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believe that a hydrogen economy that used electrolysis to generate H₂ and O₂ from water, and a fuel cell to convert H₂ and O₂ back to water and electrons, could make a substantial contribution to global energy without a much-improved oxygen electrode. The identification of this problem is not in any sense new: The redox chemistry of oxygen has been a subject of active interest (but limited success) for decades. We simply need new ideas.

Another reason to work on these big problems is that they will attract the most talented young people. Over the past 30 years, the National Institutes of Health has used stable and generous support to recruit and build a very effective community of biomedical scientists.

Solving the problems of energy and global stewardship will require the same patient, flexible, and broadly based investment, if society believes that the problems in these areas are sufficiently important to provide a life's work for its most talented young people.

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PERSPECTIVE

Toward Cost-Effective Solar Energy Use

Nathan S. Lewis

At present, solar energy conversion technologies face cost and scalability hurdles in the technologies required for a complete energy system. To provide a truly widespread primary energy source, solar energy must be captured, converted, and stored in a cost-effective fashion. New developments in nanotechnology, biotechnology, and the materials and physical sciences may enable step-change approaches to cost-effective, globally scalable systems for solar energy use.

More energy from sunlight strikes Earth in 1 hour than all of the energy consumed by humans in an entire year. In fact, the solar energy resource dwarfs all other renewable and fossil-based energy resources combined (1). With increasing attention toward carbon-neutral energy production, solar electricity—or photovoltaic (PV) technology—is receiving heightened attention as a potentially widespread approach to sustainable energy production. The global solar electricity market is currently more than \$10 billion/year, and the industry is growing at more than 30% per annum (2). However, low-cost, base-loadable, fossil-based electricity has always served as a formidable cost competitor for electrical power generation. To provide a truly widespread primary energy source, solar energy must be captured, converted, and stored in a cost-effective fashion. Even a solar electricity device that operated at near the theoretical limit of 70% efficiency would not provide the needed technology if it were expensive and if there were no cost-effective mechanism to store and dispatch the converted

solar energy upon demand (3). Hence, a complete solar-based energy system will not only require cost reduction in existing PV manufacturing methods, but will also require science and technology breakthroughs to enable, in a convenient, scalably manufacturable form, the ultralow-cost capture, conversion, and storage of sunlight.

One key step is the capture and conversion of the energy contained in solar photons. Figure 1 shows the fully amortized cost of electricity as a function of the efficiency and cost of an installed PV module (2, 4). Because the total energy provided by the Sun is fixed over the 30-year lifetime of a PV module, once the energy conversion efficiency of a PV module is established, the total amount of “product” electricity produced by the module at a representative mid-latitude location is known for the lifetime of the system. The theoretical efficiency limit for even an optimal single-band gap solar conversion device is 31%, because photons having energies lower than the absorption threshold of the active PV material are not absorbed, whereas photons having energies much higher than the band gap rapidly release heat to the lattice of the solid and therefore ultimately contain only a useful internal energy equal to that of the band gap (2). Small test cells have demonstrated efficiencies of >20%, with the remaining losses almost en-

tirely due to small reflection losses, grid shading losses, and other losses at the 5 to 10% level that any practical system will have to some extent. Shipped PV modules now have efficiencies of 15 to 20% in many cases. At such an efficiency, if the cost of a module is ~\$300/m² (2), and if we take into account the accompanying fixed costs in the so-called “balance of systems” (such as the inverter, grid connection, etc.), which add a factor of ~2 to the total installed system cost), then the sale price of grid-connected PV electricity must be \$0.25 to \$0.30 per kilowatt-hour (kWh) to recover the initial capital investment and cost of money over the lifetime of the PV installation (2, 4). Currently, however, utility-scale electrical power generation costs are much less, with current and new installations costing ~\$0.03 to \$0.05 per kWh (1). Hence, for solar electricity to be cost-competitive with fossil-based electricity at utility scale, improvements in efficiency are helpful, but manufacturing costs must be substantially reduced.

In current manufacturing schemes for Si-based solar cells, the cost of the processed and purified Si is only about 10% of the final cost of the PV module. Some of the Si is lost in cutting up boules into wafers, and other costs are incurred in polishing the wafers, making the diffused junction in the Si into a photovoltaic device, fabricating the conducting transparent glass, masking and making the electrical contacts, sealing the cells, connecting the cells together reliably into a module, and sealing the module for shipment. Hence, in such systems, the energy conversion efficiency is at a premium so as to better amortize these other fixed costs involved with making the final PV module.

Improvements in efficiency above the 31% theoretical limit are possible if the constraints that are incorporated into the so-called Shockley-Queisser theoretical efficiency limit are relaxed (2). For example, if photons having energies greater than the band gap of the absorbing material did not dissipate their excess energy as heat, but instead produced more voltage or

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generated multiple, low-energy, thermalized electrons from the energy of a single absorbed photon, theoretical efficiencies in excess of 60% would, in principle, be attainable. Absorbers having a highly quantized band structure, such as quantum wells and quantum dots, can theoretically produce the desired effects (Fig. 2). In fact, recent observations on PbSe quantum dots have demonstrated the production, with high quantum yield, of multiple excitons from a single absorbed photon, thereby establishing an existence proof for the process of interest (5). At present, how-

ever, there is no method for efficiently extracting the photogenerated carriers from the quantum dot structure to produce electricity in an external circuit. Materials with “mini-bands” or with “intermediate bands” also offer the possibility for ultrahigh energy conversion efficiency (2, 6). In this approach, different incident photon energies would promote absorption from different isolated energy levels and therefore allow for the production of different voltages (Fig. 2). The phenomenon has been described theoretically but has yet to be demonstrated in a practical im-

plementation. In addition, these materials are currently extremely costly, and methods of retaining the high performance with scalable, inexpensive manufacturing methods would also be required.

In the absence of marked increases in cell efficiency, the value of new solar cell materials rests primarily with their potential to enable an entirely different manufacturing process, such as roll-to-roll manufacturing, printing, painting, or other ultralow-cost approaches to implementation of PV technology. This area is where breakthroughs in the science and technology of solar cell materials can have the greatest impact on the cost and widespread implementation of solar electricity.

The key issue involves the trade-off between material purity and device performance. In a typical planar solar cell design, the charge carriers are collected in the same direction as light is absorbed. A minimum thickness of the cell is set by the thickness of material required to absorb >90% of the incident sunlight. However, the required thickness of the material also imposes a constraint on the required purity of the material, because the photoexcited charge carriers must live sufficiently long within the absorbing material to arrive at the electrical junction, where they can be separated to produce an electrical current flow through the metallic contacts to the cell. Impure absorber materials with short charge carrier lifetimes can therefore effectively absorb sunlight but cannot effectively convert that absorbed energy into electricity. In turn, absorber materials with the necessary purity are generally costly to produce and manufacture. Cheaper materials, such as organic polymers or inorganic particulate solids with small grain sizes, generally have short charge carrier lifetimes and/or induce recombination of charge carriers at the grain boundaries of such materials. This cost-thickness-purity constraint is largely why all current PV cells fall in the green region, labeled zone I, in Fig. 1.

Approaches to circumventing this cost/efficiency trade-off generally involve orthogonalization of the directions of light absorption and charge carrier collection. High-aspect ratio nanorods, for example, can provide a long dimension for light absorption while requiring only that carriers move radially, along the short dimension of the nanorod, to be separated by the metallurgical junction and collected as electricity (Fig. 3) (2, 7). A conceptually similar approach involves the use of interpenetrating networks of inorganic absorbers, such as CdTe “tetrapods” (8) and/or organic polymeric absorbers (9), such as the organic conducting polymer

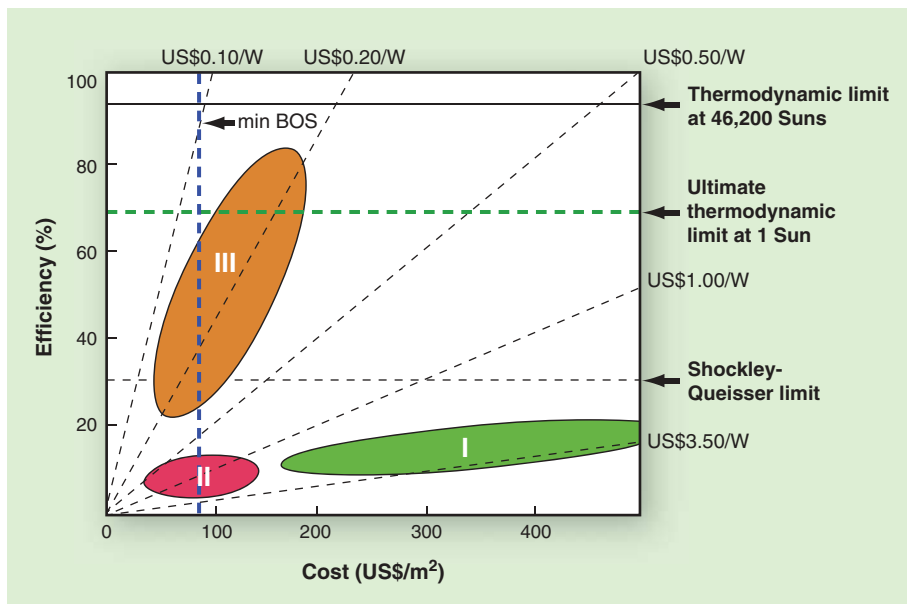


Fig. 1. Solar electricity costs as function of module efficiency and cost. The theoretical efficiencies are shown for three cases: the Shockley-Queisser limit for a quantum conversion device with a single band gap, in which carriers of lower energy are not absorbed and carriers of energy higher than the band gap thermalize to the band gap; the second-law thermodynamic limit on Earth for 1 Sun of concentration; and the second-law thermodynamic limit for any Earth-based solar conversion system. Current solar cell modules lie in zone I. The dashed lines are equi-cost lines on a cost per peak watt (W_p) basis. An estimate for the minimum balance-of-systems cost given current manufacturing methods is also indicated. A convenient conversion factor is that $\$1/W_p$ amortizes out to $\sim \$0.05/kWh$ over a 30-year lifetime of the PV module in the field. [Adapted from (4)]

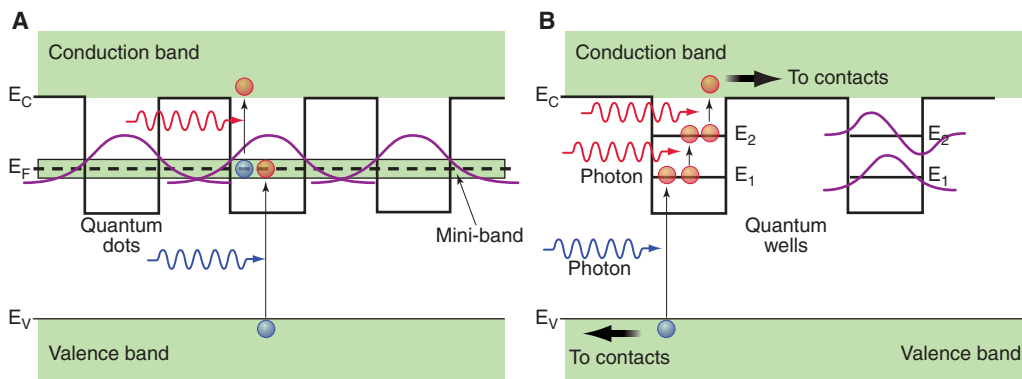


Fig. 2. Possible methods of circumventing the 31% efficiency limit for thermalized carriers in a single-band gap absorption threshold solar quantum conversion system. (A) Intermediate-band solar cell; (B) quantum-well solar cell. [Adapted from (2)]

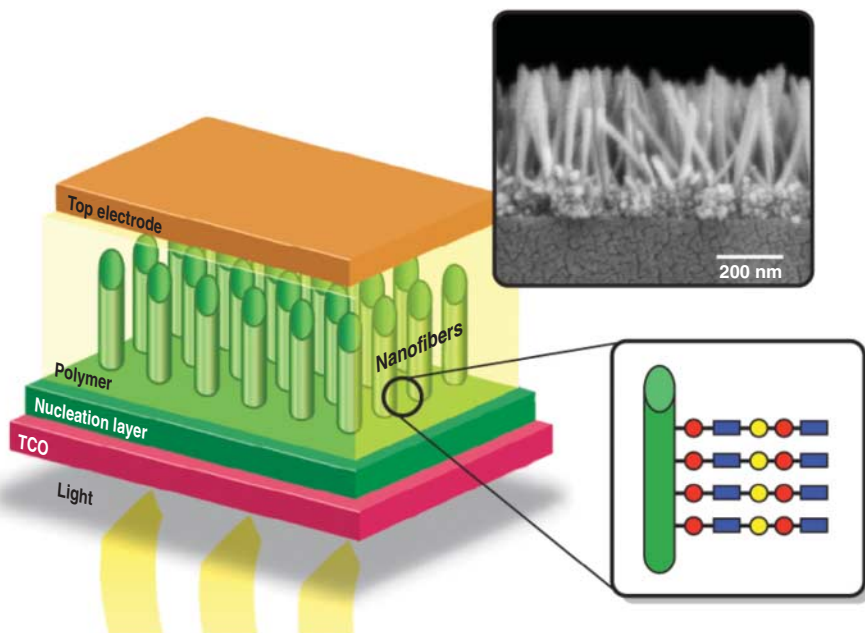


Fig. 3. Arrays of nanorods, illustrating an approach to orthogonalization of the directions of light absorption (down the length of the rods) and charge carrier collection (radially outward to the surface of the rods). [Adapted from (2)]

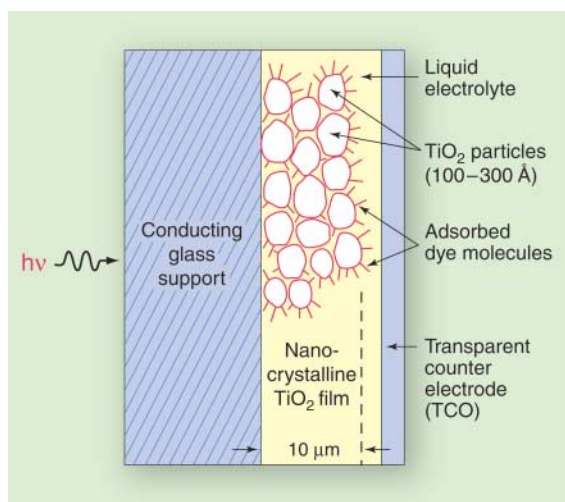


Fig. 4. Dye-sensitized solar cell, in which a nanoparticulate network provides collection of charge carriers injected into it as a result of absorption of sunlight by the adsorbed dye molecule. The oppositely charged carrier moves through the contacting liquid or polymeric phase to the counterelectrode, completing the electrical circuit in the solar cell. [Adapted from (2)]

poly(phenylenevinylene). Such systems are under widespread investigation at present, and the key is not only to obtain intimate contact between the light-absorbing and charge-collecting phases, but also to control the chemistry at the interface between the two phases that make up the device. Junction recombination is a deleterious loss pathway even in many planar solar cell devices, and such junction recombination generally becomes dominant in disordered

systems that, by definition, have a large increase in their interfacial contact area relative to their projected geometric area for light absorption. Methods for controlling the chemical properties of the surfaces and junctions of such systems, and thereby reducing their natural tendency to promote deleterious charge carrier recombination, are therefore critical. Such methods have been developed for certain well-defined semiconductor surfaces (10) and will need to be developed and implemented successfully for the high-junction area systems to obtain high (>5%) energy conversion efficiencies from such devices.

A conceptually related system is the dye-sensitized solar cell, in which a random, disordered network of inexpensive TiO_2 particles is used to collect the charge carriers. The light absorption is performed by an adsorbed dye molecule, and the interfacial contact distance is kept small by use of a liquid or conductive polymer to penetrate the pore structure of the solid and collect the other charge carrier type to complete the circuit in the cell (Fig. 4) (11). Small “champion” dye-sensitized solar cells have shown efficiencies as high as 10 to 11%, although at present large-area devices typically have efficiencies of <5%. Improvements in the efficiency of such systems will require improved

dyes, better electrolytes, and better control over the recombination at the interfacial contact area that currently limits the voltage produced by such systems to about 50 to 60% of its theoretical value. The stability of such systems will also need to be demonstrated under operational conditions for extended periods (>10 years) to allow them to be implemented in the marketplace. Clearly, advances in basic science are needed to enable all such nanostructured systems to truly offer a practical, ultralow-cost option for solar electricity production (2).

Although there is tremendous potential for growth for PV in electricity generation, solar electricity can never be a material contributor to primary energy generation without cost-effective methods for storing and distributing massive quantities of electricity (2, 3, 12). Put simply, the Sun goes out locally every night, and the intermittency imposed by the diurnal cycle must be dealt with to provide a full, base-loadable primary energy system from the Sun. The lack of cost-effective large-scale electrical storage capacity on Earth underlies the call for development of space-based solar power systems. On Earth, the cheapest method for massive electricity storage is pumped-water storage, which can be relatively efficient, but even that process does not scale well if every reservoir would have to be filled up each day and emptied each night; additionally, a staggering amount of water would be needed to compensate for the diurnal cycle if one were to provide a material contribution to the primary U.S. or global energy generation through this approach. Batteries are a natural approach to electricity storage, but for battery storage to be cost-effective over the 30-year amortized lifetime of a PV system, enormous quantities of batteries would have to be hooked up to the grid, and they would have to cost as little as lead-acid batteries while providing the cycle life of lithium-ion batteries. Innovative approaches to massive, low-cost energy storage—including potentially a superconducting global transmission grid, supercapacitors, flywheels, etc., as promoted by Smalley (12)—will be important enablers of a full solar capture, conversion, and storage energy system.

Perhaps the most attractive method for cost-effective massive energy storage is in the form of chemical bonds (i.e., chemical fuel). After all, this approach is central to photosynthesis and is the basis for much of the recent attention devoted to development of biofuels. Photosynthesis, however, saturates at about one-tenth of the intensity of normal sunlight, and consequently the yearly averaged energy storage efficiency of even the fastest-growing plants is less than 1%, and typically less than 0.3 to 0.5% (2), as compared to the >15% efficiency values displayed by current PV devices (2). Hence, to first order, land-related constraints dominate the ultimate commercial potential of biofuels as

material contributors to primary energy supply, whereas cost-related constraints dominate the ultimate commercial potential of PV-derived solar energy conversion and storage systems.

One approach to storing electrical energy in chemical bonds is through electrolysis, in which water is split into H₂ and O₂ in an electrolyzer. However, Pt-based electrolysis in acidic or neutral media is expensive and unlikely to be scalable to the levels that would be required for this process to be material in global primary energy production. Ni-based electrolysis in basic aqueous solutions is cheaper but requires scrubbing the input stream to remove the CO₂ (13); additionally, even the best fuel cells are only 50 to 60% energy-efficient and the best electrolysis units are 50 to 70% energy-efficient (13), so the full-cycle energy storage/discharge efficiency of such a system is currently only 25 to 30%. Clearly, better catalysts for the multielectron transformations involved in fuel formation are needed. Nature provides the existence proof for such catalysts, with the hydrogenase enzymes operating at the thermodynamic potential for production of H₂ from H₂O, and with the oxygen-evolving complex of

photosystem II producing O₂ from H₂O in an energy-efficient fashion. However, no human-made catalyst systems, either molecular or heterogeneous, have yet been identified that show performance even close to that of the natural enzymatic systems. Development of such catalysts would provide a key enabling technology for a full solar energy conversion and storage system.

Whether the fuel-forming system is separate, as in a PV-electrolysis combination, or integrated, as in a fully artificial photosynthetic system that uses the incipient charge-separated electron-hole pairs to directly produce fuels with no wires and with only water and sunlight as the inputs, is an interesting point of discussion from both cost and engineering perspectives. However, the key components needed to enable the whole system remain the same in either case: cost-effective and efficient capture, conversion, and storage of sunlight. Each of these functions has its own challenges, and integration of them into a fully functioning, synergistic, globally scalable system will require further advances in both basic science and engineering. Such advances, together with advances in existing technologies,

will be required if the full potential of solar energy is to be realized.

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PERSPECTIVES

Challenges in Engineering Microbes for Biofuels Production

Gregory Stephanopoulos

Economic and geopolitical factors (high oil prices, environmental concerns, and supply instability) have been prompting policy-makers to put added emphasis on renewable energy sources. For the scientific community, recent advances, embodied in new insights into basic biology and technology that can be applied to metabolic engineering, are generating considerable excitement. There is justified optimism that the full potential of biofuel production from cellulosic biomass will be obtainable in the next 10 to 15 years.

The idea of converting biomass-derived sugars to transportation biofuels was first proposed in the 1970s. Once again, the idea is being seriously contemplated as a possible substitute for petroleum-based liquid fuels. Economic and geopolitical factors (high oil prices, environmental concerns, and supply instability) have certainly played a role in reviving interest in renewable resources. However, an additional impetus is now provided by scientific and technological advances in biosciences and bioengineering that support increased optimism about realizing the full potential of biomass in the liquid fuels area within the next

10 to 15 years. New approaches to biology are being shaped by the genomics revolution; unprecedented ability to transfer genes, modulate gene expression, and engineer proteins; and a new mind-set for studying biological systems in a holistic manner [systems biology (1)]. We are also seeing advances in metabolic engineering (2–4), with the goal of overproducing useful compounds by rationally and combinatorially engineering cells and their metabolic pathways (5). Combination of concepts and methods from these fields will create a platform of technologies that are critical for overcoming remaining obstacles in cost-efficient biofuel production from cellulosic biomass.

Figure 1 shows the basic features of a biomass-to-biofuels (B2B) process (6). After harvest, biomass is reduced in size and then

treated to loosen up the lignin-cellulose fiber entanglement in a step that can take from a few minutes to many hours. Several methods have been used for this purpose, such as biomass treatment with saturated steam at 200°C, explosion with ammonia, and cooking with warm dilute acid (6). Dilute acid pretreatments are fast (minutes), whereas steam-based treatments can take up to a day. After pretreatment, the solid suspension is exposed to cellulolytic enzymes that digest the cellulosic and hemicellulosic biomass components to release the hydrolysis products, primarily six- and five-carbon sugars, respectively (along with acetic acid and lignin-derived phenolic by-products). The type of pretreatment defines the optimal enzyme mixture to be used and the composition of the hydrolysis products. The latter are fermented by ethanol-producing microorganisms such as genetically engineered yeasts, *Zymomonas mobilis* (Fig. 2), *Escherichia coli*, or *Pichia stipitis* (Fig. 3). Presently, cellulose hydrolysis and fermentation are combined in a single unit, termed the simultaneous saccharification fermentation (SSF) stage. The rationale of combining saccharification (the breaking up of complex carbohydrates into monosaccharides) and fermentation (the conversion of a carbohydrate to carbon dioxide and alcohol) in a single unit was to prevent inhibition of the hydrolytic enzymes by the reaction products (7). The SSF step typically lasts 3 to 6 days, with cellulose hydrolysis being the slow, limiting step. The product of SSF is a rather dilute ethanol stream of 4 to 4.5% from which ethanol is separated by distillation.

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