Bio-inspired constructs for sustainable energy production and use

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Résumé **Des systèmes bio-inspirés pour la production et l'utilisation de sources d'énergie renouvelable**

La production d'énergie en continu pour les besoins de l'Homme à partir de systèmes bio-inspirés et de sources d'énergie renouvelable basées sur le solaire est réalisable. Cependant, plusieurs défis doivent être relevés pour atteindre ce but. L'une des solutions consiste à coupler de manière efficace la force électromotrice de l'oxydation de l'eau à la production de carburants par voie d'électrosynthèse réductrice. Tout d'abord pour l'électrolyse de l'eau, l'utilisation efficace de l'énergie solaire nécessite d'oxyder l'eau à de faibles surpotentiels, prouesse réalisée par plusieurs enzymes dans le monde du vivant. Mais pour être utilisées dans ce contexte, ces enzymes doivent être détournées de leur source usuelle de potentiel d'oxydation vers d'autres formes comme la force électromotrice dans un conducteur métallique. Les catalyseurs biologiques peuvent aussi utiliser les électrons produits par ces réactions d'oxydation afin de synthétiser des composés à faible nombre d'atomes de carbone riches en énergie (ou de l'hydrogène), avec de faibles surpotentiels et sans trop de réactions secondaires. Mais encore une fois, pour ce faire, il serait important de faire basculer ces catalyseurs naturels de leur source de potentiel de réduction vers des potentiels d'un conducteur métallique, ou vers d'autres formes de potentiel de réduction. Dans ce but, nous avons construit dans une première étape un système hybride inspiré de la cellule de Grätzel, système dans lequel la photoanode, constituée de nanoparticules d'un semi-conducteur à large bande interdite et fonctionnalisée par un photosensibilisateur de type porphyrine, est utilisée pour la conversion photochimique de la biomasse en hydrogène.

Mots-clés **Photosynthèse artificielle, force protonmotrice, énergie solaire, catalyse biologique, bioénergétique, hydrogène, pile à combustible.**

Abstract Sustainable energy production for human use based upon solar powered bio-inspired constructs and renewable resources is achievable. However, several challenges must be overcome before this goal is realized. One is the efficient coupling of electromotive force to the oxidation of water and to the electroreductive synthesis of chemical fuels for energy storage. Beginning with the electrolysis of efficient use of solar energy requires water oxidation at minimal overpotential, a feat accomplished by enzymes found in Nature. However, in order to be used in this context, these enzymes must be switched from their usual source of oxidation potential to other forms such as electromotive force in a metallic conductor. Biological catalysts can use the electrons produced by such oxidations to carry out the synthesis of energy-rich reduced carbon compounds (or hydrogen) with little overpotential and almost no side reactions. But once again, to accomplish this technologically, it will be necessary to switch Nature's catalysts from their usual source of reduction potential to electromotive force in a metallic conductor or other forms of reduction potential. In an initial step in this direction, this article presents a hybrid system in which a porphyrin-sensitized Grätzel-type nanoparticulate wide band gap semiconductor photoanode is used for the photochemical reformation of biomass to hydrogen.

Keywords **Artificial photosynthesis, protonmotive force, solar energy, biological catalysis, bioenergetics, hydrogen, fuel cell.**

Glossary

The terms followed by an asterisk in the text are defined below.*

ATP: adenosine triphosphate.
emf: electromotive force.
NAD: nicotinamide adenine dinucleotide (oxidized form).
NADH: nicotinamide adenine dinucleotide (reduced form).
pmf: protonmotive force.
PSII: photosystem two.
P680: reaction center of PSII.
Q: 1,4-benzoquinone.
QH_2: 1,4-benzoquinol.
SHE: standard hydrogen electrod.
TiO_2: titanium(IV) oxide.
TW: terawatt.

In common with all living things, individual humans interact with the environment in ways that optimize the probability of passing on their genes. In the case of humans, organization into technologically-advanced societies and cultures has added a new dimension to this fierce evolutionary process: the material rewards of growing an ever increasing gross domestic product. The pursuit of this activity, fueled by abundant supplies of fossil fuels and supported by a well-developed technology for accessing this stored energy, has led to unsustainable energy production. Currently, societies spanning all developmental levels base their energy infrastructures on fossil fuels or unsustainably-consumed firewood.

Now, faced with the reality of anthropogenic climate change – a problem facing humanity that is no less significant than war, famine, disease, overpopulation, the plight of refugees and the guarantee of human rights across the lands – humans must find sustainable ways to power their societies. Fortunately, Nature has thrown us a lifeline. Solar energy provides the biosphere with about 10^{24} joules/year, making human needs of even a projected 10^{21} joules/year a deceptively achievable goal. Natural photosynthesis captures a fraction of the incoming solar energy to operate at above 100 TW* providing essential support for all life on Earth. The goal of research in artificial photosynthesis is to abstract the key photosynthetic processes using synthetic schemes [1-2]. Research in artificial photosynthesis can suggest hybrid systems and even ways to engineer living cells to increase the efficiency of the synthesis of energy-rich fuel materials such as hydrogen and reduced carbon compounds. The latter have the almost inestimable advantage that the infrastructure for distribution and use is in place.

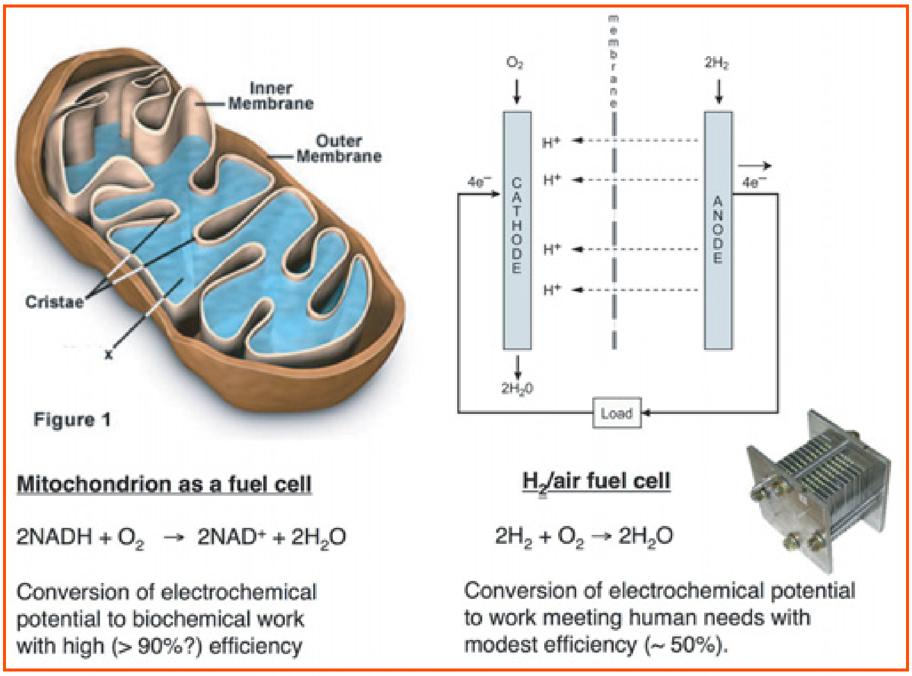
Nature's energy conversion processes

Naturally occurring respiratory and photosynthetic systems provide paradigms for all of the important energy converting processes humans would need to achieve sustainable energy production and use. In a cell respiring aerobically, energy transduction takes place in biological "fuel cells", specialized organelles known as mitochondria (*figure 1*). In the mitochondria, electrons collected by the enzymatic oxidation of reduced carbon compounds, a process that reduces NAD^+* to NADH*, are transported down their thermodynamic gradient to ultimately reduce O_2 to water. This is accomplished by a series of electron carriers known as the electron transport system. Specialized electron carriers at appropriate positions in the electron transport system use the drop in electrochemical potential to pump protons across the mitochondrial inner membrane. The resulting proton thermodynamic gradient, the difference in electrochemical potential of protons on the opposite sides of the membrane, is known as protonmotive force (pmf). The translation of redox potential to pmf by redox linked proton pumps is the most fundamental bioenergetic process of oxygen-dependent life on Earth. In subsequent reactions, living cells use pmf* or its thermodynamic equivalent, ATP*, to do synthetic chemical work, mechanical work, transport work, and signal amplification/information processing work.

Figure 1 illustrates the oxidative and reductive chemistry common to both mitochondria and fuel cells. The efficiency of hydrogen/air (O_2) fuel cells is limited by the overpotential at the oxygen-reducing cathodic electrode. This electrode typically uses noble-metal catalysts that are expensive and often easily poisoned. On the anode side, the best human-made catalysts for H_2 oxidation are platinum-based. This raises the concern that, in addition to the cost and sensitivity to chemical poisons, there may not be sufficient platinum to fabricate terawatt-level energy converting devices. In contrast, the mitochondrial energy-transducing membranes operate at near the thermodynamic limit of efficiency, using copper and iron metals at their oxygen-reducing active sites. Various hydrogenase enzymes offer other examples of catalysts that would be important in fuel cells. These enzymes catalyze the proton/hydrogen half reaction at essentially its equilibrium electrochemical potential using only iron or iron and nickel metals.

Water oxidation

In the final analysis, sustainable production of energy-rich fuels must involve water oxidation, the reverse of the O_2/H_2O half reaction of combustion, and once again Nature does this efficiently [3-6]. Photosynthetic reaction centers using Mn-based catalysts provide slightly over 1 volt (vs SHE*) to carry out the 4-electron oxidation of two water molecules to yield O_2. In commercial electrolyzers, the electrochemical reactions of the fuel cell are reversed by applying an emf*. These cells use noble-metal catalysts similar to the fuel cell and operate with an applied potential of 1.75 volts at an efficiency of 70% [7]. If a human-engineered device were to achieve an efficiency comparable to that of the natural system, it would represent a significant savings in electromotive force, a commodity that must be sustainably produced from solar, wind, geo, hydro, etc, sources. In summary, Nature's catalysts use readily available metals in combination with organic components to template oxidation-reduction energy along reaction coordinates that yield the desired products with high power conversion efficiency (little loss in overpotential and few undesirable, low-energy-conserving side reactions). The challenge is clear: we



Mitochondrion as a fuel cell

$2NADH + O_2 \rightarrow 2NAD^+ + 2H_2O$

Conversion of electrochemical potential to biochemical work with high (> 90%?) efficiency

H_2/air fuel cell

$2H_2 + O_2 \rightarrow 2H_2O$

Conversion of electrochemical potential to work meeting human needs with modest efficiency (~ 50%).

Figure 1 - Schematic of a mitochondrion and a human-engineered fuel cell illustrating that the electrochemical reduction of oxygen to water is common to both fuel cells.
The outputs are very different – pmf is the output of the mitochondrion and emf is the output of the fuel cell. Mitochondrion used with permission from M.W. Davidson.

must understand the structure, function and detailed chemical mechanisms of Nature's energy transducing processes such as photosynthesis and respiration and co-opt their essential features for human use.

Artificial photosynthesis

One approach to the development of artificial photosynthesis is to identify functional elements of the natural system and design and synthesize constructs that mimic a particular function [1-2]. In this context, it is useful to compare natural and human-engineered systems in order to identify points of functional or mechanistic similarity as starting points for design of the artificial systems and/or as interface points for the design of hybrid systems. *Figure 2* compares solar energy conversion by photovoltaic devices with natural photosynthesis. Common functional features include the absorption of light, charge separation, and coupling the output of the primary processes to the performance of work.

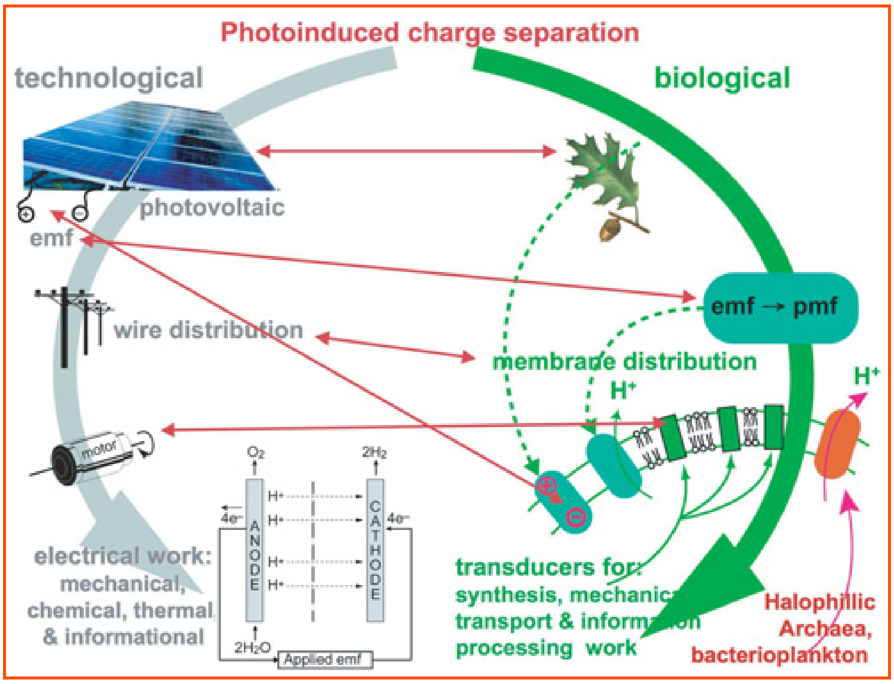


Figure 2 - Photoinduced charge separation and parallels between biological and technological solar energy conversion.

Photoinduced charge separation is common to both photovoltaic and photosynthetic processes. In photosynthesis, charge separation yields highly oxidizing and highly reducing chemical species. Nature's catalysts direct this oxidation and reduction potential along reaction coordinates that drive proton pumps that generate pmf, water oxidation that yields O_2, and carbon reduction that yields the energy-rich carbon compounds that are the building blocks of living cells. The red arrows delineate connections in function between the two systems (see text). Electrolysis is one example of the conversion of emf to redox potential; it is illustrated on the technological branch. The recent discovery of the widespread occurrence of solar energy conversion by light-driven proton pumps in certain microorganisms is indicated on the biological branch.

On the biological branch, discrete chemical species – the chlorophyll, carotenoid, and other pigments of photosynthesis – absorb light which generates excited states in which the chemical potential is increased by a fraction of the energy of the absorbed photon. Absorption of light is followed by energy transfer which ultimately generates a chlorophyll excited state in a special transmembrane chlorophyll-containing protein complex known as the reaction center. The reaction center is the site of charge separation, a process which generates vectorial redox potential across the biological membrane, indicated schematically in *figure 2*. Various mediators carry this redox potential to the catalytic sites where it drives proton pumps to generate pmf* and is used in oxidative and reductive biosynthetic processes. Pmf is distributed by the closed, bubble-like membrane which everywhere separates two aqueous phases, and is available to drive transducers that span the membrane [5-6].

On the photovoltaic branch, excitation generates electron-hole pairs in the semiconductor which translate to emf* in the attached conducting wires. Emf is distributed by the wires and is available to transducers that are connected between the wires.

Fundamental differences between biological and human-engineered solar energy conversion process are illustrated in *figure 2*. Oxidation/reduction chemistry as carried out electrochemically in the laboratory, and practically in batteries, fuel cells, etc., produces electromotive force (emf), the current and voltage carried by the metallic conductors and electrodes, which couples the chemical oxidation and reduction half reactions together. Also, emf is the energy output of photovoltaic devices. In the biological world, metallic conductors (and the corresponding emf) are not usually involved in coupling oxidizing and reducing half reactions. Rather, discrete chemical species such as co-enzymes and cytochromes act as mediators, shuttling electrons between reducing and oxidizing centers. These electron-carrying mediators (e.g., the redox components in the electron transport system described above) use the principles of molecular recognition to locate the appropriate centers for oxidation and reduction, and in this way avoid short circuit processes. In other words, the biological catalysts recognize the appropriate redox mediator and react with it so that current flow, the effective transport of electrons, is ordered. Current flow is controlled and directed in four ways: first, current flows thermodynamically down the net electrochemical gradient; second, current must flow to and through each chemical species in the order intended – it cannot skip a redox center; third, at selected redox centers allosteric and other feedback processes control electron flow in response to the needs of the cell; and fourth, if the carriers have an organization (such as across a biological membrane), then the current flow is spatially vectorial. By contrast, energy transduction carried out by human-engineered electrical devices is controlled and directed by the physical wiring of the circuit and by myriad devices that amplify, switch and otherwise modulate emf. Fuel cells, batteries, electrolyzers, etc., do require ion flow to establish a complete circuit. The context of electrical conduction by ions in these emf-based devices is different from biological electron conduction described above.

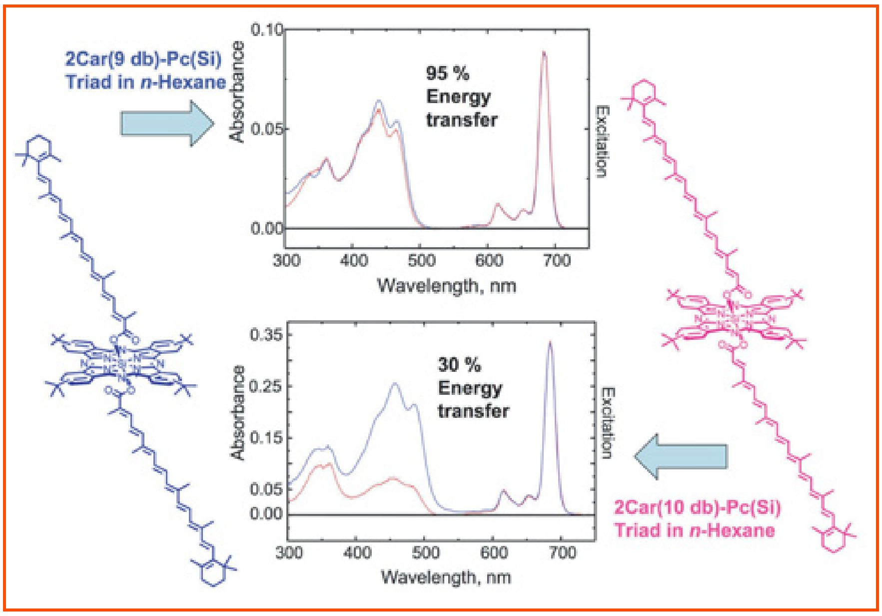


Figure 3 - Two caroteno-phthalocyanine triads that demonstrate carotenoid to tetrapyrrole singlet energy transfer.

Triads **1** and **2** differ structurally in the number of conjugated double bonds in the carotenoid moiety. The blue curve is the absorption spectrum; the red curve is the fully corrected phthalocyanine fluorescence excitation spectrum.

A fundamental difference between these systems is now clear. Nature's catalysts do not generally recognize metallic conductors and emf. It is left to human ingenuity to devise low-barrier pathways for electrons to flow across organic-metallic interfaces. Recent work in our laboratories has addressed this issue [8-9]; see references therein for work from many laboratories concerning molecule-metal conductivity.

Light harvesting and energy transfer in artificial photosynthesis

As mentioned above, artificial photosynthesis includes the design and synthesis of molecular constructs that mimic key functions found in natural photosynthetic membranes [1-2]. *Figure 3* presents an example of molecular triads designed to mimic light harvesting, energy transfer and certain elements of the control of photosynthesis found in natural photosynthetic complexes [10]. These triads illustrate that subtle changes in structure can lead to large changes in function.

Triad **1** comprises carotenoids having nine conjugated double bonds linked to a tetrapyrrole through the coordinated Si atom and demonstrates nearly quantitative singlet energy transfer from the carotenoid to the tetrapyrrole. We have shown that energy transfer occurs from several excited states in the carotenoid singlet manifold including the lowest excited singlet state, S_1, which is both relatively short lived and electric dipole forbidden. The carotenoid pigments in triad **2** have ten conjugated double bond and demonstrate remarkably different behavior from their counterparts in triad **1**. Among other things, the addition of one double bond to the conjugated chain lowers the energy of S_1, which shortens its lifetime and moves it closer to or slightly below the S_1 energy level of the phthalocyanine. The combined effect of these changes is to markedly reduce energy transfer efficiency from the carotenoid S_1 level, which in turn reduces the overall quantum yield to about 30%. Additionally, the fluorescence yield of the phthalocyanine in triad **2** is much lower at all excitation wavelengths than that of triad **1**. Quenching of tetrapyrrole excited singlet states by carotenoids in this and in similar model systems mimics the carotenoid-based control of photosynthesis in the natural system and its study leads to a deeper understanding of natural photosynthesis [11]. It is important to understand all processes that control the rate of photosynthesis in order to explore re-engineering of natural photosynthesis for increased yield. Increasing the yield of photosynthesis could have a profound impact on the food production and on sustainable energy production.

Light harvesting, energy transfer and charge separation in artificial photosynthesis

Figure 4 presents a recent example of an artificial construct that exhibits the primary photophysical functions of light absorption, energy transfer and charge separation found in natural photosynthesis [12].

The organizing framework for the heptad shown in *figure 4* is a hexaphenylbenzene that bears five light-harvesting 9,10-bis(phenylethynyl)-anthracene (BPEA) groups and a Zn porphyrin. The reaction center comprises the Zn-porphyrin as the primary electron donor and a C_{60} moiety as the acceptor. The BPEA units act as antennas to provide substantial absorption cross section in the blue-green region of the spectrum. Upon capture of a photon, excitation energy is transferred efficiently among the BPEA units (indicated by the yellow shading) until it is trapped to generate the lower-energy excited state of the Zn-porphyrin (indicated by the

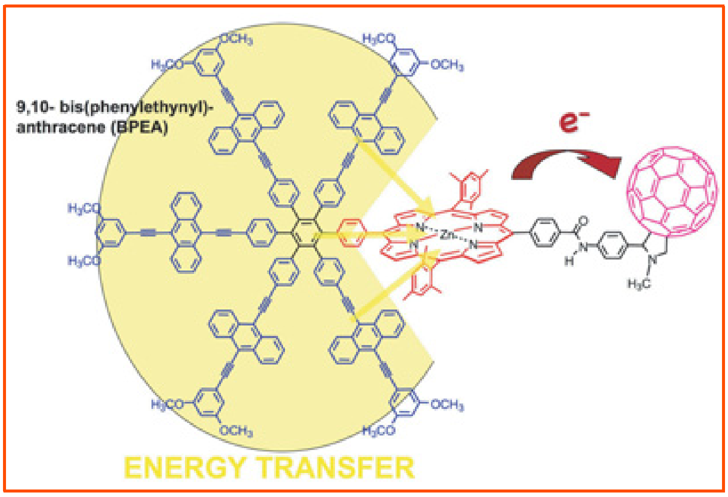


Figure 4 - A synthetic antenna-reaction center complex made up of seven active components.

yellow arrows). Once excited, the Zn-porphyrin undergoes photoinduced electron transfer (red arrow) to yield the energetic and relatively long-lived charge separated state $P_{Zn}^{\bullet +}$ -$C_{60}^{\bullet -}$. Both energy and electron transfer processes depend upon thermodynamic and electronic coupling parameters between the appropriate chromophores (fully explained in [12]). In these systems, the principles of energy transfer developed initially by Förster and Dexter can be used to design structures having the necessary electronic and thermodynamic coupling to give a high quantum yield of energy transfer. Similarly, Marcus-Hush theory is used to specify the electronic and thermodynamic parameters that will result in a high quantum yield of charge separated species which have sufficient lifetime to participate efficiently in subsequent energy conversions processes.

As indicated by the red arrows in *figure 2* linking human-engineered and natural solar conversion schemes, there are several ways to imagine taking advantage of the inherent efficiency of energy transduction in biological systems and the robustness and high efficiency of photovoltaic systems by assembling hybrid devices in which energy transduction is carried out employing biological or bioinspired catalysis coupled to human-engineered devices.

A hybrid photobiofuel cell

One approach to merging biological catalysts with emf-producing constructs is shown in *figure 5*, which presents a photobiofuel cell designed in our laboratories.

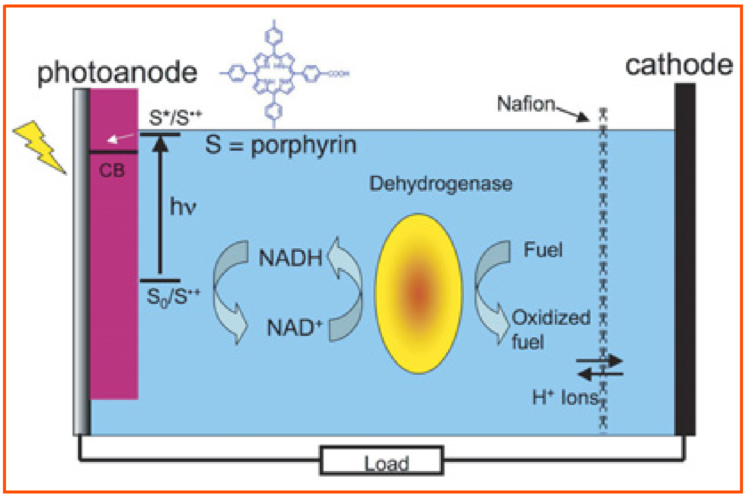


Figure 5 - A hybrid enzyme-based photoelectrochemical fuel cell producing electricity and reduced chemical species. The function of the cell is fully described in the text.

This is a non-regenerative cell in which the electrons are obtained at the anode by oxidation of biomass such as glucose or short chain alcohols; a reductive chemical reaction at the cathode and a means to transport charge between the anodic and cathodic solutions completes the circuit [13-14]. In the anode solution, a soluble dehydrogenase enzyme is used to oxidize a biological substrate and reduce NAD^+ to NADH. A porphyrin-sensitized high-surface area TiO_2* photoanode is excited by visible photons, resulting in electron injection from the first excited singlet state of the porphyrin into the conduction band of the titanium(IV) oxide. These electrons are collected at the back contact of the photoanode and passed in the connecting wire to the cathode, where any of a variety of reductive processes must occur. The porphyrin radical cation resulting from photoinduced electron injection oxidizes the NADH product of the enzymatic reactions regenerating NAD^+ and poising the NAD^+/NADH couple oxidizing. The photochemical step increases the negative potential of the electrons derived from biomass. Once injected into the TiO_2 conduction band, the electrons are conducted to the cathode where the emf is sufficient to reduce protons to hydrogen gas [15]. Under our typical operating conditions (pH 8.0), the H^+/H_2 couple is among the most reducing species encountered in biology [16], and hydrogen production is therefore considered a proxy for the synthesis of a variety of products [15]. The ability of the biohybrid photoelectrochemical cell to evolve hydrogen indicates that there is sufficient driving force for other types of bio-inspired reductive synthesis to be carried out with appropriate catalysts. In fact, the hydrogen itself could be burned, used in fuel cells, or used in the production of high-value liquid fuels [17].

A detailed study of the cell under various load conditions and with mediators other than NADH has demonstrated that NADH is essentially irreversibly oxidized at the anode so that recombination reactions (electron transfer from anode to species in the anodic solution), which severely limits the emf in some cells, is minimized [18]. The near irreversibility can be understood from the details of the NAD^+/NADH half reaction [19]. The one-electron oxidation of NADH produces $NADH^{\bullet +}$ which rapidly deprotonates to yield $NAD^{\bullet}$, the neutral radical species. $NAD^{\bullet}$ is an excellent electron donor (- 0.93 V) and is further oxidized at the anode. NAD^+ is difficult to reduce by one electron (in its role as a co-enzyme with dehydrogenases it always transfers a hydride ion) and is thus kinetically stable against electron transfer (recombination) from the anode. This is an important factor in the translation of redox potential to emf and illustrates the sensitivity of power conversion efficiency to subtle chemical features of the mediators (*vide infra*). Understanding the mechanism and consequences to the cell performance suggests that this irreversible step is a key feature to incorporate into other synthetic mediators.

An experiment was carried out to illustrate the role of the mediator in controlling the emf of the cell. As shown in *figure 5*, the cell was configured with a Pt-based cathode capable of hydrogen production at pH 8. In one case NADH was used as the sacrificial electron donor. Upon illumination of the anode, current was observed to flow in the circuit and hydrogen was formed at the cathode. A similar cell was set up with a different electron donor, hydroquinone (QH_2*), in the anodic solution. Upon illumination of the anode in this case, no current was observed to flow and no hydrogen was produced. These two cases have been further characterized electrochemically; one conclusion is that the facile participation of the quinone radical species in recombination reactions with the anode severely limits cell performance [18].

The photobiofuel cell can be thought of as functioning in two ways, depending upon the cathodic reaction. Fitted with an electrochemically-positive cathodic reaction such as the reduction of O_2 to water (assuming a suitable catalysts can be found), the work output of the cell would be emf dropped across the load shown in *figure 5*. Or, fitted with an electrochemically-negative cathodic reaction such as the reduction of H^+ to hydrogen, the electrical load would be removed and the work output would be an energy rich fuel. In either case, advantages of this cell include being able to use a variety of biomass material, limited only by the availability of NAD-linked dehydrogenase enzymes, and the relatively high emf produced as a result of photoexcitation and the electrochemical near-irreversibility of NADH oxidation at the anode.

Future challenges

The central role of pmf in biological energy transduction suggests that proton/ion pumps could be an integral part of artificial photosynthesis. Pumps require vectorial processes and therefore added organizational dimensions. These can be provided by model biological membranes separating aqueous phases and directional incorporation of artificial reaction centers. We have reported examples of this level of organizational complexity in fully synthetic, light-driven transmembrane electron transfer and in ion pumps based solidly upon the redox loop mechanisms used by Nature [20-22]. The liposome-based proton pump was further elaborated by including ATP synthase, and the light-powered synthesis of ATP was demonstrated [23].

Integrating human-engineered systems with the full range of biological processes will require the efficient interconversion of emf and pmf. *Figure 6* illustrates the initial progress we have made in the design and assembly of hybrid constructs in which a planar model biological membrane is supported between two aqueous phases so that electrochemical processes can be used to drive a molecular transmembrane proton pump [24]. In this system, the proton pump was driven by redox chemistry between ascorbate and ferricyanide; the electrodes were used to measure the ion current. In the next step, emf will be used to drive appropriate mediators on either side of the membrane so that the electrical current will be smoothly translated to pmf.

It is imagined that a source of pmf supplied concurrently with redox potential will make it possible to assemble artificial membranes that contain naturally occurring enzymes that obligatorily couple electron transfer to proton translocation. This would open the door to exploring catalytic processes as important and diverse as reducing O_2 to water with cytochrome *c* oxidase and key catalytic steps in methane synthesis requiring both reduction potential and pmf.

Conclusion

Research in artificial photosynthesis offers the possibility of finding ways to use Nature's intrinsically efficient biosynthetic and energy-transforming processes to do the bidding of humans. The paradigm is clear: during ~ 3.4 billion years of fierce evolutionary competition nature has refined energy conversion efficiency. We will not be misled; the natural examples we have before us today are the successful ones.

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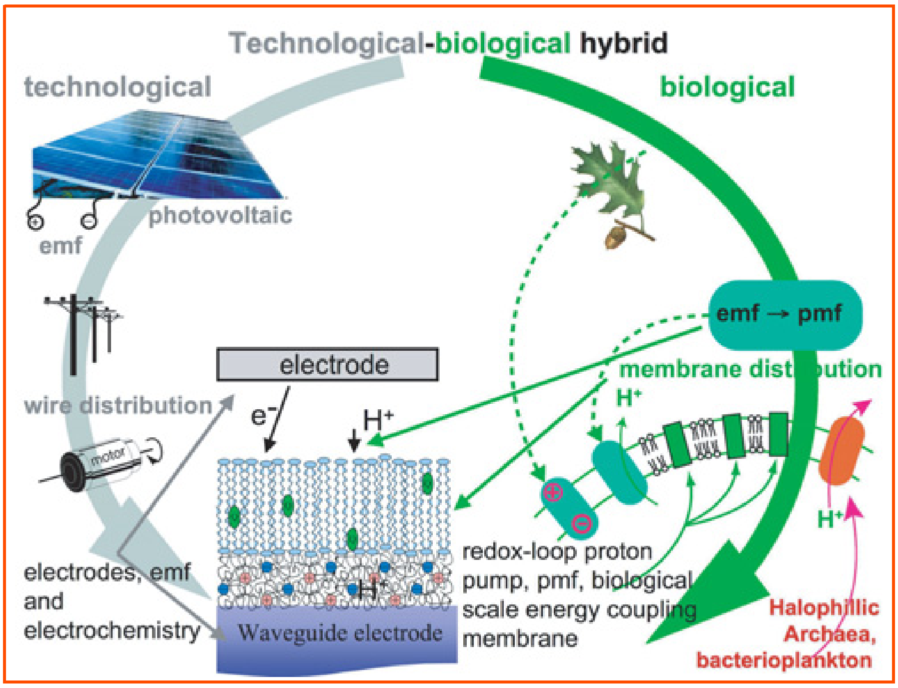

Figure 6 - A hybrid scheme in which a redox-based proton pump operating in a supported model biological membrane is coupled to electrodes and therefore to emf.
The grey arrows depict human-engineered constructs and include wires, emf and electrodes. The green arrows illustrate biological processes and include the redox-loop proton pump, pmf, and biological-scale membrane structures. The proton-carrying, lipophilic quinone is reduced at the upper electrode and oxidized at the lower one. This process is fully explained in [24]. Light-driven proton transport in *Archaea* illustrates the direct conversion of solar energy to pmf.

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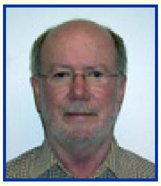

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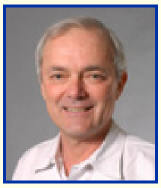

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