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Technical Assessment Report

An Assessment of Solar Energy Conversion Technologies and Research Opportunities

GCEP Energy Assessment Analysis
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Abstract

The solar energy flux reaching the Earth's surface represents a few thousand times the current use of primary energy by humans. The potential of this resource is enormous and makes solar energy a crucial component of a renewable energy portfolio aimed at reducing the global emissions of greenhouse gasses into the atmosphere. Nevertheless, the current use of this energy resource represents less than 1% of the total electricity production from renewable sources. Even though the deployment of photovoltaic systems has been increasing steadily for the last 20 years, solar technologies still suffer from some drawbacks that make them poorly competitive on an energy market dominated by fossil fuels: high capital cost, modest conversion efficiency, and intermittency. From a scientific and technical viewpoint, the development of new technologies with higher conversion efficiencies and low production costs is a key requirement for enabling the deployment of solar energy at a large scale. This report summarizes the state of the research in some mature and emerging solar technologies with high potential for large-scale energy production, and identifies fundamental research topics that are crucial for improving their performance, reliability, and competitiveness.

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Foreword

This report is one of a series of assessments on various areas of the energy landscape prepared by GCEP staff. The assessments are intended to provide an introduction to the energy area as well as context for future fundamental research activity towards reducing greenhouse gas emissions. By examining the goals and potential of the energy transformations in question as well as the current progress and research towards these ends, the assessments take a step toward elucidating the most promising areas for future research. This report, produced by GCEP Energy Analysis staff, was written by Paolo Bosshard with contributions from Wes Hermann, Emilie Hung, Rebecca Hunt, and AJ Simon. GCEP is also grateful to Professor Martin Green, UNSW, Australia, for his suggestions and comments about the sections on photovoltaics. Please address all correspondence to gcep@stanford.edu.

Introduction

Solar radiation represents the largest energy flow entering the terrestrial ecosystem. After reflection and absorption in the atmosphere, some 100,000TW hit the surface of Earth and undergo conversion to all forms of energy used by humans, with the exception of nuclear, geothermal, and tidal energy. This resource is enormous and corresponds to almost 6,000 fold the current global consumption of primary energy (13.7TW [1]). Thus, solar energy has the potential of becoming a major component of a sustainable energy portfolio with constrained greenhouse gas emissions.

Solar radiation is a renewable energy resource that has been used by humanity in all ages. Passive solar technologies were already used by ancient civilizations for warming and/or cooling habitations and for water heating; in the Renaissance, concentration of solar radiation was extensively studied and in the 19th century the first solar-based mechanical engines were built [2]. The discovery of photovoltaic effect by Becquerel in 1839 and the creation of the first photovoltaic cell in the early 1950s opened entirely new perspectives on the use of solar energy for the production of electricity. Since then, the evolution of solar technologies continues at an unprecedented rate. Nowadays, there exist an extremely large variety of solar technologies, and photovoltaics have been gaining an increasing market share for the last 20 years. Nevertheless, global generation of solar electricity is still small compared to the potential of this resource [3]. The current cost of solar technologies and their intermittent nature make them hardly competitive on an energy market still dominated by cheap fossil fuels. From a scientific and technological viewpoint, the great challenge is finding new solutions for solar energy systems to become less capital intensive and more efficient. Many research efforts are addressing these problems. Low-cost and/or high-efficiency photovoltaic device concepts are being developed. Solar thermal technologies are reaching a mature stage of development and have the potential of becoming competitive for large energy supply. Intermittency is being addressed with extended research efforts in energy storage devices, such as batteries and other electric storage systems, thermal storage, and the direct production of solar fuels (typically hydrogen). All these are valuable routes for enhancing the competitiveness and performance of solar technologies.

The aim of this report is to evaluate the potential of solar energy for low-carbon intensive and large-scale energy production and to provide a picture of the state of research in the most significant solar technologies. More than a comprehensive review, this document is intended to be an attempt at identifying interdisciplinary and fundamental research topics with high breakthrough potential for the improvement of the performance, the reliability, and the competitiveness of solar technologies. For this reason this analysis is a bottom-up approach; solar technologies are organized by energy conversion paths and the discussion focuses, when possible, on the fundamental processes and the related technical challenges. Also, the cited references are meant to indicate the state-of-the-art and not to be a comprehensive snapshot of the ongoing research. Where possible, reviews were referenced that will provide the reader with more detail.

Solar Radiation

Solar radiation is an electromagnetic wave emitted by the Sun's surface that originates in the bulk of the Sun where fusion reactions convert hydrogen atoms into helium. Every second $3.89 \cdot 10^{26}$ J of nuclear energy is released by the Sun's core [4]. This nuclear energy flux is rapidly converted into thermal energy and transported toward the surface of the star where it is released in the form of electromagnetic radiation. The power density emitted by the Sun is of the order of 64 MW/m^2 of which $\sim 1370 \text{ W/m}^2$ reach the top of the Earth's atmosphere with no significant absorption in the space. The latter quantity is called the *solar constant*.

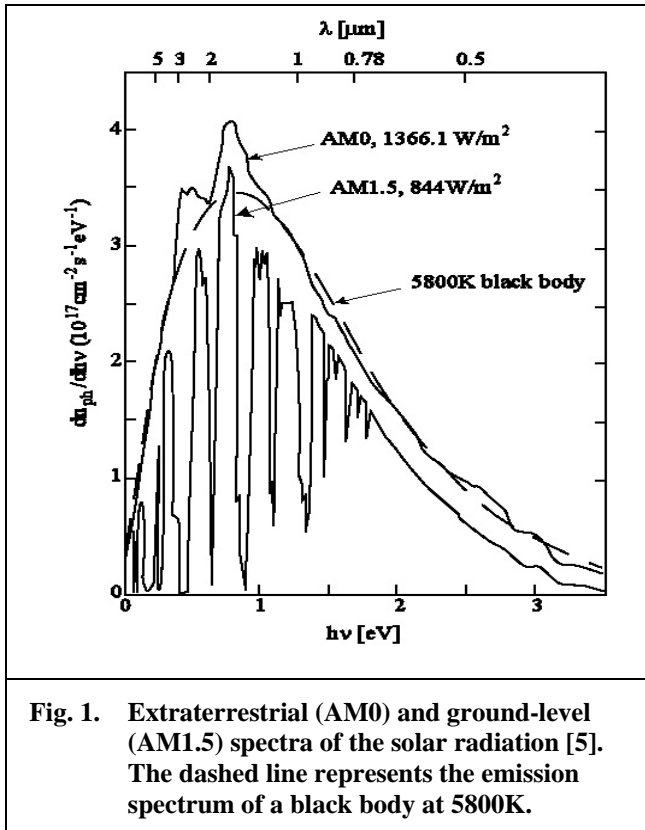


Fig. 1. Extraterrestrial (AM0) and ground-level (AM1.5) spectra of the solar radiation [5]. The dashed line represents the emission spectrum of a black body at 5800K.

The spectral range of the solar radiation is very large and encompasses nanometric wavelengths of gamma- and x-rays through metric wavelengths of radio waves. The energy flux is divided unevenly among the three large spectral categories. Ultraviolet (UV) radiation ($\lambda < 400 \text{ nm}$) accounts for less than 9% of the total; visible light (VIS) ($400 \text{ nm} < \lambda < 700 \text{ nm}$) for 39%; and infrared (IR) for about 52%.

As shown in Fig. 1, the pattern of the solar spectrum resembles closely the radiation of a perfect black body at 5800K. In the figure, AM0 indicates the *Air Mass Zero* reference spectrum measured – and partially modeled – outside the terrestrial atmosphere [5]. Radiation reaching the Earth's surface is altered by a number of factors, namely the

inclination of the Earth's axis and the atmosphere that causes both absorption and reflection (*albedo*) of part of the incoming radiation. The influence of all these elements on solar radiation is visible in the ground-level spectrum, labeled AM1.5¹ in Fig. 1, where the light absorption by the molecular elements of the atmosphere is particularly evident. Accounting for absorption by the atmosphere, reflection from cloud tops, oceans, and terrestrial surfaces, and rotation of the Earth (day/night cycles), the annual mean of the solar radiation reaching the surface is 170 W/m^2 for the oceans and 180 W/m^2 for the continents² [4]. Of this, about 75% is direct light, the balance of which is scattered by air molecules, water vapor, aerosols, and clouds.

¹ AM1.5 is the reference spectrum measured at a solar zenith angle of 48.19°

² U.S. average is 205 W/m^2

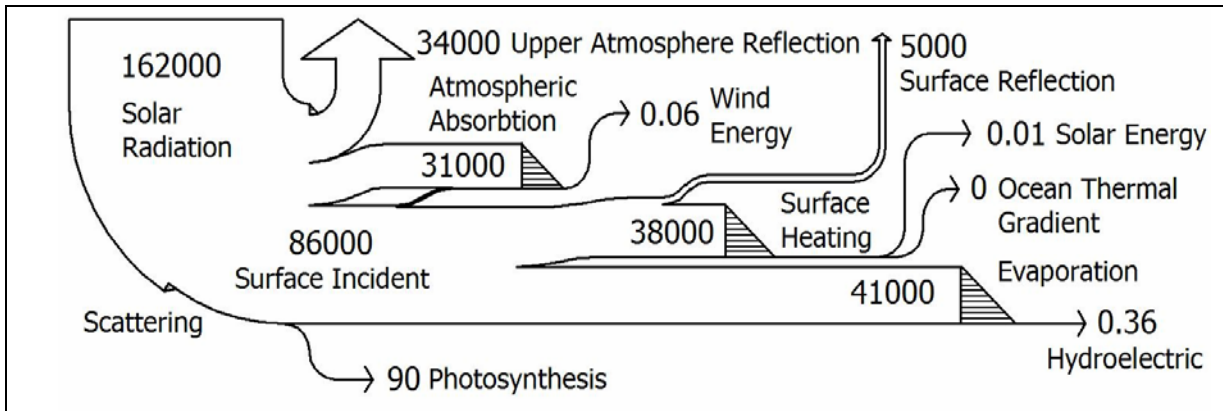


Fig. 2. Solar radiation exergy flow diagram (units in TW) [6]. Shaded surfaces represent natural exergy destruction; arrows represent human use for energy services.

The diagram in Fig. 2 illustrates the flow of the work potential, or exergy, of the solar energy into the atmosphere and the terrestrial ecosystem. This quantity represents the upper limit to the work obtainable from solar radiation conversion, a limit that is imposed by the 2nd law of thermodynamics and is independent of any conceptual device.

Of the 162PW of solar radiation reaching the Earth, 86PW hit its surface in the form of direct (75%) and diffused light (25%). The energy quality of diffused radiation is lower (75.2% of exergy content instead of 93.2% for direct light [7]), with consequences on the amount of work that can be extracted from it. 38PW hit the continents and a total exergy of 0.01TW is estimated to be destroyed during the collection and use of solar radiation for energy services. This estimation includes the use of photovoltaics and solar thermal plants for the production of electricity and hot water. Similar estimates are shown for wind energy (0.06TW), ocean thermal gradient (not yet exploited for energy production), and hydroelectric energy (0.36TW) [6].

Potential of Solar Energy

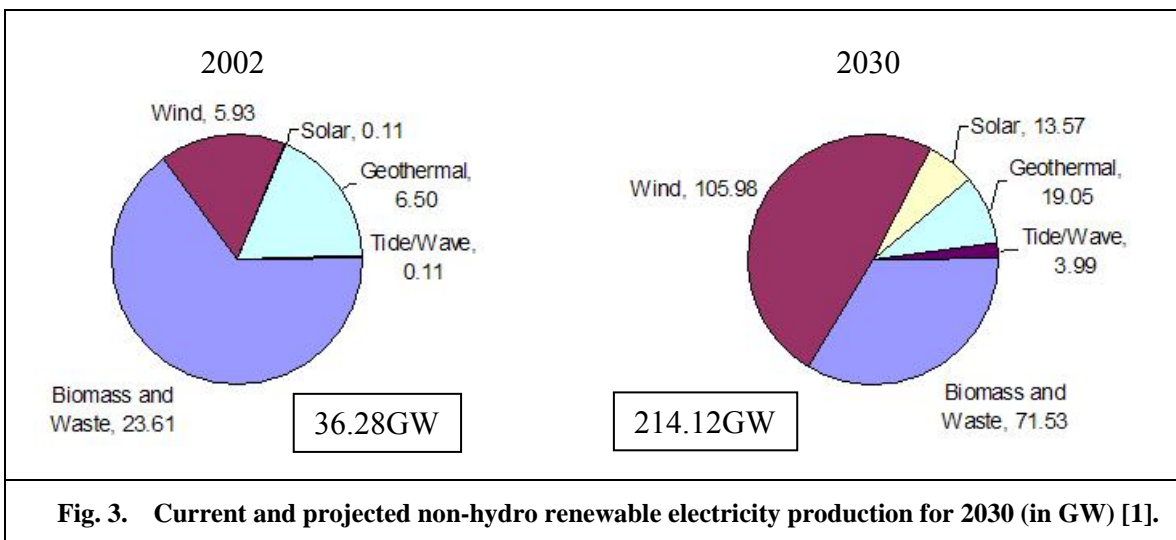
Deployment

The global solar energy potential ranges from 2.5 to 80TW (see Appendix). The lowest estimate represents around 18% of the total current primary energy consumption (13.7TW [1]), and exceeds 10% of the estimated primary energy demand by 2030 (21.84TW [1]). More optimistic assumptions give a potential for solar energy exceeding 5 fold the current global energy consumption.

Despite the relatively low power density of the solar flux, solar energy has the potential of supplying a non-negligible fraction of our energy needs. In the case of the US for example, the total electricity demand (418GW in 2002) could be satisfied by covering a land surface of 180km square with photovoltaics. This surface represents 0.35% of the total land area and roughly corresponds to the surface covered by roads in the country ($3.6 \cdot 10^{10} \text{m}^2$ [8]). All US electricity could hence be potentially produced by covering the paved roads with photovoltaic (PV) modules. Of course this cannot be applied to all

countries, where the required land fraction can be more important (e.g. 24% for Belgium [9]), with subsequent large social and environmental impacts.

The market share of solar energy is still low. Current electricity generation from PVs is only of the order of 2.6GW³ compared to 36.3GW for all renewable energies, hydroelectric power excluded [1,10]. Developed countries are steadily increasing their investments in solar power plants, and IEA projections for 2030 give an enhancement of solar electricity generation up to 13.6GW (80% of which will be from photovoltaics, and the rest (2.4GW) from solar thermal plants). However, this amount will not exceed 6% of the total electricity production from non-hydro renewable energies (see Fig. 3). It is worth noting that passive solar technologies for water heating, not included in these statistics, represent a fairly large amount of power. IEA estimates a power production of 5.3GW in 2002 and an increase up to 46GW by 2030 [1].



The major causes of the slow deployment of solar technologies are:

- The current relative high capital cost per kW installed compared with other fossil fuel based and renewable technologies;
- The intermittent nature of the energy input, and hence the requirement for energy storage systems to match the energy supply with the electricity demand and to decrease the capital cost. In a medium term, energy storage will be a key requirement for intermittent renewable energies to become more competitive versus fossil fuels. This report is not intended to analyze this issue in more detail, but the assessment of energy storage technologies is the object of a separate GCEP report [11].

³ Sandia published an exhaustive list of solar power plants (PV and/or solar thermal) with output power larger than 100kW installed worldwide in 2004 (<http://www.sandia.gov/pv/docs/PDF/Solar%20Power%20Plants%20Worldwide.pdf>).

If we want solar energy to significantly contribute to the world's energy supply, massive increases in manufacturing capacity are needed. From the research standpoint, more effort has to be put into improving efficiencies while reducing the manufacturing costs. This is a great technological challenge that requires investment of larger financial and intellectual resources to find innovative solutions.

Cost of electricity

The current higher capital cost of PV technologies compared to fossil fuels is a major barrier to large-scale deployment of solar energy. Today's price of electricity from solar energy⁴, as reported by the IEA, ranges from \$0.35/kWh to \$0.60/kWh for solar PV and from \$0.085/kWh to \$0.135/kWh for solar thermal, compared to \$0.045/kWh - \$0.055/kWh for wind and \$0.040/kWh for natural gas [1]. This large range of cost of solar energy is due to differences in the local insolation and to the estimation of the *Balance Of System* (BOS) cost relative to specific applications (namely stand-alone or grid-connected, ground-mounted or rooftop systems).

The price of the active material, the manufacturing, and the BOS components are the main elements determining the total price of PV technologies. Since the 1970's research has been exploring new processes for producing low-cost wafer silicon (both single-crystal silicon, sc-Si, and polycrystalline silicon, pc-Si), and the use of low-cost materials for thin-film PV applications, such as amorphous silicon (α -Si), III-V compounds (*e.g.* GaAs, InP), CIGS ($\text{Cu}[\text{In}_{1-x}\text{Ga}_x][\text{Se}_{1-y}\text{S}_y]_2$), cadmium telluride (CdTe), and more recently organic materials. The efficiency of thin-film laboratory cells has increased steadily in the last 20 years (see Fig. 4) and these technologies are believed to have the potential of bringing down the cost of solar energy to \$0.03/kWh - \$0.05/kWh [12].

Manufacturing scale is another key requirement for decreasing the cost of solar technologies since large-scale production lowers the cost of active materials and production. This is demonstrated by the price drop that silicon PV modules (sc-Si, pc-Si, α -Si) experienced since the early 1980's following a *progress ratio*⁵ of ~77% with cumulative production growing from 10MW to more than 1GW in 2000 [13]. If the trend continues, the price of \$1/W (~ \$0.06/kWh) will be reached when the cumulative production reaches 100GW [14], which in return will push further the deployment of solar energy systems.

Some studies (see for example [15]) suggest that this price can be reached entirely through manufacturing scale, without the need for any significant new invention. However, more research and development will increase competitiveness of solar technologies. Design and technological innovations could also decrease the cost of BOS components, and in particular of energy storage systems that represent a major fraction of

⁴ Cost of solar electricity is expressed either in \$/W (dollars per Watt-peak or Watt installed) or in \$/kWh. The translation from one unit to the other is straightforward and depends on local insolation and on the cost of money. In the case of the US, \$1/W corresponds approximately to \$0.06/kWh.

⁵ Given a *progress ratio* PR, PV modules' price decreases by 1-PR for each doubling of cumulative power; 1-PR is called the *learning factor*

the total installation cost of systems where storage is required (up to 70-80% with batteries accounting for 30-40% [16]). Such research efforts exist in the field of thermal storage associated with solar thermal technologies (in particular central receivers and parabolic troughs) and on new PV technologies with built-in storage systems, such as the dye-sensitized-cell based *photocapacitors* developed at Toim University in Yokohama [17]. Additionally, cell stability and low-cost encapsulation processes have also to be improved to maximize the lifetime of PV panels, with an incisive impact on system cost.

Organic-based photovoltaics (OPVs) are an alternative to present-day *p-n* junction photovoltaic devices for reducing the cost of solar energy. They can be deposited on lightweight, flexible and low-cost plastic substrates and thus have the potential to drop the manufacturing and installation cost by 10 to 20 fold.

The manufacturing cost for OPVs can be very low using large-throughput roll-to-roll manufacturing technology enabled with printable semiconductors and low-cost materials such as plastic substrates and polymer alternatives to Transparent Conducting Oxide (TCO) electrodes. Concerning BOS costs, packaging will remain a major concern due to the sensitivity of organic materials to oxygen and water vapor. Cost projections for electricity from organic photovoltaics based on the use of printing techniques and decrease of material cost with scaleup, are significantly below \$1/W [18].

Efficiency

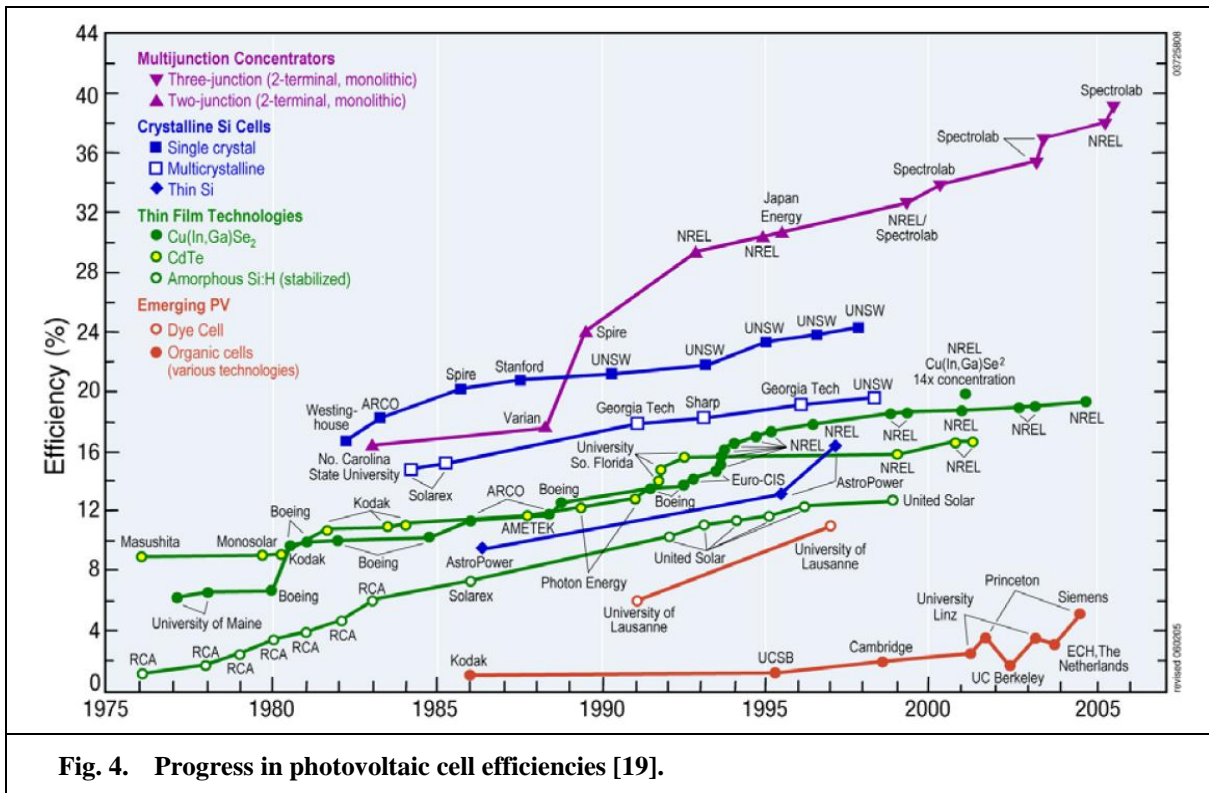


Fig. 4. Progress in photovoltaic cell efficiencies [19].

Over the past 30 years, solar cell efficiencies have continuously improved for all technologies. Among the most important accomplishments to be noted ([20] – see below

for more detail about the specific technologies) are the 24.7%-efficient c-Si solar cell (University of South Wales, Australia), the 18.4%-efficient CIGS solar cell (NREL), the 16.5%-efficient CdTe solar cell (NREL), and the 39%-efficient GaInP/GaAs/Ge triple-junction solar cell under 241-suns concentration (Spectrolab) [21]. Research on dye-sensitized solar cells (DSSCs) and organic solar cells (OSCs) began only during the last decade. The last reported record efficiencies are 10.4% for DSSCs (Ecole Polytechnique Fédérale de Lausanne, Switzerland) [22], and 5.7% for OSCs (Princeton University) [23].

Despite the notable progress made in the improvement of the efficiencies of all these technologies, achieved values are still far from the thermodynamic efficiency limits of ~31% for single junctions⁶, 50% for 3-cell stacks, impurity PVs, or up- and down-converters, and 54-68% for hot carrier- or impact ionization-based devices [24]. Furthermore, the efficiencies of commercial (or even the best prototype) modules are only about 50% to 65% of these “champion” cells [20]. Closing these gaps is the subject of ongoing research.

The solar-to-electric efficiency of solar thermal technologies varies largely depending upon the solar flux concentration factor, the temperature of the thermal intermediary, and the efficiency of the thermal cycle for the production of mechanical work and electricity. Parabolic troughs and power towers reach peak efficiencies of about 20%. Dish-Stirling systems are the most efficient, with ~30% solar-to-electric demonstrated efficiency. The performance of these systems is highly influenced by the plant availability. In the case of parabolic troughs and power towers, thermal storage increases the annual *capacity factor*⁷ from typically 20% to 50% and 75%, respectively.

Environmental Aspects of Solar Energy

Solar energy is promoted as a sustainable energy supply technology because of the renewable nature of solar radiation and the ability of solar energy conversion systems to generate greenhouse gas-free electricity during their lifetime. However, the energy requirement and the environmental impact of PV module manufacture can be further reduced, even though recent analysis of the energy and carbon cycles for PV technologies recognized that strong improvements were made both in terms of energy and carbon paybacks.

⁶ Estimation by Shockley and Quieser for a bandgap of 1.1eV [W. Shockley, H.J. Quieser, “Detailed balance limit of efficiency of *p-n* junction solar cells”, J. Appl. Phys., **32**(3), 1961, p. 510]; their approach can be used to estimate the efficiency limit for single-junction organic photovoltaics if the bandgap energy is replaced by the exciton energy [B.A. Gregg, “The photoconversion mechanisms of exciton solar cells”, MRS Bulletin, **30**, 2005, p. 20]; calculations by Peumans and Forrest give a ~20%-efficiency limit ([P. Peumans, S.R. Forrest, “Separation of geminate charge-pairs at donor–acceptor interfaces in disordered solids”, Chem. Phys. Lett., **398**(1), 2004, p. 27],[S.R. Forrest, “The limits to organic photovoltaic efficiency”, MRS Bulletin, **30**, 2005, p. 28])

⁷ Annual energy output divided by the theoretical maximum output, if the plant were running at its rated (maximum) power during all of the 8766 hours of the year.

Energy payback

In the case of pc-Si, energy payback calculations are not straightforward because today's PV industry usually recrystallizes silicon recycled from the semiconductor industry. Calculations reported in 2000 by E. Alsema [25] give estimates of the life-cycle energy requirement embodied in, respectively, frameless sc-Si and pc-Si PV modules of 1580kWh/m^2 (11.4kWh/W) and 1170kWh/m^2 (8.8kWh/W). By 2010 the requirement of electric energy for these PV technologies is forecasted to decrease to 890kWh/m^2 (5.6kWh/W) and 720kWh/m^2 (4.7kWh/W) [25]. Assuming 12% conversion efficiency (standard conditions) and 190W/m^2 of sunlight energy flux, this results in a payback time of about 4.5 years for near-term pc-Si PV modules. As illustrated in Fig. 5, more recent estimates of the energy payback time for polycrystalline silicon (pc-Si) technologies are about two years [26].

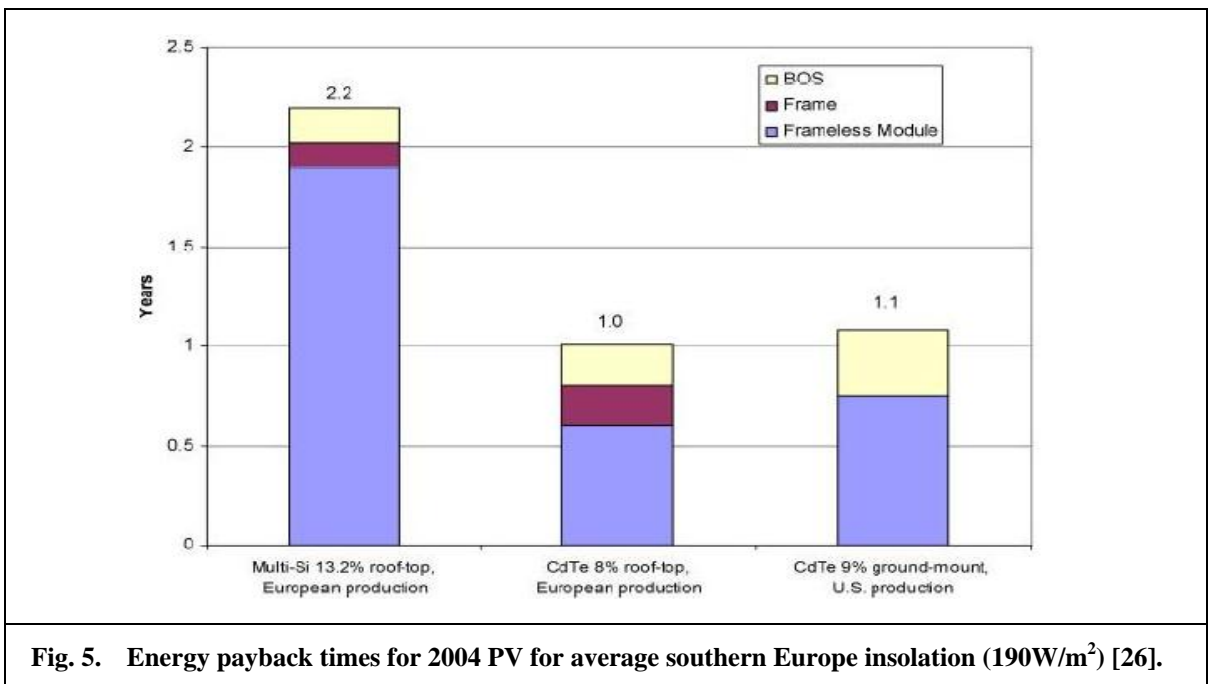


Fig. 5. Energy payback times for 2004 PV for average southern Europe insolation (190W/m^2) [26].

For thin films, the energy required to deposit the active layer is negligible compared to forming crystalline silicon wafers. Instead, the major energy sink is the energy embodied in the glass or stainless steel substrate, the film deposition process, and facility operation. These energy costs are similar for all thin-film technologies (CIGS, CdTe, α -Si), varying only in the film deposition processes. An estimate for the frameless α -Si module electricity requirement is 330kWh/m^2 (4.3kWh/W) [25]. According to these estimates and assuming 7% conversion efficiency (standard conditions) and 190W/m^2 of available sunlight flux, the payback time for current thin-film PV systems is around 2.8 years. More recent estimates give shorter payback times for thin-film technologies of about one year [26].

In a rooftop- or ground-mounted, grid-connected PV system the BOS components and module frames represent a non-negligible fraction of the total energy requirement [27]. For a rooftop-mounted system another 120kWh/m^2 should be added to the overall life-

cycle energy requirement, resulting in a payback time of about 3.5 years. Support structures for ground-mounted systems would add about another year to the payback period. Despite the wide range of payback times that can be found in the literature, all estimates remain higher than for other renewable sources such as wind (e.g. 3-4 months for wind [28]).

It is interesting to note that analysis of fossil-fuel energy production has suggested that it has similar energy payback periods to PV technologies if the costs for mining, transportation, refining, and construction are included in the calculation of the life cycle of fossil fuels [29].

Carbon payback

The CO₂ savings (other pollutants are also avoided, including NO_x, SO₂, and particulates) from displacing fossil fuels with photovoltaic systems depend upon the regional fossil fuels mix and the solar irradiance; values range from 270g to >1050g of CO₂/kWh. The world average is about 660g of CO₂/kWh [27]. Assuming an average of 5.5 hours of sunlight per day, a 1kW PV panel would give a yearly CO₂ savings of 1330kg.

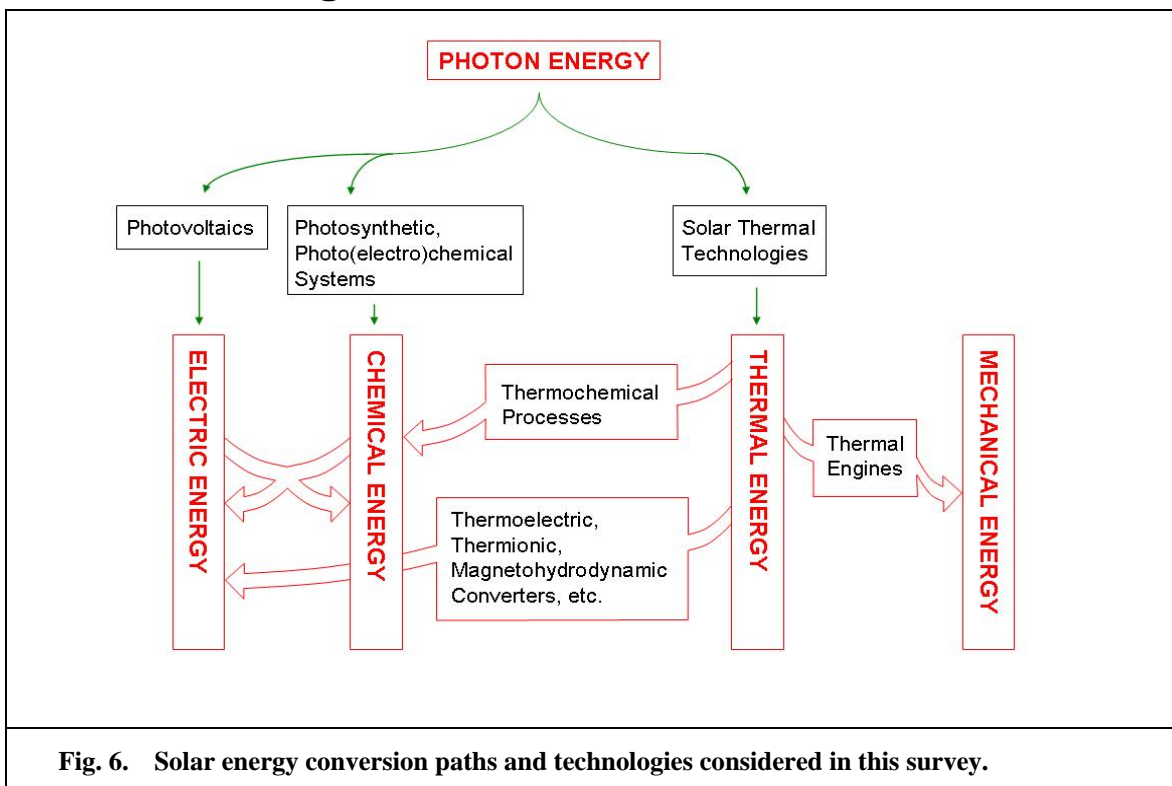
The CO₂ payback time from avoided emissions also depends on the local energy mix and the panel efficiency. Assuming an energy cost for a sc-Si panel of 600kWh/m² and the average of 660g of CO₂/kWh, the manufacture of a 1m² panel produces ~400 kg of CO₂. If we assume 12% efficiency and a solar irradiance of 1kW/m², it takes 3300kg of CO₂ to produce a 1kW PV plant, which is paid back in avoided emissions at 1330kg/year for a total time of 2.5 years. (See [14] for a more detailed analysis.) Higher cell efficiencies lower both the energy and CO₂ payback time, as do manufacturing techniques that are more energy efficient.

Safety and environmental issues

The major safety and environmental issues related to the manufacture of photovoltaics are (1) the safe handling of gases used for surface treatment or the growth of thin films (e.g. AsH₃, SiH₄, GeH₄, PH₃, B₂H₆, and H₂Se), and (2) the toxicity of some semiconductor components (e.g. Cd). (See [30] for more information.) It is generally believed that safe usage of potentially hazardous materials in PV manufacturing is possible and that the electronics industry has already made significant progress in dealing with similar materials [16]. Nevertheless, further investigation could lead to the replacement of toxic components and thus eliminate most of the concerns about the environmental risks of photovoltaics [31].

Recycling is an important strategy to be considered to enhance the public acceptance of PV technologies, to conserve rare minerals such as tellurium, and to reduce the energy requirement of PV manufacturing. Recycling cost estimates are 0.2-0.4\$/W for CdTe modules (at a process scale of 2MW), and about 0.13\$/W for c-Si cells at an operational scale of 150,000 c-Si cells per year (for comparison the production of a c-Si cell – not module – costs about 1.50\$/W) [32].

Solar technologies overview



A wide variety of solar technologies have the potential to become a large component of the future energy portfolio. Passive technologies are used for indoor lighting and heating of buildings and water for domestic use. Also, various active technologies are used to convert solar energy into various energy carriers for further utilization:

- Photovoltaics directly convert photon energy into electricity. These devices use inorganic or organic semiconductor materials that absorb photons with energy greater than their bandgap to promote energy carriers into their conduction band. Electron-hole pairs, or excitons for organic semiconductors, are subsequently separated and charges are collected at the electrodes for electricity generation.
- Solar thermal technologies convert the energy of direct light into thermal energy using concentrator devices. These systems reach temperatures of several hundred degrees with high associated exergy. Electricity can then be produced using various strategies including thermal engines (*e.g.* Stirling engines) and alternators, direct electron extraction from thermionic devices, Seebeck effect in thermoelectric generators, conversion of IR light radiated by hot bodies through thermophotovoltaic devices, and conversion of the kinetic energy of ionized gases through magneto hydrodynamic converters.
- Photosynthetic, photo(electro)chemical, thermal, and thermochemical processes are used to convert solar energy into chemical energy for energy storage in the form of chemical fuels, particularly hydrogen. Among the most significant processes for hydrogen production are direct solar water splitting in

photoelectrochemical cells or various thermochemical cycles such as the two-step water-splitting cycle using the Zn/ZnO redox system.

This document focuses on active solar technologies which are organized according to the energy conversion paths that they use to convert the energy of photons into a usable energy form: photons-to-electricity, photons-to-chemical energy, photons-to-heat-to-electricity, and photons-to-heat-to-chemical energy (see Fig. 6). This analysis focuses on the fundamental physical processes that govern the operation of the solar devices with the intent of identifying common trends or synergies between different technologies that could help identify novel research opportunities.

Photon-to-Electric Energy Conversion

Photovoltaic devices allow the direct production of electricity from light absorption. The active material in a photovoltaic system is a semiconductor capable of absorbing photons with energies equal to or greater than its bandgap. Upon photon absorption, an electron of the valence band is promoted to the conduction band and is free to move through the bulk of the semiconductor. In order for this free charge to be captured for current generation, decay to the lower energy state, *i.e.* recombination with the hole in the valence band, has to be prevented through charge separation.

In photovoltaic devices made of inorganic semiconductors, charge separation is driven by the built-in electric field at the *p-n* junction. As a consequence, their efficiency is determined by the ability of photogenerated minority carriers to reach the *p-n* junction before recombining with the majority carriers in the bulk of the material. Thus, bulk properties such as crystallinity and chemical purity often control the device efficiency.

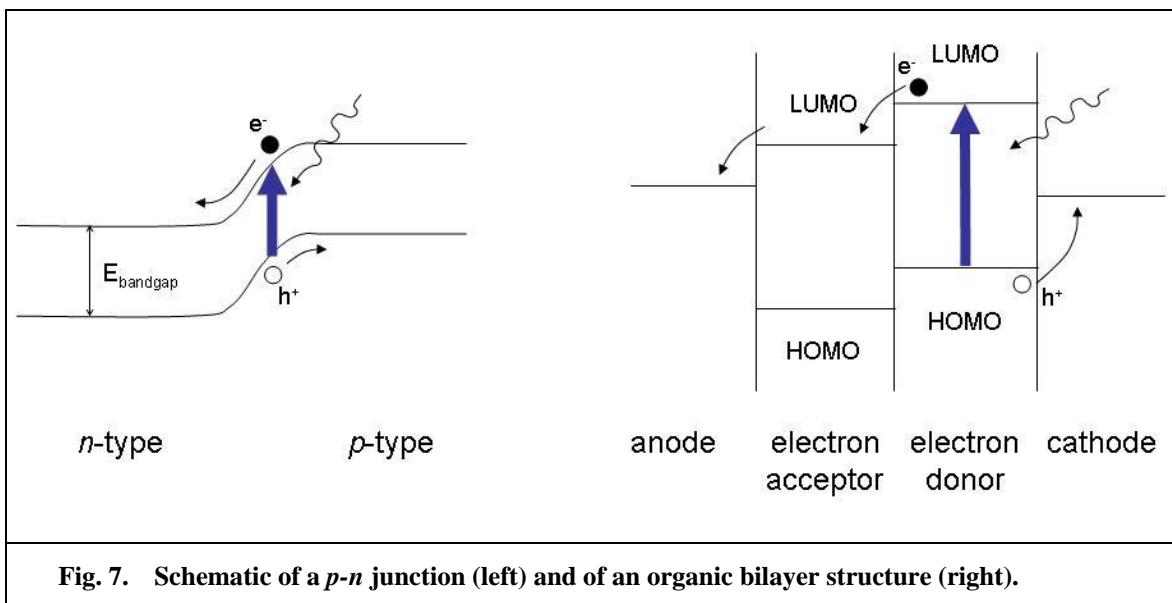


Fig. 7. Schematic of a *p-n* junction (left) and of an organic bilayer structure (right).

The operation of organic photovoltaics (OPVs) is fundamentally different. The optical and electronic properties of organic semiconductor materials are determined by the

molecular orbitals that are built up from the summation of individual atomic orbitals in the molecule.

The molecule's properties, and in particular its bandgap, are determined by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Light absorption in either small molecules or in conjugated polymers⁸ [33] leads to the formation of an exciton, *i.e.* an electron-hole pair that is bound together by Coulomb attraction, that must be dissociated. A built-in electric field can be created by sandwiching an organic semiconductor between two semiconductors with different work functions, but this method is not effective in splitting excitons. Instead, efficient exciton dissociation occurs at the interface between a donor material, where the exciton is created, and an acceptor material with an empty energy level that is lower than the LUMO of the donor (see Fig. 7). Exciton dissociation at the heterojunction produces electrons on one side of the interface already separated from the holes produced on the other side of the interface. This creates a photoinduced interfacial chemical potential energy gradient that efficiently drives the photovoltaic effect, even in the absence of a built-in electrical potential.

The efficiency of these devices is determined by the requirement that excitons reach the donor-acceptor interface, charges are transferred before recombination occurs, and charges are subsequently transported to the electrodes before electrons back-transfer from the LUMO of the acceptor to the HOMO of the donor.

In both inorganic and organic photovoltaic technologies, many strategies are under investigation for achieving efficient light absorption, charge separation, transport, and collection. The present analysis covers these fundamental processes and spans over a large range of technologies based on inorganic semiconductor materials such as silicon (c-Si, pc-Si, or α -Si), III-V compounds (*e.g.* GaAs, InP), chalcogenides (*e.g.* CdTe, CIGS), and various organic-based thin films:

- Photoelectrochemical cells, or Dye-Sensitized Solar Cells (DSSCs), where the light absorption occurs in organic dyes adsorbed on the surface of a wide-bandgap nanostructured metal oxide semiconductor substrate, usually TiO₂; upon excitation, electrons are injected into the conduction band of the oxide semiconductor and holes are scavenged by a redox couple in solution, such as iodide/triiodide (I⁻/I₃⁻). Solid-state photoelectrochemical cells use an organic semiconductor or ionic medium as a replacement to the liquid electrolyte;
- Multilayer organic planar devices, in which molecules are deposited sequentially to form a stacked device;
- Organic bulk heterojunctions, where organic donor and acceptor materials are blended on the nanoscale;

⁸ Conjugated polymers, also called Intrinsic Conducting Polymers (ICPs), have a framework of alternating single and double C-C (sometimes C-N) bonds. Delocalization of the double bonds over the entire polymer molecule produces a bandgap that lies in the range of 1.5-3eV.

- Organic/inorganic composites such as heterojunctions combining light-absorbing conjugated polymers and large-bandgap nanostructured inorganic material such as TiO₂ or ZnO;
- Artificial photosynthetic macromolecular structures where light-absorption and charge separation are realized by separated complexes within the same structure.

Additionally, advanced thin-film technologies, called “3rd generation photovoltaics”, are considered as a promising route to increasing the efficiency and/or lowering the cost of photovoltaics (see Fig. 8). Some advanced thin-film technologies included in this category are listed in the following paragraph.

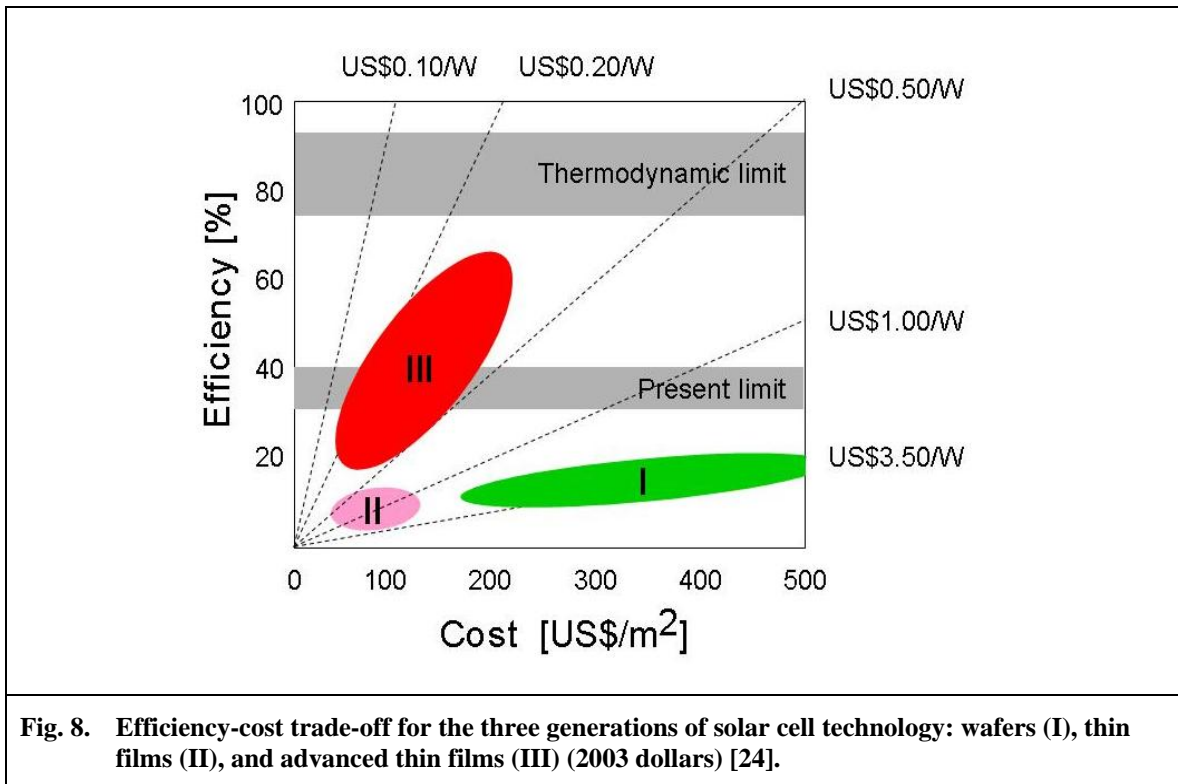


Fig. 8. Efficiency-cost trade-off for the three generations of solar cell technology: wafers (I), thin films (II), and advanced thin films (III) (2003 dollars) [24].

Photon absorption and carrier generation

One of the most critical requirements for a single junction cell is that the bandgap energy must be optimized to transfer maximum energy from the incident light to the photogenerated electron-hole pairs. The simultaneous optimization of the cell voltage, proportional to E_{bandgap} , the photogenerated current density, decreasing with E_{bandgap} , and of the fill factor, increasing with E_{bandgap} [34], gives an optimal value of $E_{\text{bandgap}} \sim 1.1-1.4\text{eV}$.

The bandgap energy of silicon (1.12eV) is almost ideal and allows absorption of photons in the near-infrared (NIR), visible, and ultraviolet spectrum. However, the indirect bandgap of crystalline silicon causes relatively poor light absorption ($<10^4\text{cm}^{-1}$) for photons with energies below 3.4eV, which is the silicon direct bandgap energy.

Therefore, typical sc-Si wafers must be 100-300 μm thick for achieving efficient light absorption.

Thin-film photovoltaic materials have a major advantage over silicon, since most of them have direct bandgap, resulting in higher optical absorption. This allows typical thin-film PV devices to use very thin layers of active material ($\sim 1\mu\text{m}$) that can thus be of lower quality. Today's most successful materials for thin-film photovoltaics are α -Si, where the optical absorption is increased by impurity scattering, CdTe, with a bandgap of 1.48eV, and CIGS, whose bandgap can be tuned around the nominal value of 1.04eV by controlling its composition and that has the highest absorption constant ($3\text{-}6 \cdot 10^5 \text{cm}^{-1}$) reported for any semiconductor. More effort is required to find new semiconductor materials combining optimal bandgap, inactive grain boundaries, stability properties, and processing ease.

Spectrum splitting through *multijunction cells* with bandgap energies designed to match the solar spectrum is a very effective route to increasing efficiency, since this method reduces the energy loss driven by the thermalization of hot electrons generated by the absorption of photons with energy $> E_{\text{bandgap}}$. Many configurations and materials have been investigated for tandem and multijunction cell concepts. Among the most interesting approaches using silicon, are: (1) the amorphous silicon-germanium alloys (a-Si,Ge:H) where the bandgap can be varied from 1.75eV down to below 1.3eV; (2) the microcrystalline and amorphous silicon tandem cells ($\mu\text{c-Si:H}$ (1.12eV)/ α -Si:H (1.75eV), also called *micromorph* [35]) with enhanced stability properties against light-induced degradation and with maximal and stable efficiencies of 14.7% and 10.7%, respectively; (3) multijunctions incorporating material alloys such as amorphous or polycrystalline silicon carbide (α -Si:C) and silicon germanium (α -Si:Ge). III-V materials have ideal bandgap energies for highly efficient photon absorption (*e.g.* 1.0-1.1eV for InGaAsN, 1.4eV for GaAs). In addition, fine-tuning of both lattice constant and bandgap can be achieved by modifying the alloy composition, resulting in a large flexibility that is exploited for growing multijunction cells. Lattice-matched and metamorphic 3-junction GaInP/GaInAs/Ge cells currently hold the efficiency records under concentrated sunlight (39% efficiency at 236 suns and $\sim 37\%$ efficiency at 310 suns, respectively) [21,36]. The cost of growing processes such as molecular beam epitaxy and metal-organic vapor phase epitaxy directed these technologies to space applications, but their inclusion in *concentrator systems* together with manufacturing scale-up might have a sensible impact on their cost for terrestrial applications [37]. To achieve this goal, however, concentrating technologies will require more technical development.

Nanoscale features are widely used in solar technologies to increase light absorption. In particular, *quantum dot sensitization* has large potential for matching the absorption spectrum of a photovoltaic cell to the solar spectrum. Nanoparticles can be built from a large variety of semiconductor materials and their bandgap can be tuned by changing the particle size and shape. Additionally, recent experimental results have demonstrated the

feasibility of multiple (2 or more) carrier generation through *impact ionization*⁹ in PbSe nanocrystals for photon energies 3 fold larger than the nanocrystals bandgap energy, E_{bandgap} . Impact ionization can potentially increase the power conversion efficiency of a solar cell based on PbSe nanocrystals by 35-40% [38].

*Extremely Thin Absorber*¹⁰ devices are another example of systems taking advantage of nanoscale structures [39]. The interest of this design is the tolerance to higher levels of defects and impurities than in flat thin-films devices, because photoinduced charge separation occurs on a length scale of a few nanometers. On the other hand, making PIN junctions (p-type semiconductor/insulator/n-type semiconductor) with such high contact area is difficult and this has hampered the performance of these cells.

Multijunction cells and multiple electron-hole pair generation are two among a set of novel approaches that could be denoted as “*3rd generation PVs*” that aim at increasing the thermodynamic efficiency limit of solar cell devices [24]. Research efforts in these technologies are increasing and the feasibility of some of them has still to be proven experimentally. The following is a non-exhaustive list of these advanced solar conversion options [24,40,41,42,43]:

- *hot carrier cells*, where the rate of photoexcited carrier cooling, caused by phonon interaction in the lattice, is slowed down to allow time for the carriers to be collected whilst they are still “hot”, thus reducing thermalization losses. Efficiency limits for these systems are of the order of 54-68%;
- *up/down converters*, converting respectively high energy photons ($>2E_{\text{bandgap}}$) into two lower-energy photons with energy $>E_{\text{bandgap}}$, and vice versa. The thermodynamic efficiency limit for a solar cell with a band-gap energy of 2eV and with an optimised up-converter attached to its rear surface is 50.7% for a non-concentrated AM1.5 spectrum;
- *multiband cells* where one or more electronic energy levels are created in the forbidden band of the bulk semiconductor material through superlattice structures based on a periodic structure of alternating layers of semiconductor materials with wide and narrow band gaps, high concentration impurities such as rare-earths in wide bandgap semiconductors, or by using semiconductors with multiple narrow bands such as I-VII and I₃-VI compounds;
- *thermophotovoltaic* devices involving the photovoltaic conversion by a receiver cell of radiation from an emitter, which could be heated by various sources including sunlight. A prime difference from normal solar photovoltaics is that

⁹ Impact ionization is an Auger-type process whereby a high-energy exciton, created in a semiconductor by absorbing a photon of energy $\geq 2E_{\text{bandgap}}$, relaxes to the band edge via energy transfer of at least $1 E_{\text{bandgap}}$ to a valence band electron, which is excited above the energy gap.

¹⁰ Extremely Thin Absorbers are conceptually close to dye-sensitized solid heterojunctions: they use a nanostructured substrate such as porous silicon or sintered films of Si nanocrystals, and an extremely thin (2-3nm) layer of a small-band-gap inorganic semiconductor, such as CuInS₂, as a replacement of the molecular dye. A hole conductor such as CuSCN is placed on top of the absorber, producing a PIN junction: p-type semiconductor/insulator/n-type semiconductor. The structure has the advantage of enhanced light harvesting due to the surface enlargement and multiple scattering.

emitted energy unable to be used by the receiver can, in principle, be recycled, allowing high conversion efficiency (up to ~54%);

- *surface plasmon* on metal nanoparticles used to enhance the light absorption of thin semiconductor layers by coupling the light with the waveguide modes of the semiconductor layer;
- *solar antenna* (or “rectenna”) *arrays* use a micro-scale antenna to convert broadband electromagnetic radiation into an AC field and optical frequency rectifiers to provide a DC electric output; theoretical efficiency limit is >85% under direct sunlight.

One of the key advantages of *organic photovoltaics* (OPVs) is that organic small-molecules and polymer materials have very high absorption coefficients, exceeding 10^5cm^{-1} , that permit the use of films with thicknesses of only several hundred nanometers. Current OPV devices exhibit high (>70%) quantum efficiency. However obtaining absorption in the NIR spectral range has proven to be challenging. Bandgaps of the active organic materials must be reduced to approach the nominally optimal value of 1.4eV while retaining good charge carrier mobility, open-circuit voltage, and the efficiency of charge separation. Conjugated polymers with bandgaps ~1.6eV have been reported in the literature [44] and various Ruthenium complex dyes absorbing up to 900nm (“black dye”¹¹) have been used in photoelectrochemical cells [45].

Combinations of active donor and acceptor materials in organic heterojunctions and of different dyes in photoelectrochemical cells can be used to broaden the absorption spectrum. In this context, light-harvesting antennae are an interesting alternative sensitizer. For example, the chromophore-loaded zeolites developed by G. Calzaferri’s group have demonstrated the ability to incorporate high densities of various dye molecules, complementing each other in their spectral features [46]. These systems also increase the dye stability by preventing their aggregation and display very efficient Förster energy transfer processes [47].

Alternatively, some 3rd generation approaches can be also applied to organic-based devices. For example, inorganic semiconductor (*e.g.* InAs or PbS) nanocrystals may be combined to organic materials for larger flexibility in terms of spectral absorption, in particular in the NIR spectral range. Sensitization properties in the infrared spectrum (1000-1600nm) have been reported for organically terminated PbS quantum dots used in conjunction with MEH-PPV¹² [48,49]. Additionally, quantum confinement can enhance the strength of absorption. Organic nanocrystals have also been used in bulk heterojunctions with enhanced light absorption properties, such as [70]PCBM¹³, a C₇₀ derivative used as acceptor material in conjunction with MDMO-PPV¹⁴ as the donor material [50].

¹¹ (tri(cyanato)-2,2’2’’-terpyridyl-4,4’4’’-tricarboxylate)Ru(II)

¹² poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene]

¹³ 3’-phenyl-3’H-cyclopropa[1,9][5,6]fullerene-C₇₀-I_h-3’butanoic acid methyl ester

¹⁴ poly[2-,ethoxy-5-(3’,7’-dimethyloctyloxy)-p-phenylene vinylene]

Tandem cells can be made of organic active layers to increase the photon absorption efficiency and the open-circuit voltage. J. Xue *and al.* [23] reported a 5.7%-efficiency tandem cell where two CuPc¹⁵/C₆₀ cells were connected in series by using a thin layer of Al nanoparticles as a recombination site in the center of the device. This strategy represents a major challenge to materials scientists to develop donor-acceptor combinations that have comparable efficiencies across the solar spectrum. The constraint that each subcell in a tandem structure must generate an equal current under 1 sun illumination intensity will most likely limit the number of cells to three. In addition, cells should be very thin in order to reduce the series resistance and thus maximize the fill factor. Innovative strategies are hence required to couple the subcells while concentrating the incident radiation directly into the regions that are most photoactive. Using surface plasmons from metal particles (collective electron surface motion excited by incident light at the resonance frequency) between the subcells is regarded as one possible technique to solve this problem [23,51]. *Parallel subcell connection* is an alternative to series connection, which would not require current matching between the individual cells. However, this configuration requires highly transparent contacts with good lateral conductivity to extract the photocurrent without incurring a significant voltage drop across the device diameter. Optically transparent nanopatterned metal films are under investigation as a replacement for ITO electrodes for high light transmission and high parallel conductivity connections in multijunction OPV cells [52].

Charge transfer and separation

Charge carriers generated upon photon absorption in inorganic semiconductors are free to move independently. Carriers that reach the depletion region across the *p-n* junction before recombination occurs get separated by the built-in electric field. Thus, the efficiency of charge separation depends upon the competition between recombination processes and charge transport, discussed in the next section.

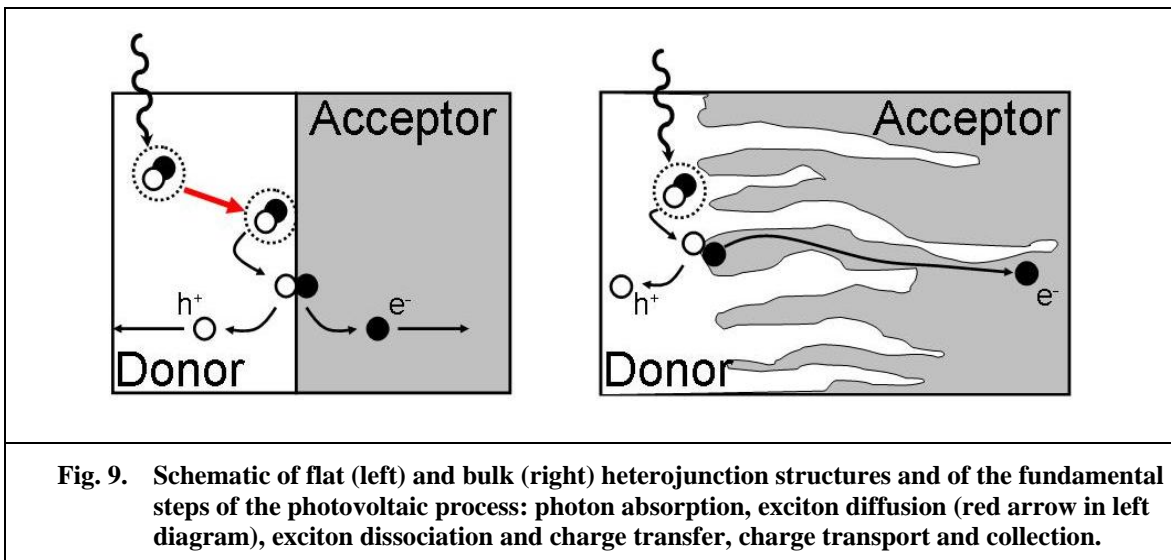
Photoexcitations in organic semiconductors result in the formation of excitons, or electron-hole pairs that are bound together by Coulomb attraction and must be dissociated. Dissociation can happen in the presence of high electric fields, at a defect site in the material, or at the interface between two materials that have sufficient mismatch in their energy levels (band offset). In most organic-based photovoltaics, exciton dissociation is governed by interfacial mechanisms. Usually the exciton dissociation is very effective, resulting in the transfer of electrons from the donor to the acceptor material and holes from the acceptor to the donor material with efficiencies approaching 100% [53] on sub-picosecond timescales such as in the case of MDMO-PPV/PCBM blends [54]. This mechanism is not well understood and there are many open questions on the kinetic requirements and on the role of interface polarizability, electric field, exciton transport rates, and interfacial electronic states [55].

Before dissociation may occur, the exciton created in either donor or acceptor material has to diffuse to the interface before recombining. As a consequence of the weak interaction between molecules, the exciton diffusion length is typically very small, on the order of 10nm. Together with light absorption efficiency, the exciton diffusion efficiency

¹⁵ copper phthalocyanine

is the most critical limit to the performance of organic PVs and constrains the cell structure. Transparent, wide bandgap and electron conducting exciton blocking layers (EBL) are used to confine the excitons close to the donor-acceptor interface and thus reduce the effective length that excitons have to travel [56]. Materials with long diffusion lengths can be used to enhance the exciton diffusion efficiency. C_{60} is an example of such a material. The use of C_{60} as the acceptor material in a double heterojunction has caused the exciton diffusion length to increase from 3nm to 40nm [53,57]. Organic materials can also be engineered to enhance the exciton diffusion, for example by introducing heavy metal ions into the structure of a molecular dye (*e.g.* Pd into porphyrin dyes [58]).

For the distance that excitons have to travel to the interface to be short, planar devices must consist of very thin active layers, thus limiting the optical density. *Bulk heterojunctions*, where donor and acceptor materials are blended on the nanoscale with a very large resulting interfacial area (see Fig. 9), solve this problem by distributing the interface throughout the device, but they face other issues related to the charge transport to the electrodes that are discussed in the next paragraph.



An additional complication to this picture is that preferential dissociation sites for excitons are not always the same. In photoelectrochemical cells based on inherently conducting polymers (ICP), exciton dissociation may occur at the ITO-polymer interface if liquid electrolytes are used [59] or at the ICP-electrolyte interface when the electrolyte is a solid polymer [60]. The influence of the cell structure and of the polymer morphology on the preferential dissociation site is not understood.

In nanocrystal-polymer blends, the interaction between organic and inorganic materials strongly impacts the cell performance. The morphology and the interfacial trap states must be controlled to increase the charge transfer efficiency. In this respect, promising results have been shown by binding phosphonic-acid-functionalized oligothiophenes to the surface of CdSe nanocrystals, leading to facilitated electronic interaction and passivation of trap states [61].

The donor/acceptor band offset, or the nature of the redox couple in the case of photoelectrochemical cells, must be optimized to yield the highest possible photovoltage. The resistance between layers must be minimized to achieve high filling factors.

Charge transport

c-Si cells need a relatively large thickness ($\sim 300\mu\text{m}$) because of mechanical constraints (Si is brittle) and the long light absorption length associated with the indirect bandgap of Si. Consequently, good material with high chemical purity and structural perfection is required to fight recombination. Surfaces must be effectively passivated to reduce recombination. Additionally, impurities and imperfections in the bulk must be avoided as they can absorb the extra energy of the conduction-band electrons and convert it into heat.

Bulk recombination is caused by lattice imperfections deriving from doping the bulk Si (*e.g.* with phosphorus and boron). Main recombination mechanisms are the Shockley-Read recombination (electron-hole recombination through imperfections, giving up the recombination energy as photons or phonons) and the Auger recombination (in which the recombination energy is given up to another free carrier). Various deposition and growing technologies, surface treatments and contact designs allowed the incremental enhancement of the electronic properties of Si wafers.

Charge transport in thin-film photovoltaics is mainly limited by grain boundary and defect states. In $\alpha\text{-Si:H}$ films, large carrier diffusion lengths require a low density of defect states in the gap. These defect states are most commonly associated with dangling-bond defects. Charge transport in CdTe cells is limited by junction interfaces and structural defects. The efficiency of these devices is enhanced by post-deposition heat treatments ($>400^\circ\text{C}$). In the case of CIGS devices, the electrical conductivity is largely determined by native defects (vacancies, interstitials and antisite defects) whose density can be decreased by optimizing the Cu/In ratio.

In organic materials the charge transport is determined by the intermolecular overlap of the frontier orbitals (HOMO and LUMO) of adjacent molecules. Charge transport in these materials is based on carrier hopping processes between molecules. Carrier mobilities in OPVs are much lower than in inorganic semiconductor materials. Hole mobilities reported for conjugated polymers range from $10^{-7}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ to $10^{-1}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, and electron mobilities from $10^{-9}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ to $10^{-4}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, compared to $475\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for holes and $1500\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for electrons in crystalline silicon. Even though mobility in organic materials is usually sufficient to allow extraction of charges in OPVs, transport time for carriers to reach the electrodes has to be decreased to compete with back recombination.

Electron and hole transport in polymers can be enhanced by chemical doping, for example by covalent attachment of functional groups. The carrier mobility in organic-based cells may be increased using heterojunctions of organic materials and inorganic

semiconductors with much higher electron mobilities (*e.g.* CdSe nanospheres [62] or nanorods [63], or CdTe tetrapods [64]).

Hole mobility in organic bulk heterojunctions is largely influenced by their morphology, which must be optimized under the constraint of allowing adequate percolation of the donor and acceptor phases. In polymer-based devices, the alignment of the polymers is also critical for charge transport. In particular, polymers with molecules π -stacking on one another are required to increase hole mobility by facilitating hopping between adjacent molecules. In devices using small-molecule materials, crystalline molecular organic phases can be synthesized to increase charge carrier transport [65].

Phase separation processes in the synthesis of bulk heterojunctions often create resistive bottlenecks and cul-de-sacs where the free charges are trapped prior to collection at the electrodes. Increasing the order of bulk heterojunctions enhances the charge separation and transport, since producing ordered structures allows control of the phase separation of the donor and acceptor to exciton diffusion length scale ($\sim 10\text{nm}$), to avoid dead ends in one of the phases by providing straight pathways to the electrodes for electrons and holes after exciton dissociation, and to align conjugated polymer chains. Various technologies have been explored to control the morphology of organic [66,67] and organic-inorganic [68,69,70] bulk heterojunctions. In particular, incorporation of polymers into a mesoporous inorganic substrate (TiO_2 , ZnO, CdS) has been achieved using various techniques, but obtaining a highly aligned polymer structure with high hole mobility needs further research. However, some self-assembled polymer structures in mesoporous substrates have already been produced [71,72].

Bio-inspired photosynthetic systems are macromolecular structures that are composed of light-harvesting pigment-protein complexes connected to reaction centers where the captured excitation energy is converted into electrochemical potential energy by photoinduced electron transfer. The light-harvesting complex consists of covalently-linked chromophores antennae that absorb light and transfer excitation energy to a central site at which charge separation occurs [73]. The synthesis of such light-harvesting molecular arrays presents many challenges. Current research aims at developing self-assembling and self-ordering modules that would allow the formation of functional and robust units. After photon absorption in the light-harvesting complex (the donor) and subsequent charge separation, efficient charge transport to the reaction center (the acceptor) is achieved by using donor-bridge-acceptor series incorporated in the macromolecular structure. The configuration of the molecular chain (the bridge) separating the donor from the acceptor has to be optimized to achieve efficient electron transport within the macromolecule. For example, energy levels and redox components have to be tuned to foster incoherent (hopping) versus coherent (superexchange) electron transport since the former is best suited for long-distance molecular transport [74,75]. More generally, understanding electron transfer in artificial photosynthetic systems needs further systematic investigation of the influence of the donor-acceptor distance and orientation, the free energy of the reaction, and electronic interaction.

Overall efficiency, stability and other technological challenges

Inorganic PV devices

The main factors limiting inorganic PV efficiency are the mismatch between the solar photon spectrum and the semiconductor bandgap, optical losses due to reflection off the cell surface or shadowing by the conductor grid that collects the electric current, recombination of electron-hole pairs, and the resistance of the metal-semiconductor contact.

Crystalline silicon technologies have potential for further incremental improvement in performance and cost reduction. The most successful c-Si cell designs of the last 15 years with efficiencies above 20% are the photolithographically-based Passivated Emitter Solar Cell (PESC) [76], the Back Point-Contact (BCP) cell (22.3% efficiency [77]), and the Passivated Emitter, Rear Locally-Diffused (PERL – 24.7% [78]). Future developments in c-Si cells are likely to be decreased wafer thickness and improved light-trapping schemes. Enhanced buried contact designs [79], and Heterojunctions with Intrinsic Thin-layer (HIT) [80], are two of the newer commercial designs. Ribbon technologies such as Edge-defined Film-fed Growth (EFG), dendritic web, and string ribbon have the potential to produce thin cells at lower cost [81,82]. Deposition of Si on foreign substrates is a possible route for obtaining low-cost cells with acceptable performances. Polycrystalline silicon on SiC graphite coated substrates [83], expansion matched conducting ceramic substrates [84], and glass substrates [85] are examples of technologies under investigation, with the latter now in commercial production.

For thin films, the technical issues include module efficiency, manufacturing scale-up, yield and throughput, and module reliability. Research in thin-film technologies often aims at incremental improvement in all these aspects. However, there are still some fundamental material properties and processes that need to be understood. For example, the light induced degradation processes of α -Si:H devices, the Staebler-Wronski effect [86], is a major challenge to enhance steady-state efficiency of this type of cell above 6-9%. The mechanisms of this degradation process are not yet fully understood and researchers try to overcome it either by developing new deposition approaches, such as the “hot wire” approach developed at NREL [87], or by reducing the thickness of the α -Si layers such as in the case of the “micromorph” cells [35].

CdTe/CdS/SnO₂ devices have shown high flexibility in terms of deposition techniques (*e.g.* spray pyrolysis, electrodeposition, vapor deposition, and close space sublimation) and high performance capabilities, with power conversion efficiencies reaching 16.5%, thanks in particular to post-deposition treatments that allow to increase the grain size, to passivate the grain boundaries, and to improve the electronic quality of the CdTe. The interdiffusion of the CdTe and CdS layers seems to improve the junction quality, but the reason for this has yet to be understood. Similarly the inclusion of p-type dopants such as Cu, Hg, Pb or Au is required to modify the CdTe contact surface, but have deleterious effect upon device durability that is only poorly understood [88]. Finally, the sensitivity of these materials to moisture is a major limitation to cell stability that is currently overcome only through encapsulation.

CIGS/CdS solar cells have major strengths related to the ease with which large grains can be grown and passivated, the material's tolerance to deviations from perfect stoichiometry, and design flexibility imparted by the ability to vary the alloy composition, *e.g.* to increase the bandgap. However, little fundamental understanding of these materials or devices is currently available, making progress in this technology largely empirical. Among the most relevant issues to be addressed include the optimization and simplification of the manufacturing processes, the moisture sensitivity, the development of lightweight flexible substrates, the replacement of CdS windows to improve environmental acceptance, and, in the long term, the limited supply of materials such as In, Ga and Se.

Organic PV devices

OPVs are compatible with plastic substrates and can be fabricated using high-throughput, low-temperature printing techniques compatible with roll-to-roll manufacturing: inkjet, screen, offset, or flexographic printing. Flexibility in the synthesis of the basic molecules allow for alteration of a wide range of properties, including molecular weight, bandgap, molecular orbital energy levels, wetting properties, structural properties (rigidity, conjugation length, molecule-to-molecule interaction, etc.), and doping. These characteristics have to be tuned in order to maximize the overall efficiency of organic photovoltaics. In particular:

- The open-circuit voltage (V_{OC}) is believed to mainly depend on the difference between the LUMO of the donor and the HOMO of the acceptor. However there is not sufficient fundamental understanding of the influence of other parameters such as the materials' work function [89];
- The short-circuit current (I_{SC}) has to be increased through photon absorption enhancement with NIR-sensitive, low-bandgap organic semiconductors or active acceptor materials, and by increasing the charge mobility and thus the charge collection.

Degradation pathways for organic photovoltaics seem to stem largely from changes in morphology, loss of interfacial adhesion, and interdiffusion of components, as opposed to strictly chemical decomposition. Thus, careful design and material engineering can substantially improve device lifetimes. Little has been published so far about the stability of these devices under illumination and UV exposure or the stability of foil-based devices with plastic substrates.

Photoelectrochemical cells with liquid electrolytes usually suffer short lifetimes because of the lack of environmental stability of the solvents traditionally used as the electrolyte host. Ionic liquid electrolytes, having extremely low vapor pressure and stable electrochemical properties, are stable electrolyte systems for photoelectrochemical cells, and effective as a replacement for liquid electrolytes based on redox-couples. In DSSCs, the interface between the nanostructured TiO_2 and the electrolyte seems to be crucial for the stability of the device [90,91]. The use of blocking layers of insulating metal oxides has been shown to prevent the adsorption of pollutants on the TiO_2 surface and to reduce

back-electron transfer. Also UV-cut-off filters may be used to prevent bandgap excitation, resulting in TiO₂ mediated oxidation processes. Further research is required to understand degradation processes and the mechanisms allowing dyes to recover when they are kept in the dark after saturation, driven by illumination at concentrated light [91]. Nevertheless, major progress has been made in increasing the lifetime of DSSCs, as demonstrated by experiments conducted by M. Grätzel who reports cells with no degradation for a period of 1000 hours at 80°C and light soaking [91].

Photon-to-Thermal-to-Electric Energy Conversion

In this section we analyze solar thermal technologies that produce electricity through concentration of solar energy for the production of heat and subsequent conversion into electric current. There are a number of options available at different stages of development¹⁶. The most developed technologies are the parabolic dish, the parabolic trough, and the power tower. The parabolic dish is already commercially available. This system is modular and can be used in single dish applications (with output power of the order of 25kW) or grouped in dish farms to create large multi-megawatt plants (see for example the 500MW solar dish farm project in Victorville, California [92]). Parabolic troughs are a proven technology and will most likely be used for deployment of solar energy in the near-term. Various large plants are currently in operation (California - 354MW) or in the planning process in the USA and in Europe. Power towers, with low cost and efficient thermal storage, promise to offer dispatchable, high capacity factor power plants in the future. Together with dish/engine systems, they offer the opportunity to achieve higher solar-to-electric efficiencies and lower cost than parabolic trough plants (see Table 1), but uncertainty remains as to whether these technologies can achieve the necessary capital cost reductions.

	Parabolic Trough	Power Tower	Dish/Engine
Size ^(a)	30-320MW	10-200MW	5-25kW
Approximate operating temperature	400°C	600°C	750°C
Annual capacity factor ^(a)	23-50%	20-77%	25%
Peak Efficiency	20% ^(b)	23%	29.4% ^(b)
Net annual efficiency ^(a)	11 ^(b) -16%	7 ^(b) -20%	12-25%
Cost [\$/W] ^(a)	4.0-2.7	4.4-2.5	12.6-1.3
Cost [\$/W _p] ^{(a)(c)}	4.0-1.3	2.4-0.9	12.6-1.1
(a) Value range indicates changes over the 1997-2030 time frame			
(b) Demonstrated values; other values are estimated or predicted			
(c) \$/W _p removes the effect of thermal storage (or hybridization for dish/engine)			
Table 1. Characteristics of major solar thermal electric power systems [93].			

All these technologies involve a thermal intermediary and thus can be readily hybridized with fossil fuel combustion and in some cases adapted to utilize thermal storage. The primary advantage of hybridization and thermal storage is that the

¹⁶ A list of the major operating concentrating solar power plants is provided by SolarPaces (http://www.solarpaces.org/csp_facilities.htm)

technologies can provide dispatchable power and operate during periods when solar energy is not available. In particular, thermal storage allows an increase in the annual capacity factor of a solar plant of 50% or more. Hybridization and thermal storage can enhance the economic value of the electricity produced and reduce its average cost.

Parabolic troughs

Parabolic trough systems use single-axis tracking parabolic mirrors to focus sunlight on thermally efficient receiver tubes that contain a heat transfer fluid (HTF). The receiver tubes are usually metallic and embedded into an evacuated glass tube that reduces heat losses. A special high-temperature coating additionally reduces radiation heat losses. The working fluid (*e.g.* thermo oil) is heated to $\sim 400^{\circ}\text{C}$ and pumped through a series of heat exchangers to produce superheated steam which powers a conventional turbine generator (Rankine cycle) to produce electricity. It is also possible to produce superheated steam directly using solar collectors. This makes the thermo oil unnecessary, and also reduces costs because the relatively expensive thermo oil and the heat exchangers are no longer needed. However, *direct steam generation* (DSG) is still in the prototype stage and more research is required to solve the thermo-mechanical issues related to working pressures above 100 bar and the presence of a two-phase fluid in the receivers [94,95].

The efficiency of a solar thermal power plant is the product of the collector efficiency, field efficiency and steam-cycle efficiency. The collector efficiency depends on the angle of incidence of the sunlight and the temperature in the absorber tube, and can reach values up to 75%. Field losses are usually below 10%. Altogether, solar thermal trough power plants can reach annual efficiencies of about 15%; the steam-cycle efficiency of about 35% has the most significant influence. Central receiver systems such as solar thermal tower plants can reach higher temperatures and therefore achieve higher efficiencies.

Current research in parabolic trough systems aims at improving performance and lifetime and at reducing manufacturing, operation, and maintenance costs with improved designs. These activities concern all critical components of the system, namely the support and tracking structure, the reflector (glass mirrors, polymeric reflectors and other alternative reflectors [96]), and the receiver tubes (absorbers, glass/metal seals, etc.).

A more fundamental research field concerns the development of new heat transfer fluids with good stability properties at higher temperatures and compatible with thermal storage systems (see paragraph on HTFs and thermal storage). In the case of DSG plants, a phase-change thermal storage may be better adapted than current thermal storage concepts [97].

A technical assessment of parabolic troughs and power towers by NREL, including forecasts for cost and performance, can be found in reference [98].

Power towers

In a power tower plant, hundreds of two-axis tracking heliostats are installed around a tower where they focus sunlight with concentrations ranging from 100 to 10,000 suns. The absorber is located on the top of the tower and can reach temperatures from 200°C to 3000°C [99]. Hot air or molten salt are usually used to transport the heat from the absorber to a steam generator where superheated steam is produced to drive a turbine and an electrical generator. Power towers are suited for large-output applications, in the 30 to 400MWe range, and need to be large to be economical. Thermal storage can be easily integrated with this type of solar systems, allowing the enhancement of the annual capacity factor from 25% to 65% and the stabilization of the power output through fluctuations in solar intensity until the stored energy is depleted.

Since the early 1980s, power towers were built in Russia, Italy, Spain, Japan, France, and the USA, with power outputs ranging from 0.5MWe to 10MWe (Solar Two, Southern California) and using various combinations of heat transfer fluids (steam, air, liquid sodium, molten nitrate, molten nitrate salt) and storage media (water/steam, nitrate salt/water, sodium, oil/rock, ceramic) [100]. The Solar Two plant has proven the feasibility of molten-salt power towers, achieving turbine operation at full capacity for three hours after sunset thanks to the two-tank (290°C/570°C) molten salt storage system (with a capacity of 110MWh). The main design challenge for this system was identifying the materials that work with molten salt, since this fluid has relatively high freezing point (220°C), low viscosity, wets metal surfaces extremely well, and is corrosive. Solar Tres (Spain, 2002) is the first commercial power tower and is a follow-up of the technologies developed for Solar Two. Its size is three fold larger, the electrical power output is 15MWe, and the thermal storage capacity 600MWh (16 hours).

The efficiency of a solar-powered steam turbine electric generator used in the power tower concept is a critical function of the temperature T_R of the receiver, which is influenced not only by the incident energy but also of several factors including the heliostat optical performance, the mirror cleanliness, the accuracy of the tracking system, and wind effects. For an ambient temperature of 340K, the efficiency is 35% for $T_R = 800K$ and 62% for $T_R = 3000K$ [101]. Solar Two achieved 13% peak efficiency with $T_R = 570^\circ C$ (the efficiency expected for a commercial plant is 23% [102]). The development of heat transfer fluids working at high temperature is a key issue for increasing the overall efficiency of power towers. Alternative systems for converting thermal energy into electricity have been explored, such as *liquid metal magnetohydrodynamic generators* (LMMHD). These systems were first investigated in the early 1980s and offer significant increases in the system thermal efficiency over the 33% considered attainable with conventional turbo-machinery. With sodium at a temperature of 650°C, the theoretical efficiency is 39.5%. A peak efficiency of 46.5% is predicted for lithium at 760°C. The thermodynamic efficiency at maximum power, with an ambient temperature of 300K and a blackbody source temperature of 6000K, is 64% and occurs at a receiver optimal temperature of 2900K [101]. Additional potential advantages are that the sodium/steam heat exchanger is eliminated in liquid metal systems, and, where LMMHD systems employ the same working fluid as the solar receiver, no recirculating pump is required as pumping power is provided directly by the cycle.

Heat transfer fluids (HTF) and thermal storage

HTF	T [°C]		Properties
	Low	High	
Synthetic oil (<i>e.g.</i> biphenyl-diphenyl)	13	395	high application temperature, flammable
Mineral oil (<i>e.g.</i> caloria)	-10	300	inexpensive, flammable
Water / Steam	0	>500	high receiver pressure required
Silicon oil	-40	400	odorless, nontoxic, expensive, flammable
Nitrate salt	220	500	high freezing temperature, high thermal stability, corrosive
Ionic liquids (<i>e.g.</i> C ₈ mimPF ₆)	-75	416	organic methyl-imidazole salts, good thermal properties, very costly, no mass product
Air	-183	>500	low energy density

Table 2. Properties of the principal HTFs for parabolic troughs and power towers [97].

The development of new heat transfer fluids (HTFs) is crucial for increasing the operating temperature of a solar thermal plant, and hence the efficiency of the steam cycle. Stability at high temperature, low flammability, low vapor pressure at high temperature, low corrosivity in standard materials, low freezing point, high boiling point, and low cost are the main required characteristics. Table 2 lists the operating temperature and the main characteristics of some HTFs considered for parabolic troughs and power towers.

Various thermal storage options are currently being considered for parabolic troughs and power towers. Some of them have already been demonstrated but many need further research, particularly concerning the optimization of the HTF materials. Here are some among the most significant technologies:

- *Concrete* – This system would use a HTF in the solar field and pass it through an array of pipes imbedded in concrete. The highest uncertainty is the long-term stability of the concrete material itself after thousands of charging cycles.
- *Indirect two-tank molten-salt* – In current applications, a synthetic oil (*e.g.* biphenyl-diphenyl oxide) is used as HTF in the solar field and for heating molten salt through a heat exchanger in the thermal storage system. Two separate tanks are used for this system. The excess heat of the solar collector field heats up the molten salt, which is pumped from the cold to the hot tank. If the solar collector field cannot produce enough heat to drive the turbine, the molten salt is pumped back from the hot to the cold tank, and heats up the heat transfer fluid. The molten salt, as it was used in the Solar-Two solar tower pilot demonstration plant [102], is a binary mixture of 60% sodium nitrate (NaNO₃) and 40% potassium nitrate (KNO₃) salt. The feasibility of this system was proven and the concept seems to have low technological risk despite the relatively high freezing point (~225°C) of the salt.

- *Thermocline storage* – Thermoclines use a single storage tank. A low-cost filler material (e.g. quartzite and silica sand) acts as the primary thermal storage medium and replaces approximately two-thirds of the molten salt that would be needed in a two-tank system. With the hot and cold fluid in a single tank, the thermocline storage system relies on thermal buoyancy to maintain thermal stratification. The thermocline is the region of the tank between the two temperature resources, with a temperature difference of about 60°C [103]. Thermoclines can maintain their integrity over a three-day no-operation period.
- *Molten-salt HTF* – Using a lower temperature molten salt as the HTF in the solar field allows the same fluid to be used in both the solar field and the thermal storage field, leading to significant cost reduction for the thermal storage, especially when used in the thermocline configuration. This also allows the solar field to be operated at higher outlet temperatures, increasing the power cycle efficiency and further reducing the cost of thermal storage. Major technical barriers to this option include the challenges of high freezing temperature salts (of the order of 120°C) and with higher operating temperatures leading to higher heat losses and requiring new materials and components.
- *Organic molten-salt HTF* – Organic salts, or ionic liquids, have the advantage of being liquid at room temperature. Additionally they can be synthesized to have specific properties desirable for solar applications, namely low freezing point, high thermal stability, low corrosivity, good heat transfer and thermal properties, and low cost. The development of organic salts is relatively new and more research is required to optimize all these characteristics, particularly to lower the materials cost.

Dish-engine systems

Dish-engine systems can be used to generate electricity in the kilowatts range. A parabolic concave mirror concentrates sunlight; the two-axis tracked mirror must follow the sun with a high degree of accuracy in order to achieve high efficiencies. At the focus is a receiver which is heated up over 700°C. The absorbed heat drives a thermal engine which converts the heat into motive energy and drives a generator to produce electricity. If sufficient sunlight is not available, combustion heat from either fossil fuels or biofuels can also drive the engine and generate electricity. The solar-to-electric conversion efficiency of dish-engine systems can be as high as 30%, with large potential for low-cost deployment. For the moment, the electricity generation costs of these systems are much higher than those for trough or tower power plants, and only series production can achieve further significant cost reductions for dish-engine systems. A number of prototype dish-engine systems are currently operating in Nevada, Arizona, Colorado, and Spain. High levels of performance have been established; durability remains to be proven, although some systems have operated for more than 10,000 hours.

Most research and development efforts aim at incrementally enhancing the reliability, performance, and cost-effectiveness of all major components of these systems: concentrators, receivers, and engines. The development of high-efficiency low-cost thermal engines or alternative heat-to-electric conversion systems is the most critical requirement for these systems to become economical.

Various thermodynamic cycles have been considered for dish-engine systems. Stirling and open Brayton (gas turbine) cycles have shown the best performances to date. *Stirling engines* have a potential for high efficiency and external heating makes them easily adaptable to solar dishes. Modern, high-performance Stirling engines use hydrogen or helium working gas at temperatures over 700°C and pressures as high as 20MPa, resulting in thermal-to-electric conversion efficiencies of about 40% [104]. The main disadvantage of these types of engines is their manufacturing cost, mainly determined by the materials used for the hot part heat exchanger (stainless steel, high-temperature alloys or ceramic materials) and by the design of the cooling system. In a *dish-Brayton system*, solar heat is used to replace or supplement the fuel at the entrance of the gas turbine. Current designs include pressure ratios of ~2.5, turbine inlet temperatures of about 850°C, and recuperation of waste heat, with predicted efficiencies over 30% [105]. Dish-Brayton systems are still at an early stage of development.

Alternative dish systems replace the thermal engine with high-efficiency (>30%) multijunction photovoltaic cells working with concentrated sunlight (see section on photovoltaics), or with thermoelectric or thermionic devices for direct current extraction from the high temperature receiver. *Thermoelectrics* can convert thermal energy into electrical energy through the Seebeck effect. Theoretical efficiency limits are below 30% of the Carnot efficiency $\Delta T/T_{\text{high}}$ for *figure of merit*¹⁷ (ZT) values <1. The challenge in designing efficient thermoelectric materials is enhancing electrical conductivity (*e.g.* by using crystalline, high-bandgap, heavily doped semiconductors) while minimizing thermal conductivity, as described in the “phonon-glass electron-single-crystal” (PGEC) concept by G.A. Slack [106]. Lattice thermal conductivity, the major contribution to thermal conductivity, can be minimized by increasing the phonon scattering by introducing heavy atoms, disorder, large unit cells, clusters, and rattling atoms. Using these principles, a variety of high ZT materials have been developed with different operation temperature ranges. Skutterudite material systems and complex chalcogenide structures are some representative examples of such materials [107]. Low-dimensional (nanostructured) thermoelectric materials have high potential for achieving figure of merit values of 2 and higher [107]. In fact, quantum and size effects may enhance the Seebeck coefficient and the electrical conductivity, while boundary phonon scattering would lead to a large reduction in thermal conductivity.

In contrast with thermoelectric devices, electron transport in *thermionic converters* is not diffusive but ballistic, the emitter and collector electrodes being physically separated to prevent thermal diffusion along a solid lattice. Thermionics are an old technology that was widely developed from the 1950’s to the mid-1970’s. The development efforts were virtually abandoned because of the lack of electrode materials with combined low working functions (~1eV) and low vapor pressures (for long-term stability); the low

¹⁷ The non-dimensional thermoelectric figure of merit, denoted ZT , controls the efficiency of a thermoelectric device and is defined as $ZT = \frac{a^2}{\kappa\rho} \Delta T$, where a is the Seebeck coefficient, κ the thermal conductivity and ρ the resistivity. In traditional materials the upper limit of ZT is acknowledged to be ~1.

performance (heat-to-electric conversion efficiency <10%) and the high operating temperatures (>1400K); and the technical challenges related to manufacturing devices with an interelectrode spacing <10 μ m needed to decrease the negative-space-charge effect in vacuum thermionic converters. High-pressure cesium diode thermionic converters with refractory-metal electrodes (having low vapor pressure) showed better performances, with output-power densities ranging from 1W/cm² to 30W/cm² and efficiencies from 5% to 20% with emitter temperatures T_E between 1500K and 2000K [108], the theoretical efficiency limit for thermionic conversion being 30% ($0.65\eta_{\text{Carnot}}$ for emitter and collector temperatures of 1800K and 900K, respectively) [108,109]. The development of nanotechnologies led to realizing devices with interelectrode spacing as small as 1-10nm, allowing tunneling of hot electrons and thus higher conversion efficiencies. As in the case of thermoelectric devices, extensive research efforts are focused on low temperature applications such as cooling at temperatures below room temperature or power generation from waste heat at temperatures <400-500K. For high temperature applications, effective high-energy electron selectivity [110], and decreasing the large (up to 50%) power losses caused by the charge-space effect [109], are among the main fundamental issues that are currently being addressed to enhance the efficiency of thermionics.

Solar chimneys

In contrast with the previously described thermal technologies, solar chimneys convert into electricity not only direct normal irradiance but global irradiance. A solar chimney power plant has a high chimney, up to 1000m, and is surrounded by a large collector roof up to 130m in diameter, that consists of glass or resistive plastic supported on a framework. Towards its centre, the roof curves upwards to join the chimney, creating a funnel. The sun heats up the ground and the air underneath the collector roof, and the heated air follows the roof until it reaches the chimney. There, it flows at high speed (35mph) through the chimney and drives multiple wind turbines at its bottom. The ground under the collector roof behaves as a storage medium, and can even heat up the air for a significant time after sunset. The efficiency of the solar chimney power plant is below 2%, and depends mainly on the height of the tower. However, the whole power plant is not without other uses, as the outer area under the collector roof can also be utilized as a greenhouse for agricultural purposes. As with trough and tower plants, the minimum economical size of solar chimney power plants is also in the multi-megawatt range. A 1,000m tall pilot solar chimney of 200MW is planned for construction in Australia in 2006 [111]. Solar chimneys use well-known technologies, so research and development is needed in design and construction rather than in fundamental physics.

Photon-to-Chemical Energy Conversion

Photoconversion processes are used for producing a large variety of chemicals with clear energetic and environmental advantages compared to conventional technical processes [112]. This section focuses on the synthesis of chemical fuels – *e.g.* ammonia, methane, or hydrogen (see also the GCEP report on hydrogen technologies [113]) – since this application has the largest potential in terms of energy production. Moreover, it

could partially solve one of the principle shortcomings of conventional solar technologies, which is the lack of capacity for energy storage. Among the large variety of identified processes and technologies, we consider here three main categories of solar-to-chemical conversion processes: photo(electro)chemical processes, thermochemical processes, and photosynthetic processes in natural systems. Photochemical and photoelectrochemical systems use light-sensitive materials (in aqueous suspension or in the form of bulk electrodes, respectively) for absorbing photon energy and producing electrons with sufficient energy for splitting water. In thermochemical technologies, concentrated solar flux is used to produce the high-temperatures necessary to drive endothermic reactions such as syngas production from natural gas, water thermal decomposition, and water splitting through high-temperature chemical cycles. Some biological systems (algae, bacteria, yeasts) produce hydrogen in their metabolic activities. Research in this field aims at overcoming the oxygen sensitivity of the hydrogen-evolving enzyme systems and at increasing the hydrogen production yield. In parallel, biomimetic systems (see page 23) are being investigated. These systems are capable of absorbing light, separating charges, and acting as catalysts for water redox. Biomass, which can be considered as a form of chemical storage for solar energy, and biomass-derived fuels are analyzed in more detail in a separate GCEP report [114].

Photo(electro)chemical water splitting

The efficiency limit of a photoelectrochemical cell used for splitting water is 41% for a photoanode bandgap that just matches the free energy of the water splitting reaction (1.23eV at 25°C and 1atm). The efficiency decreases to ~18% for a bandgap of 2eV and to 0.05% for 3eV (the bandgap energies of TiO₂ and SrTiO₃, respectively) [101]. Accounting for the thermodynamic potential needed for water splitting, overvoltage losses, and the energy required for driving the reaction, 1.6-1.8V have to be provided to produce hydrogen from water. In photoelectrochemistry, this voltage is provided by a semiconductor material with bandgap $1.6\text{eV} < E_g < 2.2\text{eV}$ immersed in aqueous solution. Major barriers in this research field are finding efficient light-absorbing materials and catalysts with corrosion-resistance properties in water and energy levels that match the reduction and oxidation half-reactions. Combinatorial techniques are often used to screen a large variety of photoanode and photocathode materials (including binary, ternary, and quaternary compounds; these techniques also allow to study doping effects) and to test them against photon absorption efficiency, photocatalytic activity, and resistance to corrosion. A report from the IEA on photoelectric production of hydrogen [115] includes an extended analysis of recent research results in this field and a list of high potential materials and systems. Some significant examples are tungsten trioxide (WO₃), ferric oxide (Fe₂O₃), silver-chloride (AgCl) and silver-sulfide (Ag₂S) clusters (zeolite A), titanium dioxide (TiO₂), and zinc oxide (ZnO). Light-absorption of photosensitive electrodes is often insufficient or inappropriate to match with the electric current needs of integrated counter-electrodes or photovoltaic bias in photoelectrochemical systems. Therefore, light absorption and photocurrent have to be enhanced by means of sensitizers (*e.g.*, ruthenium-based dye sensitizers on nanocrystalline TiO₂ – DDSCs or Grätzel cells –, dye-loaded zeolite antennae on various receptor semiconductor materials – see [46]) or doping agents (platinum or ruthenium in WO₃, various metal dopants in Fe₂O₃ or ZnO),

respectively. Furthermore, the most stable semiconductors in aqueous solutions are oxides, which usually have bandgap energies that are too large. Lowering the bandgap of stable oxide-based semiconductors is therefore an important research activity. Photoelectrode stability is also addressed by separating the generation of hydrogen and oxygen with a photocatalyst membrane [116], by modifying the nature of the electrolyte, or by covering materials with ideal solar absorption but poor stability with adequate protective coatings. Tandem or multi-junction cells are particularly interesting in this sense since the absorption efficiency can be enhanced by complementary spectrum absorption (see chapter on photovoltaics), while a corrosion-resistant material can be used as the top-junction (*e.g.*, WO₃ on GaInP₂).

Finally, the energetics and kinetics of the redox reaction are determined by the chemistry of the semiconductor/electrolyte interface. The development of high-activity resistant catalysts is hence crucial for the success of this technology. Molecular catalysts are a promising lower-cost, higher turnover alternative to heterogeneous catalyst (*e.g.* platinum particles). One leading strategy is mimicking natural hydrogenase enzymes with functional catalyst systems with low-valent redox-rich iron and cobalt platforms.

Research on catalysts for water oxidation is less advanced, and relatively little progress has been made in the last 20 years. Main barriers are poor stability, large overpotential, and slow-turnover. Oxidation of water to hydrogen peroxide might be a way to address the formation of dioxygen, which is a particularly expensive process from a thermodynamic viewpoint.

Thermal and thermochemical processes

Concentration of solar light in solar thermal plants reaches 5,000 suns and produces temperatures of several hundred degrees. Therefore, it can be used for some specific thermal or thermochemical processes where high-temperature is required. The spectrum of applications is wide and includes [117,118]:

- Hybrid solar/fossil processes such as (1) carbothermic reduction of metal oxides using coke or natural gas as chemical reducing agent. The deployment of such processes could substantially reduce greenhouse-gas emissions in industrial applications (up to 59% of CO₂-equivalent emission reductions for zinc production); (2) solar thermal decomposition, or “pyrolysis”, of fossil fuels or biomass, solar steam reforming of natural gas (950-1200K – efficiency ranging from 65-75% [119]), or solar steam gasification of heavy hydrocarbons [120] or coal (1350-1600K).
- Hydrogen production through direct solar water thermal dissociation (>2500K). Theoretical efficiencies are about 40% at 2500K and 2mbar [121]. H₂/O₂ separation is the main technical barrier; quenching (a rapid cooling separation technique) is the simplest technology but introduces large irreversibility.
- Hydrogen production through thermochemical cycles were proposed to bypass the H₂/O₂ separation problem of direct water dissociation since hydrogen and oxygen

are produced at different steps.

Two-step systems, with theoretical efficiencies above 30%, are based on metal oxide redox reactions: (1) solar reduction of the metal oxide at elevated temperatures (either thermal or carbothermal, where C or CH₄ are reducing agents); (2) exothermic oxidation (hydrolysis) of the metal below 800K. To date, the highest potential cycles in this category are the ZnO/Zn cycle [122], with theoretical efficiencies of ~50% at 2300K, and Fe₃O₄/FeO cycle, with theoretical efficiencies of ~60% at 1900K. In both cases, separation of the product gases from the intermediate chemical agents (usually by quenching) is limiting the yield of the latter and the overall energy efficiency.

Multi-step cycles are more complex to implement but allow the use of relatively moderate temperatures. Their overall exergy efficiency is limited by irreversibilities associated with heat transfer and product separation. Some examples are the 3-step iodine-sulfur cycle at 1140K, with an efficiency limit ~50%, and the 4-step UT-3 cycle, based on the hydrolysis of CaBr₂ at 1020K and of FeBr₂ at 870K, with a comparable efficiency limit.

Although 2000 to 3000 cycles have already been identified, only very few have been investigated in the last 20 years. Many fundamental and technical problems have still to be solved, including the development of materials with excellent thermal and corrosion resistance; the increase of the yield of intermediate chemical agents, limited by the efficiency of gas separation technologies that also limits the overall energy efficiency; and the matching of the reaction rates of the individual steps of the cycles.

Biological systems

Current efficiency of fuel production from biomass is quite low: less than 1% of the incident insolation is stored as chemical fuels. Improvements in the efficiency of photosynthesis may be obtained by addressing all fundamental steps leading from the capture of light and the production of biomass to the formation of polysaccharides and their conversion into liquid fuels. Genetic engineering of biological systems is explored to increase the cellulose production yield [123]; molecular models are developed to understand cellulose structure [124] and the activity of the enzymes that hydrolyze it, together with the limitations to their performance; various genetically modified organisms are developed which may ferment multiple sugars without being inhibited by other compounds that are naturally present in biomass or are produced in the cellulose-to-sugar conversion process [125].

Photobiological hydrogen technologies use certain photosynthetic microbes that produce hydrogen from water in their metabolic activities using light energy. Normally, photosynthetic systems do not evolve hydrogen, but rather reduce CO₂ to carbohydrates. However, it is possible to modify conditions such that the reducing end of the photosynthetic process (Photosystem-I) is coupled to a hydrogen-evolving enzyme, such

as hydrogenase (*e.g.* in green algae) or nitrogenase (*e.g.* in cyanobacteria). Photon-to-hydrogen conversion efficiency under ideal conditions approaches ~10%, and recently 7.5% was obtained in green algal photosynthesis [126]. A major difficulty is that the algal systems saturate at solar irradiances above ~0.03 suns, where the photon absorption rate exceeds the rate at which photosynthesis can utilize them, resulting in dissipation and loss of the excess photons (up to 95% of absorbed photons [127]) as fluorescence or heat. Thus, genetic engineering is required to reduce the size and/or effectiveness of the light-harvesting antenna chlorophyll pool to allow greater solar conversion efficiencies and higher photosynthetic productivity.

Another problem concerns the stability of hydrogen evolving enzymes in the presence of oxygen. Because oxygen is produced along with the hydrogen, the technology must overcome the limitation of oxygen sensitivity of the hydrogen-evolving enzyme systems. Researchers are addressing this issue by screening for naturally occurring organisms that are more tolerant of oxygen, and by creating new genetic forms of the organisms that can sustain hydrogen production in the presence of oxygen [128].

Practical applications of biological systems for hydrogen synthesis are still far away since the current understanding of biological processes is too limited. More fundamental research is required to understand, among others, molecular mechanisms, the structure and functionality of enzyme catalysts, and the kinetics of biological hydrogen metabolism. Biological systems for hydrogen production are assessed in a separate GCEP report dedicated to hydrogen production, storage, and usage [113].

Conclusion

The deployment of solar technologies for energy production at a large scale requires the involvement of both political and economical players, but also further improvements in the conversion efficiency and reduction of manufacturing cost. A large ongoing research effort aims to find innovative solutions to overcome these barriers. In the last decade, photovoltaic technologies have experienced an astonishing evolution that led to the increase of the efficiency of crystal-silicon solar cells up to 25% and of thin-film devices up to 19%. Recently, nano-technology, innovative deposition and growth techniques, and novel materials opened routes for reaching higher performances (multijunction devices and other 3rd generation photovoltaics) and for developing very low-cost devices such as organic-based PVs. All these technologies face comparable fundamental issues related to the steps involved in the conversion of photon energy into electricity: photon absorption, charge carrier generation, charge separation, and charge transport. Both fundamental research and technical development are critical requirements for these technologies to become more efficient, stable, and reliable. Solar thermal systems are at the demonstration stage and some installations are already operational. Their ability to overcome the intermittency problem using hybridization and thermal storage renders these technologies particularly suitable for large-scale electricity production. Direct production of chemicals fuels, and particularly hydrogen, from solar energy is a promising alternative to using fossil fuels for the development of a sustainable carbon-free fuel economy. Thermochemical and biological conversion processes are

promising technologies with potential for high efficiency. However, only a few thermochemical processes have been investigated to date and biological systems require more understating of genetics and biological conversion to become efficient and stable. Solar energy has a large potential to be a major fraction of a future carbon-free energy portfolio, but technological advances and breakthroughs are necessary to overcome low conversion efficiency and high cost of presently available systems.

Appendix

Global solar energy technical potential

Table 3 gives an estimate of the global solar energy potential for electricity generation based on the annual average irradiance and sky clearance in 11 different geographical regions worldwide (from [8]). In this calculation we assumed that 1% to 10% of the unused land surface could be available to solar energy, that 1m² of flat-plate PV collector module requires typically 2m² of available land, and we used a conversion efficiency of 10%.

Region	Irradiance ^(a)		Sky clearance ^(b)		Unused land ^(c) [Mha]	Solar energy technical potential ^(d)	
	[kW/m ²]		[%]			Min	Max
	Min	Ma x	Min	Ma x			
North America	0.22	0.45	0.44	0.88	594.0	0.29	11.76
Latin America and the Caribbean	0.29	0.46	0.48	0.91	256.7	0.18	5.37
Sub-Saharan Africa	0.31	0.48	0.55	0.91	692.5	0.59	15.12
Middle East and North Africa	0.29	0.47	0.55	0.91	820.9	0.65	17.55
Western Europe	0.21	0.42	0.44	0.80	86.4	0.04	1.45
Central and Eastern Europe	0.23	0.43	0.44	0.80	14.2	0.01	0.24
New states from former Soviet Union	0.18	0.43	0.44	0.80	798.7	0.32	13.74
Pacific OECD states	0.28	0.46	0.48	0.91	171.6	0.12	3.59
Other Pacific Asia	0.32	0.48	0.55	0.89	73.9	0.07	1.58
Centrally planned Asia and China	0.26	0.45	0.44	0.91	320.6	0.18	6.56
South Asia	0.27	0.45	0.44	0.91	103.8	0.06	2.13
Total					3933.1	2.50	79.11
Ratio to the current annual primary energy consumption (13.7TW)						0.18	5.77
Ratio to the annual primary energy consumption projected for 2030 (21.84TW)						0.11	3.62
(a) Assumed annual average clear sky irradiance							
(b) Assumed annual average							
(c) 1% - 10% of unused land surface were assumed available for solar energy							
(d) Assumed 10% conversion efficiency and 2m ² of available land used for 1m ² of solar panels							
Table 3. Global solar energy technical potential (adapted from R. Sims [8]).							

The global solar energy potential ranges from 2.5 to 80TW. The lowest estimate represents ~18% of the total current primary energy consumption (13.7TW [1]), and exceeds 10% of the estimated primary energy demand by 2030 (21.84TW [1]). The highest estimate of the potential for solar energy exceeds 5 fold the current global energy consumption. Additional information on photovoltaic energy capacity of other WEC – World Energy Council - member countries can be found in [129].

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