A perspective on Organic Photovoltaics

Garry Rumbles
• Research cell efficiencies

• Driving force for electron transfer and the relationship to $V_{oc}$

• Charge-Transfer states, Charge-Separated states, and the state of separated charges

• IP, $E_A$, $v$, $E_{ox}$, $E_{red}$

Funding by the Solar Photochemistry Program
Division of Chemical Sciences, Geosciences, and Biosciences

U.S. DEPARTMENT OF ENERGY
Office of Science
Best Research-Cell Efficiencies

- Multijunction Cells (2-terminal, monolithic)
- LM = lattice matched
- MM = metamorphic
- IMM = inverted, metamorphic
- Three-junction (concentrator)
- Three-junction (non-concentrator)
- Two-junction (concentrator)
- Two-junction (non-concentrator)
- Four-junction or more (concentrator)
- Four-junction or more (non-concentrator)

- Thin-Film Technologies
  - CIGS (concentrator)
  - CIGS
  - CdTe
  - Amorphous Si:H (stabilized)

- Emerging PV
  - Dye-sensitized cells
  - Perovskite cells (not stabilized)
  - Organic cells (various types)
  - Organic tandem cells
  - Inorganic cells (CZTSSe)
  - Quantum dot cells (various types)

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

- Crystalline Si Cells
  - Single crystal (concentrator)
  - Single crystal (non-concentrator)
  - Multicrystalline
  - Silicon heterostructures (HT)
  - Thin-film crystal

- NREL efficiency chart (https://www.nrel.gov/pv/assets/images/efficiency-chart.png)
Tracking Research Cell Progress

Power conversion efficiency (%) vs Year

- Dye-sensitized Solar Cells
- Mitsubishi Chemical
- Tandem-junction OPV
- Solution-processed Thermally-evaporated (Heliatek)

Polymer-based Single-junctions:
- PPV
- P3HT
- Benzothiadiazole-based
- Benzodithiophene-based
- Konarka
- Plextronics
- Solarmer
- MEH-PPV:PC61BM
- P3HT:PC71BM
- MDMO-PPV:PC61BM
- MDMO-PPV:PC71BM
- P3HT:bis-PC61BM
- P3HT:[60]ICBA
- U. Toronto
- NREL
- Semiconductor Nanocrystals
Interactive: Record-Breaking PV Cells

The world’s leading PV research labs use this chart to track record-breaking solar cells. New champs appear as soon as they are certified.

There’s often a lot of hype when solar companies claim to set new records. But to see how different PV technologies really stack up, it’s important to compare standardized and independent efficiency tests. Here, we present the records that have been independently verified by the world’s three leading independent labs.

For explanation of the cell types, cell categories, and additional analysis, please see “What Makes a Good PV Technology?”

Due to the dense nature of the data, this graphic is best viewed on a large display.

Best Research Cell Efficiencies (Version: 2017-09-21)

Each line on the chart represents a different type of PV cell, and each dot represents a new verified efficiency record. Lines are colored according to the five categories of cells listed below.

- Crystalline Si Cells
- Emerging PV
- Multijunction Cells
- Single-junction GaAs
- Thin-film Technologies

Credit: IEEE Spectrum/NREL. Infographic: Josh Romero
IEEE Spectrum (spectrum.ieee.org/static/interactive-record-breaking-pv-cells)
Solar cell efficiency tables

Martin A. Green, Yoshihiro Hishikawa, Ewan D. Dunlop, Dean H. Levi, Jochen Hohl-Ebinger, Anita W.Y. Ho-Baillie

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Solar cell efficiency tables (version 51)

<table>
<thead>
<tr>
<th>Classification</th>
<th>Efficiency, %</th>
<th>Area, cm²</th>
<th>$V_{oc}$, V</th>
<th>$J_{sc}$, mA/cm²</th>
<th>Fill Factor, %</th>
<th>Test Centre (date)</th>
<th>Description</th>
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<tbody>
<tr>
<td>Cells (silicon)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Si (crystalline)</td>
<td>25.0 ± 0.5</td>
<td>4.00 (da)</td>
<td>0.706</td>
<td>42.70</td>
<td>82.8</td>
<td>UNSW p-type PERC</td>
<td>UNSW p-type PERC top/rear contacts57</td>
</tr>
<tr>
<td>Si (crystalline)</td>
<td>25.8 ± 0.5</td>
<td>4.008 (da)</td>
<td>0.7241</td>
<td>42.87</td>
<td>83.1</td>
<td>FhG-ISE (7/17)</td>
<td>FhG-ISE, n-type top/rear contacts59</td>
</tr>
<tr>
<td>Si (large)</td>
<td>26.6 ± 0.5</td>
<td>179.74 (da)</td>
<td>0.7403</td>
<td>42.50</td>
<td>84.7</td>
<td>FhG-ISE (11/16)</td>
<td>Kaneka, n-type rear IBC3</td>
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<tr>
<td>Si (multicrystalline)</td>
<td>22.0 ± 0.4</td>
<td>245.83 (t)</td>
<td>0.6717</td>
<td>40.53</td>
<td>80.9</td>
<td>FhG-ISE (9/17)</td>
<td>Jinko solar, large p-type39</td>
</tr>
<tr>
<td>GaInP</td>
<td>21.4 ± 0.3</td>
<td>0.2504 (ap)</td>
<td>1.4932</td>
<td>16.31</td>
<td>87.7</td>
<td>NREL (9/16)</td>
<td>LG electronics, high bandgap60</td>
</tr>
<tr>
<td>GaInAs/GaInAs</td>
<td>32.6 ± 1.4</td>
<td>0.248 (ap)</td>
<td>2.024</td>
<td>19.51</td>
<td>82.5</td>
<td>NREL (10/17)</td>
<td>NREL, monolithic tandem</td>
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<tr>
<td>Cells (chalcogenide)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CIGS (thin-film)</td>
<td>22.6 ± 0.5</td>
<td>0.4092 (da)</td>
<td>0.7411</td>
<td>37.76</td>
<td>80.6</td>
<td>FhG-ISE (2/16)</td>
<td>ZSW on glass41</td>
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<tr>
<td>CIGSS (Cd free)</td>
<td>22.0 ± 0.5</td>
<td>0.512 (da)</td>
<td>0.7170</td>
<td>39.45</td>
<td>77.9</td>
<td>FhG-ISE (2/16)</td>
<td>Solar frontier on glass50</td>
</tr>
<tr>
<td>CdTe (thin-film)</td>
<td>22.1 ± 0.5</td>
<td>0.4798 (da)</td>
<td>0.8872</td>
<td>31.69</td>
<td>78.5</td>
<td>Newport (11/15)</td>
<td>First solar on glass42</td>
</tr>
<tr>
<td>CZTSS (thin-film)</td>
<td>12.6 ± 0.3</td>
<td>0.4209 (ap)</td>
<td>0.5134</td>
<td>35.21</td>
<td>69.8</td>
<td>Newport (7/13)</td>
<td>IBM solution grown43</td>
</tr>
<tr>
<td>CZTS (thin-film)</td>
<td>11.0 ± 0.2</td>
<td>0.2339 (da)</td>
<td>0.7306</td>
<td>21.74</td>
<td>69.3</td>
<td>NREL (3/17)</td>
<td>UNSW on glass12</td>
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<tr>
<td>Cells (other)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perovskite (thin-film)</td>
<td>22.7 ± 0.8</td>
<td>0.0935 (ap)</td>
<td>1.144</td>
<td>24.92</td>
<td>79.6</td>
<td>Newport (7/17)</td>
<td>KRICT15</td>
</tr>
<tr>
<td>Organic (thin-film)</td>
<td>12.1 ± 0.3</td>
<td>0.0407 (ap)</td>
<td>0.8150</td>
<td>20.27</td>
<td>73.5</td>
<td>Newport (2/17)</td>
<td>Phillips 66</td>
</tr>
</tbody>
</table>

"Notable exceptions": "Top 10" confirmed cell and module results not class records measured under the global AM1.5 spectrum (1000 Wm$^{-2}$) at 25°C (IEC 60904-3: 2008, ASTM G-173-03 global)
Consequently, an impressive PCE of 13.0% was recorded for the PBDB-T-SF:IT-4F-based device, which was certified as 13.1% by the National Institute of Metrology, China (NIM), suggesting that the results obtained in our lab are reliable.
Efficient Organic Solar Cells Processed From Hydrocarbon Solvents.

Zhao, J.; Li, Y.; Yang, G.; Jiang, K.; Lin, H.; Ade, H.; Ma, W.; Yan, H.

Efficient Organic Solar Cells Processed From Hydrocarbon Solvents.

Motivation:

- Connect molecular, photo-induced electron transfer theory to the bulk heterojunction solar cell
- Identify role of states intermediate between excitation and free carriers
- Establish the nature of the pathway(s) for recombination
- Understand the role of solid-state microstructure

\[ \text{Rhodobacter sphaeroides Reaction Center} \]
Motivation:

- Connect molecular, photo-induced electron transfer theory to the bulk heterojunction solar cell
- Identify role of states intermediate between excitation and free carriers
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- Understand the role of solid-state microstructure

\[
k_{ET} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\lambda + \Delta G^o)^2}{4\lambda k_B T}\right)
\]
Why is this important? (Using type II model)

\[ \alpha = \text{LUMO}_{\text{Acceptor}} - \text{LUMO}_{\text{Donor}} \]

\[ \beta = \text{LUMO}_{\text{Acceptor}} - \text{HOMO}_{\text{Donor}} \]

\[ \approx V_{oc} \]

1. Energy loss associated with exciton dissociation
2. Charge generation mechanism at interface
Exciton* $\rightarrow$ CS* state  
CT* state $\leftrightarrow$ Carriers  

↓  
Ground State  

Transient Absorption  
Photoluminescence  
Microwave Conductivity
Processes

\[ D + A^* \xrightarrow{k_1} X^* \xleftarrow{k_2} D^+ + A^- \]
\[ \downarrow k_A \quad \downarrow k_X \]

GS

Transient Absorption

Photoluminescence

Microwave Conductivity
appended electron donors, which has proven crucial in be an important factor in designing high-performance organic that control PDI aggregation and reduce excimer formation, PDIs are easily modi...ff,

Additionally, an increase in The tendency of PDIs to...50 quantum yield of 60 V versus ferrocene (V versus SCE). Linking in toluene solution features maxima at 60 nm. By comparison with the emission experiments were carried out in a 2-methyltetrahydrofuran glass...1 to 2945


All in low dielectric constant solvents (<7.6)
A Highly C$_{70}$ Selective Shape-Persistent Rectangular Prism Constructed through One-Step Alkyne Metathesis. 
*Journal of the American Chemical Society*, 133(51), 20995–21001.

$\Delta G_{CS}$ in toluene = -0.27 eV; $\Delta G_{CS}$ in Benzonitrile = -0.95 eV
\[ \Delta E^0_{CT} = N_A \left\{ e\left[ E^0(D^{+\ast} / D) - E^0(A / A^{-\ast}) \right] + \frac{z(D^{+\ast})z(A^{-\ast})e^2}{4\pi\varepsilon_0\varepsilon_r a^2} \right\} - \Delta E_{0,0} \]

\[ \Delta E_T^0 = IP_D - EA_A - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r a} - E_{Exciton} \]

\[ \Delta G_{CS} = (IP_D - E_{Exciton}) - EA_A = LUMO_D^{opt} - LUMO_A^{elec} \]
\[
\Delta_{ET}G^o = N_A \left\{ e \left[ E^o(D^{**} / D) - E^o(A / A^{-*}) \right] - \Delta E_{0,0} + \frac{z(D^{**})z(A^{-*})e^2}{4\pi\varepsilon_0\varepsilon_r r_{DA}} - \frac{z(D^{**})z(A^{-*})e^2}{4\pi\varepsilon_0} \left[ \frac{1}{2r_D} + \frac{1}{2r_A} \right] \left( \frac{1}{\varepsilon_{EC}} - \frac{1}{\varepsilon_S} \right) \right\}
\]
1:1 Complex and Static Quenching

(a) Absorbance (OD) vs. Wavelength (nm)

[C$_{70}$]:[COP-5] in Tol
- 0.0
- 0.16
- 0.46
- 0.79
- 0.98
- 1.2
- 1.6
- 2.0

(b) Absorbance at 710 nm (mOD) vs. [C$_{70}$]:[COP-5]

(d) τ$_F$ = 9.8 ns

λ$_{em}$ = 660 nm

(c) Absorbance (mOD) vs. Wavelength (nm)

Abs

CT emission

Abs emission int. (a.u.)
Long-lived charge-transfer state of a $\text{C}_{70}$-encapsulated bisporphyrin covalent organic polyhedron in a low dielectric medium.

Michael Ortiz, Sung Cho, Jens Niklas, Seonah Kim, Oleg G. Poluektov, Wei Zhang, Garry Rumbles, Jaehong Park

J. Am. Chem. Soc. 2017, 139, 4286–4289
molecular triad (C) to undergo photoinduced electron transfer from the porphyrin first excited singlet state or to the fullerene •- to solvent and temperature. The quantum yield of C•+ of C energies of the charge-separated states of fullerene-based systems are only about half as sensitive to changes.

Introduction

Although this triad is a useful mimic of several aspects of components of such supramolecular species. After the first report, the major product of the reaction has the ylides (Prato reaction) can result in 8 di-

RESULTS

The arrangement is reminiscent of that of the special pair of porphyrin dyad successful, due in part to favorable energetics, low reorganization parameters for the electron and energy transfer processes in dyad these constructs feature a single chemical linkage joining the porphyrin and fullerene, and electron transfer between the two these isomers, an adduct to a C10•+ model fullerene are •-phenylene vinylene)–fulleropyrrolidine dyad

These results have motivated their use in a number of supra-

photoactive materials.

Yield

Separation or recombination time /seconds

2%PCBM + RR-p3HT

PCBM
A complex conjugated polymer:fullerene blend
• Research cell efficiencies
  - Notable exceptions
  - Device area
  - Certification

• Driving force for electron transfer and the relationship to $V_{oc}$
  - Weller equation and Gibbs energy, not LUMO offset
  - Reorganiz(s)ation energy $\Delta G$

• Charge-Transfer states, Charge-Separated states, and the state of separated charges
  - CT states absorb and emit
  - CS states absorb very weakly, are generally associated with molecular triads and photosynthesis reaction center
  - State of separated charges are free of coulomb attraction, are extracted by devices and can be readily detected using microwave conductivity

• $IP, E_A, \nu E_{ox}, E_{red}$
  - Caution with connecting or combining these data
Director's Postdoctoral Fellowship

Have you completed your Ph.D. within the last two years? Can you demonstrate a promising career of research and leadership?

The NREL Director’s Fellowship attracts the next generation of exceptionally qualified scientists and engineers with outstanding talent and credentials in renewable energy research and related disciplines. One of the fellowship positions is named the Nozik Fellowship, in recognition of Emeritus Senior Research Fellow Dr. Arthur J. Nozik and his outstanding scientific contributions to renewable energy.

The Director’s Fellowship application process is held four times a year as follows:

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<th>Application Window Closes*</th>
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<tr>
<td>March 1</td>
<td>July 1</td>
</tr>
</tbody>
</table>

*Applications submitted after the closing date will not be reviewed.

Candidates are selected based on eligibility, program expectations, and research proposals. Overriding consideration, when evaluating the application, will be the quality of the candidate. Successful candidates will serve a two-year term, with a possible third-year renewal paid with program funding (maximum three-year appointments). The Director’s Fellowship includes a premium salary rate, additional funding for conferences/presentations, competitive benefits package, and relocation assistance (for moves greater than 50 miles from NREL).