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Maturity of Photovoltaic Solar-Energy Conversion

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1. Introduction

In this chapter, the author explains the present technological and scientific maturity of the field of solar-energy conversion. The author builds on scientific foundations to generalize several upper limits of solar-energy conversion as a function of the geometric-concentration factor. These limits are used to define a high-efficiency regime for the terrestrial conversion of solar-energy. The current world-record efficiency is measured in solar cells composed of three junctions operating in tandem under a geometric-concentration factor of 454 Suns. By illustrating that the current world-record efficiency is clearly within the high-efficiency regime, the author argues that the field of photovoltaic solar-energy conversion is far removed from its infancy. Inasmuch that the world-record efficiency is less than half of the theoretical terrestrial limit, the author argues that there is significant space for scientific innovation. In addition, by noting that the world-record efficiency, which is measured with a tandem solar cell with three junctions operating at 454 Suns, is 9% less than the physical limit of a tandem solar cells with two junctions operating under the same number of Suns, the author makes apparent the potential for improvement to the present technological paradigm. The author concludes that solar-energy science and technology has significantly more challenges to address and innovations to realize before it may be considered a fully mature field.

The remainder of this chapter is organized as follows. In Section 2, the author describes an ideal p - n junction solar cell and distinguishes the solar cell's absorber, its function, and its relation to the other essential components of the solar cell. In Section 3, the author reviews three important approaches that establish upper-limiting efficiencies of solar-energy conversion: the radiation-in-radiation-out approach of Landsberg and Tonge, the omni-colour approach of DeVos, Grosjean, and Pauwels, and the detailed-balance approach of Shockley and Queisser. The detailed-balance approach establishes the maximum-power conversion-efficiency of a single p - n junction solar cell in the terrestrial environment as 40.7%. Yet, the omni-colour approach establishes the maximum-power conversion-efficiency of solar energy in the terrestrial environment as 86.8%. In Section 4, the author reviews four approaches for realizing a global efficiency enhancement with respect to the maximum-power conversion-efficiency of a single p - n junction solar cell. The current technological paradigm experimentally demonstrates high-efficiencies by using stacks of p - n junction solar cells operating in tandem. Other next-generation approaches propose the incorporation of one or more physical phenomena (*e.g.*, multiple transitions, multiple electron-hole pair generation, and hot carriers) to reach high-efficiencies. In Section 5, the author offers concluding remarks.

2. Ideal p - n junction solar cell

In Figure 1, the present author illustrates the ideal electronic structure of a photovoltaic solar cell (Würfel, 2002; Würfel, 2004), a device that converts the energy of radiation into electrical energy. The ideal structure of the solar cell is comprised of several components: an absorber, two emitters and two contacts. The absorber enables photo-chemical conversion, the emitters enable electro-chemical conversion, and the contacts enable useful work to be performed by an external load. In the following paragraphs, the present author describes an ideal solar cell in more detail.

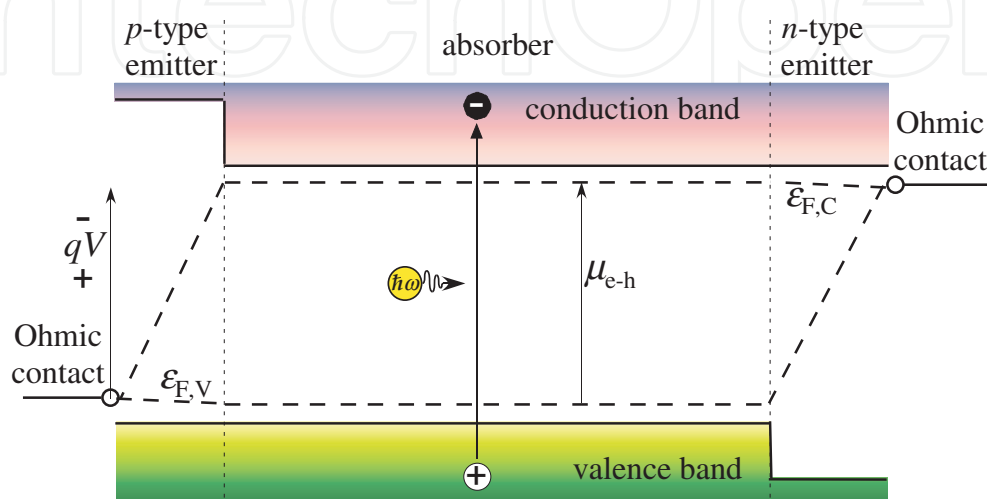


Fig. 1. Ideal structure of a solar cell. Shown is the absorber, which is sandwiched between an n -type emitter and a p -type emitter. An Ohmic contact is made to each of the emitters. A voltage, V , exists between the contacts of the solar cell.

An absorber is in the center of the solar cell. The absorber is a medium whose electronic states form a conduction band and a valence band. The conduction and valence bands are separated by an energetic gap that is characterized by the absence of electronic states. The occupancy of the electronic states of the conduction band and valence band are described by the quasi-Fermi energies $\varepsilon_{F,C}$ and $\varepsilon_{F,V}$, respectively. The absorber is the region of the solar cell where the absorption of photons occurs and where the subsequent photogeneration of electrons and holes takes place. Ideally, each photon with energy greater than that of the energetic gap may generate a single electron-hole pair. In such case, the energy of each photon with energy greater than the bandgap is converted to the chemical energy of an electron-hole pair, μ_{e-h} , where $\mu_{e-h} = \varepsilon_{F,C} - \varepsilon_{F,V}$ (Würfel, 2002; Würfel, 2004).

The absorber is sandwiched between two semi-permeable emitters (Würfel, 2002; Würfel, 2004). The emitters are selected to produce an asymmetry in the band structure. The electronegativity and bandgap of the emitter on the right (*i.e.*, the n -type emitter) are selected so that the (i) electrons largely or completely permeate through and (ii) holes largely or completely do not (Würfel, 2002; Würfel, 2004). A small gradient drives the majority carriers (*i.e.*, holes) to the right so that a beneficial current is produced. A large gradient drives minority carriers (*i.e.*, electrons) to the right so that a detrimental current is produced. The latter current is very small, resulting from the relative impermeability of the rightmost emitter to electrons. The emitter on the left is similarly selected, except that it is the holes that permeate through and yield a beneficial current.

On the external surface of both emitters is a metallic contact. The carriers in the contacts are in equilibrium with one another, so where the contact interfaces with the emitter the occupancy of holes and electrons are described by the same Fermi energy. The absolute value of the Fermi energy at the contact of the n -type emitter is roughly equal to the absolute value of the quasi-Fermi energy of majority carriers at the interface between the absorber interfaces with the n -type emitter. An analog of this statement holds for the contact to the p -type emitter. Thus, between the two contacts there is a voltage, V , that is proportional to the potential difference $\varepsilon_{FC} - \varepsilon_{FV}$ as $V = (\varepsilon_{FC} - \varepsilon_{FV}) / q$, where q is the elementary charge. Therefore, the chemical energy of each electron-hole pair, μ_{e-h} , is converted to electrical energy by a unit pulse of charge current, q , at the voltage V . In the following subsection, the present author reviews various limits describing the efficiency of solar-energy conversion.

3. Limits to ideal solar-energy conversion

In this section, the present author reviews three distinct approaches to upper-bound the efficiency of solar-energy conversion. In Section 3.1, the present author offers a schematic of a generalized converter and uses the schematic to define the conversion efficiency. In sections 3.2, 3.3, and 3.4, the present author reviews the Landsberg-Tonge limit, the Shockley-Queisser limit, and the omni-colour limit, respectively. In Section 3.5, the present author compares and contrasts these three approaches. Finally, in Section 3.6, the present author draws conclusions regarding the upper-theoretical efficiency of converting solar energy to electricity in the terrestrial environment. The present author concludes that though the efficiency limit of a single p - n junction solar cell is large, a significant efficiency enhancement is possible. This is because, in the first approximation, the terrestrial limits of a single p - n junction solar cell are 40.7% and 24.0%, whereas those of an omni-colour converter are 86.8% and 52.9% for fully-concentrated and non-concentrated sunlight, respectively.

3.1 Generalized energy converter

Figure 2 is a schematic of a generalized energy converter (*c.f.* the converter in Landsberg & Tonge (1980)). The converter is pumped with a power flow, \dot{E}_p , and a rate of entropy flow, \dot{S}_p . Analogously, the converter, which maintains a temperature T_c , sinks a power flow, \dot{E}_s , and a rate of entropy flow, \dot{S}_s . Meanwhile, a rate of useable work, \dot{W} , is delivered and a rate of heat flow, \dot{Q} , is transmitted to the ambient. Internally, the converter experiences a rate change of energy, \dot{E} , and a rate change of entropy, \dot{S} . In addition, the converter, by its own internal processes, generates a rate of entropy, \dot{S}_g .

The first-law conversion efficiency, η , is defined as the ratio of the useable power over the energy flow pumped into the converter, so that (Landsberg & Tonge, 1980)

$$\eta \doteq \frac{\dot{W}}{\dot{E}_p}. \quad (1)$$

Typically, in the science of solar-energy conversion, no more than two radiation flows pump the converter (see Figure 3). Always present is a direct source of radiation from the sun, which is assumed a black body with a surface temperature T_s , yielding an energy flux, $\dot{U}_{p,s}$. Sometimes present, depending on the geometric-concentration factor, C , is a diffuse source of radiation scattered from the Earth's atmosphere, which is assumed to be a black body with a surface temperature T_E , yielding an energy flux, $\dot{U}_{p,E}$. Considering the dilution factor of solar radiation, $D [2.16 \times 10^{-5}]$, which is linearly related to the solid angle subtended by the sun on

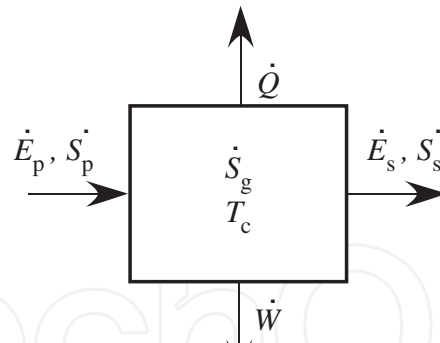


Fig. 2. Generalized schematic diagram of an energy converter. In the radiative limit, the energy flows pumped to and sunk by the converter (*i.e.* \dot{E}_p and \dot{E}_s) are limited to the radiant energy flux [$\text{J m}^{-2} \text{s}^{-1}$] pumped to and sunk by the converter: \dot{E}_p and \dot{E}_s , respectively.

the earth (Shockley & Queisser, 1961), and a geometric-concentration factor of solar energy, C , which may range between unity and $1/D$ (De Vos, 1992), the total energy flux impinging upon the converter, \dot{E}_p , is written with the Stefan-Boltzmann constant, σ [$5.67 \times 10^{-8} \text{ W/m}^2/\text{K}^4$], as

$$\dot{E}_p = \sigma \left[C D T_S^4 + (1 - C D) T_E^4 \right]. \quad (2)$$

Meanwhile, the quantification of the power density generated by the converter depends on the specific details of the converter. As this section only discusses a generalized converter, no further mathematical form of the power density is specified.

Calculating the performance measure by substituting the right-hand side of Equation (1) into the denominator of Equation (2) is different from the manner of calculating the performance measure as done in the detailed-balance work of many references (Bremner et al., n.d.; Brown & Green, 2002a;b; De Vos, 1980; 1992; De Vos & Desoete, 1998; Levy & Honsberg, 2006; Luque & Martí, 2001; Martí & Araújo, 1996; Shockley & Queisser, 1961; Werner, Brendel & Oueisser, 1994). In the latter references, though the particle flux impinging upon the solar cell is given in terms of the dual source, the performance measure is calculated with respect to the energy flux from the sun, $\dot{U}_{p,s}$. This distorts the performance measure of the device, resulting in efficiencies $\left[1 + \frac{1-CD}{CD} \left(\frac{T_E}{T_S} \right)^4 \right]$ times those obtained using the first-law efficiency (Levy & Honsberg, 2008a). . In the following subsection, the present author reviews an approach to upper bound the efficiency limit of converting solar energy to useful work.

3.2 Landsberg-Tonge limit

Landsberg and Tonge present thermodynamic efficiencies for the conversion of solar radiation into work (Landsberg & Tonge, 1980). The converter is pumped with all the radiation emitted from a black body, which maintains a surface temperature T_p . The converter is also given as a black body, however its temperature is maintained at T_c . The converter, therefore, sinks black-body radiation associated with this temperature. With the use of two balance equations, for energy and for entropy, Landsberg and Tonge derive the following inequality for the

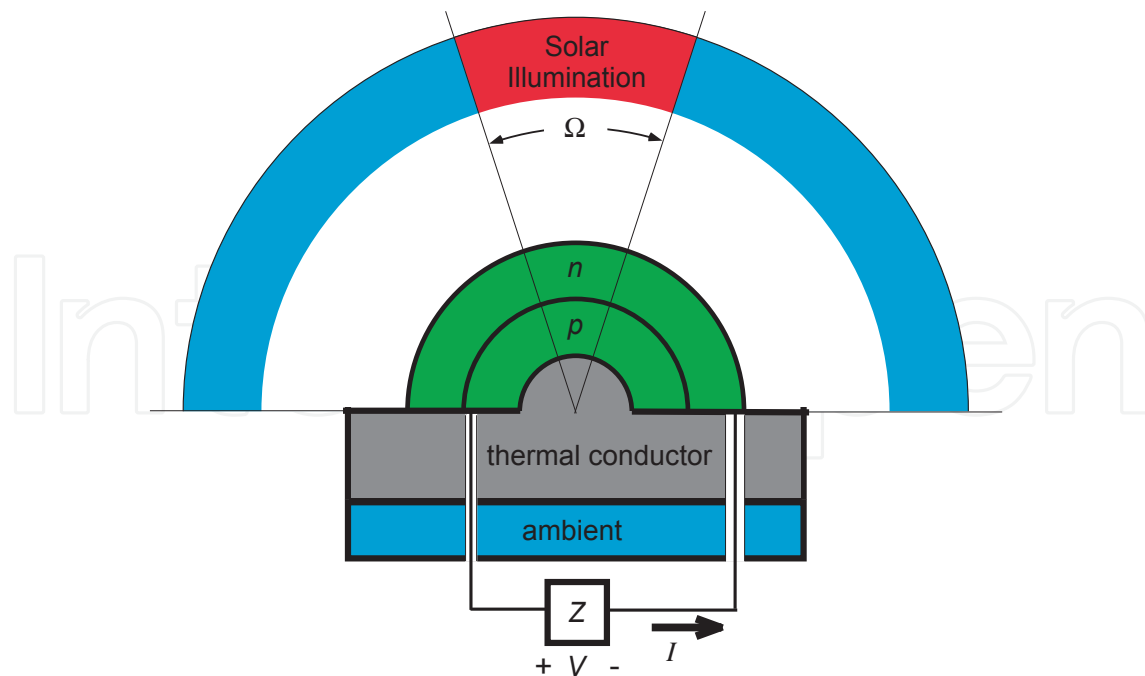


Fig. 3. Cross section of an abstracted p - n junction solar cell with spherical symmetry. The exaggerated physical symmetry reinforces the solar geometry, where a solid angle of the solar cell's surface, Ω , is subtended by direct insolation from the sun and the remainder of the hemisphere is subtended by diffuse radiation from the atmosphere. The solid angle may be adjusted by geometrical concentration of the sun's light. The solar cell is maintained at the ambient temperature, the surface terrestrial temperature, by a thermal conductor.

first-law efficiency:

$$\eta \leq 1 - \frac{4}{3} \frac{T_c}{T_p} + \frac{1}{3} \left(\frac{T_c}{T_p} \right)^4. \quad (3)$$

In arriving at the above inequality, Landsberg and Tonge assume steady-state conditions. Equality holds for the special case where there is no internal entropy generation (*i.e.* $\dot{S}_g = 0$). The resulting equality is first derived by Patela by considering the exergy of heat radiation (Petela, 1964). The Landsberg-Tonge limit may be extended so as to model the dual sources of the solar geometry (Würfel, 2002). In the case of two black-body sources simultaneously pumping the converter, a derivation similar to that of Landsberg and Tonge yields a first-law efficiency given as

$$\eta \leq \frac{(CD) \left(T_S^4 - \frac{4}{3} T_c T_S^3 + \frac{1}{3} T_c^4 \right) + (1 - CD) \left(T_E^4 - \frac{4}{3} T_c T_E^3 + \frac{1}{3} T_c^4 \right)}{(CD) T_S^4 + (1 - CD) T_E^4}. \quad (4)$$

Figure 4 illustrates the Landsberg-Tonge efficiency limit. In Section 3.3, the detailed-balance method of Shockley and Queisser is presented and applied to a single p - n junction solar cell.

3.3 Shockley-Queisser limit

Shockley and Queisser present a framework to analyze the efficiency limit of solar-energy conversion by a single p - n junction (Shockley & Queisser, 1961). They name this limit the detailed-balance limit for it is derived from the notion that, in principle, all recombination

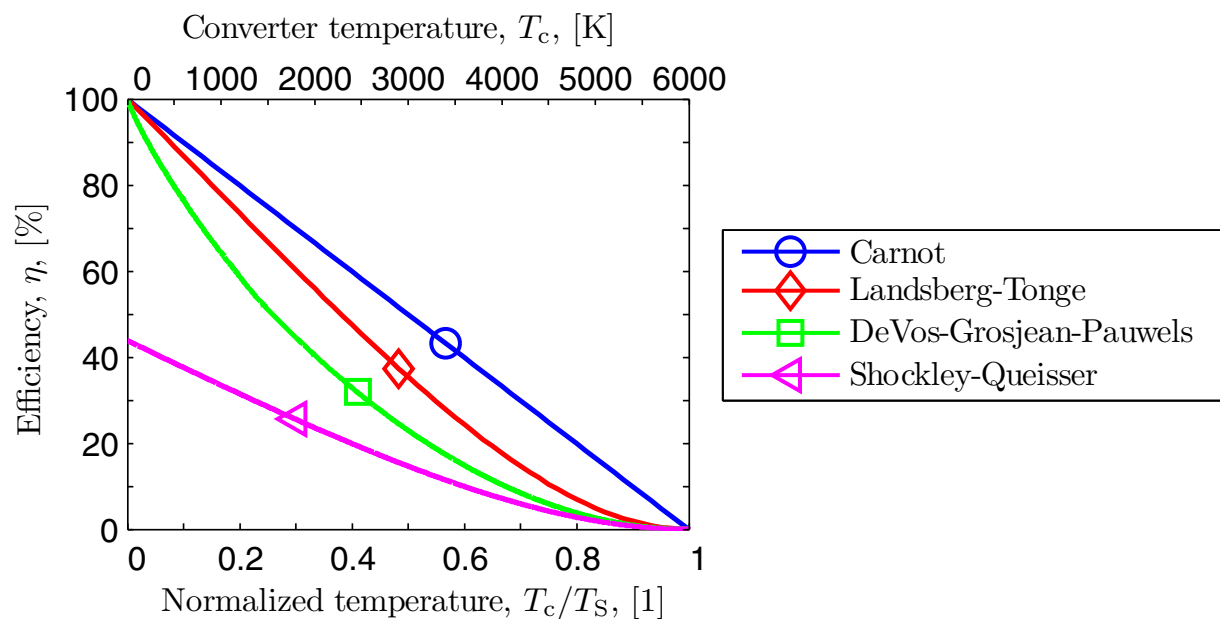


Fig. 4. Efficiency limits of ideal solar-energy converters as a function of the ratio of the converter's temperature, T_c , to the pump's temperature, T_s . Shown are the Landsberg-Tonge closed-form efficiencies of the radiation-in-radiation-out converter, the DeVos-Grosjean-Pauwels analytic efficiencies of the omni-colour converter, and the Shockley-Queisser numerical efficiencies of the p - n junction converter. All efficiencies are for fully-concentrated solar irradiance. As a visual aid, the Carnot efficiencies are presented.

processes may be limited to photo-induced processes and balanced by photo-induced generation processes. Their *ab initio* limit – as opposed to a semi-empirical limit based on factors such as measured carrier lifetimes – represents an upper-theoretical limit above which a single p - n junction solar cell may not perform. In addition, it is a reference for experimental measurements of single-junction solar cells in terms of future potential.

In their framework, Shockley and Queisser identify several factors that may degrade the efficiency of energy conversion and ideally allow that the degrading factors are perfectly mitigated. Therefore, in the detailed balance limit it is permissible that:

- the fractions of recombination and generation events that are coupled to radiative processes are both unity,
- the probability that incident photons with energy greater than or equal to the semiconductors band-gap are transmitted into the solar cell is unity,
- the probability with which a transmitted photon creates an electron-hole pair is unity,
- the probability that an electron-hole pair yields a charge current pulse through an external load is unity, and,
- the fraction of solid angle subtended by the sun may be unity- *i.e.*, the sun's radiation is completely concentrated onto the solar cell (see Figure 3 on page 5).

Figure 4 illustrates the upper-efficiency limit of solar-energy conversion by a single p - n solar cell. The Shockley-Queisser model predicts that the the upper limiting efficiency of a p - n junction solar cell is 44%. This efficiency limit is valid only when the solar cell's temperature is held to absolute zero. In Section 3.4, the omni-colour limit is presented.

3.4 Omni-colour limit

In principle, the detailed-balance method may be applied to omni-colour converters (De Vos, 1980; 1992; De Vos et al., 1982). The omni-colour limit may be derived in terms of either photovoltaic processes (Araújo & Martí, 1994; De Vos, 1980; 1992; De Vos et al., 1982; Würfel, 2004), photothermal processes (De Vos, 1992), or hybrids thereof (De Vos, 1992; Luque & Martí, 1999). In either case, as the number of layers in a stack of photovoltaic converters (Alvi et al., 1976; De Vos, 1992; Jackson, 1955; Loferski, 1976; Wolf, 1960) or in a stack of photothermal converters (De Vos, 1992; De Vos & Vyncke, 1984) approach infinity, the solar-energy conversion efficiencies approach the same limit (De Vos, 1980; 1992; De Vos & Vyncke, 1984) – the omni-colour limit. Figure 4 illustrates the upper-efficiency limit of omni-colour solar-energy conversion. In Section 3.5, the present author compares and contrasts the efficiency limits that are heretofore reviewed.

3.5 Comparative analysis

In Section 3.2 through Section 3.4, the present author reviews several approaches that quantify the efficiency limits of solar-energy conversion. The aforementioned limits are now compared and contrasted.

All of the limits reviewed in this Section 3 have in common an efficiency limit of zero when the converter's temperature is that of the pump. In addition, several of the limits approach the Carnot limit for the special case where the converter's temperature is absolute zero. These include the Landsberg-Tonge limit and the De Vos-Grosjean-Pauwels limit. At absolute zero the Shockley-Queisser limit is substantially lower (44%) than the Carnot limit. It is interesting to note that the Landsberg-Tonge limit (see Equation 4 on page 5) and the omni-colour limit (De Vos, 1980) both approach unity for regardless of the geometric-concentration factor of solar irradiance.

The large differences between the Shockley-Queisser limit and the other limits are attributed to the relationship between the energetic gap of the semiconductor comprising the p - n junction and the range of photon energies comprising the broadband spectrum of black-body radiation. Sub-bandgap photons do not yield a photovoltaic effect and so do not participate in generating charge current. Meanwhile, the conversion of each supra-bandgap photon uniformly generates a single electron-hole pair at a voltage limited by the bandgap. Therefore, the portion of each supra-bandgap photon's energy in excess of the bandgap does not contribute to useful work. By using an omni-colour converter, the efficiency degradation caused by the relationship between the energetic gap of the semiconductors comprising the tandem stack and the broadband nature of the solar spectrum are eliminated. Therefore, the difference between the De Vos-Grosjean-Pauwels limit and the Landsberg-Tonge limit is attributed to the generation of internal irreversible entropy. Except for the two temperature extremes aforementioned, each layer of the omni-colour converter generates a rate of irreversible entropy resulting from its internal processes. This is so even though each layer of the omni-colour converter operates at its maximum-power point and converts monochromatic light (Würfel, 2004).

As illustrated by the present author in Figure 4, the efficiency limits reviewed heretofore may be given in descending order as Carnot, Landsberg-Tonge, De Vos-Grosjean-Pauwels, and Shockley-Queisser. Photovoltaic converters may not exceed the De Vos-Grosjean-Pauwels limit for their internal processes are associated with a rate of irreversible internal entropy generation (Markvart, 2007; Würfel, 1982). In Section 3.6, the present author concludes these findings by describing limits to the conversion of solar energy in the terrestrial environment.

3.6 Terrestrial conversion limits

Table 1 lists the upper-efficiency limits of the terrestrial conversion of solar energy. As is convention in the science of solar-energy conversion, all efficiencies are calculated for a surface solar temperature of 6000 K, a surface terrestrial temperature of 300 K, and a converter maintained at the surface terrestrial temperature. In addition, the geometric dilution factor is taken as 2.16×10^{-5} (De Vos, 1992). For each type of converter listed, the upper-efficiency limit is given for fully-concentrated sunlight and, in some cases, for non-concentrated sunlight. The values listed depend only on the sun's surface temperature, the earth's surface temperature, and the geometric-concentration factor, as opposed to consideration regarding the air mass of the Earth and other secondary phenomena. The present author concludes that though the upper-efficiency limit of a single p - n junction solar cell is large, a significant efficiency enhancement is possible. This is true because the terrestrial limits of a single p - n junction solar cell is 40.7% and 24.0%, whereas the terrestrial limits of an omni-colour converter is 86.8% and 52.9% for fully-concentrated and non-concentrated sunlight, respectively. In Section 4, the present author defines the notion of high-efficiency approaches to solar-energy conversion and briefly reviews various proposed high-efficiency approaches.

4. High-efficiency approaches

In this section, Section 4, the present author reviews several distinct approaches for high-efficiency solar cells. In Section 4.1, the present author defines "high-efficiency" in terms of the upper-conversion efficiencies of the Shockley-Queisser model and the De Vos-Grosjean-Pauwels model. In Section 4.2, the present author reviews the current technological paradigm to realize high-efficiency solar cells: stacks of single p - n junction solar cells operating in tandem. In sections 4.3, 4.4, and 4.5, the present author reviews three next-generation approaches to realize high-efficiency solar cells: the carrier-multiplication solar cell, the hot-carrier solar cell, and the multiple-transition solar cell, respectively. Finally, in Section 4.6, the present author draws conclusions regarding the justification for researching and developing next-generation approaches. Though stacks of single p - n junction solar cells operating in tandem are the only high-efficiency approach with demonstrated high-efficiency performance, the present author concludes that development on a next-generation solar cell is justified in that a (i) next-generation solar cells offer a global-efficiency enhancement in themselves and (i) also per layer if incorporated in a stack of solar cells operating in tandem. Immediately below in Section 4.1, the present author defines what is meant by high-efficiency performance.

4.1 Global efficiency enhancement

There are several proposals for high-efficiency solar cells. In this chapter, similar to Anderson in his discussion of the efficiency enhancements in quantum-well solar cells (Anderson, 2002), the present author defines high-efficiency in terms of a global efficiency enhancement. Shown in Figure 5 are the upper-efficiency conversion limits of the single-junction solar cell and the omni-colour solar cell. In Figure 5, the upper-efficiency conversion limits are given as a function of the geometric-concentration factor, C . The present author defines "high efficiency" in terms of the numerical data given in Figure 5. The present author asserts that, for any and all geometric concentration factor, a proposal for high-efficiency solar cell must, when optimized, offer an efficiency greater than that of an optimized Shockley-Queisser solar cell at that same geometric-concentration factor. For example, according to the present author's definition, under non-concentrated sunlight a high-efficiency proposal, when optimized,

Converter	$\eta _{\text{Ter}}, [\%]$	
	$C = 1/D$	$C = 1$
Carnot	95.0	95.0
Landsberg-Tonge	93.3 ^a	72.4 ^b
De Vos-Grosjean-Pauwels	86.8 ^c	52.9 ^d
Shockley-Queisser	40.7 ^e	24.0 ^f

[†] Listed values are first-law efficiencies that are calculated by including the energy flow absorbed due to direct solar radiation and the energy flow due to diffuse atmospheric radiation. The listed values are likely to be less than what are previously recorded in the literature. See Section 3.1 on page 3 for a more comprehensive discussion.

^a Calculated from Equation (3) on page 5.

^b Calculated from Equation (4) on page 5.

^c Obtained from reference (De Vos, 1980) and reference (Würfel, 2004).

^d Adjusted from the value 68.2% recorded in reference (De Vos, 1980) and independently calculated by the present author.

^e Obtained from reference (Bremner et al., n.d.).

^f Adjusted from the value 31.0% recorded in reference (Martí & Araújo, 1996).

Table 1. Upper-efficiency limits of the terrestrial conversion of solar energy, $\eta|_{\text{Ter}}$. All efficiencies calculated for a surface solar temperature of 6000 K, a surface terrestrial temperature of 300 K, a solar cell maintained at the surface terrestrial temperature, a geometric dilution factor, D , of 2.16×10^{-5} , and a geometric-concentration factor, C , that is either 1 (non-concentrated sunlight) or $1/D$ (fully-concentrated sunlight).

must have an upper-efficiency limit greater than 24.0%. Clearly, for physical consistency, the optimized theoretical performance of the high-efficiency proposal must be less than that of the omni-colour solar cell at that geometric concentration factor. Furthermore, the present author asserts that any fabricated solar cell that claims to be a high-efficiency solar cell must demonstrate a global efficiency enhancement with respect to an optimized Shockley-Queisser solar cell. For example, to substantiate a claim of high-efficiency, a solar cell maintained at the terrestrial surface temperature and under a geometric concentration of 240 suns must demonstrate an efficiency greater than 35.7% – the efficiency of an optimized Shockley-Queisser solar cell operating under those conditions. Before moving on to Section 4.2, where the present author reviews the tandem solar cell, the reader is encouraged to view the high-efficiency regime as illustrated in Figure 5. The reader will note that there is a significant efficiency enhancement that is scientifically plausible.

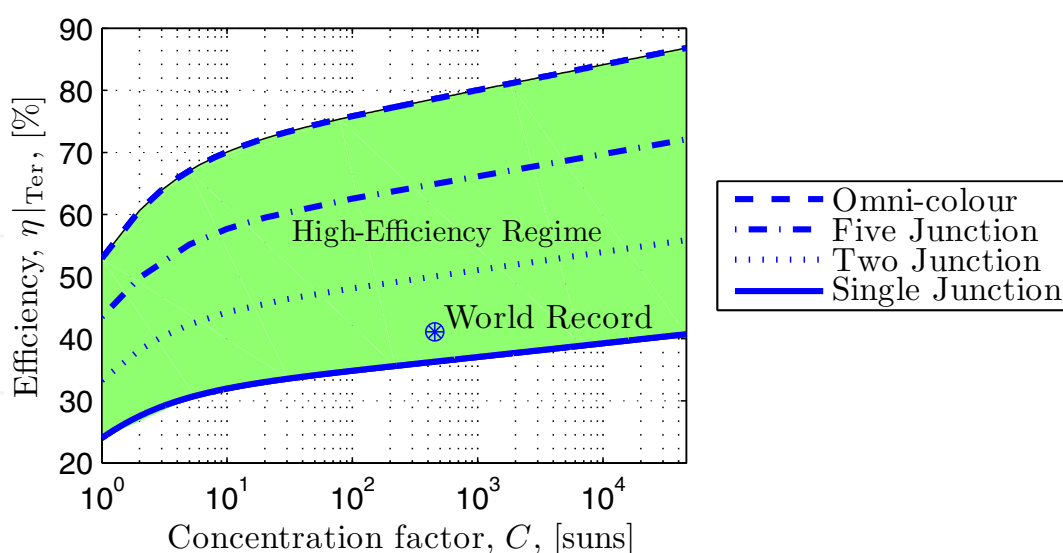


Fig. 5. The region of high-efficiency solar-energy conversion as a function of the geometric-concentration factor. The high-efficiency region (shaded) is defined as that region offering a global-efficiency enhancement with respect to the maximum single-junction efficiencies (lower edge) and the maximum omni-colour efficiencies (upper edge). The efficiency required to demonstrate a global efficiency enhancement varies as a function of the geometric-concentration factor. For illustrative purposes, the terrestrial efficiencies (see Table 2) of a two-stack tandem solar cell and a five-stack tandem solar cell are given. Finally, for illustrative purposes, the present world-record solar cell efficiency is given (*i.e.*, 41.1% under a concentration of 454 suns (Guter et al., 2009)).

4.2 Tandem solar cell

The utilization of a stack of p - n junction solar cells operating in tandem is proposed to exceed the performance of one p - n junction solar cell operating alone (Jackson, 1955). The upper-efficiency limits for N -stack tandems ($1 \leq N \leq 8$) are recorded in Table 2 on page 11. As the number of solar cells operating in a tandem stack increases to infinity, the upper-limiting efficiency of the stack increases to the upper-limiting efficiency of the omni-colour solar cell (De Vos, 1980; 1992; De Vos & Vyncke, 1984). This is explained in Section 3.4 on page 7. In practice, solar cells may be integrated into a tandem stack via a vertical architecture or a lateral architecture. An example of a vertical architecture is a monolithic solar cell. Until now, the largest demonstrated efficiency of a monolithic solar cell – or for any solar cell – is the metamorphic solar-cell fabricated by Fraunhofer Institute for Solar Energy Systems (Guter et al., 2009). This tandem is a three-junction metamorphic solar cell and operates with a conversion efficiency of 41.1% under a concentration of 454 suns (Guter et al., 2009). An example of horizontal architectures are the solar cells of references (Barnett et al., 2006; Green & Ho-Baillie, 2010), which utilize spectral-beam splitters (Imenes & Mills, 2004) that direct the light onto their constituent solar cells. The present author now reviews the carrier-multiplication solar cell, the first of three next-generation proposals to be reviewed in this chapter.

4.3 Carrier-multiplication solar cell

Carrier-multiplication solar cells are theorized to exceed the Shockley-Queisser limit (De Vos & Desoete, 1998; Landsberg et al., 1993; Werner, Brendel & Oueisser,

Converter	$\eta _{\text{Ter}}, [\%]$	
	$C = 1/D$	$C = 1$
Infinite-Stack Tandem [*]	86.8 ^a	52.9 ^b
Eight-Stack Photovoltaic Tandem	77.63 ^c	46.12 ^e
Seven-Stack Photovoltaic Tandem	76.22 ^c	46.12 ^e
Six-Stack Photovoltaic Tandem	74.40 ^c	44.96 ^e
Five-Stack Photovoltaic Tandem	72.00 ^c	43.43 ^e
Four-Stack Photovoltaic Tandem	68.66 ^c	41.31 ^e
Three-Stack Photovoltaic Tandem	63.747 ^c	38.21 ^e
Two-Stack Photovoltaic Tandem	55.80 ^c	33.24 ^e
One-Stack Photovoltaic Solar Cell ^{**}	40.74 ^c	24.01 ^e

[†] Listed values are first-law efficiencies that are calculated by including the energy flow absorbed due to direct solar radiation and the energy flow due to diffuse atmospheric radiation. The listed values are likely to be less than what are previously recorded in the literature. See Section 3.1 on page 3 for a more comprehensive discussion.

^{*} Recorded values are identical to those of the omni-colour converter of Table 1 on page 9.

^{**} Recorded values are identical to those of the Shockley-Queisser converter of Table 1 on page 9.

^a Obtained from reference (De Vos, 1980) and independently calculated by the present author.

^b Adjusted from the value 68.2% recorded in reference (De Vos, 1980) and independently calculated by the present author.

^c Obtained from reference (Bremner et al., n.d.) and independently calculated by the present author.

^d Adjusted from the values recorded in reference (Martí & Araújo, 1996) and independently calculated by the present author.

^e Calculated independently by the present author. Values are not previously published in the literature.

Table 2. Upper-efficiency limits, $\eta|_{\text{Ter}}$, of the terrestrial conversion of stacks of single-transition single p - n junction solar cells operating in tandem. All efficiencies calculated for a surface solar temperature of 6000 K, a surface terrestrial temperature of 300 K, a solar cell maintained at the surface terrestrial temperature, a geometric dilution factor, D , of 2.16×10^{-5} , and a geometric-concentration factor, C , that is either 1 (non-concentrated sunlight) or $1/D$ (fully-concentrated sunlight).

1994; Werner, Kolodinski & Queisser, 1994), thus they may be correctly viewed as a high-efficiency approach. These solar cells produce an efficiency enhancement by generating more than one electron-hole pair per absorbed photon via

inverse-Auger processes (Werner, Kolodinski & Queisser, 1994) or via impact-ionization processes (Kolodinski et al., 1993; Landsberg et al., 1993). The efficiency enhancement is calculated by several authors (Landsberg et al., 1993; Werner, Brendel & Oueisser, 1994; Werner, Kolodinski & Queisser, 1994). Depending on the assumptions, the upper limit to terrestrial conversion of solar energy using the carrier-multiple solar cell is 85.4% (Werner, Brendel & Oueisser, 1994) or 85.9% (De Vos & Desoete, 1998). Though the carrier-multiple solar cell is close to the upper-efficiency limit of the De Vos-Grosjean-Pauwels solar cell, the latter is larger than the former because the former is a two-terminal device. The present author now reviews the hot-carrier solar cell, the second of three next-generation proposals to be reviewed in this chapter.

4.4 Hot-carrier solar cell

Hot-carrier solar cells are theorized to exceed the Shockley-Queisser limit (Markvart, 2007; Ross, 1982; Würfel et al., 2005), thus they may be correctly viewed as a high-efficiency approach. These solar cells generate one electron-hole pair per photon absorbed. In describing this solar cell, it is assumed that carriers in the conduction band may interact with themselves and thus equilibrate to the same chemical potential and same temperature (Markvart, 2007; Ross, 1982; Würfel et al., 2005). The same may be said about the carriers in the valence band (Markvart, 2007; Ross, 1982; Würfel et al., 2005). However, the carriers do not interact with phonons and thus are thermally insulated from the absorber. Resulting from a mono-energetic contact to the conduction band and a mono-energetic contact to the valence band, it may be shown that (i), the output voltage may be greater than the conduction-to-valence bandgap and that (ii) the temperature of the carriers in the absorber may be elevated with respect to the absorber. The efficiency enhancement is calculated by several authors (Markvart, 2007; Ross, 1982; Würfel et al., 2005). Depending on the assumptions, the upper-conversion efficiency of any hot-carrier solar cell is asserted to be 85% (Würfel, 2004) or 86% (Würfel et al., 2005). The present author now reviews the multiple-transition solar cell, the third of three next-generation proposals to be reviewed in this chapter.

4.5 Multiple-transition solar cell

The multi-transition solar cell is an approach that may offer an improvement to solar-energy conversion as compared to a single $p-n$ junction, single-transition solar cell (Wolf, 1960). The multi-transition solar cell utilizes energy levels that are situated at energies below the conduction band edge and above the valence band edge. The energy levels allow the absorption of a photon with energy less than that of the conduction-to-valence band gap. Wolf uses a semi-empirical approach to quantify the solar-energy conversion efficiency of a three-transition solar cell and a four-transition solar cell (Wolf, 1960). Wolf calculates an upper-efficiency limit of 51% for the three-transition solar cell and 65% four-transition solar cell (Wolf, 1960).

Subsequently, as opposed to the semi-empirical approach of Wolf, the detailed-balance approach is applied to multi-transition solar cells (Luque & Martí, 1997). The upper-efficiency limit of the three-transition solar cell is now established at 63.2 (Brown et al., 2002; Levy & Honsberg, 2008b; Luque & Martí, 1997). In addition, the upper-conversion efficiency limits of N -transition solar cells are examined (Brown & Green, 2002b; 2003). Depending on the assumptions, the upper-conversion efficiency of any multi-transition solar cell is asserted to be 77.2% (Brown & Green, 2002b) or 85.0% (Brown & Green, 2003). These upper-limits

justify the claim that the multiple-transition solar cell is a high-efficiency approach. Resulting from internal current constraints and voltage constraints, the upper-efficiency limit of the multi-transition solar cell is asserted to be less than that of the De Vos-Grosjean-Pauwels converter (Brown & Green, 2002b; 2003). That said, it has been shown (Levy & Honsberg, 2009) that the absorption characteristic of multiple-transition solar cells may lead to both incomplete absorption and absorption overlap (Cuadra et al., 2004). Either of these phenomena would significantly diminish the efficiencies of these solar cells.

4.6 Comparative analysis

In Section 4.1, the present author defined the high-efficiency regime of a solar cell. In Sections 4.2-4.5, the present author reviewed several approaches that are proposed to exceed the Shockley-Queisser limit and reach towards De Vos-Grosjean-Pauwels limit. Of all the approaches, only a stack of p - n junctions operating in tandem has experimentally demonstrated an efficiency greater than the Shockley-Queisser limit. The current world-record efficiency is 41.1% for a tandem solar cell operating at 454 suns (Guter et al., 2009). The significance of this is now more deeply explored.

The fact that the experimental efficiency of solar-energy conversion by a photovoltaic solar cell has surpassed Shockley-Queisser limit is a major scientific and technological accomplishment. This accomplishment demonstrates that the field of solar energy science and technology is no longer in its infancy. However, as may be seen from Figure 5 on page 10 there is still significant space for further maturation of this field. Foremost, the present world record is less than half of the terrestrial limit (86.8%). Reaching closer to the terrestrial limit will require designing solar cells that operate under significantly larger geometric concentration factors and designing tandem solar cells with more junctions. That said, there is significant room for improvement even with respect to the present technologic paradigm used to obtain the world record. The world-record experimental conversion efficiency of 41.1% is recorded for a solar cell composed of three-junctions operating in tandem under 454 suns. Yet, this experimental efficiency is fully 9 percentage points and 16 percentage points less than the theoretical upper limit of a solar cell composed of a two-junction tandem and three-junction tandem (i.e., 50.1%), respectively, operating in tandem at 454 suns (i.e., 50.1%) and 16 percentage points less than the theoretical upper limit of a solar cell composed of three-junctions (i.e., 57.2%) operating at 454 suns. The author now offers concluding remarks.

5. Conclusions

The author begins this chapter by reviewing the operation of an idealized single-transition, single p - n junction solar cell. The present author concludes that though the upper-efficiency limit of a single p - n junction solar cell is large, a significant efficiency enhancement is possible. This is so because the terrestrial limits of a single p - n junction solar cell is 40.7% and 24.0%, whereas the terrestrial limits of an omni-colour converter is 86.8% and 52.9% for fully-concentrated and non-concentrated sunlight, respectively. There are several high-efficiency approaches proposed to bridge the gap between the single-junction limit and the omni-colour limit. Only the current technological paradigm of stacks of single p - n junctions operating in tandem experimentally demonstrates efficiencies with a global efficiency enhancement. The fact that any solar cells operates with an efficiency greater than the Shockley-Queisser limit is a major scientific and technological accomplishment, which demonstrates that the field of solar energy science and technology is no longer in its infancy. That being said, the differences between the present technological record (41.1%) and

sound physical models indicates significant room to continue to enhance the performance of solar-energy conversion.

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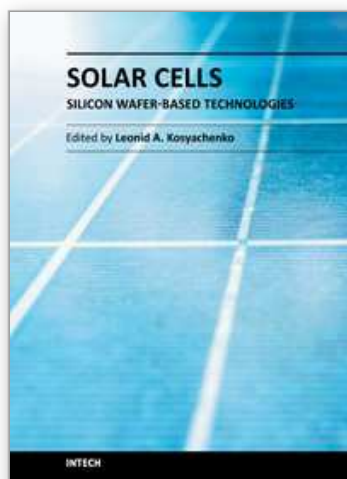
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