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Biotechnological Storage and Utilization of Entrapped Solar Energy

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Abstract

Our laboratory has recently developed a device employing immobilized F_0F_1 adenosine triphosphatase (ATPase) that allows synthesis of adenosine triphosphate (ATP) from adenosine 5'-diphosphate and inorganic phosphate using solar energy. We present estimates of total solar energy received by Earth's land area and demonstrate that its efficient capture may allow conversion of solar energy and storage into bonds of biochemicals using devices harboring either immobilized ATPase or NADH dehydrogenase. Capture and storage of solar energy into biochemicals may also enable fixation of CO_2 emanating from polluting units. The cofactors ATP and NADH synthesized using solar energy could be used for regeneration of acceptor D-ribulose-1,5-bisphosphate from 3-phosphoglycerate formed during CO_2 fixation.

Index Entries: Solar energy; F_0F_1 adenosine triphosphatase; immobilization; land area; CO_2 fixation.

Introduction

Land plants, aquatic plants, cyanobacteria, and other photosynthetic bacteria including some thermophiles are known for efficient conversion of solar energy into chemical energy by their photosynthetic apparatus *(1–3)*. This photosynthetic process has inspired the development of several interdisciplinary research technologies (including artificial antennas) for entrapment of solar energy *(4–6)*. There are three requirements for successful entrapment of solar energy and its conversion into chemical energy by artificial means: (1) absorption of light energy and its conversion into

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electronic excitation, (2) efficient utilization of electronic excitation to efficiently drive directed work with minimal loss of energy (such as by heat), and (3) utilization of the photoexcited charge to perform specific chemical transformations for storage of solar energy in usable products *(7)*. Of these three requirements, the semiconductors have successfully met the first two criteria: acting as excellent light absorbers and providing electronic excitation and directed work *(7)*.

Throughout the biologic world, the F_0F_1 adenosine triphosphatase (ATPase) acts as a great energy transducer. For an average human body at resting phase that demand necessitates a turnover of about 65 kg of adenosine triphosphate (ATP)/d *(8)*. Using artificial antennas and immobilized ATPase in liposomes, it has been demonstrated that light-driven proton pumping may drive enzyme-mediated ATP synthesis *(9)*. At 200 mV, 10 protons are needed for three molecules of ATP generation, rendering the system at about 63% average efficiency *(8,9)* (see Appendix A).

In this article, we examine a number of issues related to biotechnological utilization of solar energy, including optimization of methods for entrapment of solar energy, application of these methods for storage and utilization of solar energy, and the quantitative potential for exploitation of global solar energy supply by such methodologies.

Materials and Methods

Immobilization of Enzyme

A biotin tag was incorporated in the **c**-subunit of F_0 ATPase by insertion of the biotin-binding domain of transcarboxylase in the **c**-subunit. The codons for the 123 (Val_{18}-Tyr_{140}) and 105 (Lys_{20}-Leu_{124}) amino acid residues of the transcarboxylase biotin-binding domain were inserted between Met-1 and Ser-3 of the **c**-subunit in plasmid pBWU13 using polymerase chain reaction, which resulted in biotin-bound subunit **c**. This approach has been proven successful for F_0F_1 ATPase immobilization *(10,11)*. The biotin tag would remain confined to a specific region of the **c**-subunit of F_0 ATPase and the complex would be immobilized in a similar fashion as has been done with other proteins *(10)*. All subunits of F_0/F_1 complex were expressed from a plasmid, pBWU13, with mutant subunit substituted in the place of wild-type subunit *(10,12)* in *Escherichia coli* strain DK8 (Δ*unc*), which lacks the F_0/F_1 gene *(13)*. An asymmetric semipermeable styrene-isoprene-styrene block copolymer membrane was synthesized *(14)*. A self-assembled monolayer (SAM) was formed on semipermeable membranes using hexadecanethiol following standard techniques *(15,16)*. The semipermeable membrane was covered with a mixed SAM consisting of biotinylated thiols and an excess of ω-hydroxy-undecanethiol (HTA) to which streptavidin would be bound *(15–17)*. The excess HTA forms a film (SAM) and allows electrical conductance across the entrance and exit channels of F_0. A lipid layer was applied above the polymer matrix harboring immobilized F_0/F_1 ATPase, ensuring a composite layer formation (poly-

mer and the HTA or lipid) such that any conduction would be owing to ATP synthase. The polymer matrix and HTA or lipid composite provide means in which F_0 is embedded and allow application of electric field across the entrance and exit of F_0. F_0 is immobilized on the polymer membrane and the HTA SAM forms a thin monolayer covering the F_0 and providing necessary insulation.

Device

F_0/F_1 bacterial ATPase was immobilized (by a biotin-mediated process) on a semipermeable membrane catalytic reaction chamber containing 50 m*M* Tris-Cl buffer. The membrane separated the reaction chamber into two subchambers; in one chamber, a buffer containing adenosine 5'-diphosphate (ADP) and P_i was more acidic (pH 7.0 vs 7.8). This pH difference was maintained by an electrochemical gradient of 200–250 mV using solar energy. A solar cell connected to the chamber for maintenance of electrical potential enabled forward driving of the ATP synthesis by the immobilized ATP synthase.

Results

The flux of irradiant solar energy that falls on Earth is about 1367 W/m^2. Earth has a land area of 1.27×10^{14} m^2. The urban area is 30% of the total surface area of Earth. If the flux of irradiated energy is completely captured by the land area of Earth or even the urban usable area, then the global energy requirement could be either substantially supplemented or entirely met with this source alone, depending on the efficiency of capture and subsequent transformation losses (see Appendix B). Consider that most building structures actually add to the surface area that could be potentially used for capture. For example, a land area of 4 m^2 used for construction of a building theoretically should provide a roof with approximately the same surface area and, in addition, walls that could also be used for solar energy capture. Additionally, the surface area for capture can be enhanced by structural design and with design modification of transducers that may aid in capture and storage of this energy. The classic energy capture devices are photovoltaic cells, and their efficiency is usually 10 to 20%. Under certain experimental conditions, maximum efficiency has been reached using photovoltaic cells, which is about 34%. The global energy demand is 3.5×10^{20} J/yr. A land area of 8.118×10^9 m^2 will be required to meet the global energy requirement. Considering a 20% average capture and provided that all available land area is used, the land area required would be 4×10^{10} m^2. US energy consumption is 0.8×10^{20} J/yr and the available land area is 9×10^{12} m^2. The total capture of energy would require an area of 1.856×10^9 m^2. However, using the 20% capture efficiency will necessitate approximately an area of 9.28×10^9 m^2 (see Appendix C). The overall efficiency of energy transduction in the biologic systems using F_0F_1 ATPase varies between 47.5 and 78 % (see Appendix A).

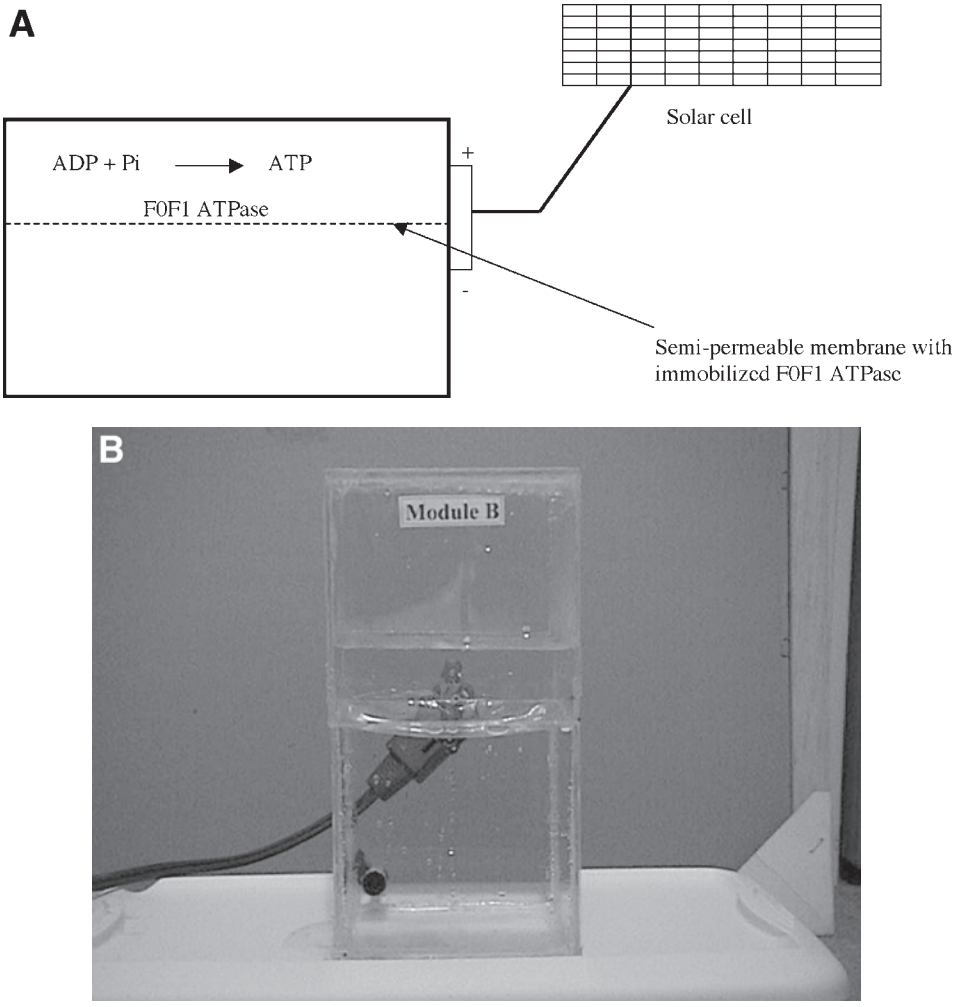

Fig. 1. **(A)** Schematic diagram of a uniformly oriented immobilized F_0F_1 ATPase. **(B)** The device for transduction of solar energy into ATP. The device uses a uniformly oriented immobilized ATPase on a semipermeable membrane. The captured solar energy transduced by a semiconductor sets an electrochemical gradient across the two chambers resulting in ATP synthesis by the enzyme using ATP and P_i.

Using directionally oriented immobilized ATPase, we demonstrate that ATP could be generated from constituent ATP and P_i using solar energy (Fig. 1A,B). The artificial matrix is robust and allows scale-up operations. This system is amenable to use in combination with other devices, and it is possible to build practical devices for conversion of solar chemical energy using this device.

For uniformly oriented immobilized enzyme, we exploited the biotin-tagged F_0/F_1 ATPase protein complex. A practical device for conversion of solar energy into ATP using uniformly oriented F_0F_1 ATPase has been made (Fig. 1). In the device there are two chambers, and between the two cham-

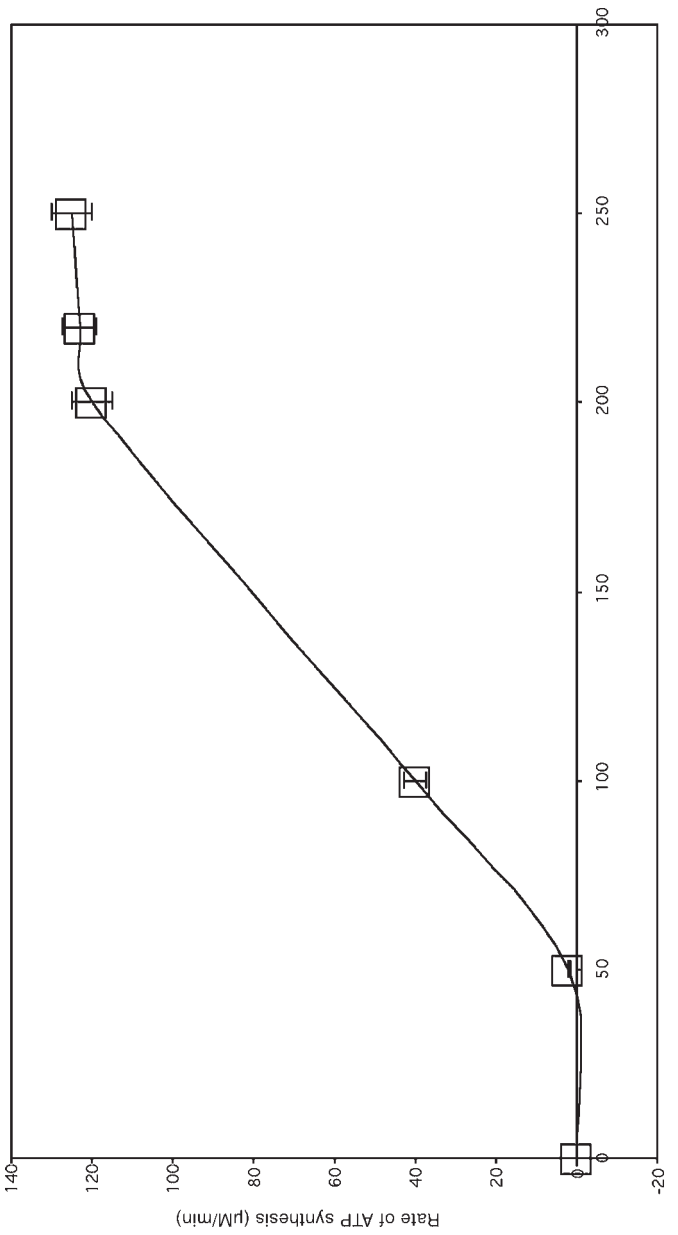

Fig. 2. Synthesis of ATP by transduction of captured solar energy in F_0/F_1 ATPase chamber.

bers a semipermeable membrane retains the uniformly oriented immobilized enzyme. The uniform orientation ensures that transduction of energy does not result in wasteful hydrolysis of ATP or formation of other unwanted products. Figure 2 shows the conversion of solar energy into ATP. The device harboring uniformly oriented ATPase is quite efficient compared to biologic transduction in cells.

Discussion

The results of our studies demonstrate a working prototype apparatus that can be used to drive enzymatic ATP synthesis on an artificial membrane. It is therefore possible to use solar energy trapped using semiconductors and to store and meet a substantial part of the local energy demands in certain parts of the globe. We therefore have a source of energy, although it has a cyclic but daily availability and a great degree of variation. An efficient transducer of energy (ATPase) is also available. The questions are, thus, Is there an efficient capture or can one be made and linked to the transducer in an effective way? Can it be rendered useful for different stationary and mobile consumers? Is a biotechnological solution possible? The power of a horse, like a human *(8)*, is derived from captured solar energy (photosynthesis activating the turnover of ATP, which is utilized for the enzymatic synthesis of simple and complex sugars and other building blocks). Is it possible to quantify the amount of energy needed for requirements of an average home or a car in terms of ATP, and is it possible to determine a quantity of ATPase that would be needed for such conversion? How can such stored energy be most effectively utilized? Our preliminary investigations indicate that such issues may be resolved in practical terms.

Planar lipid bilayers can be formed from monolayers of monounsaturated monoglycerides and lecithins *(18)*. This system can be used for a number of coupled devices such as in vitro synthesis of poly (3-hydroxybutyric acid) with an enzymatic coenzyme A recycling system *(19)*, interfacial catalysis and production of leukotriene A4 by 5-lipoxygenase in a phospholipase A_2–coupled reaction *(20)*, or in vitro synthesis of semisynthetic penicillins using coupled enzymatic systems *(21)*. Recently, a biocatalytic CO_2 fixation system, recyclable with respect to the acceptor, that employs an efficient enzymatic capture step *(22)* and is suitable for small, medium, and large stationary CO_2-emitting units has been invented *(23,24)*. One possible large-scale use of such chemical energy is in regeneration of the acceptor *(25)* utilizing cofactor ATP *(26)* as well as NADH.

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Appendix A

Efficiency and Other Details of ATPase-Based Enzymatic Transduction System

The conversion efficiency of the ATPase system has been determined as follows: Yeast ATP synthase generates about three ATP molecules every 10 protons *(8)*. The mitochondrial potential difference of 200 mV drives ATP generation. The charge on a single proton is 1.6×10^{-19} C. Electrical

work (W) is charge (q) × potential difference (dV). Thus, 10 protons perform work equivalent to 16×10^{-19} C × 200×10^{-3} V, which is 3.2×10^{-19} J. Bond energy in ATP is about 7.3 kcal/mol or 30.51 kJ/mol. For three molecules, the stored bond energy would be $[3 \times (0.166 \times 10^{-23}$ molecule/mol) × $30.51 \times 10^3]$ J = $0.498 \times 10^{-23} \times 30.51 \times 10^3$ J = 1.52×10^{-19} J. Thus, the efficiency of the system can be estimated as 1.52×10^{-19} J/3.2×10^{-19} J × 100, which is about 47.5%. However, 7.3 kcal or 30.51 kJ/mol, is the energy that is released on average on hydrolysis of ATP at 25°C, but the terminal bond formation of ATP may take as high as about 12 kcal/mol or 50.16 kJ/mol, making the stored energy close to $0.498 \times 10^{-23} \times 50.16 \times 10^3$ J = 2.5×10^{-19} J. Efficiency therefore becomes 2.5×10^{-19} J/3.2×10^{-19} J × 100, or 78%. Thus, average efficiency of the ATPase system is about 63%.

Some other facts about ATP are as follows *(8)*:

- Requirement of average human at rest of about 420 kJ/h.
- Power provided by the ATP synthase of 90%.
- 522 amp or 3×10^{21} protons/s.
- Reformation of ATP at a rate of 9×10^{20} molecules/s.
- Turnover of ATP of 65 kg/d.

This necessitates in humans about 380 L of O_2 every day.

Appendix B

Details of Solar Energy

The sun's rate of emission from the photosphere assuming total emissivity would be

$$\text{Energy flux } (I) = \text{constant } (\sigma) \times (\text{Temperature of sun's photosphere } T, \text{ Kelvin})$$

$$I = \sigma \cdot T^4 = (\sigma = 5.67 \times 10^{-8}\,\text{W}/[\text{m}^2 \cdot \text{K}^4]) \times (T = 6000\ \text{K})^4 = 73.5 \times 10^6\,\text{W/m}^2$$

The total energy emitted by the sun's photosphere is

$$\text{W} = (\text{energy/m}^2) \times [\text{area of photosphere} = (4 \cdot \pi \cdot r_{\text{sun}}{}^2)]$$
$$= (73.5 \times 10^6) \times [4 \cdot 3.14 \cdot (r_{\text{sun}} = 647 \times 10^6\ \text{m})^2] = 3.865 \times 10^{26}\ \text{W}$$

in which $r_{\text{sun}} = 647 \times 10^6$ m.

The sun's energy radiates in all directions and spreads out over the surface of a sphere of ever-increasing volume and surface area. At the distance of Earth, this sphere has a radius equal to Earth's average distance from the sun, which is about 150×10^9 m. The surface area of this sphere will be

$$4 \cdot \pi \cdot r_{\text{sun-Earth}}{}^2 = 4 \cdot \pi \cdot (150 \times 10^9)^2 = 2.83 \times 10^{23}\ \text{m}^2$$

Thus, 3.865×10^{26} W would be spread over this area.

Average flux of solar energy as it approaches Earth = Total energy emitted by photosphere of sun/surface area of sphere between sun and Earth

$$= 3.87 \times 10^{26}\ \text{W}/2.83 \times 10^{23}\ \text{m}^2 = 1367\ \text{W/m}^2 = \text{Earth's solar constant } (S_o)$$

Earth's solar constant can be independently determined experimentally:

$$W = m \cdot S \cdot dT = 4186 \times \text{J/kg} \times {}^{\circ}\text{C} \times \text{mass of water} \times \text{average } dT/\text{time} \times 2 \text{ (correction factor for glass)} \times 1.4 \text{ (correction factor for atmosphere)}$$

The average energy falling on Earth (the energy falling on an average square meter) is calculated as follows:

$$\text{Average flux of energy input on Earth} = \text{Total energy intercepted/surface area of Earth} = (S_o)\cdot(\pi \cdot r_{\text{Earth}}{}^2)/4\cdot\pi\cdot r_{\text{Earth}}{}^2 = S_o/4 = 1367/4 = 342 \text{ W/m}^2$$

$$\text{Total energy intercepted by Earth } (W) = (\text{solar constant}) \times (\text{area of Earth's disk/sphere}) = (S_o)\cdot(\pi \cdot r_{\text{Earth}}{}^2)$$

$$\text{Surface area of Earth} = 4\cdot\pi\cdot r_{\text{Earth}}{}^2$$

The input solar energy has two components: one that is absorbed by Earth and the other that is reflected back in space and referred to as "albedo." Only the absorbed energy component is available to heat Earth and, hence, it is less than $(S_o/4)$. Earth's "planetary albedo" is estimated to be 30%, or 0.3. Therefore, the absorbed energy is 70%, or 0.7, of the incoming energy. Thus,

$$\text{Available real energy flux} = (S_o/4) \times 0.7 = (341 \text{ W/m}^2) \times 0.7 = 239.2 \text{ W/m}^2$$

There is atmospheric interference with the incoming and outgoing energy in addition to the planetary albedo equal. The Earth-sun distance varies throughout the course of a year—from 147 million km at Perihelion (January 3) to 152 million km at Aphelion (July 5), which affects the sphere in which solar radiation is spread out.

Appendix C

Land Area Available to Trap Solar Energy and Comparison With Energy Consumption

Total surface area of the earth is 5.1×10^{14} m^2 and total amount of sun's energy per year over all earth is 1.1×10^{25} J/yr $\times$ 0.5 = 5.5×10^{24} J/yr (only half of the Earth gets sun at any time). United States land surface is about 9×10^{12} m^2 and receives about 1×10^{23} J/yr from sun that is about 1000 times more solar energy than energy used in the United States. Global energy and US energy consumptions are about 3.5×10^{20} and 0.8×10^{20} J/yr respectively. The United States, however, gets only an average of 8 h of useful light per day and even then only about 1/600th of land area is sufficient for capture of total necessary energy with 100% capture. Photovoltaic cells are about 10% efficient, which will thus require about 1/60th of US land area for this energy capture or about 1.5×10^{11} m^2. About 1/6th of total energy 8×10^{20} J/year is used in homes (about 75 million homes), giving about 2×10^{11} J/yr per home. A useable roof area of 10 m by 10 m, or 100 m^2 of useable roof area, will allow capturing 6×10^{11} J/roof per year.