Theoretical limit for efficiency of silicon solar cells

"The Shockley-Queisser Limit and Beyond "

Gonçalo Monteiro Albuquerque – 47242

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ABSTRACT: This study was based on the analysis of the paper "*Detailed Balance limit of Efficiency of p-n Junction Solar Cells*" written by William Shockley and Hans J. Queisser. This study starts with a small introduction on the solar cells' parameters and calculation of efficiency from IV characteristic curve and then it goes more deeply into the Shockley-Queisser paper where I try to simplify at most the paper fundamentals, variables and main ideas and vision of the paper. Lastly, was given some recent and current solar cells that try to exceed or avoid the Shockley-Queisser limit.

1. Introduction: Solar Cells Parameters and Efficiency

The efficiency is one of the most commonly used parameters to compare different solar cells performances. The most widely way to calculate the efficiency of a solar is by looking to its parameters in order to obtain values that can afterwards be translate as ratio of energy output from the solar cell to input energy from the sun. However, the efficiency of a solar cells is not fully described if the spectrum and intensity of the incident sunlight and the temperature of the solar cell are not included, once they depend from each other. Therefore, in order to compare different solar cells, conditions must be carefully controlled and maintained under which efficiency is being measured. It's well known that terrestrial solar cells are measured under AM1.5 conditions and at a temperature of 25ºC (~300K)., while if we plan on building a spatial solar powerplant or spacecrafts powered by solar energy, the ambient conditions would be AM0.

The efficiency of a solar cell is determined as the fraction of incident power which is converted to electricity and is defined as:

$$P_{max} = V_{oc} \times I_{SC} \times FF \qquad [1]$$

$$\eta = \frac{V_{oc} \times I_{SC} \times FF}{P_{in}} \qquad [2]$$

Where V_{oc} is the open-circuit voltage, I_{SC} is the short-circuit current, FF is the fill-factor, P_{in} is the incident power flux from the sun, calculated by multiplying the irradiance, normally 1000 W/m^2 by the area of the solar cell, and η is the efficiency.

The open Circuit voltage, V_{oc},is the maximum voltage from a solar cell and occurs when the net current through the device is zero, $I_{SC} = 0$, and is given by the following equation:

$$V_{oc} = \frac{n \times k \times T}{q} \times \ln(\frac{I_L}{I_0} + 1) \quad [3]$$

Where n is the ideality factor, kT/q is the thermal voltage at 300K, q is the electron charge and k is the Boltzman's constant, I_L is the light generated current and I_0 is the dark saturation current. The short-circuit current, I_{SC}, is the maximum current from a solar cell and occurs when the voltage across the devices is zero, $V_{oc} = 0$. It can be described through the following equation, derivate from diode equation (or an ideal solar cell equation):

$$I = I_L - I_D = I_L - I_S \times [e^{\left(\frac{q \times V}{k \times T}\right)} - 1] \quad [4]$$

The "fill factor" is a parameter which, in conjunction with Voc and Isc, determines the maximum power from a solar cell. Its defined as the ratio of the maximum power from the solar cell to the product of Voc and Isc. Graphically, the FF is a measurement of the "squareness" of the solar cell and is also the area of the largest rectangle which will fit in the IV curve, as it is illustrated below:

$$FF = \frac{V_{MP} \times I_{MP}}{V_{oc} \times I_{sc}} = \frac{Area\ A}{Area\ B} \quad [5]$$

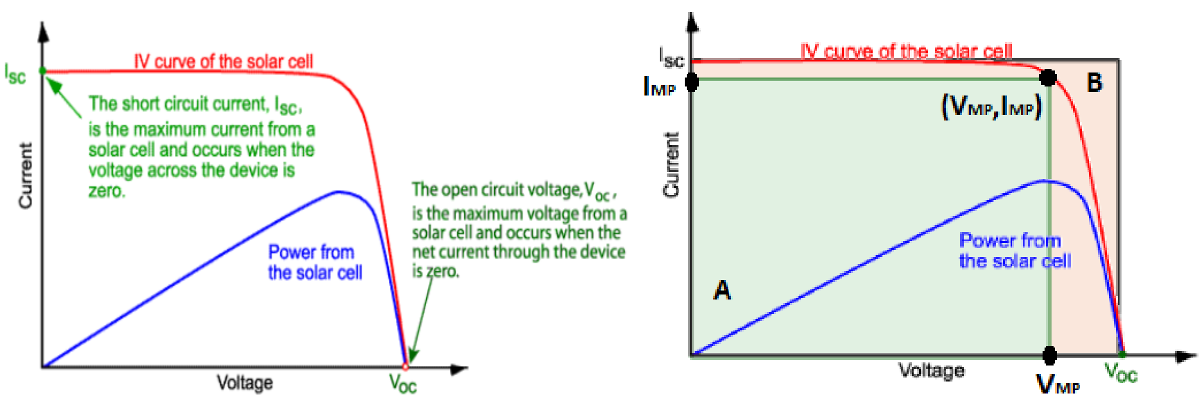


Illustration 1 - I-V characteristic curve with the meaning for I_sc and V_oc respectively, as well as the fill factor illustration.

2. Detailed Balance Limit of Efficiency – Shockley-Queisser Limit

In the mid-50s, many papers were written in order to proof a potential maximum limit of efficiency for silicon solar cell, which included several well-known scientists such as Chapin, Fuller and Pearson in 1954, and Pfann and van Roosbroeck also in 1954. Prince in 1955 gave a further study in which the efficiency was calculated as a function of the energy gap and Loferski explained the dependency of efficiency upon energy gap in more detail processes. However, all these papers were based on empirical values for the constants describing the characteristics of the solar cell, which predict certain limits of observed efficiencies and had become general accepted theoretical limits. Although, William Shockley and Hans J. Queisser did not agree with this statement since it was based on certain empirical values of lifetime, etc, and they suggested to change the name to "semiempirical limit". They were certain that there was a theoretical justifiable upper limit as a consequence of the nature of atomic processes required by the basic laws of physics, particularly the principle of detailed balance, which they called "detailed balance limit". Comparing the two limits, "semiempirical limit" and "detailed balance limit", the difference is much more significant in potential for improvements, since the detailed balance limit achieved values twice as high as the "semiempirical limit", thus suggesting much greater possible improvements.

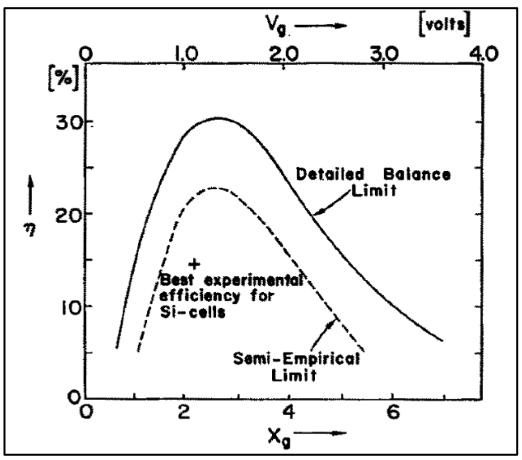


Illustration 2 - Comparison of the "semiempirical limit" of efficiency of solar cells with the "detailed balance limit", derived from J. Appl. Phys. 32, 510 (1961); doi: 10.1063/1.1736034. + represents the "best experiment efficiency to date" (1960) for silicon solar cells.

At their paper, "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells", Shockley and Queisser, as the paper said, made an approach to calculate the maximum upper theoretical limit of efficiency for p-n junctions solar cells using the detailed balance equations, which is a thermodynamic perspective, and several fundamental assumptions such as:

- Radiative recombination sets an upper limit to minority carrier lifetime and it determines the detailed balance limit for efficiency.
- The concentration of one sun.
- Temperature of the sun: $kT_s = qV_s$ (k is Boltzmann's constant, q is the electronic charge).
- Temperature of the solar cell: $kT_c = qV_c$
- Energy Band gap (E_g): $E_g = h\nu_g = qV_g$ (h is the Planck's constant)

- The efficiency is found to involve only the two following ratios: $\boldsymbol{x_g} = \frac{\boldsymbol{E_g}}{\boldsymbol{kT_s}}$ and $\boldsymbol{x_c} = \frac{\boldsymbol{T_c}}{\boldsymbol{T_s}}$
- Photons with energy greater than $\boldsymbol{hv_g} > \boldsymbol{E_g}$ produce precisely the same effect as photons of energy equal to $\boldsymbol{hv_g}$ and the absorption coefficient is unity.
- Solar cell is subjected to blackbody radiation, therefore **T_s = 6000 K** and **T_c = 300 K**
- Carriers on the semiconductor have **infinite mobility**.

Shockley and Queisser start this theory by calculating the maximum efficiency of a solar cell for an ideal solar cell, which has an spherical shape and therefore receives radiation from all directions, they assumed that the cell's temperature is zero (T_c = 0 K) and the sun's temperature is 6000 K, and it is represented and the figure below, extracted from the Shockley-Queisser paper (1960).

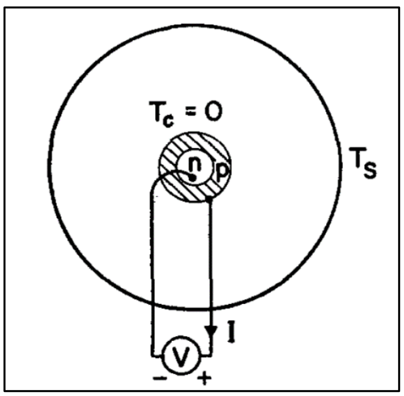


Illustration 3 – Spherical solar cell at the centre receiving radiation from the sun from all directions with Tc =0K and Ts=6000K.

The efficiency was then calculated by the following expression:

$$\boldsymbol{\eta = u(x_g) = \frac{generated\ photon\ energy}{input\ power} = \frac{hv_g Q_s}{P_s}} \qquad [6]$$

In order to calculate the photon generated energy, it's necessary to define the **Q_s**, number of photons absorbed, which they assumed for photon's energy greater than the band gap ($\boldsymbol{hv_g > E_g}$) will be absorbed. To calculate the **Q_s**, was used the Planck's law, which gives the spectral irradiance power given by the following expression:

$$\boldsymbol{I(\lambda, T)} = \frac{2\boldsymbol{hv}^3}{\boldsymbol{c}^2} \times \frac{1}{\boldsymbol{e}^{\frac{\boldsymbol{hv}}{\boldsymbol{k_B T}}} - 1} \qquad [7]$$

Now, it is possible to calculate the number of photons absorbed, **Q_s**, by taking the integral of the number incoming photons at each light frequency that correspond to the band gap of the cell until infinity, expressing by the following expressions and resolutions:

$$\boldsymbol{Q_s = Q(v_g, T_s)} = \frac{2\boldsymbol{\pi}}{\boldsymbol{c}^2} \int_{v_g}^{\infty} \frac{\boldsymbol{v}^2}{\boldsymbol{e}^{\frac{\boldsymbol{hv}}{\boldsymbol{kT_s}}} - 1} \boldsymbol{dv} = \frac{2\boldsymbol{\pi}(\boldsymbol{kT_s})^3}{\boldsymbol{c}^2\boldsymbol{h}^3} \int_{x_g}^{\infty} \frac{\boldsymbol{x}^2}{\boldsymbol{e}^{\boldsymbol{x}} - 1} \boldsymbol{dx} \qquad [8]$$

To calculate the input power, **P_s**, they integrated the power spectrum density of Planck's law [9] over the different wavelength, from wavelength of zero until infinity, which is also the approximately the Stefan-Boltzmann's law, described by the following expression:

$$\boldsymbol{P_s} = \frac{2\pi h}{c^2}\int_{o}^{\infty}\frac{v^2}{e^{\frac{hv}{kT_s}}-1}dv = \frac{2\pi(kT_s)^4}{c^2h^3}\int_{0}^{\infty}\frac{x^3}{e^x-1}dx \qquad [9]$$

After calculating these two parameters, $\boldsymbol{Q_s}$ and $\boldsymbol{P_s}$, it is now possible to obtain the maximum efficiency for each energy gap of a p-n junction silicon solar cell with T_c = 0 K, by using the expression [6] demonstrated above. By plotting the efficiency in function of the energy gap, Shockley and Queisser obtained the following graph:

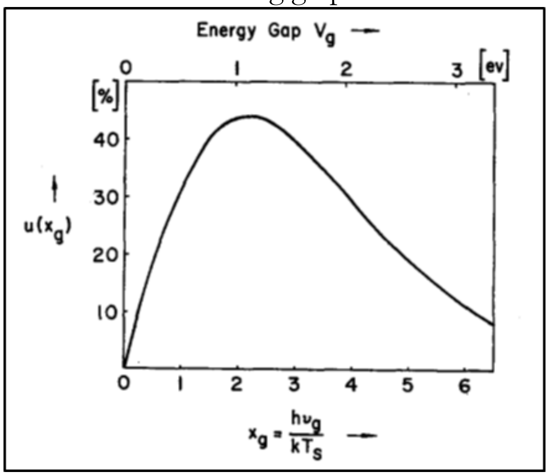


Illustration 4 – Dependence of the ultimate efficiency u(xg) upon the energy gap Vg of the semiconductor.

The maximum efficiency for a cell's temperature of zero kelvin, for an ideal solar cell is about 44% of a band gap equal to ~ 1,1 eV.

However, this is for an ideal solar cell. When they looked to a realistic case of a solar cell, with T_c=300K (ambient temperature) acting as a blackbody, therefore emitting radiation of its own and consider the solar cell to have a planar shape, as it is demonstrated at the following illustration 5, with a specific angle of the sun incident radiation upon the area of the solar cell, so it does not receives radiation from all directions. It also has a load (resistance) connected to the circuit (R_L) extracting energy out of the cell, which has a specific resistance.

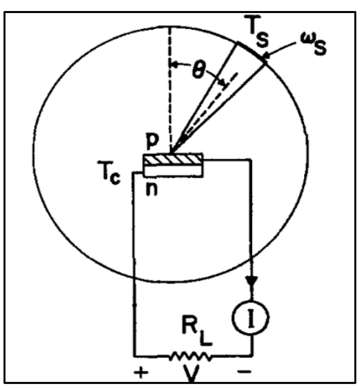


Illustration 5 - A planar cell irradiated by a spherical sun subtending a solid angle ω, at angle of incidence ϑ.

Now, to calculate the ultimate efficiency of this "realistic" solar cell they consider the number of absorbed photons, Q_s, where they had to take into account that only one side of the cell receives incoming radiation of a specific area, $\boldsymbol{A_p}$, as well as the radiation came from a specific angle and direction (orientation). So, to calculate Q_s they had to take into consideration the geometric shape of the solar cell. Another thing Shockley and Queisser had to take into consideration is that the solar cell is considered to be a blackbody and therefore emits radiation from an area of **2*$\boldsymbol{A_p}$**, and it is surrounded by another "shell" or cavity. So, to calculate the radiation from the cell, Q_c, Shockley and Queisser assumed the cell and the "shell" are in thermodynamic equilibrium therefore the temperature of the "shell" ,T, is equal to the temperature of the cell, $\mathbf{T_c = 300K}$, with zero voltage (V = 0V), therefore the radiation absorbed by the cell is equal to the radiation emitted ($\mathbf{R_{abs} = R_{emit}}$). This emitted radiation coming out of the cell is considered to come only from radiative recombination process of electron-holes, which was very praised, once the other scientists at that time were evaluate this phenomenon by approaching semiconductors perspective, and not assuming the solar cell as a blackbody. This way, to calculate the radiation from the cell, $\mathbf{Q_c}$, Shockley and Queisser used again Planck's Law [10] and assumed the following expression, that relates the spectral irradiance which is greater than the band gap with the temperature of the cell (blackbody):

$$\boldsymbol{Q}_c = \boldsymbol{Q}(\boldsymbol{v}_g, \boldsymbol{T}_c) = \frac{2\boldsymbol{\pi}(\boldsymbol{kT}_c)^3}{\boldsymbol{c}^2\boldsymbol{h}^3} \int_{x_g/x_c}^{\infty} \frac{\boldsymbol{x}^2}{\boldsymbol{e}^{\boldsymbol{x}} - 1} \boldsymbol{dx} \tag{10}$$

To calculate the total amount of radiation leaving the cell (radiative recombination), Shockley and Queisser used the following expression:

$$\boldsymbol{R_{RR_{V=0V}}} = 2\boldsymbol{A_p t_c Q_c} \tag{11}$$

Where $\mathbf{t_c}$ represents the probability that an incident photon of energy greater than E_g will enter the body and produce a hole-electron pair. However, at normal conditions the applied voltage is not operating at zero and to calculate the recombination at a specific voltage, Shockley and Queisser used the knowledge of semiconductors, which was highly known at that time. At semiconductors, the radiative recombination is directly proportional to the product of number of electrons (n) and holes (p). So, when zero voltage is applied the radiative recombination is $\boldsymbol{R_{RR}} \propto \boldsymbol{n}_0\boldsymbol{p}_0$ and when voltage, V, is applied the radiative recombination is translated by: $\boldsymbol{R_{RR_V}} \propto \boldsymbol{np} = \boldsymbol{n}_0\boldsymbol{p}_0\boldsymbol{e}^{\frac{qV}{kT}}$. From these two equations, now we can obtain a similar expression as expression [14] by integrating an applied voltage, as the following:

$$\boldsymbol{F_C(V)} = \boldsymbol{R_{RR_V}} = 2\boldsymbol{A_p t_c Q_c e^{\frac{qV}{kT}}} \tag{12}$$

Having the total energy loss as radiative recombination by expression [12], now to calculate the energy extracted from the cell (maximum power) they calculate the useful current, ***I***, by using the expression [4] above defined, based on the diode equation but instead of I_L they wrote I_{sh} which represents the short circuit current when zero voltage is applied and for the case of a planar cell of projected area $\mathbf{A_p}$, such as:

$$\boldsymbol{I} = \boldsymbol{I_{sh}} - \boldsymbol{I}_0\boldsymbol{e^{\frac{qV}{kT}}} \tag{13}$$

$$\boldsymbol{I_{sh}} = \boldsymbol{q}(\boldsymbol{F_s} - \boldsymbol{F_c(V)}) \tag{14}$$

$$\boldsymbol{F_s} = \boldsymbol{Af_w t_s Q_s} \tag{15}$$

Where $\boldsymbol{A}$ is the area of the body, $\boldsymbol{f_w}$ is a geometrical factor, taking into account the limited angle from which the solar energy falls upon the body (ω_s) and $\boldsymbol{t_s}$ is the probability that incident photons will produce a hole-electron pair and may differ from $\boldsymbol{t_c}$ because of the difference in the spectral distribution of the blackbody radiation at temperature Tc and Ts. The open-circuit voltage $\mathbf{V_{op}}$ is chosen in a way that the product IV is at maximum and is obtain from the arrangement of the expression [3], such as:

$$\boldsymbol{V_{op} = \frac{k \times T_c}{q} \times \ln(f \times \frac{Q_s}{Q_c})} \quad [16]$$

Where f represents the product between $\mathbf{f_c}$, $\mathbf{f_w}$ and $\mathbf{t_s}$ divided by product of 2 times **tc**. The factor 2 comes from the fact that sunlight falls on only one of the two sides of the planar cell. The nominal efficiency is then obtained by the following expression:

[17]

$$\boldsymbol{P_{inc} = f_w A P_s} \quad [18]$$

By plotting the IV characteristic curve, it is possible to obtain the maximum power point for the current and voltage and then it is possible to obtain the limit efficiency, expressed as a function of the four variables $\mathbf{x_g}$, $\mathbf{x_c}$, $\mathbf{t_s}$ and $\mathbf{f}$, of Shockley-Queisser by the following formula:

$$\boldsymbol{\eta(x_g, x_c, t_s, f) = \frac{V_{max} I_{V_{max}}}{P_{inc}}} \quad [19]$$

The following graph is the famous limit efficiency (%) of Shockley-Queisser for p-n junctions in function of the energy band gap (eV):

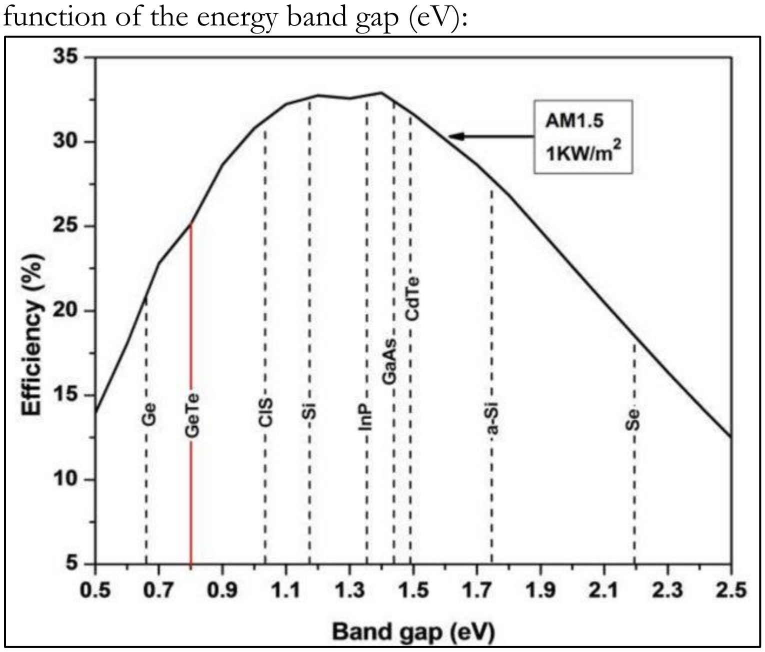


Illustration 6 - S.Q. efficiency limit in function of the energy band gap and the correspondence for different solar cells materials.

The maximum efficiency is reached around 33,7% for a single pn-junction PV cell, assuming AM 1.5 solar spectrum and a temperature of the cell of 300 K and it occurs at a band gap of 1.34eV, which is very close for silicon solar cells, which have a band gap of 1.12eV.

3. Beyond Shockley-Queisser Limit

There are three main PV generations known and accepted: (I) high quality pn-junctions; (II) thin film PV; (III) new approaches. These three PV generations have different cost per efficiency as expressed at the following image:

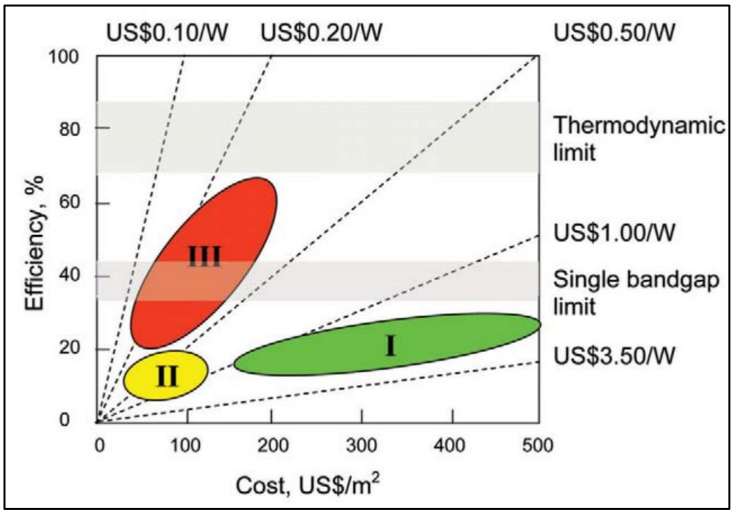
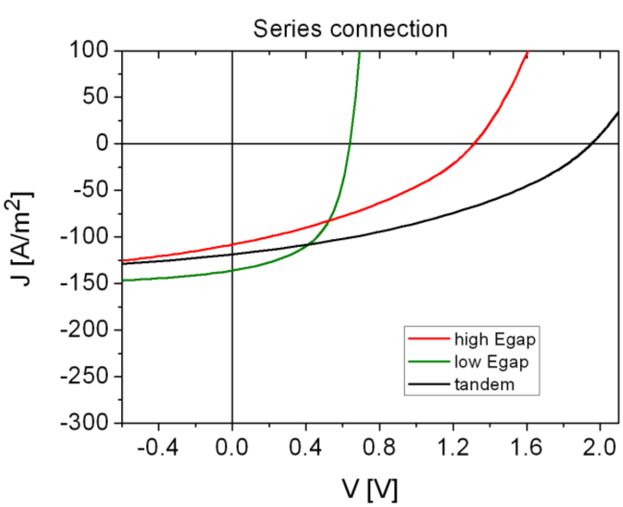


Illustration 7 - The three PV generations expressed in function of efficiency per cost.

The third PV generation is the one that try to avoid the S.Q. limit, or losses as much as possible. There is a way to improve the efficiency of solar cells without changing the design of solar cells, which is by attaching concentrators, since you have more light it enhances the $\mathbf{V_{oc}}$ and therefore offers a higher efficiency. Another way to improve the efficiency of the solar cells is multi-junction solar cells. Multi-junction solar cells basically split the spectral irradiance in order to absorb as many wavelengths as possible, this way avoiding thermalisation losses. A way to this is by using two absorbers, instead of one, which the first one absorbs high energy (high band gap cell) and another one below which absorb low energy (low band gap cell). This way, dependently if the cell is connected in series or in parallel, the final output power will increase, as shown at the following image.



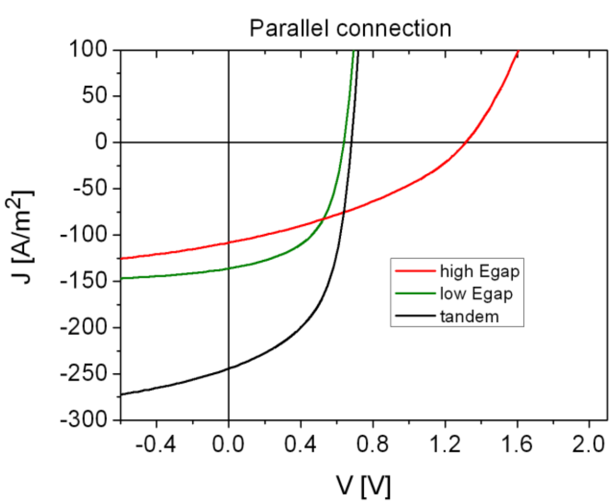


Illustration 8 - Series and parallel connection for tandem cells and the respectively IV curve.

In series, the total voltage will be the sum of the voltages across the multiple junctions and the current remains the same. In parallel, the total current will be the sum of the currents across the multiple junctions and the voltage remains equal, explained by Kirkoff laws.

Nowadays, there are several real multi-junctions (2, 3 and 4 junctions) solar cells which already achieved higher efficiencies than the S.Q. limit. At the graph below, it shows all the best research-cell efficiencies around the world made by NREL, where it is possible to see that the S.Q. was already exceeded or avoided.

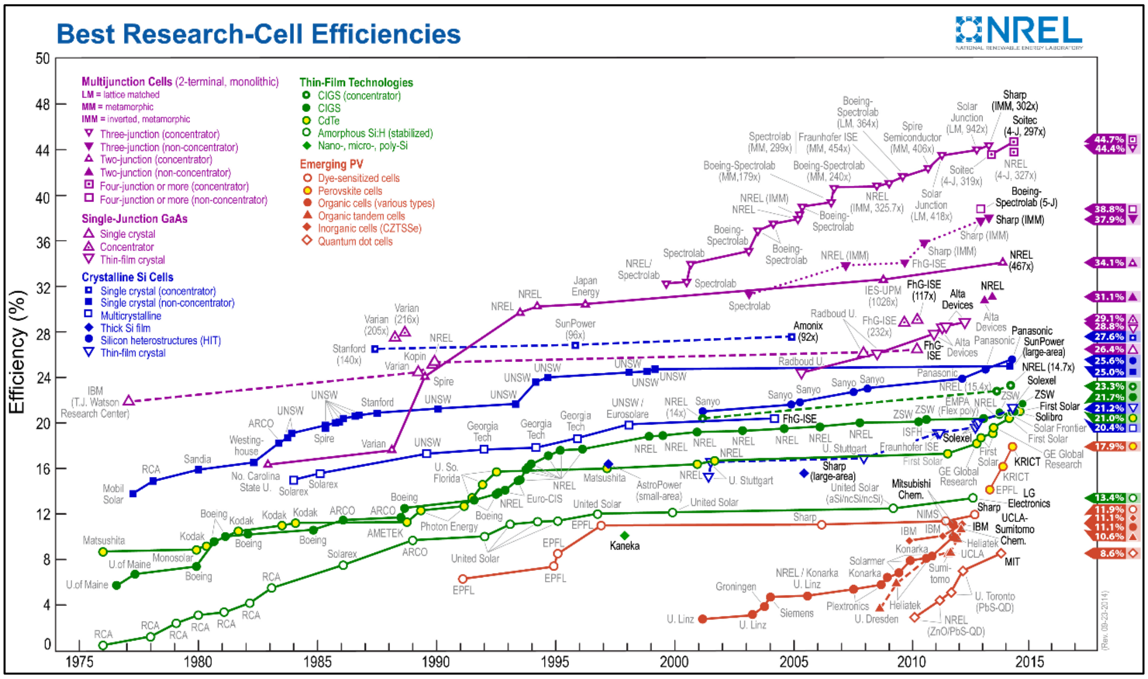


Illustration 9 - Best research-cell efficiencies around the world until 2017, made by NREL.

4. Conclusion

Shockley and Queisser were essential to develop a theoretical limit of efficiency for pn-junction, which gave a lot of contribution to the future development of solar cells in which more than 8000 papers cited their paper for further studies. The largest losses that they consider are either from photons that are not absorbed, or they thermalize. Nowadays there are more attempts to avoid the S.Q. limit (third PV generation), in which multi-junction solar cells are already available on the market. But there are other technologies that are still to come, such as hot-carrier collection (Le Bris and Guillemoles, Appl. Phys. Lett. 97, 113506), multiple-exciton generation (Beard et al., Science 334, 1530 (2011)) and intermediate band gaps (M.A. Grenn, Prog. Photovolt: Res. Appl. 9, 137), which I leave here for further studies on SES.