Classifiying advanced concepts to assess device requirements for high efficiency solar cells

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***Abstract*—**

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I. Introduction

The efficiency of terrestrial solar energy conversion is fundamentally limited by the Landsberg limit of 93%. Single junction solar cells can, however, reach only about a third of this efficiency, a limitation first formulated by Shockley and Queisser [1]. Many concepts have been proposed to overcome this Shockley-Queisser (SQ) limit for single junction solar cells. In this contribution, we are going to explore the classification of these concepts according to the processes that occur in them and explain how this affects model-building for these devices and the requirements they have to fulfil.

Arguably the simplest extension of the single junction solar cell is the two-terminal multi-junction solar cell, in which p-n junctions of materials with different band gaps are stacked on top of each other and connected with a tunnel junction. The different p-n junctions are connected in series and a Venn diagram for advanced concept solar cell classification (see Figure 1) therefore places those devices in the ellipse labelled "series".

Series connection demands the same current flow in each component. Such a device therefore requires nearly equal photon flux absorbed in each of the p-n junctions which imposes strict conditions on the band gaps of the different materials. These conditions can be somewhat relaxed if the p-n junctions with the higher band gap materials show a very high internal luminescence efficiency, so that the total recombination is dominated by radiative processes. In this case, some of the photon flux can be redistributed from the high band gap top junctions to the lower band gap bottom junctions without a significant loss in conversion efficiency compared to the perfectly matched case [3], [4]. The importance of luminescent redistribution of excitations in such a device places it also in the "luminescence" ellipse of the venn diagram of advanced concept solar cells. Note that the series connection condition for two junction terminals can be broken by adding more terminals. A three-terminal device adds a parallel element, and therefore a requirement to match voltages instead [5].

The requirement for making an electrical connection between two different materials in order to surpass the SQ limit, inherent in multi-junction solar cells, can be circumvented by making an optical connection via luminescence. In this case, one material with at least two optical transitions is used to up- or down-convert a portion of the incoming light so that it can be used more efficiently by the actual solar cell [6], [7]. When translating the luminescence and absorption processes in this spectral converter into an equivalent circuit diagram, this spectral shaping inevitably involves a parallel connection between two competing luminescence emission pathways which operate in parallel. Whether high- or low-energy emission predominates is determined by the alignment of the energy gaps between the emitting states and the 'etendue of the absorbed and emitted radiation for each transition.

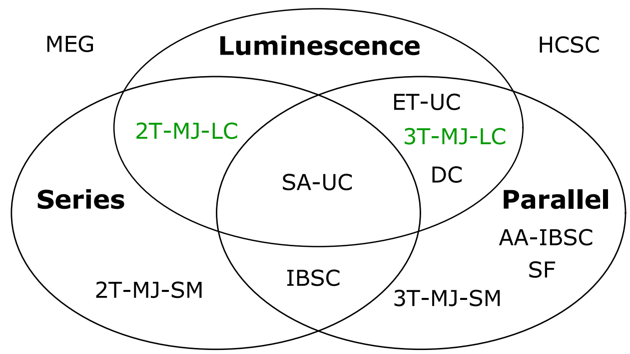

Fig. 1. A venn diagram of the different advanced concept solar cells; two terminal multi-junction with selective mirror (2T-MJ-SM) or with luminescent coupling (2T-MJ-LC) through luminescent transfer of excitations between junctions, three terminal multi-junction with selective mirror (3T-MJ-SM) or with luminescent coupling (3T-MJ-LC), up-conversion through sequential absorption (SA-UC), or through energy transfer processes (ET-UC), down-conversion (DC), intermediate band solar cell (IBSC), energy transfer intermediate band solar cell (ET-IBSC), singlet fission and injection (SF) solar cell. Different elements can be connected in series, they can be connected in parallel or via luminescence. Multi-exciton generation (MEG) and hot carrier solar cell (HCSC) do not fit into this scheme and are left outside the venn diagram. Only the two concepts in green have been realised with efficiencies beyond the Shockley Queisser limit. Adapted from [2].

For low concentration of sunlight, efficient up-conversion thus requires an energy relaxation step from the low-energy absorbing states to long-lived intermediate states that interact with each other to produce a highly excited state. Every known up-converting material has such a relaxation step, resulting in exothermic up-conversion that releases heat to the environment. Down-conversion of sunlight could, in principle, occur even as an endothermic process, where heat is taken from the environment so that the sum of the energy of the down-converted photons is larger than the energy of the absorbed high-energy photon.

The same materials that enable up-conversion or down-conversion of sunlight could also be applied to the solar cells such that they could transfer the excitations electrically into the absorber material instead of via luminescence. The Singlet Fission solar cell creates two low-energy triplet excitations at the front of the solar cell [8], which are subsequently transferred into a p-n junction absorber that has a band gap below the triplet energy. This would enhance the available current for this device. It still contains a parallel connection between the high energy singlet and the low-energy triplets.

The Auger-assisted IBSC could, for example, consist of a p-n junction with an embedded molecular up-converter material [9], [10]. Triplet-triplet annihilation of the low energy triplets, which absorb below the band gap of the p-n junction absorber leads to high energy singlets with energies above the band gap. These singlets can transfer their energy directly to the absorber material and create additional electron hole pairs. For this process to occur the relative position of the quasi-Fermi levels of all these excitations is again important and they again operate in parallel, which again leads to the necessity of relaxation, or ratchet, steps at low concentration.

Intermediate band solar cells (IBSCs) [11] have been envisaged as a way to directly introduce three absorption edges into one material and thus enable a simpler architecture that could have similar efficiency limits to a triple-junction device. The idea is that sequential absorption from valence band into intermediate band (IB) and from the IB into the conduction band turns two below band gap photons into one electron hole pair. This sequential absorption constitutes a series connection between the two transitions, while it is also connected in parallel to the conventional above band gap absorption.

The voltages of the below band gap excitations and the above band gap excitation are not matched at low concentration. This leads to a voltage loss compared to the single junction device that can only be compensated if the current gained from the below band gap part is substantial [12]. The introduction of an energy relaxation, or ratchet, step in the sequential absorption process could lead to higher effiencies at low concentration [13] and also for low absorption strength of the intermediate transitions [12] because it allows for a matching of the voltages between the different parallel absorption pathways.

Multi-exciton generation (MEG) [14] and hot carrier solar cells (HCSCs) [15] stand somewhat outside of this diagram. In MEG, electron cooling due to phonons competes with impact ionization processes that multiply the available excitations from high energy photons. Understanding MEG requires a non-equilibrium analysis [16] that does not lend itself to an equivalent circuit analysis and a classification into parallel or series connected devices. HCSCs in their ideal implementation have more in common with thermal heat engines and the attempted classification is not suited for understanding them. This means that they present interesting numerical simulation challenges.

References

[1] W. Shockley and H. J. Queisser, "Detailed balance limit of efficiency of p-n junction solar cells," *Journal of Applied Physics*, vol. 32, no. 3, pp. 510–519, 1961. [Online]. Available: http://scitation.aip.org/content/aip/journal/jap/32/3/10.1063/1.1736034

[2] A. Pusch and N. J. Ekins-Daukes, "Voltage matching, étendue, and ratchet steps in advanced-concept solar cells," *Phys. Rev. Applied*, vol. 12, p. 044055, Oct 2019. [Online]. Available: https://link.aps.org/doi/10.1103/PhysRevApplied.12.044055

[3] A. Brown and M. Green, "Radiative Coupling as a Means to Reduce Spectral Mismatch in Monolithic Tandem Solar Cell Stacks-Theoretical Considerations," in *Proc. 29th IEEE Photovoltaic Specialists Conference*, 2002, p. 868.

[4] A. Pusch, P. Pearce, and N. J. Ekins-Daukes, "Analytical expressions for the efficiency limits of radiatively coupled tandem solar cells," *IEEE Journal of Photovoltaics*, vol. 9, no. 3, pp. 679–687, May 2019.

[5] W. McMahon, H. Schulte-Huxel, J. Buencuerpo, M. Young, T. Klein, J. Geisz, A. Tamboli, and E. Warren, "Voltage-matched strings using 3-terminal tandems: Fundamentals and end losses," in *2020 47th IEEE Photovoltaic Specialists Conference (PVSC)*, 2020, pp. 0266–0266.

[6] T. Trupke, M. A. Green, and P. Würfel, "Improving solar cell efficiencies by up-conversion of sub-band-gap light," *Journal of Applied Physics*, vol. 92, no. 7, pp. 4117–4122, 2002. [Online]. Available: https://doi.org/10.1063/1.1505677

[7] ——, "Improving solar cell efficiencies by down-conversion of high-energy photons," *Journal of Applied Physics*, vol. 92, no. 3, pp. 1668–1674, 2002. [Online]. Available: https://doi.org/10.1063/1.1492021

[8] M. J. Y. Tayebjee, A. A. Gray-Weale, and T. W. Schmidt, "Thermodynamic limit of exciton fission solar cell efficiency," *The Journal of Physical Chemistry Letters*, vol. 3, no. 19, pp. 2749–2754, 2012. [Online]. Available: https://doi.org/10.1021/jz301069u

[9] N. J. Ekins-Daukes and T. W. Schmidt, "A molecular approach to the intermediate band solar cell: The symmetric case," *Applied Physics Letters*, vol. 93, no. 6, p. 063507, 2008. [Online]. Available: https://doi.org/10.1063/1.2970157

[10] C. Simpson, T. M. Clarke, R. W. MacQueen, Y. Y. Cheng, A. J. Trevitt, A. J. Mozer, P. Wagner, T. W. Schmidt, and A. Nattestad, "An intermediate band dye-sensitised solar cell using triplet–triplet annihilation," *Phys. Chem. Chem. Phys.*, vol. 17, pp. 24 826–24 830, 2015. [Online]. Available: http://dx.doi.org/10.1039/C5CP04825G

[11] A. Luque and A. Martí, "Increasing the efficiency of ideal solar cells by photon induced transitions at intermediate levels," *Phys. Rev. Lett.*, vol. 78, pp. 5014–5017, Jun 1997. [Online]. Available: http://link.aps.org/doi/10.1103/PhysRevLett.78.5014

[12] A. Pusch, M. Yoshida, N. P. Hylton, A. Mellor, C. C. Phillips, O. Hess, and N. J. Ekins-Daukes, "Limiting efficiencies for intermediate band solar cells with partial absorptivity: the case for a quantum ratchet," *Progress in Photovoltaics*, vol. 24, no. 5, pp. 656–662, 2016. [Online]. Available: ¡Go to ISI¿://WOS:000373624100006

[13] M. Yoshida, N. J. Ekins-Daukes, D. J. Farrell, and C. C. Phillips, "Photon ratchet intermediate band solar cells," *Applied Physics Letters*, vol. 100, no. 26, pp. –, 2012. [Online]. Available: http://scitation.aip.org/content/aip/journal/apl/100/26/10.1063/1.4731277

[14] J. H. Werner, R. Brendel, and H. Queisser, "Radiative efficiency limit of terrestrial solar cells with internal carrier multiplication," *Applied Physics Letters*, vol. 67, no. 7, pp. 1028–1030, 1995. [Online]. Available: https://doi.org/10.1063/1.114719

[15] R. T. Ross and A. J. Nozik, "Efficiency of hot-carrier solar energy converters," *Journal of Applied Physics*, vol. 53, no. 5, pp. 3813–3818, 1982. [Online]. Available: https://doi.org/10.1063/1.331124

[16] A. Pusch, S. P. Bremner, M. J. Y. Tayebjee, and N. J. E. Daukes, "Microscopic reversibility demands lower open circuit voltage in multiple exciton generation solar cells," *Applied Physics Letters*, vol. 118, no. 15, p. 151103, 2021. [Online]. Available: https://doi.org/10.1063/5.0049120