Lec03 - Solar energy

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The resource

In the first lecture of the course we considered the gigantic amount of solar power hitting spaceship earth (around 88 000 TW of *thermodynamic free energy* every second at the surface), but we also established the absurdity of viewing all this as a harvest-able resource when comparing to present or projected future societal energy demand. Starting from the simplistic assumption that 5%[1] of the global land mass (*i.e.* large parts of deserts, resting agricultural land, building roofs etc.) can ultimately be covered by solar harvesting systems what do we get? 5% of global land mass is an area of 7.4 million km^2 (equivalent to 77% of the United States or China) and if it were evenly distributed globally, it would correspond to an average irradiated free energy of about 1280 TW.[2] The technologies for *direct solar harvesting* (*v.i.*) are all trying to tap this resource, but there are, however, other indirect ways to collect solar energy which do not require covering large areas with anything.

How can we harvest sunlight (direct/indirect)

It makes sense to make a simple taxonomy to categorize the many different approaches to solar energy capture and harvesting. Firstly, we can divide the solar harvesting into direct methods and indirect methods. A direct method is one which directly turns sunlight into the desired (energy containing) product. Some common examples of direct solar harvesting include: Food crops (product: energy for human metabolism), photovoltaic solar cells (product: electrical energy), solar thermal collectors (product: hot water)

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[1] It is, of course, trivial to scale the resulting numbers up or down by the relevant factor in case you think 5% is unrealistic.

[2] In practice, most deserts have above-average solar input so we could argue that this should be adjusted up slightly – but on the flip-side as mentioned in the lecture 1 notes, the simple Carnot efficiency free energy over-estimates how much energy is actually harvestable, so all in all, a resource of around 1300 TW for 5% of the landmass is probably not far from reality.

etc. Much more common, however, is indirect solar harvesting which is often less efficient than the direct route (and sometimes by orders of magnitude as we shall see). Examples of indirect solar harvesting include: Wind power and hydro power, most bio-fuels, and much more.

Example: Hydro power

The "face value" efficiency of hydro power is very high. A water turbine can turn perhaps 0.9 times the potential energy of the water into electricity.

$$E_{hydro} = \eta_{turbine} mgh \tag{1}$$

where we take $\eta_{turbine}$ to be 0.9, m is the mass of water, g is the gravitational constant ($9.81\,\mathrm{m/s^2}$) and h is the height difference across the water dam. The potential energy of elevated water is pure *thermodynamic free energy*. So the direct water-to-electricity efficiency is great (90%), but from a solar energy perspective, the efficiency is actually rather horrendous. In order to move water from the ocean to behind the dam the sun must provide energy to evaporate the water. The heat of evaporation for water, is a around $E_{evaporation} \sim 2.26\,\mathrm{MJ\,kg^{-1}}$, so if the dam height is $100\,\mathrm{m}$ we get a solar-to-electricity efficiency of

$$E_{hydro,solar} = \eta_{turbine} mgh / E_{evaporation}$$

$$\sim \frac{0.9 \times 1\,\mathrm{kg} \times 9.81\,\mathrm{m/s^2} \times 100\,\mathrm{m}}{1\,\mathrm{kg} \times 2.26\,\mathrm{MJ\,kg^{-1}}} = 0.00039$$

So if viewed as a solar harvesting technology, the efficiency is actually only around 0.04% depending on the dam height. This is so bad that it makes even photosynthesis look good. . .

Of course, if the desired product of solar capture is not electricity, but *e.g.* hydrogen, a technology like photovoltaic capture+electrolysis is actually an indirect technique since we're making the hydrogen via electricity as an intermediate. The same is true for solar-thermal electricity production where we go from sunlight via heat to electricity.

From a thermodynamic point of view it is almost always more attractive to find a direct route to the desired product. This is particularly true if the intermediate is not a high quality energy (high quality energy/low entropy energy is energy where the *thermodynamic free energy* is almost the same as the total energy such as electricity or high energy photons; low quality energy is the opposite - typically heat, while many chemical forms of energy are often of intermediate quality). By this logic, going from sunlight to hydrogen via electricity might not be so bad -despite being indirect- be-

cause the intermediate is electricity, while going from sunlight to electricity via heat (solar thermal electric) is inherently a bad idea from an efficiency standpoint (although perhaps not from an economic standpoint).

Near term solar technology

Ignoring food production since that is more than "just" energy harvesting, the undisputed king of solar harvesting in at 2020 is ... hydro power!! Wind comes in second place, far behind hydro power. This is in spite of both hydro power and wind power being indirect solar harvesting techniques with minuscule solar-to-electricity efficiency they both (still) dominate over the direct harvesting techniques. The reason is simple: The act of grabbing the sunlight itself (which requires covering enormous areas with something) comes for free (courtesy of the oceans). You "just" have to build a dam on a river or stick a turbine into the air. On the other hand with direct solar capture we must pay for every square meter of solar capture area. Nevertheless, the future of solar energy looks like it will be dominated by direct harvesting.

There are many places in the World were much domestic hot water is supplied by small solar heaters. Hard numbers are difficult to find, but no doubt many, many GW worth of solar power is caught this way. Particularly in developing countries with good solar resources. On a larger scale, direct solar heating is sometimes used - *e.g.* as an input for district heating systems. In Denmark, for example, where district heating is quite common, there are many large-ish solar harvesters for heating the district heating water and it seems that this (very cheap and highly efficient) technology has plenty of room to grow. In fact, a very substantial fraction of global energy use is for space heating and for heating tap water. More fancy solar collectors such as evacuated tubes can heat water to a boil - even in the winter in Scandinavia (as long as the tubes face direct sunlight). Regardless of the $\sim 1\,\mathrm{TW}$ global potential for direct solar heating, the largest potential of any direct solar harvesting process seems to be photovoltaics, *i.e.* direct solar-to-electricity harvesting.

Photovoltaics

Solar cells are fascinating (demonstrate one to any 10 year old child and observe the amazement). There is something almost magical about a thin cell which can drive *e.g.* an electric motor indefinitely when illuminated.

There are many flavors of solar cells, but the market is totally dominated by single-junction solar cells based on semiconductors. In essence, a semiconducting material can absorb a photon of light and temporarily store

most of its energy as an electron-hole pair. If you somehow attach two wires to the semiconductor - one in which the electrons can flow to (but the holes cannot) and another where the holes can flow to (but electrons cannot) a difference in electrostatic potential will develop between the wires when light is absorbed by the semiconductor and thus they can drive an external load. Violà - power directly from the sun.

The main *figures of merit* for a solar cell are:

U_{oc} The open circuit voltage, [Volt]. This is the maximum voltage the illuminated cell can reach (when no current is flowing).

j_{sc} The short circuit current density, [Ampere/m^2]. This is the maximum current (per unit of illuminated cell area) that the cell can deliver to the external wire (when no voltage is requested).

FF The "fill factor", $FF \in [0 \dots 1]$ (no unit). This is the maximum power the cell can deliver at the optimum working voltage divided by the product of the open circuit voltage and the short circuit current:

$$FF = \frac{P_{max}/A}{U_{oc} \times j_{sc}} = \frac{U_{mpp} \times j_{mpp}}{U_{oc} \times j_{sc}} \tag{2}$$

Where P_{max} is the maximum power delivered by the optimally loaded cell and A is the illuminated area. U_{mpp} and j_{mpp} are the voltage and current density at the *Maximum Power Point* (the optimal load condition) of the cell. You might be wondering why $FF < 1$ - *i.e.* why $U_{mpp} < U_{oc}$ and $j_{mpp} < j_{sc}$. This shortfall is due to both non-ideal nature of real cells but also due to fundamental thermodynamic limits. The first non-ideality is that any real cell must have a finite internal resistance (the so-called *series resistance*), R_s. Then, according to Ohm's law, any finite current must give rise to a voltage loss of $U_{loss} = IR_s$ so the U is always less than U_{oc}. Moreover, any real cell with a potential difference from front to back will have a small, unwanted internal leakage current (in addition to the desired external current) due to a parasitic *shunt resistance*, R_{shunt}. This results in a loss of current $I_{loss} = U/R_{shunt}$.

Clearly, R_s must be minimized and R_{shunt} must be maximized, but it turns out at even with $R_s \to 0 \land R_{shunt} \to \infty$ (*i.e.* an ideal cell) we still have

$$U_{oc} - U_{mpp} \gtrapprox 100 \, \text{meV}$$

This difference is a substantial loss and it is a fundamental thermodynamic price we must pay to separate the electrons from the holes (because the cell must operate at finite temperature). It can be shown that the relation between U_{mpp} and U_{oc} under ideal conditions at temperature T is:

$$U_{mpp} = U_{oc} - \frac{k_B T}{e} ln \left(\frac{e U_{mpp}}{k_B T} - 1 \right) \tag{3}$$

where k_B is Boltzmann's constant and e is the elementary charge. In order to isolate U_{mpp} this calls for the *Lambert function*, W, with the property $y = xe^x \Leftrightarrow x = W(y)$ which can be used to give:

$$U_{mpp} = \frac{k_B T}{e} W(e^{\left(\frac{eU_{oc}}{k_B T}\right)})$$ (4)

Example: Theoretical U_{oc} to U_{mpp} voltage difference

Setting the cell temperature to 50°C so that $k_B T = 28\,\text{meV}$ and using a numerical calculator to evaluate W we get:

$$U_{oc} = 700\,\text{mV} \Rightarrow U_{mpp} = 614\,\text{mV}(\text{a loss of } 86\,\text{mV } (12\%))$$
$$U_{oc} = 1000\,\text{mV} \Rightarrow U_{mpp} = 903\,\text{mV}(\text{a loss of } 97\,\text{mV } (9.7\%))$$

Thus we see that the theoretical minimum voltage loss is on the order of $80\,\text{mV}$ to $100\,\text{mV}$ which motivates the statement, that in practice at least $100\,\text{mV}$ is lost here. This is equivalent to saying that there is a hard thermodynamic limit (due to finite cell temperature) on the FF. For the first cell in the example the FF is limited to 88% and to 90.3% for the second cell.

You might now be wondering what determines U_{oc}. It is determined by the ratio of the short circuit current and the reverse (dark) saturation current, j_s:

$$U_{oc} = \frac{k_B T}{e} ln\left(1 + \frac{j_{sc}}{j_s}\right) + \frac{k_B T}{e} ln(\eta_{external})$$ (5)

$\eta_{external}$ is the external luminescence efficiency of the cell - *i.e.* how good the cell is at not wasting excitations on non-radiative processes. $\eta_{external}$ can in principle approach 1 - in which case the second term drops out. j_s, which should be as low as possible, is determined by thermal excitation of electron-hole pairs even in the absence of light. We won't go into how this is calculated, but it essentially scales inversely with the exponential of the ratio of the semiconductor band gap to the temperature. *I.e.* j_s improves exponentially, as cell temperature is decreased or the bandgap is increased (see figure 1).[3]

This leads to the relation between the semiconductor band gap, Eg, and the open circuit voltage shown in figure 2. Notice that the U_{oc} increases linearly with band gap, but the slope is slightly less than 1 - and that there is an offset which significantly decreases the attractiveness of low band gap solar cells.

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[3] j_{sc} also depends on the bandgap because only photons with an energy above the bandgap energy can be absorbed by the semiconductor, but compared to the exponential dependence of j_s this variation is negligible.
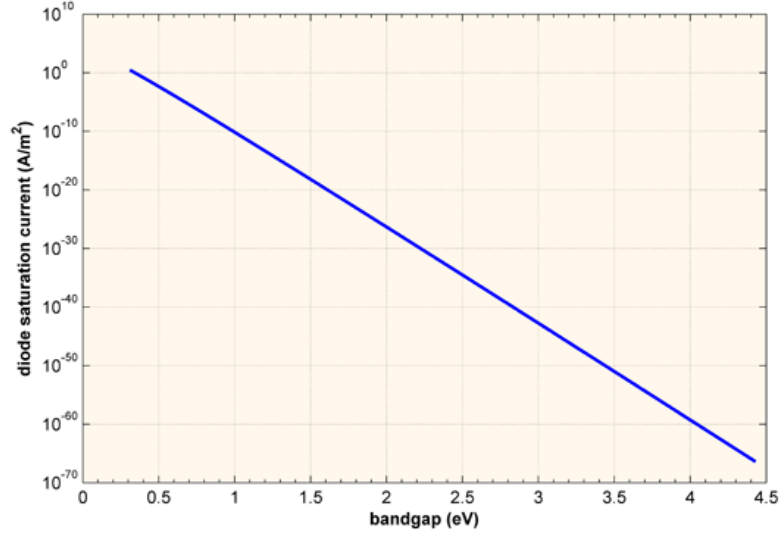
Figure 1: Ideal dark saturation current, j_s, as a function of absorber band gap at $T = 300\,\mathrm{K}$. From `www.pveducation.org/pvcdrom/solar-cell-operation/open-circuit-voltage`
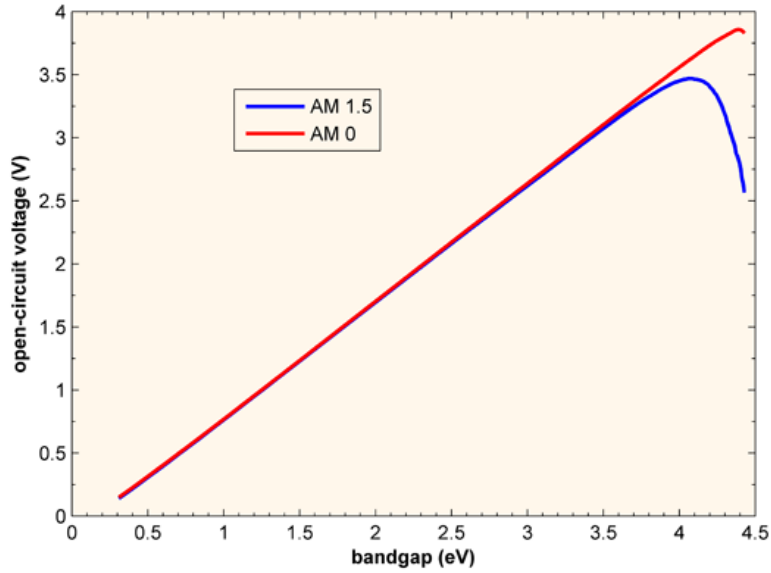

Figure 2: Theoretical open circuit voltage, U_{oc}, as a function of semiconductor bandgap at $T = 300\,\mathrm{K}$. AM0 is solar spectrum outside of the earth's atmosphere, while AM1.5 is the standard spectrum on earth. From: `<www.pveducation.org/pvcdrom/solar-cell-operation/open-circuit-voltage`

We should point out that the plot shows the (ideal) best case U_{oc}, and that for most real cells (including excellent Si-based cells) the second term due to $\eta_{external} < 1$ does not drop out and often costs amounts to hundreds of mV so the intersection of the red line in the illustration and the zero of U_{oc} is closer to a band gap of $0.4\,\mathrm{V}$ than $0.15\,\mathrm{V}$.

Finally, you might be tempted to think that because a higher bandgap gives a higher U_{oc} that a very high bandgap gives the best efficiency, but that's not the case. In fact, for the spectrum of light, we get here on earth the optimum band gap for a single junction solar cell is

$$Eg_{(optimum,AM1.5G)} \sim 1.25\,\mathrm{eV} \pm 0.15\,\mathrm{eV} \tag{6}$$

The reason is that increasing the band gap is the same as increasing the threshold energy which photons must have in order to be absorbed. This means that increasing the band gap causes a drop in j_{sc} and since the power scales with the product of U_{oc} and j_{sc} (and FF) the bandgap is inherently a compromise between increasing current without decreasing voltage too much. A careful analysis (the so-called detailed balance calculation) leads to the famous *Shockley-Queisser* limit. The SQ limit is works out to give a solar-to-electricity efficiency of $\sim 33\%$ for the solar spectrum on earth and at room temperature. This is the maximum thermodynamically possible efficiency any single-junction solar cell can ever reach. For context the best Si-solar cells are around 25% efficiency, so that technology is already 76% towards the SQ limit for an ideal cell (actually 80% towards the real limit for silicon due to its band gap of $1.1\,\mathrm{eV}$ and the fact that its is an indirect gap semiconductor). There aren't many technologies in the market closer to their fundamental theoretical limits than solar cells!

Improving photovoltaics

Since photovoltaics were introduced in the market more than 50 years ago their efficiency has increased dramatically (figure 3).

Today, there are multiple technologies in the market place which achieve solar-to-electricity efficiency between 20% and 25% on the module level (the efficiency of a full module is always less than that of a small champion research cell!): Crystalline silicon (c-Si), CdTe and CIGS (and GaAs for niche markets) all deliver $> 20\%$ efficiency which is very impressive indeed. c-Si dominates in terms of market share due to its attractive features: Low price, no dependence on rare, expensive or poisonous elements, great module stability and good "bankability" [4].

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[4]The term bankability covers how easy (and cheap) it is to get financing for a solar plant. Plants based on known technology offering only incremental improvements over "tried and tested" technology will have much easier access to money than any radically new designs. Thus bankability causes a great deal of conservatism in solar technology.
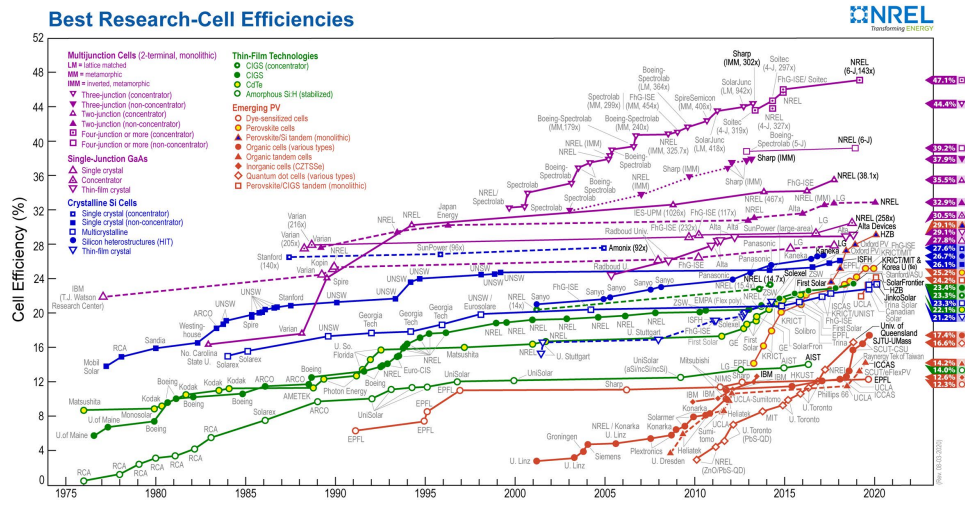
Figure 3: Timeline of world record photovoltaic (research) cell conversion efficiency. The SQ limit for single junction cells without optical concentration is around 33%. GaAs at 29.1% is *very* close to this limit.

Besides the relentless increase in efficiency, an even more impressive development has been the fantastic drop in price. Photovoltaics seem to follow Swanson's "law"/the solar learning curve whereby the market price for solar modules drop by around 23% for every doubling of the total cumulative production (figure 4). This is, of course, a purely empirical relation, but it captures how industrial production of photovoltaic panels becomes ever more optimized and gains "economy of scale" as the production grows.

Clearly, for the cost of photovoltaic power to drop along with the panel cost the other costs must follow the panel cost down. Fortunately the costs related to inverters (and other electronics), mounting hardware and the like has also dropped fast. Even the process of installation of hardware (manual work) has been coming down thanks to ever more clever mounting systems optimized for fast and reliable installation or even semi-automated installation. In fact in many countries it is now the "soft costs" [5] which pose the main drag on the overall price drop.

Leaving the soft cost problem to others, engineers are still looking to reduce hardware costs. Given that many costs scale with proportionally with the area of a photovoltaic installation there is a clear economic driver motivating increased module efficiency (even at a slightly higher $/W figure). So realizing that the state of the art photovoltaic cells are getting very close

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[5]Soft costs cover everything not directly related to erecting the installation. Things like permitting, customer acquisition, legal expenses, financing overhead etc. (Bean counting, in short).
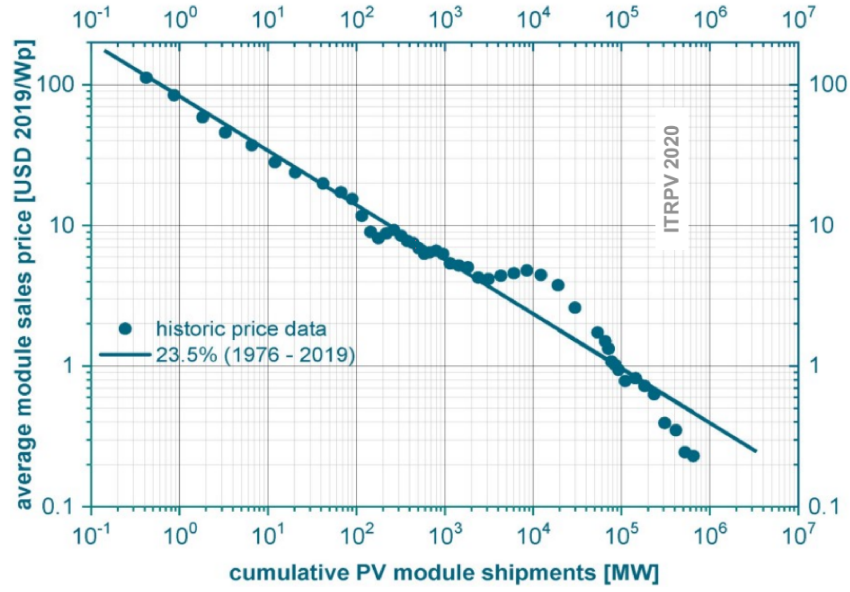
Figure 4: Market price of photovoltaic modules as a function of the total cumulative production (log-log plot). There is one datum for each year since 1976. The data line represents a decrease in price of 23.5% for every doubling of the total photovoltaic production. The plot also shows that cumulative solar production up to 2019 was around 6.5×10^5 MW - *i.e.* 650 GW. The temporary departure from the trend line in the early 2000s was when demand for high purity silicon for c-Si solar outgrew the available supply of scrap silicon from the microchip industry and new silicon production dedicated to photovoltaics had to be built. Today, c-Si photovoltaics is uses many, many times more high-purity silicon then the microchip industry and prices for high purity silicon have come down substantially. From: ITRPV 2020 report, https://itrpv.vdma.org/

to the SQ limit there is a serious global research effort underway to look into (cheap) options which might move the efficiency limit beyond 33%.

Fundamental research areas (future tech – hopefully)

One of the most promising approaches to moving the theoretical limit beyond the SQ limit is to upgrade from a single-junction cell architecture to multi-junction photovoltaic cells. Especially two- (tandem) or even triple-junction cell designs seem promising. A tandem design moves the SQ limit up to 42% (a gain of 9% absolute) while a triple-junction design is pushes the limit further to 49% [6]. Of course extra layers add manufacturing complexity (*i.e.* cost), but also -and more subtly- cells with many layers only perform well when illuminated with the exact design optical spectrum, and this is a problem because sunlight around noon is much more rich in blue light (high energy photons) than morning/evening light which severely lacks the blue photons. Thus a multi-junction cell optimized for mid-day performance will severely under perform in the morning and evening. For these reasons tandems are the primary focus of research and it seems reasonable, that we might one day have tandem panels on the market reaching 80% of their theoretical limit - *i.e.* around 34% solar-to-electricity efficiency. Lab-cells combining a perovskite top cell with a silicon rear cell have already reached 29.1% as can be seen in the figure 3. A tandem cell increases the maximum efficiency above that of the single junction cell because it allows the front cell to be optimized for blue and green light (*i.e.* with a high band gap and the correspondingly high voltage) while the rear cell can still absorb the red in near-infrared photons. So while the tandem can harvest the same number of photons as the single junction cell made from the rear cell material (typically c-Si) – it gets more voltage out of half of them. The result is that the current is half that of the single junction cell – but the voltage is more than doubled for an overall gain in power (and thus efficiency). In order for this to work, the band gap of the front cell should be matched to that of the rear cell so that they have matched photocurrent. In principle a careful numerical analysis is called for, but in practice the optimum is usually close to the point where the difference in band-gap is 680 meV or so. Thus in order to find a matched semiconductor for use as a front cell with a c-Si rear cell (band gap for c-Si is 1100 meV) you would for a semiconductor with a band gap of ca 1750 meV.

Besides multi-junction cells other avenues to overcome the SQ limit are also being explored. These include photon up- or down-conversion concepts

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[6]With an "infinite" number of junctions (obviously impractical), the SQ limit becomes 68%.
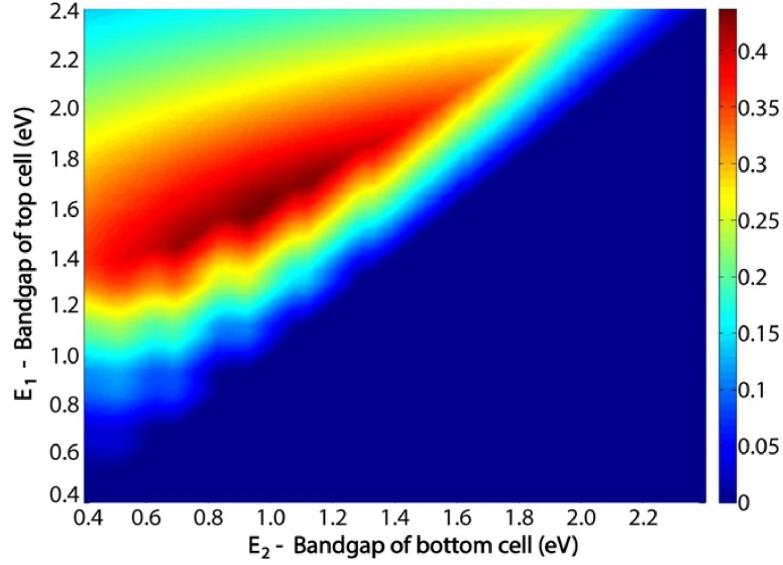
Figure 5: Map of SQ efficiency of a tandem (2-bandgap stacked) solar cell as a function of the two bandgaps. The global maximum is around 42% solar-to-electricity. Adapted from https://doi.org/10.1038/srep32349

where *e.g.* one blue photon is *down converted* to two near infrared photons to be absorbed in *e.g.* a c-Si cell; and *hot carrier* photovoltaic cells where the excited electrons in the semiconductor are captured before they *thermalize* - *i.e.* they are captured within femtoseconds so that their surplus energy is not wasted as heat. Another research field is to integrate electrochemical conversion directly on the solar absorber to store the energy by upgrading the energy content of chemicals. Sometimes called *artificial photosynthesis* or *photoelectrochemistry, PEC* the aim here is not to boost efficiency, but rather to store the solar energy for later use - for example as fuels.

Such advanced concepts (and many more besides) are, however, mostly just research projects with little-to-no market penetration yet.