

# Assessing Possibilities and Limits for Solar Cells

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What are the solar cell efficiencies that we can strive towards? We show here that several simple criteria, based on cell and module performance data, serve to evaluate and compare all types of today's solar cells. Analyzing these data allows to gauge in how far significant progress can be expected for the various cell types and, most importantly from both the science and technology points of view, if basic bounds, beyond those known today, may exist, that can limit such progress. This is important, because half a century after Shockley and Queisser (SQ) presented limits, based on detailed balance calculations for single absorber solar cells, those are still held to be the only ones, we need to consider; most efforts to go beyond SQ are directed towards attempts to circumvent them, primarily via smart optics, or optoelectronics. After formulating the criteria and analyzing known loss mechanisms, use of such criteria suggests—additional limits for newer types of cells, Organic and Dye-Sensitized ones, and their siblings,—prospects for progress and—further characterization needs, all of which should help focusing research and predictions for the future.

## 1. Introduction

What are the limits for photovoltaic (PV) energy conversion? Shockley and Queisser (SQ)<sup>[1]</sup> formulated fundamental limits from a detailed balance (radiation in/radiation out) analysis for PV conversion with one absorber (see ref. [2] for an intuitive, thermodynamic photosynthetic conversion efficiency estimate), without manipulation of the incident solar spectrum, such as concentration or wavelength shifting, or possible use of non-linear optical or electronic effects.<sup>[3]</sup> SQ provides presently the only limit, soundly based on our understanding of the physics and thermodynamics of the PV cells. Great attempts have and are made to find practical ways for light/photon manipulations to go beyond the SQ limits.<sup>[4]</sup> The enormous efforts in PV research and development justify, though, to consider also the possible existence of limitations, in addition to the SQ one.<sup>[5]</sup> Finding such limits should stimulate work to see if they can be circumvented and in how far

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they present basic scientific bounds, so as to focus efforts on possible routes for progress in different solar cell types.

Here we look for, and identify some such possible bounds from summaries and analyses of the experimental performance data, obtained on the various solar cell types. To this end we define several criteria, viz., the ratio of:

-a- efficiency of the best commercially available module to that of the best laboratory cell,  $\eta_{CM}/\eta_{LC}$ , indicating possible industrial/scale-up limits;

-b- short circuit current,  $J_{SC}$ , of the laboratory cell with the highest reported efficiency, to the maximal theoretical possible current for this cell,  $J_{SC}^{MAX}$ , using the absorber's optical absorption edge,  $E_G^{[6-9]}$ , and assuming 1 electron/absorbed photon, and of this cell's current at maximal power (MP),  $J_{MP}$ , to  $J_{SC}^{MAX}$ , where  $J_{SC}^{MAX} = q \int_{\lambda=0}^{\lambda=E_G} \phi(\lambda) d\lambda$  (with  $q$  the elementary charge,  $\lambda$  the wavelength, and  $\phi$

the photon flux); these ratios are  $J_{SC}/J_{SC}^{MAX}$  and  $J_{MP}/J_{SC}^{MAX}$ ;

-c- open circuit voltage,  $V_{OC}$ , of the laboratory cell with the highest reported efficiency, to the voltage corresponding to the bandgap or effective optical absorption edge energy of the cell's absorber,  $E_G/q$ , and of the voltage at MP of this cell,  $V_{MP}$ , to  $E_G/q$ ,  $qV_{OC}/E_G$  and  $qV_{MP}/E_G$ ; the last ratio also yields  $(E_G - qV_{MP})$ , the cell's energy loss;

The total absorbed energy, after photogeneration of carriers, for a given cell with is  $E_G/q \cdot J_{SC}^{MAX}$ . Hence the internal efficiency for absorbed solar to electrical power can be given by  $\eta = [V_{MP} \cdot J_{MP}] / [(E_G/q) \cdot J_{SC}^{MAX}]$ .<sup>[10]</sup> Ideally,  $V_{MP}$  is determined by  $V_{OC}$  (which depends on  $E_G$ ) and the diode quality factor.<sup>[11]</sup>  $J_{MP}$  is ideally governed by  $J_{SC}^{MAX}$  and the diode quality factor. Hence, comparing the ratios  $J_{MP}/J_{SC}^{MAX}$  and  $qV_{MP}/E_G$  for various solar cell types (with a range of  $E_G$ ) can point to underlying differences between cell types and practical limitations to a given type of cell. An additional ratio that has been used at times, is that of (best laboratory cell efficiency)/(Shockley-Queisser efficiency),  $\eta_{LC}/\eta_{SQ}$ .<sup>[12]</sup> Comparing actual results to SQ (detailed balance) calculations reflects not only research ability but may also indicate the existence of additional limits that may affect industrial promise.

## 2. Results and Discussion

Tables 1, 2, and 3 give the numerical values for criteria -a-, -b- and -c-. Figures 1 and 2 illustrate the use of criteria -b- and -c-.

**Table 1.** Comparison of PV conversion efficiency values of best commercial modules and best single cell conversion efficiencies. Data taken from refs. [7,8] and manufacturers' information.

Technology (area if <600 cm <sup>2</sup> )	Efficiency [%] rated/minimum	Manufacturer	$\eta_{CM}/\eta_{LC}$ best commercial module/best cell efficiency
Single-crystal Si non-standard junction	19.3/?	SunPower	0.77
Single-crystal Si HIP junction	17.1/15.9	Sanyo	0.74
Multi crystal Si standard junction	14.7/12.6	Q-Cells	0.72
EFG(ribbon) Si standard junction	13.4/12.7	Evergreen	0.75
CIGS	12.0/9.3	Q-Cells (Solibro)	0.61
CIGS	11.9/9.2	AVANCIS	0.61
CdTe	11.1/9.7	First Solar	0.66
a-Si:H single junction <sup>a)</sup>	6.3/?	Kaneka	0.62
a-Si:H, triple junction <sup>a)</sup>	6.7/6.3	Uni-Solar	0.54
Dye (225)	5 <sup>b)</sup>	3GSolar	0.46
Organic polymer	1.7	Konarka	0.20
Organic polymer (225)	3.9 <sup>b)</sup>	Solarmer	0.24

<sup>a)</sup>Stabilized values; <sup>b)</sup>Pilot modules; no stability information yet; not yet commercially available.

**Table 2.** Comparison of actual SC, MP and maximum possible currents for various solar cell types. Data from refs. [7,8] and references therein, unless noted otherwise.

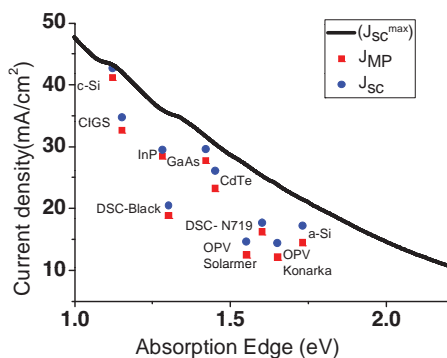
Cell type (absorber)	RT bandgap/abs. edge [eV]	$J_{MP}^a)$ [mA/cm <sup>2</sup> ]	$J_{SC}^{MAX}$	$J_{MP}/J_{SC}^{MAX}$ [%]	$J_{SC}^a)$ [mA/cm <sup>2</sup> ]	$J_{SC}/J_{SC}^{MAX}$ [%]
sc-Si (c-Si)	1.12	41.2	43.3	95	42.7	99
GaAs	1.42	27.8 <sup>b)</sup>	31.7	88	29.6	93
InP	1.28	28.5	36.0	79	29.5	82
CdTe	1.45	23.3	30.5	76	26.1	86
Cu(In <sub>0.7</sub> Ga <sub>0.3</sub> )Se (CIGS)	~1.15 <sup>c)</sup>	32.7	42.1	~78	34.8	~83
a-Si:H (a-Si) <sup>d)</sup>	~1.73	14.5	21.5	~67	17.28	~80
DSSC (black dye) <sup>e)</sup>	~1.3 <sup>g)</sup>	18.9	35.4	~53	20.5	~58
(red N719) <sup>f)</sup>	~1.6 <sup>h)</sup>	16.3	25.3	~64	17.7	~70
Org. polymer (P3HT-PCBM-like)						
Solarmer	~1.55 <sup>c)</sup>	12.5 <sup>b)</sup>	27	~46	14.7	~54
Konarka	~1.65 <sup>c)</sup>	12.2 <sup>b)</sup>	23.9	~51	14.5	~61

<sup>a)</sup>for best performing cell; <sup>b)</sup>based on our estimates; see ref. [54]; <sup>c)</sup>no published optical absorption data available; value from EQE onset; <sup>d),e),f)</sup>Efficiencies are comparable to those from ref. [7] (for a-Si:H<sup>[55]</sup> and the black dye<sup>[56]</sup> entries), but now with all the data, relevant for our analyses. N719 data are from<sup>[57]</sup>; <sup>g)</sup>Absorption onset of "black dye"[tri(cyanato)-2,2'-terpyridyl-4,4'-tricarboxylate] Ru(II) on TiO<sub>2</sub> is 950 nm (1.30 eV); cf. ref. [58]; <sup>h)</sup>The 1.6 eV absorption onset of N719 dye (di-tetrabutylammonium cis-bis(isothio-cyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)Ru(II) on TiO<sub>2</sub> is from ref.[45].

**Table 3.** Comparison of reported OC and MP voltages for cells with best conversion efficiencies, to the optical bandgap/absorption edge of the cell's lowest energy absorber. Data from ref. [7,8] and references therein, unless noted otherwise.

Cell type(absorber)	Room temp. bandgap/ abs. edge [eV]	$qV_{OC}^a)$ [eV]	$qV_{OC}/E_G$ [%]	$qV_{MP}^a)$ [eV]	Energy loss ( $E_G - qV_{MP}$ ) [eV]	$qV_{MP}/E_G$ [%]
sc-Si (c-Si)	1.12	0.71	63	0.61	0.51	54
GaAs	1.42	1.11	78	0.99 <sup>b)</sup>	0.43	70
InP	1.28	0.88	69	0.75	0.53	59
CdTe	1.45	0.84	58	0.71	0.74	49
Cu(In <sub>0.7</sub> Ga <sub>0.3</sub> )Se (CIGS)	~1.15 <sup>c)</sup>	0.72	~62	0.60	~0.55	~52
a-Si:H (a-Si) <sup>d)</sup>	~1.73	0.88	~51	0.70	~1.03	~40
DSSC (black dye) <sup>e)</sup>	~1.3 <sup>g)</sup>	0.71	~55	0.55	~0.75	~42
(red N719) <sup>f)</sup>	~1.6 <sup>h)</sup>	0.85	~53	0.69	~0.91	~43
Org. polymer (P3HT-PCBM-like)						
Solarmer	~1.55 <sup>c)</sup>	0.76	~49	0.63 <sup>b)</sup>	~0.92	~41
Konarka	~1.65 <sup>c)</sup>	0.82	~49	0.68 <sup>b)</sup>	~0.97	~41
Photosynthesis (PS)→ fuel	~1.8		–	(0.75)	1.05 <sup>i)</sup>	(42)

<sup>a)-h)</sup>See Table 2; <sup>i)</sup>from ref. [26]



**Figure 1.** Maximal possible vs. experimental photocurrents at short circuit (SC) and maximal power (MP) for best solar cells at AM 1.5. Labels in the figure correspond to the left-most column in Table 2. DSC: Dye-sensitized cell. OPV: Organic photo voltaic (cell).

### 2.1. Scale-up Limits

$\eta_{CM}/\eta_{LC}$  (Table 1) reflects manufacturing maturity of a cell type into *modules*. The reasoning is that the basic science, underlying PV conversion by a given cell, will not change from cell to module. The significantly higher CdTe than CIGS values, and the single than multi-junction a-Si:H ones, can be taken to reflect more progress on the industrial learning curve. The low dye-sensitized (DS) and organic cells values and the high ones for c-Si cell types represent extreme cases, with the latter showing what we can hope to achieve with the former.

### 2.2. Limits of current efficiency

Data for  $J_{SC}/J_{SC}^{MAX}$  and  $J_{MP}/J_{SC}^{MAX}$  are shown in Table 2. Compiling  $J_{SC}/J_{SC}^{MAX}$  data show that most developed cells achieve close to theoretical limits of current efficiency. For cells made with inorganic electronic materials the ratio is 80–99%, a value that decreases with decreasing degree of atomic order of the materials, responsible for the cell's PV activity. Figure 1 gives a visual summary of these data, by introducing them in a plot of  $J_{SC}^{MAX}$  as function of  $E_G$ .

$J_{MP}/J_{SC}^{MAX}$  values show a difference between the single crystal, polycrystalline and other solar cells, similar to that for  $\eta_{CM}/\eta_{LC}$ , which now, though, can be taken to indicate progress of *cell* development. The single crystal Si value is remarkably high, also considering its indirect bandgap. The lower values for GaAs and esp. for InP probably reflect the lower development level of single junction III-V cells. There is a clear difference between the two current ratios for the crystalline and CIGS cells and the a-Si:H one, with the CdTe one intermediate, reflecting the lower collection efficiencies of the last two cells. For a-Si:H this can be explained by the low mobility in the amorphous material, while for CdTe it reflects probably losses at grain boundaries (GB), due to its GB chemistry and physics<sup>[13]</sup> (see also below).

#### 2.2.1. Organic and DS Cells

Organic and DS cells give values, significantly lower than those for other cells, which begs the question if this reflects a mere

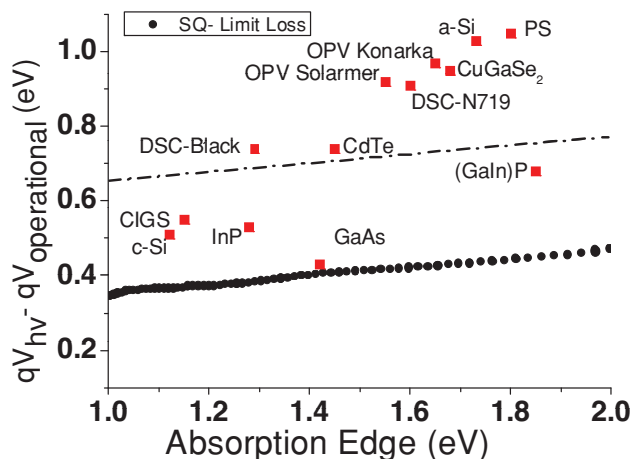
development lag or basic reasons, considering that both these cell types are studied for several decades. The lower values for the organic cells than for a-Si:H suggest the reason cannot only be lack of structural order.

Organic PV cells differ from their inorganic counterparts in several ways. Differences in the charge separation step<sup>[14,15]</sup> are especially relevant for their current collection efficiency. The excitons (electrically neutral, bound electron-hole pair) that form upon photogeneration, need to diffuse (see also refs.<sup>[16,17]</sup>) to the Donor-Acceptor (D-A) interface for efficient separation of the electronic charge carriers, while typical exciton diffusion lengths in the organic PV absorber materials are ~10 nm.<sup>[18]</sup> Optimal charge separation at the interface requires a large interface area and strong D-A electronic coupling.<sup>[19]</sup> However, efficient charge collection at the electrodes requires long lifetime of the charge-separated states, which requires minimum interface area (to minimize recombination) and weak electronic D-A coupling. These opposite requirements need to be balanced, and, hence, will put a limit on the optimal efficiency of these cells.<sup>[20]</sup>

The low carrier mobility in most organic materials favours recombination before collection. For the DS cell the high carrier mobility in nanocrystalline TiO<sub>2</sub> conveys an advantage over all-organic cells. For the paradigmatic poly(3-hexylthiophene) (P3HT)-phenyl-C61-butyric acid methyl ester (PCBM) bulk heterojunction (BHJ) blend, full absorption in the P3HT polymer yields  $J_{SC}^{MAX} \sim 19 \text{ mA} \cdot \text{cm}^{-2}$ .<sup>[5]</sup> However, electronic charge carriers, generated in a disordered absorber need to percolate through the material to the electrodes before recombining. This process, whose efficiency is expressed in the carrier mobility and diffusion length, limits the absorber layer width in what, anyhow, are meant to be *thin film* cells. With an optically thick layer of 400 nm,  $J_{SC}^{MAX}(\text{eff}) \approx 13 \text{ mA} \cdot \text{cm}^{-2}$ , while for small area P3HT:PCBM cells  $J_{SC} \sim 11 \text{ mA} \cdot \text{cm}^{-2}$  is obtained.<sup>[5]</sup> New polymers, absorbing farther in the red, yield higher currents (Table 2). Still, till now the external or internal quantum efficiency (EQE or IQE: spectrum of electrons out/incident or absorbed photons) of organic cells is <100% over a wide spectral range,<sup>[7,8]</sup> due to broad absorption peaks, rather than the sharp absorption edge of “classical” inorganic cells. Because carrier mobility and diffusion lengths limit how thick an organic semiconductor can be used in a PV cell, making them optically thick may lower the power conversion efficiency.

#### 2.2.2. Tail States: Defining the Absorption Edge

The minimal energy required for photon absorption is not an absolute number, because some materials have tail absorption, very small cross sections at energies, lower than their main absorption range. In principle, this need not affect PV performance, because with sufficiently thick materials, also tail absorption can become complete. However, even if thick systems are possible, photons absorbed via tail states may still not be useable for PV. Such is the case for a-Si:H, where the effective absorption edge will be at the minimal energy, needed to excite electrons to above the mobility edge.<sup>[21]</sup> For organic semiconductors, already materials of high crystallinity show low energy tail absorption,<sup>[22]</sup> rather than a sharp absorption edge.<sup>[23]</sup> The tail state effect is even more pronounced for the non-crystalline



**Figure 2.** Shockley-Queisser limit (dots) and experimental energy cost vs. excitation energy. Labels in the figure correspond to the left-most column in Table 3. DSC: Dye-sensitized cell. OPV: Organic photovoltaic (cell). PS: (natural) photosynthesis. Data for (GaIn)P (the high band gap cell of the NREL tandem cell) are from ref.[59]. Data for CuGaSe<sub>2</sub> are from ref.[60]. The dot-dashed line represents the SQ limit cost line, shifted by 0.3 eV, as argued for a-Si:H cells<sup>[34]</sup> and for organic cells.<sup>[35]</sup> Data for PS are from ref.[26], with a -1.05 eV “cost” (“overpotential” in ref. [26]).

materials used in BHJ cells (see section 2.3.1 for tail state effect on  $V_{OC}$ ).

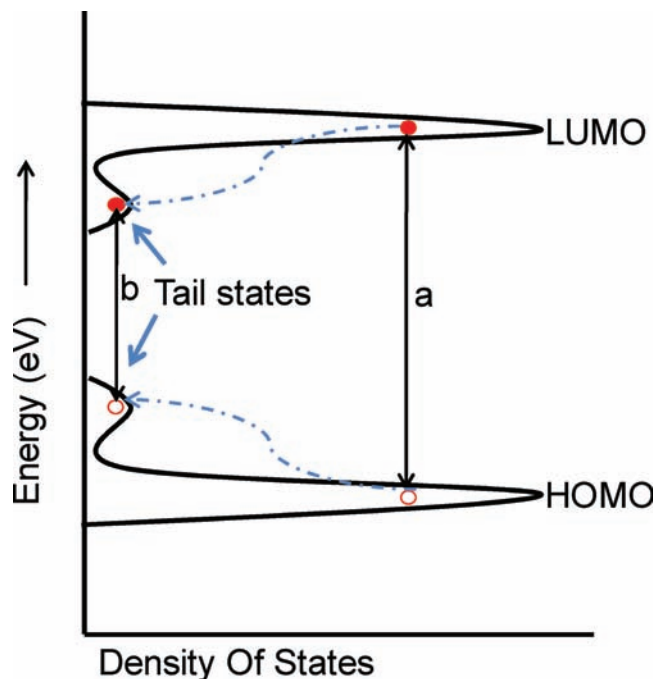
The small-grained (~1 μm) polycrystalline inorganics (CdTe, CIGS) are intermediate between single crystal and amorphous materials.

In general the low IQE values of in organic cells have been linked to carrier transport problems, perhaps impurities, processing problems, because of poor film forming ability and low materials solubility.<sup>[24]</sup> Much of the work in organic BHJ (and in DS) cells is directed to lower bandgap absorbers, (but see ref.<sup>[25]</sup>), which are likely used in recent record cells (cf. Table 2).

### 2.3. Energy Loss

$qV_{OC}/E_G$  and especially  $qV_{MP}/E_G$  express a major limit for several new solar cell types. Using the SQ photon to energy conversion limit on a single absorber system (Figure 2, inspired by plots in Supporting Information ref. [26]) shows the energy cost, imposed by the SQ limit, as function of excitation energy (cf. also Figure 16 in ref. [5]).

In Table 3  $qV_{OC}/E_G$  and  $qV_{MP}/E_G$  express a limit, related to the SQ one, as can be seen also from the summary analysis in ref.<sup>[27]</sup> but the data hold more information. The lower value for c-Si than for GaAs and InP, can be related to the indirect bandgap of c-Si, and the direct one of the two III-V materials (see below). The significant difference in  $qV_{OC}/E_G$  (and  $qV_{MP}/E_G$ ) between the three inorganic thin film cells, a-Si:H on the one hand and CdTe and CIGS cells on the other hand, reflects the different physics (importance of a-Si:H tail states; cf. discussion in section 2.2.2 and Figure 3); the difference between CdTe and CIGS is suggestive of the different GB energetics in these polycrystalline systems<sup>[13,28]</sup>: the higher voltage



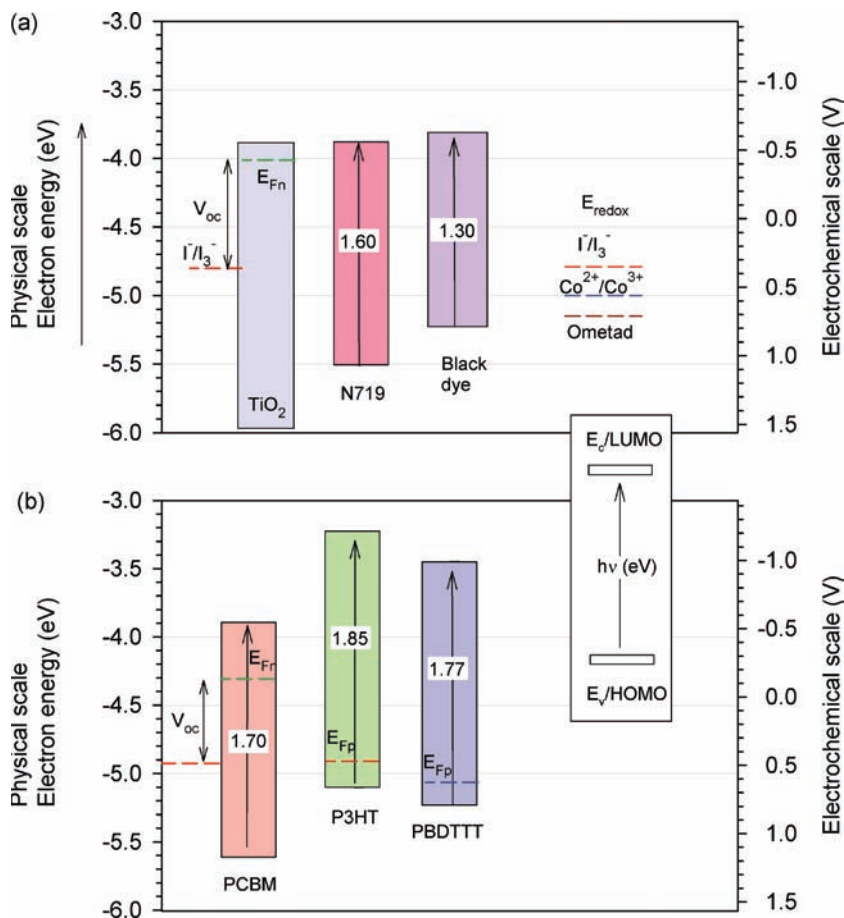
**Figure 3.** Schematic of electron/hole thermalization in the LUMO (or CB)/in the HOMO (or VB) to tail states. The result is that the energy that can be extracted is “b” instead of “a” eV. The dashed-dotted lines illustrate thermalization of the carriers. LUMO and HOMO are equivalent to mobility edges in amorphous materials.

price for CdTe than for CIGS cells results from the strong inversion at the CdTe GBs, with large conduction and valence band (CB and VB) differences between bulk and GB,<sup>[13,29]</sup> while for CIGS the CB around and at the GB remains rather flat and inversion results mostly from the composition-induced change in VB.<sup>[28]</sup> Comparing the (single) crystalline and polycrystalline thin film cell data in the Tables shows that deviation from high crystallinity demands a voltage price.

#### 2.3.1. Organic solarcells

For organic solar cells, the present common understanding is that  $V_{OC}$  is primarily limited by  $\Delta\{LUMO(A)-HOMO(D)\}$ <sup>[30,31]</sup>(cf. 2.3.2 (a) Below, and Figure 4). However, data are accumulating that indicate that this  $\Delta$  is not the sole  $V_{OC}$ -determining factor,<sup>[32,33]</sup> explaining the need to look for additional factors, to determine more realistic limits to the  $V_{OC}$ .

**Importance of Tail States:** In 1981 Tiedje analyzed the a-Si:H cell's physics and concluded that the non-periodic structure of the absorber and the resulting tail states (cf. Figure 3) exerts a price of several 100 mV, compared to what is the case for perfect crystalline cells,<sup>[34]</sup> a concept that was recently applied to the polymer-fullerene cells,<sup>[35]</sup> based on earlier analyses of these cells.<sup>[33,36]</sup> Experimental evidence for the presence of tail states in organic semiconductors can be found in refs. [37–39]. Though the effective absorption edge will be at higher energy, the electrons and holes will quickly thermalize into the tail states and, thus, the voltage that can be extracted, which is determined by the quasi-Fermi levels, will be decreased as tail state, rather



**Figure 4.** Schematic energy diagrams of the materials components of (a) Dye-sensitized and (b) Organic bulk heterojunction solar cells. Standard energy levels are given on the solid state, one electron energy scale, while the origin of the electrochemical scale is taken at the  $-4.44$  eV IUPAC value<sup>[61]</sup> (a new  $4.28$  eV value was proposed<sup>[62]</sup>; cf. also endnote 25 in ref.[63]).  $E_{Fn}$  and  $E_{Fp}$  are the quasi-Fermi levels of electrons and holes (the  $I^-/I_3^-$  redox potential in most DS cells). Their difference relates to  $V_{oc}$  as indicated.  $TiO_2$  and dyes' energy levels depend on the solution components; dye levels may also depend on criteria for the absorption onset. Data from<sup>[45,58]</sup> and from<sup>[64]</sup> for PBDTTT (poly{4,8-bis-substituted-benzo(1,2-b:4,5-b)dithiophene-2,6-diyl-alt-4-substituted-thieno{3, 4-b}thiophene-2,6-diyl}).

than band (mobility) edge energies will become the relevant ones (cf. Figure 3).<sup>[40,41]</sup>

In DS cells the states in the  $TiO_2$  gap, near the band edge, are quickly filled, as carriers in the filled tail states have sufficiently long lifetime<sup>[42,43]</sup> (in contrast to what is the case of a-Si:H). Therefore, here the CB edge, rather than the tail of the edge states, matters for determining  $V_{oc}$  (but see refs. [44–46]).

**High Bandgap → High Cost?:** At first sight Figure 2 suggests that the energy cost increases with absorption edge energy. Adding the crystalline (Ga,In)P entry shows that this need not be so, if high enough crystalline quality material is used. The energy cost for present day organic cells is close to that of the highly developed single junction a-Si:H. Both should be viewed with the above-discussed  $\sim 0.3$  eV for disordered systems in mind, as shown by the dashed-dotted line in Figure 2. Also shown is an entry for natural photosynthesis, which is comparable to that for the organic and a-Si:H cells. Naturally, the latter information should be combined with the electron transfer rate

of photosynthesis which, if expressed as current, is  $\sim 10^{-2}$  mA·cm<sup>-2</sup>, outside the range of Figure 1. While the DS cell's absolute energy cost with the lower absorption edge black dye is less than with the more common N719 dye, the relative losses,  $qV_{MP}/E_G$ , are similar. The gain in current with the black dye is significantly less than could be hoped for, as expressed by their  $J_{MP}/J_{SC}^{MAX}$  values. Irrespective of other issues, such as stability, these results drive home the reason why black dye DS cells did not (yet) give the hoped-for efficiency increases, which, though, may come with further development.

### 2.3.2. Summarizing the Data for Existing Thin Film Solar Cells

The energy loss ( $E_G - qV_{MP}$ ) is far more than what the SQ limit dictates, particularly for DS and organic cells. While we can invoke the  $0.3$  V loss due to tail states (Figure 2),<sup>[34]</sup> as these are disordered or poorly crystalline systems, this still leaves a large extra loss, suggesting additional limits for such cells. While possible factors were considered in various studies<sup>[5,33,35]</sup> we cannot (yet) determine them, but can point to loss mechanisms that can add to the SQ limits for DS and organic solar cells.

(a) **Dielectric Constant Effect and Vibronic Coupling:** In an inorganic semiconductor the binding energy of the photogenerated exciton is  $\leq kT$  and the built-in electric field in a  $p-n$  junction suffices to break the electron-hole pair. In conjugated organics this binding energy is 100s of meV, due to their low dielectric constant ( $\epsilon_r = \sim 3.5$ ). BHJ organic and DS cells rely on a nm-scale mixture of materials for fast  $e^-h^+$  pair separation into distinct electron and hole carrier materials, requiring a driving force, different from the electric field in "classical" cells. Energy diagrams for both types of cells are given in Figure 4 (energy levels values are indicative, as they vary, depending on device conditions). Based on accumulated data from the literature,  $\geq 0.3$  eV is required for efficient charge separation in the low dielectric constant organic PV materials. Part of the absorbed photon energy provides this by having the absorber's LUMO (its electron affinity)  $\geq -0.3$  eV higher than the CB of the electron transporter in a DS cell or the LUMO of the electron acceptor (e.g., PCBM) in a BHJ cell. In the P3HT/PCBM BHJ cell, optical absorption is practically restricted to P3HT, which acts both as absorber and hole transporter. In this cell the LUMO of the acceptor ( $\sim n$ ) material is much lower than that of the donor ( $\sim p$ ) material, Figure 4. Such mismatch limits the attainable  $V_{oc}$ , which, for any generic solar cell is given by the separation of electron ( $E_{Fn}$ ) and hole ( $E_{Fp}$ ) quasi-Fermi levels, the acceptor LUMO and donor HOMO levels in the BHJ cell.

While for DS cells the electron conductor (esp.  $\text{TiO}_2$  with  $\epsilon_r \approx -60$ ; for  $\text{ZnO}$   $\epsilon_r \approx -8.5$ ) and the ionic electrolyte screen the charged carriers from each other,<sup>[42]</sup> in organic cells their separation probability depends on overcoming, after initial charge transfer, the Coulomb attraction across the organic–organic interface,<sup>[47]</sup> which is significant, because of the low dielectric constant ( $\epsilon_r$ ). Assuming  $\epsilon_r = 3.5$  and 1 nm separation, this binding energy can be  $\sim 0.4$  eV. Excess energy can exist in the vibronic modes of molecules (yielding a hot Coulomb-bound pair) after charge transfer. Monte Carlo simulations<sup>[48]</sup> show that the excess thermal energy that the system possesses depends on  $\Delta\text{LUMO}$  (D–A). If charge separation is faster than thermalization of the vibronic modes, separated states can be formed without need of additional energy (Onsager mechanism<sup>[49]</sup>).<sup>[50]</sup> An extreme possibility with minimal energy loss could be if strong electron-phonon coupling leads to large overlap of the vibronic states, involved in the charge transfer, and subsequent charge separation states. Such a case implies polaron formation. Polaron formation has been suggested as the cause for  $V_{\text{OC}}$  loss,<sup>[51]</sup> but polaron binding energies in organic PV materials range from  $\sim 1\text{--}2 \cdot kT$  (30–50 meV) for rigid molecules, like pentacene, fullerenes, and phthalocyanines, to  $\sim 0.1$  eV for those such as pentathienoacene,<sup>[52]</sup> which, with many internal degrees of freedom, is more akin to the PV polymers, i.e.,  $\ll 0.3$  eV.

In any case, the energy requirement to produce the charge separated state in a molecular organic system puts a limit on how much of the  $E_G$  energy (in the absorber) can be converted into  $qV_{\text{OC}}$  (and  $qV_{\text{MP}}$ ). While decreasing the energy, driving charge separation, increases  $V_{\text{OC}}$ , it will decrease electron transfer/injection so much that overall cell performance will decrease.<sup>[46]</sup>

(b) *Injection and Regeneration Loss*: In a DS cell the same type of consideration as given above for the organic cells, applies for the transfer of a hole to the hole conductor. This is a major limitation on the efficiency, because the best carrier, the  $\text{I}_3^-/\text{I}^-$  redox couple in organic solvent, has a redox energy (“solution Fermi level”; Figure 4) leading to  $\sim 500$  mV loss, due to its position relative to the dye HOMO. This explains the search for a hole conductor with a redox energy closer to the dye HOMO, such as Co-based redox couples or organic solids. Up to now such replacements result in higher recombination rate or lower hole mobility (diffusion).<sup>[53]</sup>

These possible limitations (a)–(b) for organic and DS cells should not affect the inorganic polycrystalline thin film cells.

### 3. Conclusions

The need to identify and define basic limitations, beyond that given by SQ, and to distinguish such limitations from lack of development effort and of maturity is becoming critical for future thin film cell development, especially of newer types, inorganic, molecular organic or other ones. For organic molecular cells we can, with some *hubris*, use our analysis and find that the low dielectric constant, non- or poorly crystalline, molecular systems will have an extra energy loss of some 500–750 meV, compared to the “classical” PV cells. One immediate, obvious, but possibly iconoclastic implication of this conclusion, visually expressed in Figure 2, is that one should move

away from low  $E_G$  absorbers with such materials, because these losses gain importance as  $E_G$  decreases. This conclusion suggests that the focus on  $\sim 1.4$  eV absorbers, based on pure SQ analysis, central to much PV development, is misguided for molecular cells.

We conclude that in addition to the general “terawatt check” for any alternative energy direction, i.e., assume all goes as we hope, and taking into account also the need for sustainable material choices, “how will we get several TW of power?”, the  $\eta_{\text{CM}}/\eta_{\text{LC}}$  (Table 1),  $J_{\text{MP}}/J_{\text{SC}}^{\text{MAX}}$  (Table 2),  $qV_{\text{MP}}/E_G$  and  $E_G - qV_{\text{MP}}$  (Table 3) criteria can help to put order in the enormous parameter space that we face, making our choices for the future, and help define research directions.

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