Limits to efficiency of photovoltaic energy conversion

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Energy from the Sun

USA: ~200 Wm\(^{-2}\)
6500 kW solar resource
1500 W electricity
10 kW total energy

UK: 125 Wm\(^{-2}\)
500 kW solar resource
700 W electricity
5 kW total energy

Cote d’Ivoire: ~250 Wm\(^{-2}\)
4500 kW solar resource
20 W electricity
0.5 kW total energy
Photons in, electrons out

Photovoltaic energy conversion requires:

- photon absorption across an energy gap
- separation of photogenerated charges
- asymmetric contacts to an external circuit
Photons in, electrons out
Photons in, electrons out

p type silicon

n type silicon
p type silicon
n type
efficiency
~ 15-20%
power rating
~ 100-200 W_p

Applications, large and small

CIS Tower, Manchester
0.4 MW_p (Solar Century)

Solar powered refrigeration
~100 W_p

~1 mW_p
• Photovoltaic energy conversion

• Limiting efficiency of solar cells

• Where next?

• Routes to more work per photon

• Molecular solar cells
Detailed balance limit

(i) One electron hole pair per photon with $h\nu > E_g$.

(ii) Carriers relax to form separate Fermi distributions at lattice temperature $T_{\text{ambient}}$ with quasi Fermi levels separated by $\Delta \mu$.

(iii) All electrons extracted with same electrochemical potential $\Delta \mu = eV$.

(iv) Only loss process is spontaneous emission.
A fraction $X\beta$ of the “sky” emits solar radiation at a black body temperature of $T_{\text{sun}}$.

A fraction $(1 - X\beta)$ of the “sky” emits ambient radiation at a black body temperature of $T_{\text{ambient}}$.

The photovoltaic energy converter emits ambient radiation at a black body temperature of $T_{\text{ambient}}$ and a chemical potential of $\Delta\mu$.

The remaining charge pairs provide a current of electrons with chemical potential of $\Delta\mu$. 
Calculation of limiting efficiency

\[
\frac{J}{e} = X\beta \int_{E_g}^{\infty} b_{\text{sun}}(E) \, dE + (1 - X\beta) \int_{E_g}^{\infty} b_{\text{ambient}}(E) \, dE - e^{\Delta\mu/kT} \int_{E_g}^{\infty} b_{\text{ambient}}(E) \, dE
\]

\[
J = J_{sc} - J_0 \left( e^{eV/kT} - 1 \right)
\]

\[P = JV\]
Limit to efficiency: the Goldilocks story

Photon energy / eV

E gap
Limit to efficiency: the Goldilocks story

Photon energy / eV

Current

Energy gap

Voltage

Energy gap

Power

Energy gap
Limit to efficiency: the Goldilocks story

- Photon energy / eV
- Current
- Voltage
- Power

Energy gap

- Current
- Voltage
- Power

Energy gap
Limit to efficiency: the Goldilocks story
Limiting efficiency of single band gap cell

Optimum cell converts 31% of power

Power spectrum from black body sun at 5760K

Lost by transmission

Lost by thermalisation

Optimum cell converts 31% of power
Practical and limiting efficiencies

![Graph showing efficiency vs. bandgap for different materials.]( Courtesy:Ned Ekins-Daukes)
How bad are the assumptions?

(i) One electron hole pair per photon with $h\nu > E_g$,  
Overestimate current by 10-20%

(ii) Carriers relax to form separate Fermi distributions at lattice temperature $T_{\text{ambient}}$ with quasi Fermi levels separated by $\Delta\mu$.  
~ OK

(iii) All electrons extracted with same electrochemical potential $\Delta\mu = eV$  
Overestimate $eV_{oc}$ by $O(0.1 \text{ eV})$

(iv) Only loss process is spontaneous emission  
Overestimate $eV_{oc}$ by few 0.1 eV  
Overestimate fill factor
Highest efficiency single junction: thin film GaAs

Device with absorbing substrate

Thin-film device

Limiting efficiency: 30.4 %
Actual efficiency: 24.8 %

Limiting efficiency: 32.4 %
Actual efficiency: 28.8 %

Spire Corp, IEEE Tr. Electron Dev. 37, 469 (1990)
Alta Devices, Prog. Photovoltaics 20, 606 (2012)
Outline

• Photovoltaic energy conversion

• Limiting efficiency of solar cells

• Where next?

• Routes to more work per photon

• Molecular solar cells
• Installed PV capacity growing at > 30% per annum for ~15 years
• Mainly based on crystalline Si technology
• Where next?
Cost reductions follow maturing of Si technology through innovations in manufacturing and design.

Cost evolution typical of a semiconductor technology not a conventional energy technology

Role for technical innovation?
PV technologies

Best Research-Cell Efficiencies

Efficiency vs. Cost/area

- I: Si
- II: thin film
- III: Higher efficiency routes

Emerging technologies:
- Dye-sensitized cells
- Organic cells (various types)
- Organic tandem cells
- Inorganic cells
- Quantum dot cells

Multijunction Concentrators
- Three-junction (intermetallic, monolithic)
- Two-junction (GaInP, GaAs)

Single-Junction GaAs
- Single crystal
- Concentrator
- Thin film

Crystalline Si Cells
- Single crystal
- Multicrystalline
- Thin film

Thin Film Technologies
- Cu(In, Ga)Se₂
- CdTe
- Amorphous Si (a-Si)

Emerging PV:
- Organic cells (various types)
- Inorganic tandem cells
- Quantum dot cells

Cost/area vs. Efficiency


Solar cells timeline and efficiency improvements by year.
Outline

- Photovoltaic energy conversion
- Limiting efficiency of solar cells
- Where next?
- Routes to more work per photon
- Molecular solar cells
Routes to more work per photon

- Power spectrum from black body sun at 5760K
- Optimum cell converts 31% of power
- Lost by thermalisation
- Lost by transmission
- More band gaps
- Slow carrier cooling
- Spectral conversion

Irradiance (W m\(^{-2}\) eV\(^{-1}\))

Photon Energy (eV)
Route 1: Multiple band gaps

- Multi-junction structures or spectral splitting
• Wide range of band gaps available but seek combinations with similar lattice constant
• Record of 43.5% by Solar Junction (April 2011) for a triple junction using dilute nitride (InGaP/GaAs/InGaAsN)

This works, but multijunction III-V structures are expensive to grow
Route 2: More work per photon by slowed cooling

- Generation
- Equilibration
- Cooling
- Recombination

Optimum cell converts 31% of power

Power spectrum from black body sun at 5760K

Lost by thermalisation

Lost by transmission

Optimum cell converts 31% of power
Strategies for slowing carrier cooling

- Exploit limited electronic and photon states in nano- or molecular systems

- Carrier cooling slowed down in quantum dots by ‘phonon bottleneck’ effect

- Enhance this with strategies to prevent recombination
  - Core-shell structure, interface passivation, ligands
  - Cooling slowed by 3 orders

Evidence for slowed cooling but tiny effect at solar intensities
Route 3: Reshaping the spectrum by up and down-conversion

Power spectrum from black body sun at 5760K

Optimum cell converts 31% of power

Lost by thermalisation

Lost by transmission
Molecular up-conversion: applied to a-Si solar cell

- Absorption in red absorbing molecules $\rightarrow$ triplet formation $\rightarrow$ triplet transfer to emitter $\rightarrow$ singlet regeneration $\rightarrow$ emission
- Applied to a-Si:H solar cell to increase EQE in red.

Evidence for both up- and down-conversion, but small impact on total photocurrent
Outline

• Photovoltaic energy conversion
• Limiting efficiency of solar cells
• Where next?
• Routes to more work per photon
• Molecular solar cells
**Thin films and emerging technologies**

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_g$ (eV)</th>
<th>Grain size (µm)</th>
<th>Max $J_{sc}$ (mAcm$^{-2}$)</th>
<th>Actual $J_{sc}$ (mAcm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>Efficiency (%)</th>
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</thead>
<tbody>
<tr>
<td>Crystalline silicon</td>
<td>1.1</td>
<td>$&gt;10^4$</td>
<td>43</td>
<td>42.7</td>
<td>0.706</td>
<td>25.0</td>
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<tr>
<td>Crystalline GaAs</td>
<td>1.4</td>
<td>$&gt;10^4$</td>
<td>32</td>
<td>29.7</td>
<td>1.122</td>
<td>28.8</td>
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<tr>
<td>Polycrystalline Silicon</td>
<td>1.1</td>
<td>10-100</td>
<td>42</td>
<td>38.0</td>
<td>0.664</td>
<td>20.4</td>
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<tr>
<td>CuInGaSe$_2$</td>
<td>&gt; 1.0</td>
<td>1</td>
<td>&lt; 45</td>
<td>34.8</td>
<td>0.713</td>
<td>19.6</td>
</tr>
<tr>
<td>Cd Te</td>
<td>1.4</td>
<td>1</td>
<td>42</td>
<td>26.1</td>
<td>0.845</td>
<td>16.7</td>
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<tr>
<td>Amorphous Si</td>
<td>~1.7</td>
<td>$&lt;10^{-2}$</td>
<td>~ 23</td>
<td>16.7</td>
<td>0.886</td>
<td>10.1</td>
</tr>
<tr>
<td>Organic</td>
<td>~1.6</td>
<td>$&lt;10^{-2}$</td>
<td>~24</td>
<td>16.7</td>
<td>0.899</td>
<td>10.0</td>
</tr>
</tbody>
</table>

**Notes:**
- Single junction: Limiting $\eta$ as above
- Practical $\eta$ limited by recombination: small grains
- Heterojunction: What limits $\eta$?
Molecular photovoltaic materials

- Excited states are localised:
  - Photogenerated charge pairs don’t separate
  - Separated charges move slowly

- Charge separation induced by doping with electron acceptors
Molecular photovoltaic conversion

Energy diagram:
- $E_{L}^{D}$, $E_{H}^{D}$, $E_{L}^{A}$, $E_{H}^{A}$
- $\Delta E_{LL}$, $\Delta E_{HH}$

Free energy diagram:
- $S_{1}^{A}$, $S_{1}^{D}$, $E_{g}$, $E_{CT}$, $E_{CS}$
- $-\Delta G_{CT}$

Donor and acceptor interactions:
- Molecular structures
- Redox potential diagram

Direction of electron flow:
- $H_{2}O \rightarrow 2e^{-} + \frac{1}{2}O_{2}$
- NADPH, NADP
State of the Art in Molecular Photovoltaics

- Successive layers deposited from solution
- Cell efficiency > 10%
- Modules follow slowly.

Figure: courtesy Rene Janssen, 2012

Graph:
- Efficiency (%)
- Single junction
- Tandem junction
Molecular Photovoltaics: Energy efficiency

• Motivation is lower manufacture cost, but also lower energy intensity
• Enable larger impact on CO₂ emissions in short term, especially if lower cost stimulates faster uptake
• In long term, higher power conversion efficiency is key
Limiting efficiency in molecular heterojunction

- Optical gap > electrical gap
- In detailed balance limit, charges recombine radiatively across electrical gap
- Introduce sub-gap states of finite oscillator strength
Limiting efficiency in molecular heterojunction

- Limiting $\eta$ is lower and optimum $E_g$ larger than for single junction
- Most models predict 20%, practical best is 10%
- Where are losses?
- How large must $(E_g - E_{CS})$ be?

Size of energetic losses in molecular heterojunction

- Probe energy of charge pair at interface, $E_{CT}$ with electroluminescence
- Modulate $E_{CT}$ for same $E_g$ by varying fullerene acceptor
- Find
  - photocurrent is generated only when $(E_g - E_{CT}) > 0.35$ eV (with exceptions)
  - $eV_{oc}$ is smaller than $E_{CT}$ (and $E_{CS}$) by $\sim 0.4$ eV
Size of energetic losses in molecular heterojunction

- **Charge separation loss** $\Delta E_C$ normally $> 0.3$ eV. Absent in inorganics.

- Non-geminate **recombination loss** $\Delta E_R \sim 0.4$ eV, similar to inorganics

- Net $E_g - eV_{oc} > 0.6$ eV, c.f $0.4$ eV for inorganic single junctions
Size of energetic losses in molecular heterojunction

- **Inorganic junctions:**
  \[ \Delta E_{\text{g}} \approx 0.4 \text{ eV in best cases.} \]
  Efficiency within \(~5\%\) of DB limit

- **Molecular heterojunctions**
  \[ \Delta E_{\text{g}} \approx 0.6 \text{ eV} \]

- Can we reduce \( \Delta E_{\text{C}} \)?

- Yes – in some cases, \( \Delta E_{\text{C}} \) as low as 0.1 eV
  - Function of chemical structure
  - But compensated by high \( \Delta E_{\text{R}} \)
  - Need to understand why!
Molecular higher efficiency approaches?

- **Multi junctions:**
  - Tandems demonstrated.
  - Easy to manufacture

- **Spectral conversion:**
  - Singlet exciton fission for downconversion
  - Triplet-triplet annihilation for upconversion

- **Slow carrier thermalisation?**
  - Helps to reduce losses to trapping at interfaces and in transport
  - *Might* give access to hot carrier effects if energy selective contacts possible
Where do we go from here?

- Solar electricity is abundant, sustainable, versatile and available
- Existing technologies operate within a factor of 2 of the physical limit of 30%
- Goal is to reach similar or higher efficiencies with low energy technologies that can grow quickly.
- Challenges remain for physicists, chemists and materials scientists – but none of them known to be insurmountable

Thank you for your attention!