Ideal Solar Cell Efficiencies

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In a recent paper, Guillemoles *et al*[1] attempt to clarify and explain the often cited paper by Shockley and Queisser[2] (SQ) which defines the limits to photovoltaic conversion by a single-junction solar cell. The SQ paper is not easy to read and is therefore easily misunderstood. As modern solar cells approach theoretical efficiency limits, the fundamentals become particularly important and the effort by Guillemoles *et al* is therefore to be welcome. However, in doing so, the authors have fallen into several pitfalls, and the aim of the present note is to clarify a number of misconceptions and correct some errors in that paper for specialists and non-specialists alike to help disentangle the complexities of the SQ paper.

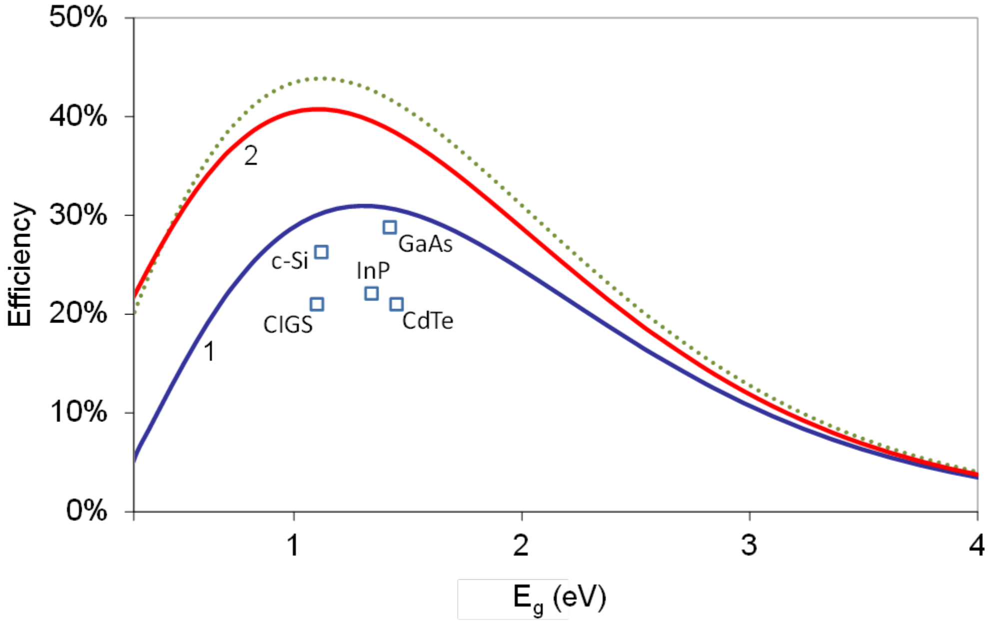

Fig. 1. The most frequently quoted Shockley-Queisser efficiency curves shown alongside the best measured solar cell efficiencies (points): Curve 1 – under “one-sun” illumination, and 2 – under sunlight at maximum concentration ratio of approximately 46,000. Also shown, by the dotted line, is the Trivich-Flinn efficiency (1). Sunlight modelled as black-body radiation at 6000K, cell temperature 300K.

Shockley and Queisser described their result as a detailed balance limit which - in an intuitive manner - describes the balance between the incident and emitted photon fluxes rather than a similar thermodynamic term of detailed balancing (also referred to as microscopic reversibility[3]), more akin to an earlier paper by van Roosbroeck and Shockley[4] and more recent reciprocity theorems (see e.g. Rau[5]). The key underpinning principles of the SQ paper are that the maximum efficiency of a solar cell depends solely on the photon fluxes of the incident and emitted radiation, and that light absorption by the solar cell can be described by a well-defined threshold energy E_g - the semiconductor bandgap. This assumption holds well for virtually all crystalline inorganic semiconductors which form the basis for the SQ theory, and makes it possible to make a clear comparison between actual efficiencies and theoretical limits at each relevant bandgap (see Fig. 1 for a typical example).

Guillemoles *et al* claim to consider only the SQ curve that corresponds to one sun illumination. This leads them to ascribe – incorrectly – a major part of voltage from the "ideal" value of E_g/q to electrical work of transferring a charge carrier between the contacts (labelled as "isothermal losses" in ref. 1). In fact, the largest part of this loss is of optical nature, a fundamental and unavoidable loss contained in the SQ theory and visible in Fig. 1 as the difference between the maximum-concentration and one-sun efficiencies, due to the expansion in size (étendue) from the incident to emitted beam. Sometimes called optical entropy generation, [6,7] this is a subtle but important loss, with an origin closer to Planck's radiation thermodynamics[8] than to traditional optics, that is easily misunderstood.[9] Emitted photons are in thermal equilibrium with the electron-hole pairs that emit them, and with whom they share the common temperature and chemical potential. The optical entropy generation – which implies that heat is absorbed from the low temperature heat bath that cannot be converted to useful work - reduces the chemical potential of the emitted photons. This, in turn, reduces the voltage that the electron-hole pairs can generate, at or away from the open circuit. The magnitude of this loss is about 0.28 V in voltage terms; the resulting efficiency loss exceeds the nonradiative and residual radiative losses (in other words, the difference of the measured efficiency from the SQ one-sun curve) in the best solar cells (see Fig. 1), and is similar to these losses in standard production cells. It is important to emphasize that this loss cannot be reduced by changing the electronic parameters of the solar cell but only by manipulating the incident and emitted beams. Interestingly, irreversible entropy generation is also at the root of the loss of full power at short circuit, not always discussed in the textbooks on photovoltaics in any detail.

In identifying the "real" voltage losses relative to the SQ value in Eq. (3), Guillemoles *et al* define somewhat novel figures of merit rather than use more conventional parameters (see e.g. refs. [10, 11,12]). Doing so leads to some confusion and an incorrect estimate of one of these parameters (F_{em}), usually defined in terms of emitted photon fluxes rather than via the dark saturation current of the solar cell – for example, F_{em} parallels the t_c parameter of Shockley and Queisser, equal to the probability that a photon at the temperature of the solar cell is absorbed and produces and electron-hole pair. Indeed, if $J_o^{real} = J_o^{QE} / Q_e^{lum}$, as defined in Table 1of ref. 1, where Q_e^{lum} is the efficiency of luminescent emission by the solar cell when operating as a light-emitting diode then, by optoelectronic reciprocity[5], $J_o^{QE} = EQE_o J_o^{SQ}$, where

EQE_o is the external quantum efficiency for the emitted light. It therefore follows that the parameter F_{em} of ref. 1 is just the reciprocal of EQE_o and never smaller than unity, contrary to the claim on p.504. This conclusion can be easily understood in physical terms: because of lower efficiency, a real solar cell will always emit a photon flux no higher than an ideal (SQ) cell with the same bandgap, and therefore $F_{em} \geq 1$ - in contrast to the higher dark saturation current obtained by dividing with Q_e^{lum}. It is also worth noting that this result is a consequence of both potentially lower-than-unit emissivity at the emission wavelengths (losses in Stage A, as attributed in ref. 1), but also due to losses in carrier transport to junction, and therefore originating from losses in Stage C.

The inequality $F_{em} \geq 1$ is a rigorous consequence of the SQ model with a well-defined absorption edge at the bandgap, and is amply confirmed by solar cell data (for example, F_{em} may range from 5 in standard to about 1.5 in best crystalline silicon solar cells. The observation of F_{em} below unity is therefore an indication of inapplicability of the SQ model. This may arise, for example, in the case of band tails and below-bandgap absorption which may be significant in some materials, including thin films, organic semiconductors and perovskites. If this is the case, situations may also arise when $F_{SC}>1$, contradicting further the claims in ref. 1. Attempts have been made to extend the SQ detailed balance to allow for such features in optical absorption (see, for example, refs. 12 and 13) but, at the present time, it is far from clear what connection and/or corrections to the SQ model will emerge.

More subtle but nevertheless important from the fundamental viewpoint is the fact that the construction in Fig. 2b of ref. 1 is not due to Shockley and Queisser, as least not what is generally understood to be their acclaimed work leading to the efficiencies shown by the full lines in Fig. 1. In fact, the maximum efficiency implied in Fig. 2b of ref. 1, as given by

$$\eta_{TF} = E_g \int_{E_g}^{\infty} \Phi(E)dE \bigg/ \int_0^{\infty} E\Phi(E)dE \qquad (1)$$

is due to Trivich and Flinn (TF),[14] published some six years before the paper by Shockley and Queisser who reproduce this efficiency under the name of “ultimate efficiency”, shown by the dotted line in Fig. 1.

Although the difference between the TF model and the SQ efficiency at maximum concentration is numerically less than about 3% of absolute efficiency, it has nevertheless profound conceptual implications. The TF method is independent of the intensity of the incident sunlight, and therefore prevents a direct deduction of the most useful SQ efficiency curve: that under one-sun illumination which, as we have seen earlier, is a consequence of the balance between the incident and emitted light beams.

The construction in Fig. 2b is due to Henry[15] who shows the full complexity of obtaining the measured solar cell parameters by this technique and whose construction clearly highlights the difference between the “maximum concentration” and “ one sun” efficiencies discussed earlier in this note. The use of TF efficiency (1) in place of the true SQ efficiency results in an error (which seems to have disappeared from Fig. 2a of ref. 1), already contained in ref. 16, where the TF efficiency is also incorrectly used as the starting point.

In conclusion, the Shockley - Queisser detailed balance provides a powerful insight into the operation of solar cells near their theoretical potential, and its understanding is becoming essential for all researchers working at the cutting edge of photovoltaics. Notwithstanding, the model may be easily misunderstood, if only due to a subtle interplay between the broad range of disciplines which contribute to fine details of the theory. There is a need, clearly, for a further interpretation, clarification and explanation. But, as Einstein once observed, the explanation should be made as simple as possible, but no simpler.

Competing interests

The author declares no competing interests

Acknowledgement

Centre for Advanced Photovoltaics is supported by the Czech Ministry of Education, Youth and Sport. CZ.02.1.01/0.0/0.0/15_003/0000464.

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