Continuum Models of
Dye-Sensitized Solar Cells

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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.
LUMO - HOMO = energy harvest/photon
LUMO verses HOMO

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Spectrum and IPCE

**Solar Radiation Spectrum**

![Diagram of solar radiation spectrum](image)

- **Sunlight at Top of the Atmosphere**
- **5250°C Blackbody Spectrum**
- **Radiation at Sea Level**
- **Absorption Bands**

**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/m² and a reference wave-length of λ = 500nm. From the photonic energy relation

\[ E_{\text{photon}} = \frac{hc}{\lambda}, \]

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

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

The incident photon flux is thus

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

Using Avagadro’s number = 6.02 × 10²³/mole, yields the photonic molar flux

\[ N_{\text{inc}} = 4 \times 10^{-3}\frac{\text{moles}}{m^2s}. \]
Dancing in the Dark

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

\[
I_{\text{inc}} = \frac{N_{\text{inc}}}{F} = 4 \times 10^{-2} \text{ A cm}^2.
\]

The dye density is roughly, 1 molar = $10^3 \text{ moles/m}^3$.

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

\[
\text{Hits} < \frac{N_{\text{inc}}}{l_d \times \text{Dye density}} = \frac{4 \times 10^{-3} \text{ moles}}{5 \times 10^{-6} \text{ m} \times 10^3 \text{ moles/m}^3} = 0.8 \text{ photon/s},
\]

less than one hit a second. Better estimate is one hit every 5 seconds.
Energy Levels and Kinetics

Forward Reactions
\[ h\nu + D \rightarrow_{R_{\text{inj}}} D^+ + e^- (\text{TiO}_2) \]
\[ 3I^- + 2D^+ \rightarrow_{R_{\text{regen}}} I_3^- + 2D \]
\[ I_3^- + 2e^- (\text{cathode}) \rightarrow_{R_{\text{cath}}} 3I^- \]

Back Reactions
\[ I_3^- + 2e^- (\text{TiO}_2) \rightarrow_{R_{\text{back}}} 3I^- \]
\[ D^+ + e^- (\text{TiO}_2) \rightarrow D \]

The open-circuit (max) voltage depends upon back-reaction and is bounded by
\[ V_{\text{OC}} \leq V_{\text{Fermi}} - V_{\text{electrolyte}}. \]

The short-circuit (max) current depends upon the light-capture efficiency.
Fermi-Levels and Transport

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, $k_{et}$, between solvated ions/interfaces. Incorporates rearrangement energy, $\lambda$, of solvation spheres required after charge transfer

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

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

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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 $V_{OC} = 0.7 - 0.8V$ and $I_{SC} = 10 - 15$ 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

\[ C_D = D^+ + D, \]
\[ C_I = 2I_2 + I^- + 3I_3^-, \]
\[ I^- + I_3^- + n_c = Li^+ + D^+. \]

The buffering reaction is fast, which yields the equilibrium relation

\[ \frac{I_2I^-}{I_3^-} = \frac{k^-}{k^+} = k_{bf} = 10^{-7}. \]

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

\[ \frac{dn_c}{dt} = R_{inj} - 2R_{back} - 2R_{cath}. \]

and the oxidized dye

\[ \frac{dD^+}{dt} = R_{inj} - 2R_{regen}. \]
The cell voltage is either prescribed or set via an external resistance relation

\[ V = J_{\text{cell}} \Omega_{\text{ext}} = 2R_{\text{cath}} \Omega_{\text{ext}}, \]

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