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SHORT COMMUNICATION

Radiative efficiency of state-of-the-art photovoltaic cells

Martin A. Green*

School of Photovoltaic and Renewable Energy Engineering, University of New South Wales (UNSW), Sydney, Australia 2052

ABSTRACT

Maximum possible photovoltaic performance is reached when solar cells are 100% radiatively efficient, with different photovoltaic technologies at different stages in their evolution towards this ideal. An external radiative efficiency is defined, which can be unambiguously determined from standard cell efficiency measurements. Comparisons between state-of-the-art devices from the representative cell technologies produce some interesting conclusions. Copyright © 2011 John Wiley & Sons, Ltd.

KEYWORDS
radiative efficiency; efficiency limits

***Correspondence**
Martin A. Green, School of Photovoltaic and Renewable Energy Engineering, University of New South Wales (UNSW), Sydney 2052, Australia.
E-mail: m.green@unsw.edu.au

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1. INTRODUCTION

It has long been appreciated that the limiting photovoltaic solar cell performance is obtained when recombination in the cell is dominated by radiative processes. Shockley and Queisser [1] determined the limiting performance of single-junction devices by recognising that any nett recombination in a solar cell in this limiting case would result in emission of a photon of energy above the bandgap, with the integrated emission determining the total nett radiative recombination current. These authors also investigated the effect of parallel non-radiative processes upon device performance.

Figure 1 shows the results of applying the same analysis to limiting performance under the recently adopted IEC 60904:Ed.2 (2008) Air Mass 1.5 (AM1.5) Global Spectrum (ASTM173-03 G) [2]. Also shown as dashed line are the effects of less than ideal recombination properties of the devices as well as the best certified experimental energy conversion efficiencies under this new spectrum [3,4].

The effect of parallel non-radiative processes can be described in terms of what will be described as the external radiative efficiency (ERE). This is defined as the fraction of the total dark current recombination in the device that results in radiative emission from the device. Because this fraction may vary in general with the voltage across the device, the open-circuit voltage (V_{oc}) is chosen as the reference voltage (the ERE is closely related to the external quantum efficiency of a light-emitting diode operating at the corresponding injection level). Due to total internal reflection and photon recycling, the ERE will generally be smaller than what will be termed the internal radiative efficiency (IRE), the fraction of internal recombination events that are radiative, such as is determined by the ratio of total lifetime to the radiative lifetime. For silicon devices, the IRE can be several times the ERE [5], but obviously this ratio must decrease towards unity as both approach 100%.

The dashed lines in Figure 1 show the limiting efficiencies for ERE between 1% and 10^{-6}% with the best cells lying between the limits for 1% and 0.01%. As will be shown, actual ERE can be appreciably higher because effects other than radiative inefficiencies also decrease the experimental efficiency below the ideal limits.

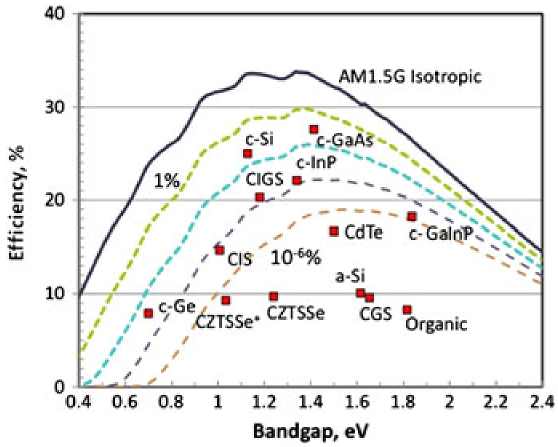

Figure 1. Shockley–Queisser limits on the efficiency of conventional single-junction cells as well as limits for cells of 1%, 0.01%, 0.0001% and 0.000001% external radiative efficiency. The best confirmed experimental results are also shown.

2. EXPERIMENTAL RADIATIVE EFFICIENCY

Experimental ERE can be deduced by taking advantage of a surprising yet fundamental reciprocal relationship recently identified by Rau [6]. The Shockley–Queisser analysis models the radiation emitted by the cell at energies above its bandgap E_g as room-temperature blackbody radiation exponentially enhanced by the cell voltage, as given by Eq. (1):

$$\text{Photons emitted/unit area} = \frac{2\pi}{h^3c^2}\exp\left(\frac{qV_{oc}}{kT}\right)\int_{E_g}^{\infty}\frac{E^2 \mathrm{d}E}{\exp(E/kT)-1} \quad (1)$$

E is the photon energy, c the vacuum light velocity, q the electronic charge, h Planck's constant, k Boltzmann's constant and T is device temperature.

Rau showed that, under conditions that are often closely approached in practice, actual cells emit radiation with this distribution multiplied at each wavelength by the external quantum efficiency (EQE) of the device, as measured for the device operating as a solar cell (i.e. electrons/incident photon). In terms of hemispherical emission:

$$\text{Photons emitted/unit area} = \frac{2\pi}{h^3c^2}\exp\left(\frac{qV_{oc}}{kT}\right)\int_{0}^{\infty}\frac{\overline{EQE}_{abs}E^2 dE}{\exp(E/kT)-1} \quad (2)$$

where $\overline{\mathrm{EQE}}_{abs}$ is the angularly weighted value of the EQE. This remarkable relationship has been confirmed for a number of experimental devices [7–9] as well as being consistent with modelling prior to its recognition [10].

The cell EQE is a required measurement for a calibrated measurement of cell efficiency, to adjust for spectral mismatch between the spectrum used for illuminating the cell during measurement and the tabulated reference spectrum [2]. This means that each calibrated cell measurement yields sufficient information to allow calculation of ERE.

On cell open circuit, the photogeneration of carriers within a cell is balanced by recombination within the device, globally if not at each point within the device. The open-circuit voltage measured at the cell terminals is the voltage that increases recombination within the active region of the device to the level required to balance the photocurrent able to be collected by the junction. Assuming reasonable device quality so that parasitic resistances are not excessive and also assuming that the collection probability of carriers is not strongly voltage dependent, the photocurrent density collected by the junction on open circuit will equal the short-circuit current density. The light emitted due to the forward bias that balances the photocurrent will be the EQE-weighted, exponentially enhanced blackbody radiation previously described, allowing the ERE to be calculated as follows:

$$\mathrm{ERE} = \frac{\frac{2\pi q}{h^3c^2}\exp\left(\frac{qV_{\mathrm{oc}}}{kT}\right)\int\frac{\overline{\mathrm{EQE}}_{abs}E^2\mathrm{d}E}{\exp(E/kT)-1}}{J_{\mathrm{sc}}} = \frac{\exp\left(\frac{qV_{\mathrm{oc}}}{kT}\right)\int\overline{\mathrm{EQE}}_{rel}N_{BB}(E)\mathrm{d}E}{\int \mathrm{EQE}_{rel}N_{AM1.5}(E)\mathrm{d}E} \quad (3)$$

EQE is the value for the solar cell for near-perpendicular incident light in either absolute or relative terms, with $\overline{\mathrm{EQE}}$ the appropriately weighted value over all angles of incident light. For a high quality cell, this will not differ greatly from the near-perpendicular value [11]. EQE is generally measured either in absolute or relative terms with a midrange relative accuracy of about 3%. The major contributions to the integration on the numerator come from the long wavelength region of the spectral response, from the region where this response begins to fall rapidly to the low value near the absorption threshold, whereas the main contribution to the denominator comes from the region near the peak photon density in the AM1.5 spectrum in the 600–700 nm range.

Some of the sources of inaccuracies in the evaluation of ERE have already been suggested. An isotropic response needs to be assumed for evaluation from standard near-perpendicular EQE data. Collection probabilities may be voltage dependent so that the short-circuit condition, where EQE is normally evaluated, may not represent conditions at open circuit. The reciprocal relation itself also is only strictly valid under conditions where the *quasi-fermi* level separation at the junction is constant [6], which would not be the case for resistive devices even at open circuit because of circulating currents. Cell parameters such as carrier lifetimes and surface recombination properties should not be injection-level dependent [6,12], although an ERE could still be defined in such cases, as for EQE. However, such effects are expected to be minor for cells of respectable performance, particularly in relation to the large differences in ERE noted between different devices and different technologies.

3. STATE-OF-THE-ART DEVICES

External radiative efficiency was calculated for a range of representative state-of-the-art cells [3,4]. The absolute EQE for these cells is shown in Figure 2a, deduced from the relative EQE by normalising to the experimental J_{sc} measured for the devices. The calculated spectral luminescence from these devices on open circuit are shown in Figure 2b. Units are ampere/square metres/nanometres, representing the current density required on open circuit to support the different spectral components shown. Due to large differences between technologies, different scaling factors are applied to the different results, although the same scaling factor is applied to cells of the same type, except for the GaAs cells.

Until recently [3], the most efficient non-concentrating, single-junction cell was a 26.4% efficient GaAs cell fabricated by the Fraunhofer Institute for Solar Energy (GaAs ISE) with parameters shown in Table I. Integrating the spectral luminescence gives an ERE of 1.26%. Given

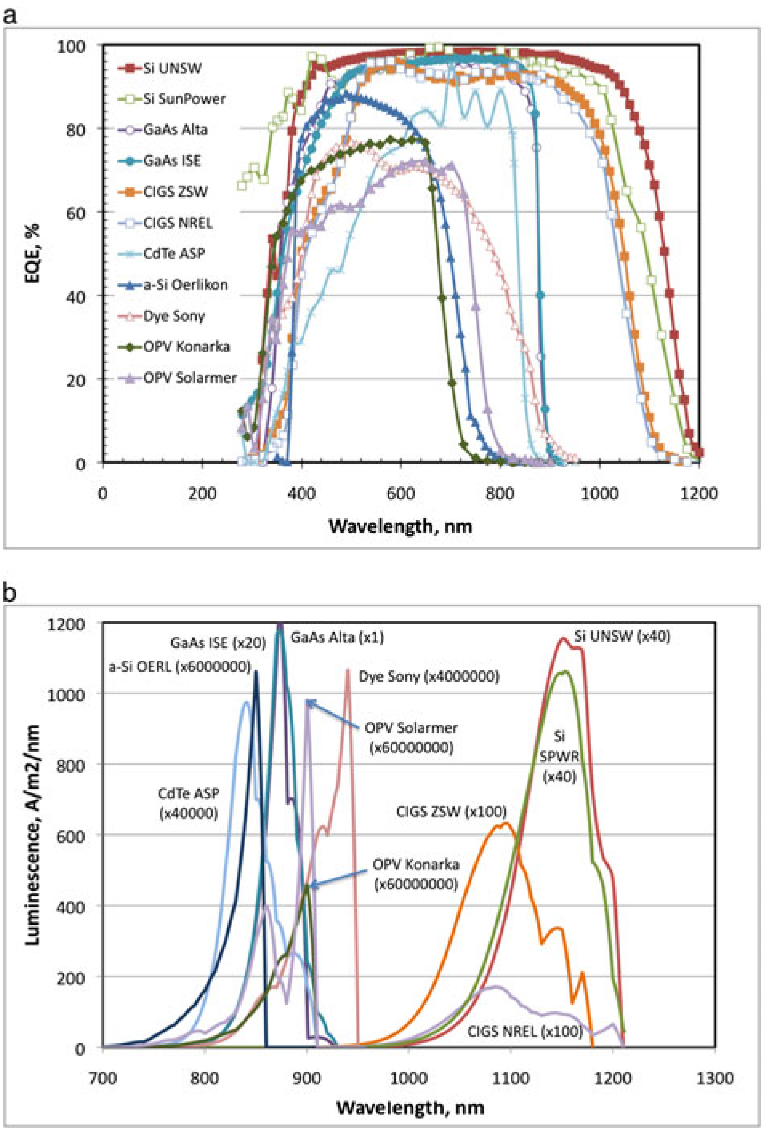

Figure 2. (a) EQE for the different cells described in the text; (b) calculated spectral luminescence from the different cells due to dark current recombination on open circuit, with widely varying multiplication factors.

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Table I. External radiative efficiency (ERE) and other relevant performance parameters at 25 °C for the state-of-the-art devices [3,4] included in the present study.

Device	V_{oc} (mV)	J_{sc} (mA/cm^2)	Efficiency (%)	ERE (%)
Si UNSW	706	42.7	25.0	0.57
Si SPWR	721	40.5	24.2	0.56
GaAs Alta	1107	29.6	27.6	22.5
GaAs ISE	1030	29.8	26.4	1.26
CIGS ZSW	740	35.4	20.3	0.19
CIGS NREL	713	34.8	19.6	0.057
CdTe* ASP	838	21.2	12.5	1.0E−4
a-Si Oerlikon	886	16.8	10.1	5.3E−6
Dye* Sony	719	19.4	9.9	7.2E−6
OPV Konarka	816	14.5	8.3	2.7E−7
OPV Solarmer	759	15.9	8.1	3.8E−7

*Minimodule: results on a 'per cell' basis.

that this device was fabricated on a GaAs substrate, it is speculated that IRE would have been appreciably higher because n^2 more radiation would have been emitted into the substrate than into air (where n is the substrate refractive index).

In October 2010 [4], this record was surpassed with 27.6% efficiency measured for a thin-film GaAs device fabricated by Alta Solar (GaAs Alta). As shown in Figure 2a, this has an almost identical spectral response to cell GaAs ISE, but as in Figure 2b, the luminescent intensity on open circuit is almost 20 times higher, corresponding to a greatly improved ERE of 22.5%. This high value suggests that photons emitted during radiative recombination events towards the rear of the device are not wasted, as speculated for the GaAs ISE device, but a reasonable number are reflected back into active device regions.

With radiative recombination forming such a large fraction of total recombination in this device, further improvements in ERE will result in immediate benefits. As ERE is increased towards 100%, an additional gain in V_{oc} of up to 40 mV is expected with a corresponding fill factor improvement.

The ERE for the two crystalline silicon devices investigated are not appreciably lower than the second-rated GaAs device, with both Si devices displaying an ERE of about 0.6%. This is similar to the electroluminescent quantum efficiency directly measured for similar devices [10], again confirming the accuracy of the present approach. Because the Sunpower device (Si SPWR) with less than 200 μm thickness is appreciably thinner than the University of New South Wales device (Si UNSW) with 400 μm thickness and has possibly poorer rear reflection, the EQE is notably poorer at long wavelength, with J_{sc} also appreciably lower. This is compensated by a higher V_{oc} due to the smaller volume of the bulk region combined with likely better surface passivation. From Figure 2b, the two devices have almost identical open-circuit voltage luminescence.

Comparison of two recent copper–indium–gallium–selenide (CIGS) devices also produces interesting results. One is a small-area 20.3% efficient device fabricated by Zentrum für Sonnenenergie-und Wasserstoff-Forschung (CIGS ZSW), and the second is for a larger (1 cm^2) device of 19.6% efficiency fabricated by the US National Renewable Energy Laboratory (CIGS NREL). Both devices can be seen in Figure 2a to have similar spectral responses, although the CIGS ZSW device has a much stronger emission on open circuit with ERE of 0.19% compared with 0.06% for the NREL device. This indicates fundamentally better quality material in the ZSW device, although this may be partly due to its smaller size given the strong areal dependence of CIGS cell performance.

The next three devices to be discussed include recent record CdTe, a-Si and dye-sensitised devices [3,4]. The CdTe device is a small 12.5% efficient submodule with ERE of 1.0×10^{-4}% fabricated by Advanced Solar Power (ASP). Smaller cells could be expected to have higher ERE, whereas commercial CdTe modules, now averaging 11.3% aperture area efficiency, would be expected to have lower ERE. The best a-Si cell to date fabricated by Oerlikon (OERL) has quite a low ERE of 5.3×10^{-6}%. However, from Figure 1, its bandgap can be seen to be in an appropriate region for highest possible conversion efficiency with such low ERE.

The dye-sensitised device is again a small 9.9% efficient submodule, although with energy conversion performance close to the best-performing small-area cell (11.2%). Although the operational principles of a dye-sensitised cell are vastly different from the previous p–n junction devices, the reciprocity relationships giving rise to Rau's relationship are expected still to apply [13]. ERE is 7.2×10^{-6}%, similar to but slightly higher than the a-Si device.

The final two devices are two of the first organic photovoltaic (OPV) devices to exceed 8% energy conversion efficiency [4], with very different energy absorption thresholds, as apparent from Figure 2a. Both devices however display very similar ERE in the 3–4 $\times 10^{-7}$% range.

Even though organic light-emitting diodes of efficiency of 20% and higher have been reported, the different requirements for photovoltaics [14] greatly reduce the radiative efficiency. In particular, the blending required to produce bulk heterojunction devices with high carrier collection greatly reduces the radiative efficiency.

4. CONCLUSIONS

The ERE, able to be unambiguously deduced from standard solar cell efficiency measurements, is shown to be a useful parameter in comparing the performance of cells of both the same and completely different technologies. Comparison for state-of-the-art cells of Si, GaAs, CIGS, CdTe, a-Si, dye-sensitised and OPV technologies shows some interesting similarities and some surprising differences. As each technology matures, ERE will evolve towards the 100% value required for limiting performance.

REFERENCES

1. Shockley W, Queisser HJ. Detailed balance limit of efficiency of p–n junction solar cells. *Journal of Applied Physics* 1961; **32**: 510–519.
2. International Standard, IEC 60904–3, Edition 2, 2008, Photovoltaic devices—Part 3: Measurement principles for terrestrial photovoltaic (PV) solar devices with reference spectral irradiance data. ISBN 2-8318-9705-X, *International Electrotechnical Commission*, April 2008.
3. Green MA, Emery K, Hishikawa Y, Warta W. Solar cell efficiency tables (Version 36). *Progress in Photovoltaics* 2010; **18**(5): 346–352.
4. Green MA, Emery K, Hishikawa Y, Warta W. Solar cell efficiency tables (Version 37). *Progress in Photovoltaics* 2011; **19**: 84–92.
5. Trupke T, Zhao J, Wang A, Corkish R, Green MA. Very efficient light emission from bulk crystalline silicon. *Applied Physics Letters* 2003; **82**: 2996–2998.
6. Rau U. Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells. *Physical Review B* 2007; **76**: 085303.
7. Kirchartz T, Rau U. Electroluminescence analysis of high efficiency Cu(In, Ga)Se_2 solar cells. *Journal of Applied Physics* 2007; **102**: 104510.
8. Kirchartz T, Helbig A, Rau U. Note on the interpretation of electroluminescence images using their spectral information. *Solar Energy Materials and Solar Cells* 2008; **92**: 1621–1627.
9. Kirchartz T, Helbig A, Reetz W, Reuter M, Werner JH, Rau U. Reciprocity between electroluminescence and quantum efficiency used for the characterization of silicon solar cells. *Progress in Photovoltaics* 2009; **17**: 394–402.
10. Green MA, Zhao J, Wang A, Reece PJ, Gal M. Efficient silicon light emitting diodes. *Nature* 2001; **412**: 805–808.
11. Ferraioli L, Maddalena P, Massera E, Parretta A, Green MA, Wang A, Zhao J. "Evidence for generalised Kirtchhoff's law from angle-resolved electroluminescence of high efficiency silicon solar cells". *Applied Physics Letters* 2004; **85**: 2484–2486.
12. Green MA. "Generalized relationship between dark carrier distribution and photocarrier collection in solar cells". *Journal Applied Physics* 1997; **81**: 268–271.
13. Trupke T, Würfel P, Uhlendorf I, Lauermann I. Electroluminescence of the dye-sensitized solar cell. *The Journal of Physical Chemistry B* 1999; **103**(11): 1905–1910.
14. Kirchartz T, Mattheis J, Rau U. Detailed balance theory of excitonic and bulk heterojunction solar cells. *Physical Review B* 2008; **78**: 235320.