = 0.8\frac{\rm photon}{\rm s},}$$

less than one hit a second. Better estimate is one hit every 5 seconds.

Energy Levels and Kinetics



Forward Reactions

$$\mathrm{h}\nu + \mathrm{D} \rightarrow_{R_{\mathrm{inj}}} \mathrm{D}^+ + \mathrm{e}^-(\mathrm{TiO_2})$$
$$3\mathrm{I}^- + 2\mathrm{D}^+ \rightarrow_{R_{\mathrm{regen}}} \mathrm{I}_3^- + 2\mathrm{D}$$
$$\mathrm{I}_3^- + 2\mathrm{e}^-(\mathrm{cathode}) \rightarrow_{R_{\mathrm{cath}}} 3\mathrm{I}^-$$

Back Reactions

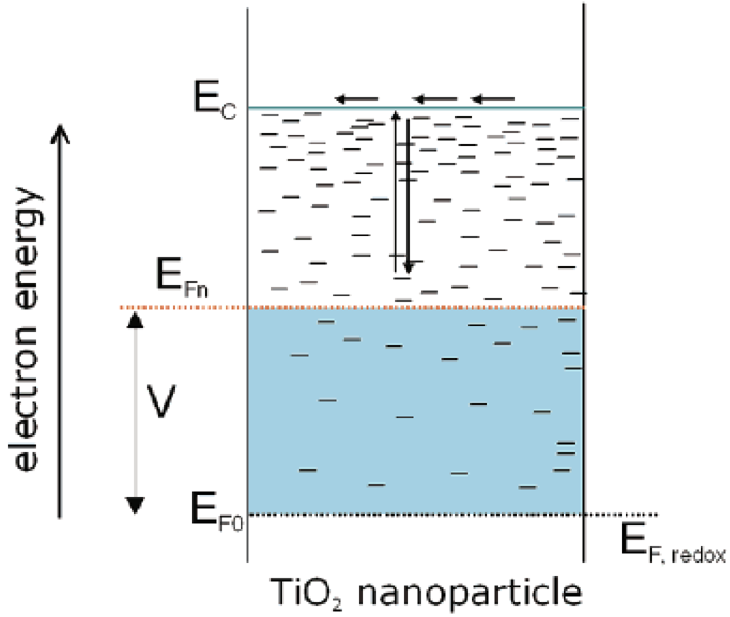
$$\mathrm{I}_3^- + 2\mathrm{e}^-(\mathrm{TiO_2}) \rightarrow_{R_{\mathrm{back}}} 3\mathrm{I}^-$$
$$\mathrm{D}^+ + \mathrm{e}^-(\mathrm{TiO_2}) \rightarrow D$$

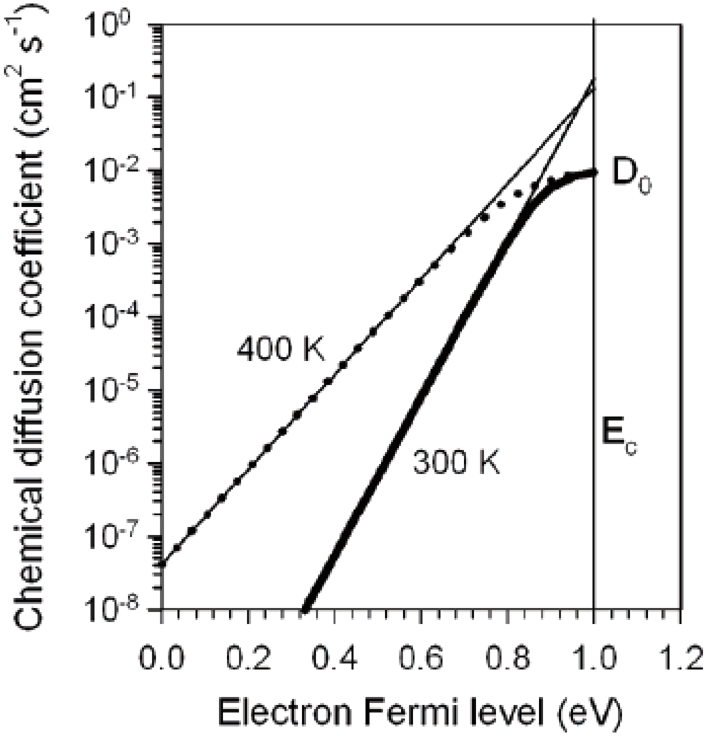
The open-circuit (max) voltage depends upon back-reaction and is bounded by

$$V_{\mathrm{OC}} \leq V_{\mathrm{Fermi}} - V_{\mathrm{electrolyte}}.$$

The short-ciruit (max) current depends upon the light-capture efficiency.

Fermi-Levels and Transport





Juan Bisquert *J. Phys. Chem. B* **110** (2006).

Fermi-Level Dependence

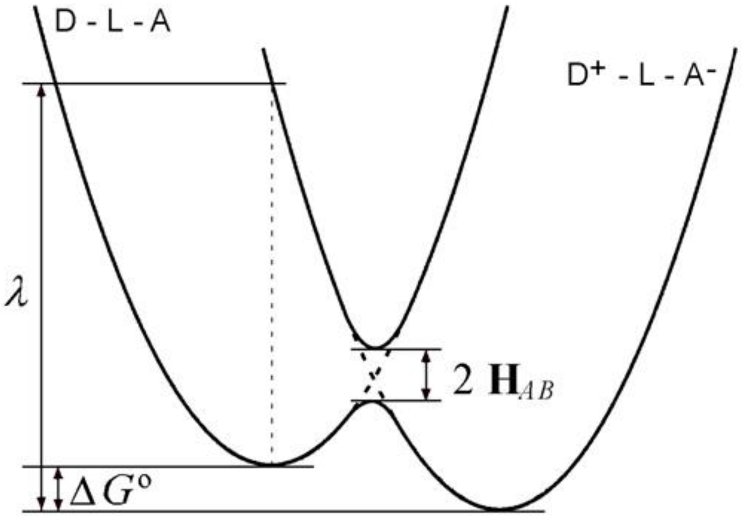
Further work is needed to determine whether the density and energetic distribution of electron traps is an intrinsic property of the oxide or whether it also depends on factors such as the composition and ionic strength of the electrolyte phase, as might be expected if trapping is due to electron−ion interactions rather than defect states in the oxide.

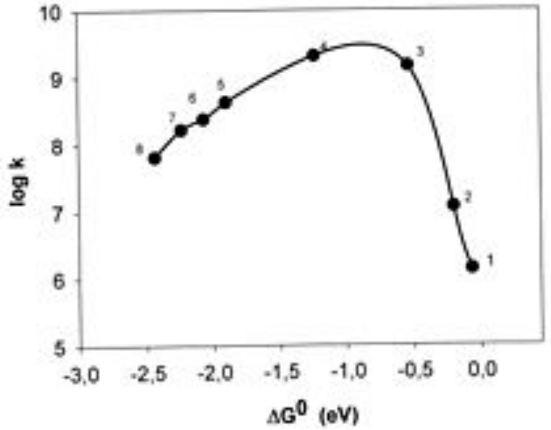
From survey article: Laurence Peter *Accounts of Chemical Research* **42** (2009).

Marcus Theory– Back Reaction Rates

Predicts rate of electron transfer, $\boldsymbol{k}_{\mathrm{et}}$, between solvated ions/interfaces. Incorporates rearrangement energy, $\boldsymbol{\lambda}$, of solvation spheres required after charge transfer

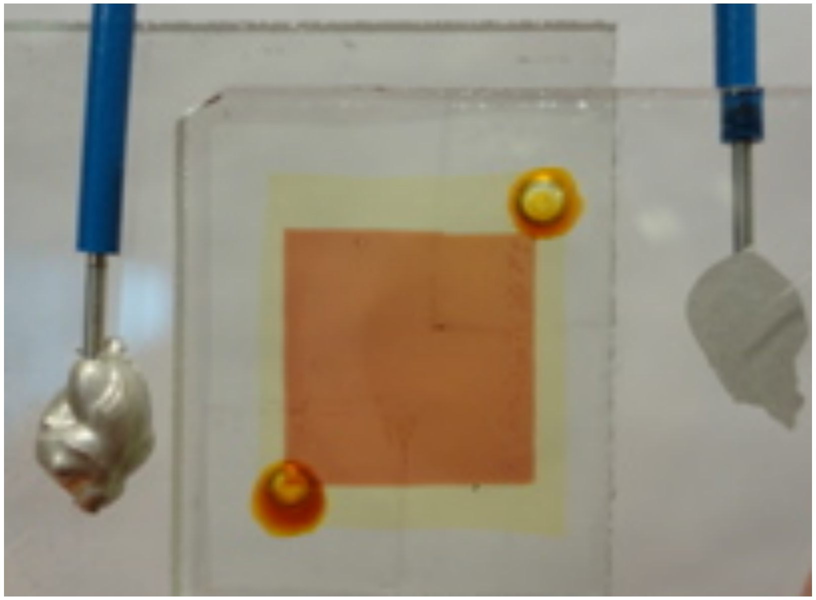
$$\boxed{k_{\mathrm{et}} = \frac{2\pi}{\hbar}\frac{|H_{AB}|^2}{\sqrt{4\pi\lambda k_b T}}\exp\left(-\frac{(\lambda+\Delta G^\circ)^2}{4\lambda k_b T}\right).}$$

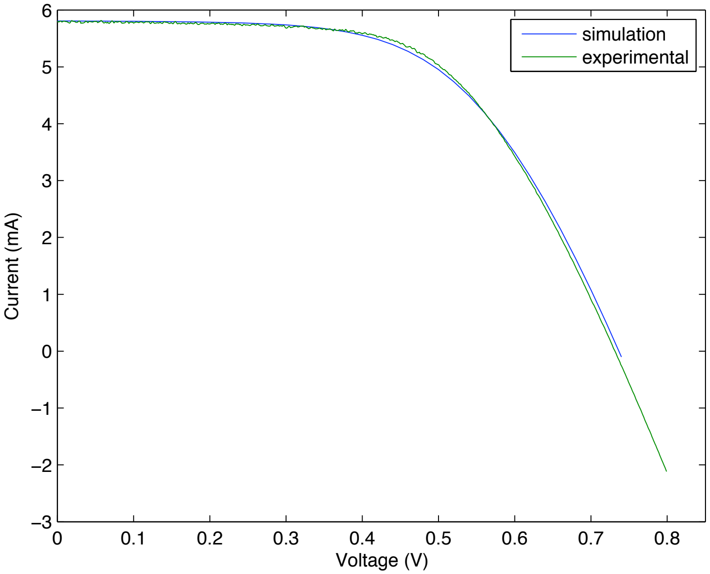




(left) Free energy verses 'reaction coordinate', showing strength of coupling, $\boldsymbol{H}_{\mathrm{AB}}$, between donor and acceptor states, liberated (Gibbs) free energy $\boldsymbol{\Delta G^\circ}$, and the reorganization energy, $\boldsymbol{\lambda}$. (right) $\ln k_{\mathrm{et}}$ verses $\boldsymbol{\Delta G^\circ}$ for transfer to an acceptor with differing numbers of aromatic hydrocarbons, and hence differing $\boldsymbol{\Delta G^\circ}$.

J-V Curves



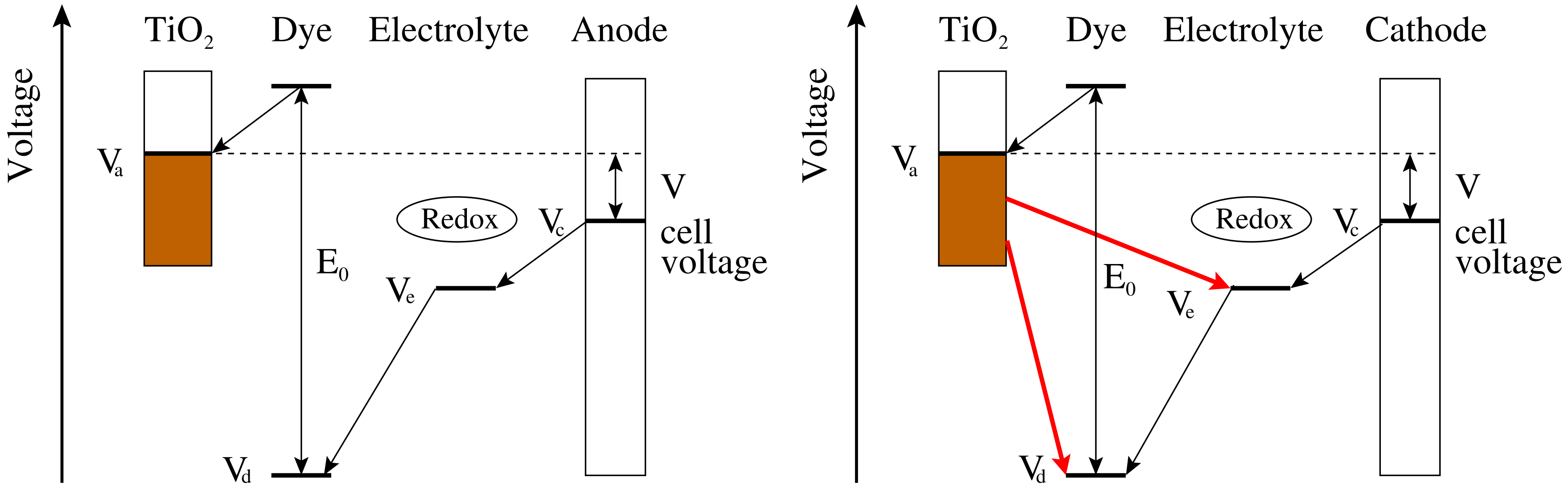


Open Circuit Voltage (OCV), Short Circuit Current (SCC), Incident Photon Conversion Efficiency (IPCE), Fill Factor (FF), Cell Efficiency.

A simple model reproduces the experimental current-voltage relations.

Typical DSSCs have $V_{\mathrm{OC}} = 0.7 - 0.8V$ and $I_{\mathrm{SC}} = 10 - 15$ mA/cm^2, with conversion efficiencies of 11%.

Vanilla Cell Model



(Left) Typical voltages in the DSSC in the absence of back reaction. The TiO_2 fills trap levels raising the Fermi level. The fill rate decreases as the difference between the excited dye state, $V_d + E_0$ and the trap level V_c decrease. Photons excite the dye from its HOMO V_d to its LUMO level $V_d + E_0$. The observed cell voltage V is difference between cathode and anode voltages. The redox shuttle recharges the oxidized dye at a rate dependent upon the voltage difference $V_e - V_d$. (Right) Back reactions, depicted in red, can recombine trapped electrons from the TiO_2 to oxidized dye states D^+ or to the redox shuttle, at rates that depend upon the voltage differences.

Rate Equations

The total dye concentration, total Iodine, and charge balance

$$C_D = D^+ + D,$$

$$C_{\mathrm{I}} = 2\mathrm{I}_2 + \mathrm{I}^- + 3\mathrm{I}_3^-,$$

$$I^- + I_3^- + n_c = Li^+ + D^+.$$

The buffering reaction is fast, which yields the equilibrium relation

$$\frac{\mathrm{I}_2\mathrm{I}^-}{\mathrm{I}_3^-} = \frac{k_{\mathrm{bf}}^-}{k_{\mathrm{bf}}^+} = k_{\mathrm{bf}} = 10^{-7}.$$

The remaining, dynamic variables are the concentration of electrons in the conduction band

$$\frac{dn_c}{dt} = \overbrace{R_{\mathrm{inj}}}^{\text{injection rate}} - \overbrace{2R_{\mathrm{back}}}^{\text{back reaction rate}} - \overbrace{2R_{\mathrm{cath}}}^{\text{cathode rate}}.$$

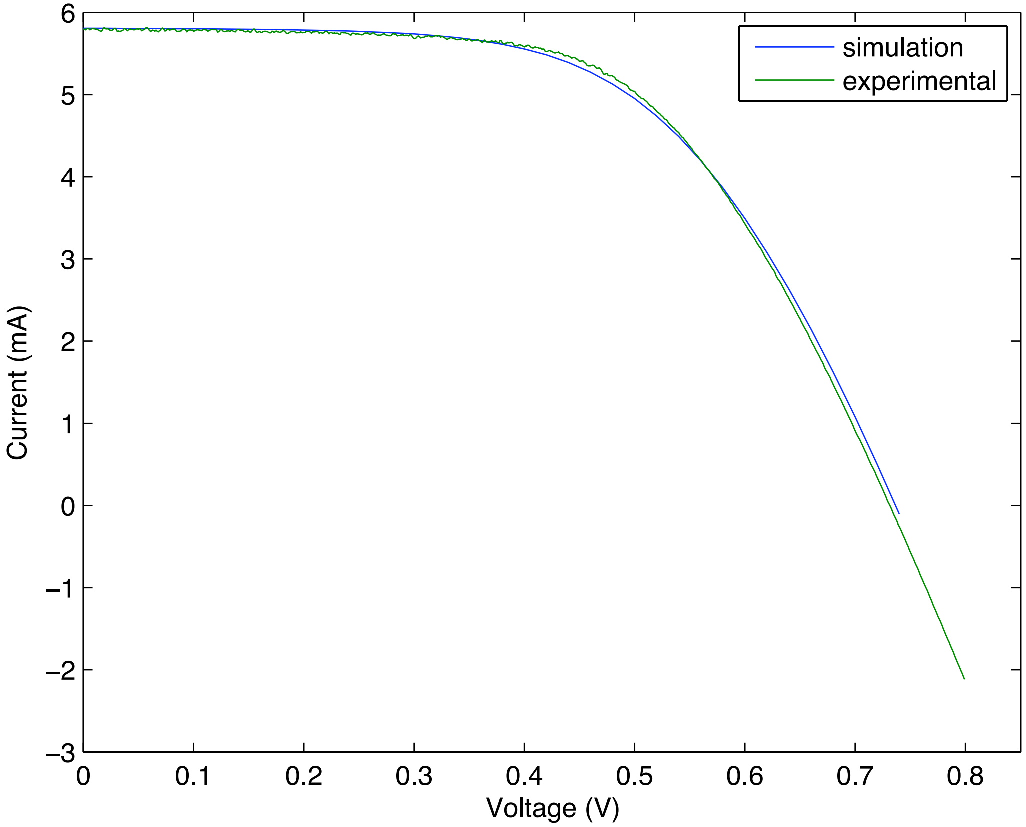
and the oxidized dye

$$\frac{dD^+}{dt} = R_{\mathrm{inj}} - 2R_{\mathrm{regen}}.$$

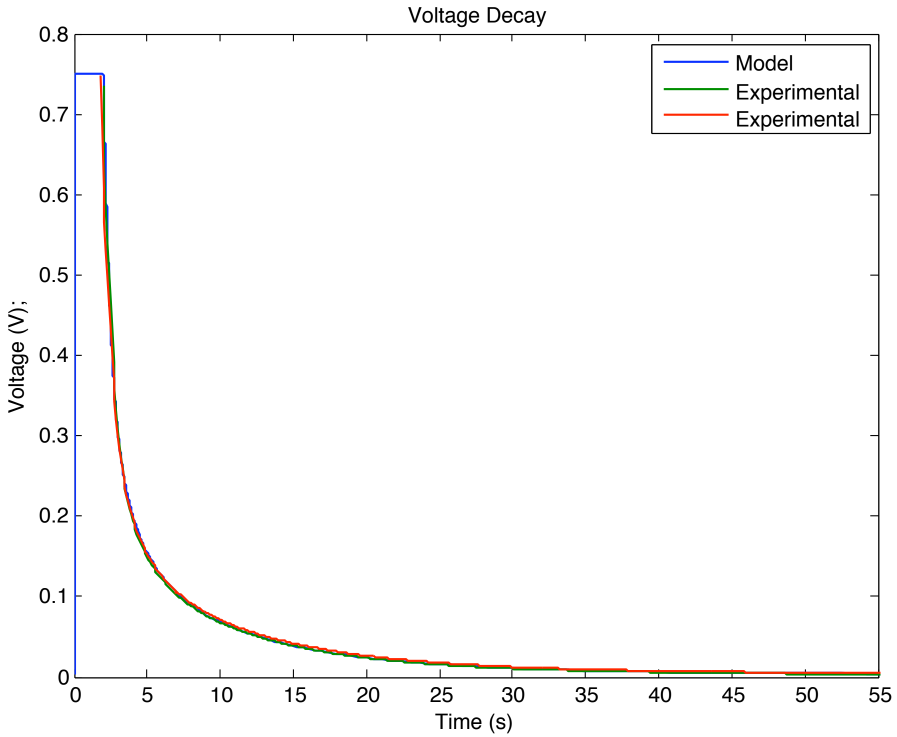
The cell voltage is either prescribed or set via an external resistance relation

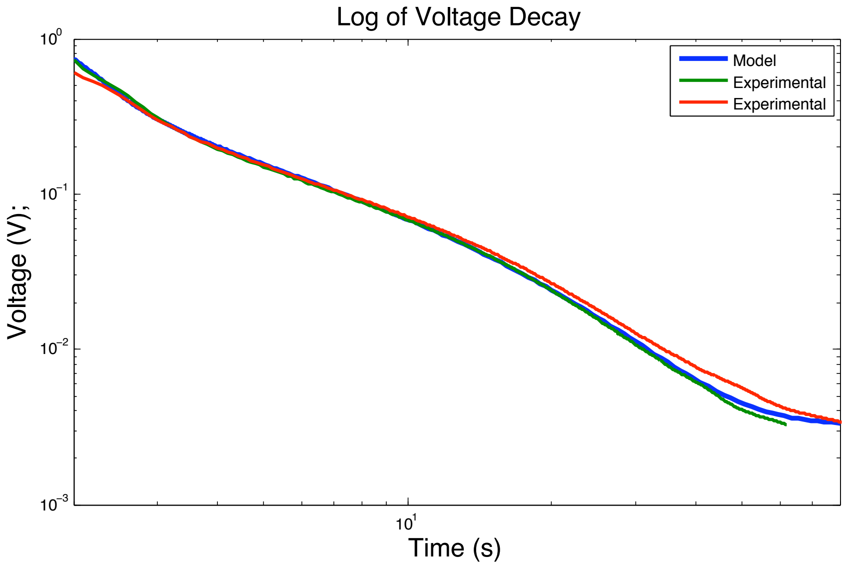
$$V = J_{\mathrm{cell}}\Omega_{\mathrm{ext}} = 2R_{\mathrm{cath}}\Omega_{\mathrm{ext}},$$

where the cell current is equal to twice the cathode reaction rate.



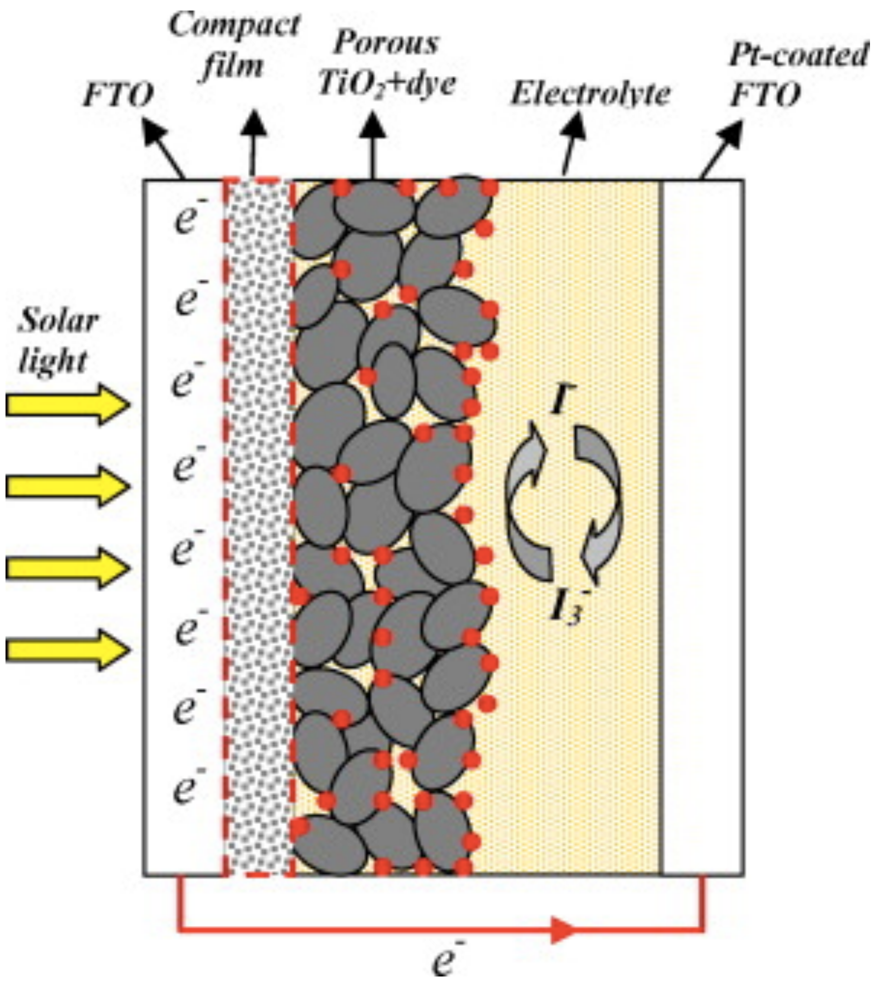
Dark-Cell Decay

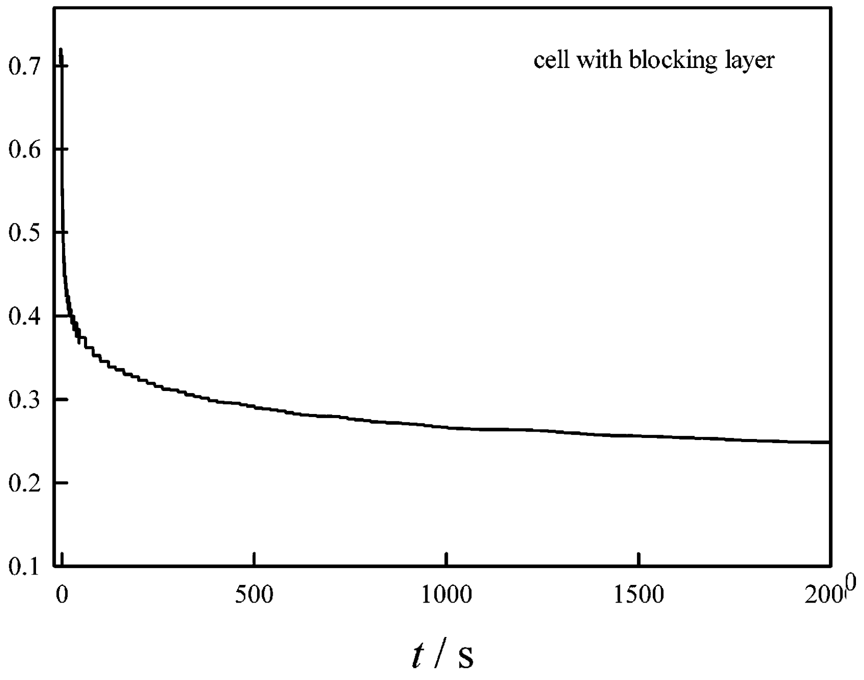




A better diagnostic experiment is the dark-cell decay:
A cell is illuminated until steady-state, the light is extinguished and the voltage is recorded as a function of time. This gives a strong measurement of the back reaction rate.

Blocking Layer





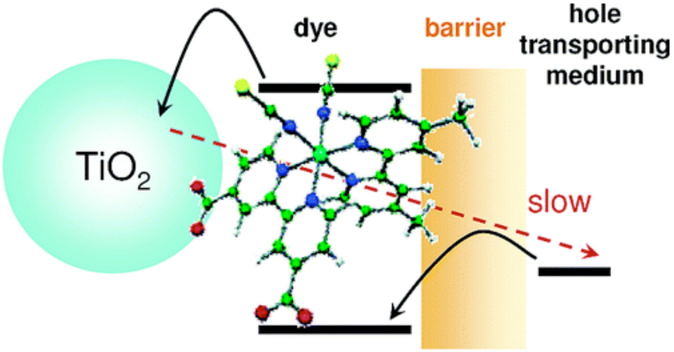
Much of the back reaction is from the transparent fluorine doped tin oxide (SnO_2:F) or FTO collection plate, adding a blocking layer of pure TiO_2 greatly reduces this mode of back reaction.

How to Improve DSSCs?

- Replace Ruthenium with a cheaper (organic) dye
- Replace Pt electrode with a non-precious metal (Exfolieated Graphene)
- Reduce the back reaction by replacing electrolyte mixtures.
- Eliminate volatility of the electrolyte, which leads to leakage, evaporation, and expansion upon freezing.

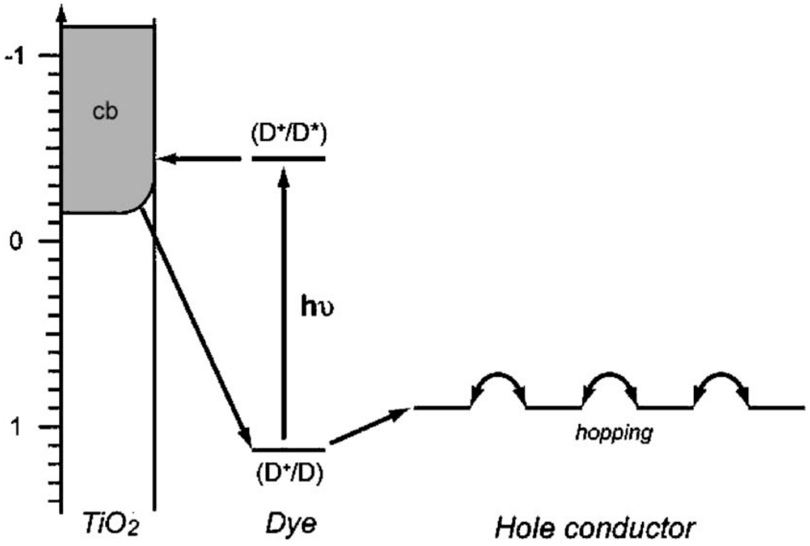
Replace electrolyte with

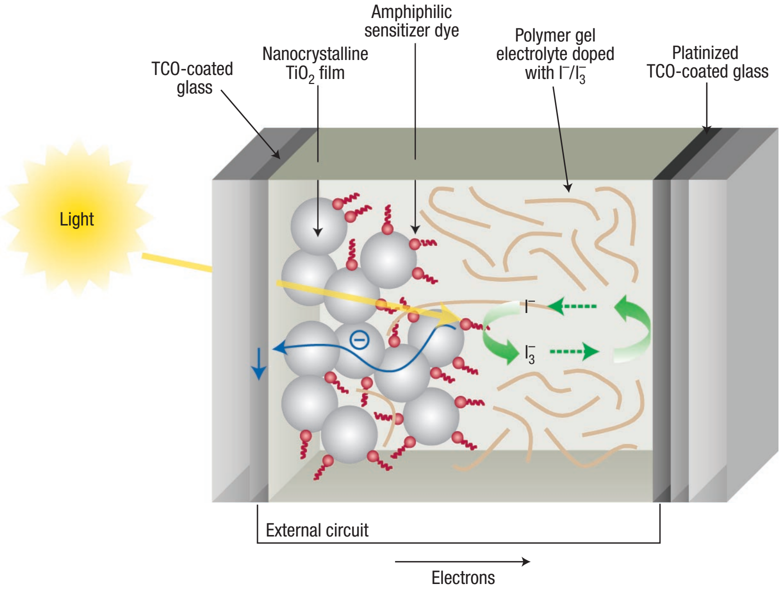
- Organic and inorganic hole-transport materials
- Polymers and poly-electrolyte gels
- Ionic Liquids



Caveats: Pay attention to compatibility of new electronic transporter with TiO_2/dye and potential back-reaction rates.

Solid-State (Polymer) Hole Transport Polymers verses Gels





- Solid State Polymer hole conductors have no volatile solvents, but generically have poor connectivity to the dye molecules.
- Embedding the iodine redox shuttle in a polymer gel matrix reduces need for Lithium, and entraps solvent in a porous network that dramatically limits its volatility and swelling, yet may preserve its role as a charge transfer mediator at the dye interface.