ing P, or these neutron stars must turn off at relatively short periods. It has been argued by Flowers and Ruderman[11] that α in fact *increases* with time, and hence P. It would appear therefore that pulsars with near-perpendicular fields must die young, well before their period reaches 1s. We suggest that this is due to a cut-off in particle production or acceleration. We note that this could be reasonable in pulsar models such as that of Ruderman and Sutherland[12] which require one particular sense of field alignment with respect to the rotation axis.

In conclusion, the interpulse of the new millisecond pulsar provides supporting evidence that short period pulsars have highly elongated beams, and hence a higher probability for interpulses. A measurement and analysis of the polarisation swings in the main pulse and interpulse of the new pulsar will be of great value in testing our conclusions. We expect such measurements to indicate a large offset of the line of sight from the magnetic poles, as is already suggested by the observed high degree of average linear polarisation .

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1. Backer, D. C; Kulkarni, S. R., Heiles, C., Davis, M. M. and Goss, W. M., *Nature* (*London*), 1982, **300**, 615.
2. Manchester, R. N. and Taylor, J., *Pulsars*, 1977, Freeman, San Francisco.
3. Narayan, R. and Vivekanand, M., *Astron. Astrophys.*, 1982, **113**, L3.
4. Narayan, R. and Vivekanand, M., submitted to *Astrophys. J.*
5. Radhakrishnan, V. and Srinivasan, G., *Curr. Sci.*, 1982, **51**, 1096.
6. Srinivasan, G. and van den Heuvel, E. P. J., *Astron. Astrophys.*, 1982, **108**, 143.
7. Alpar, M. A., Cheng, A. F., Ruderman, M. A. and Shaham, J., *Nature* (*London*), 1982, **300**, 728.
8. Narayan, R. and Vivekanand, M., to appear in *Astron. Astrophys.*
9. Radhakrishnan, V. and Cooke, D. J., *Astrophys. Lett.*, 1969, **3**, 225.
10. Taylor, J. H., 1981, I.A. U. Symp. No. 95 on PULSARS, Eds. W. Sieber and R. Wielebinski, Reidel, Dordrecht, p. 361.
11. Flowers, E. and Ruderman, M. A., *Astrophys. J.*, 1977, **215**, 302.
12. Ruderman, M. A. and Sutherland, P. G., *Astrophys. J.*; 1975, **196**, 51.
13. Hankins, T. H., 1980, Reported at the I.A.U Symp. No. 95 on PULSARS; unpublished.

Note added in Proof: We have recently received a preprint by M. Ashworth, A. G. Lyne and F. G. Smith (kindly sent by A.G. Lyne) describing polarisation observations on PSR 1937+214 which show a total sweep range of the position angle of less than 10° and 20° in the main pulse and interpulse respectively These values are consistent with our expectation that the line of sight in the pulsar is offset by large angles from the magnetic poles.

It has also been drawn to our attention that PSR 1822–09. which has a well-established interpulse (Cady and Ritchings, *Nature* (*London*), **269**, 126, 1977; Fowler, Wright and Morris, *Astron. Astrophys.*, **93**, 54, 1981), is not included in our list. We regret this unfortunate oversight.

APPLICATION OF PHOTOSYNTHETIC PIGMENTS IN LIGHT ENERGY TRANSDUCTION

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ABSTRACT

The potentials of the application of recently discovered photosynthetic pigment bacteriorhodopsin in light energy transduction are discussed.

INTRODUCTION

ONE of the major problems associated with solar energy conversion lies in the wide spectral distribution of sunlight. The sun at about 6000° K is essentially a black body emitter, this emission is partially scattered and absorbed by the earth's atmosphere. Roughly half of the sun's emitted energy is in the form of visible and ultraviolet light of which less than 5% of the energy actually striking the earth's surface is in the ultraviolet region of the spectrum. The remaining half of the sun's energy consists of near-infrared and infrared light. This is the region of the spectrum not energetic enough to promote electronic

excitations needed to break chemical bonds because covalent bond energies exceed the energy available from such light. Thus it is the visible component of the solar energy which can be converted into useful form of energy either as fuel or electricity. The transduction of solar energy to chemical or electrical energy is an important but long range option available for substantiating our depleting sources of energy. The sun can contribute greatly to our energy demands if efficient, inexpensive and technologically feasible mechanisms for solar energy conversion are devised. Till the middle of seventies the emphasis has been on the development of solid state photovoltaic devices (*i.e.* the development of low costing solar cells) and then the development of other photochemical systems (such as valence isomerization, photogalvanic cell, semiconductor/liquid junction, photolysis of water, etc.) took over as possible economic means of solar energy conversion[1]. However, during the past few years there has been a growing interest in solar energy conversion using biological systems[2-5]. A number of biological systems that have been investigated include the microbiological conversion of carbohydrates into hydrogen, methane and lower alcohols, using enzymes and photosynthetic pigments (plant) for photodecomposition of water and the biochemical fuel cells which utilise the enzymatic catalysis of electrode processes.

Recently a new photosynthetic pigment, bacteriorhodopsin[6] has been discovered which is mechanistically much simpler and more elegant than the well known photosynthetic pigment chlorophyll. Bacteriorhodopsin is a relatively small (M. wt. 27,000, number of amino acids 247) chromo protein which is found in the purple membrane of halobacteria. The chromophore retinal is bound to *216 amino acid* (Lysine) from the N-terminal of the polypeptide chain through a protonated Schiff base linkage[7]. The bacteriorhodopsin in the purple membrane functions as a light driven proton pump. As a consequence, an electrochemical proton gradient is developed across the membrane In other words, the bacteriodrhodopsin in the purple membrae converts light energy into chemical energy which is stored as a H' ion concentration gradient and the membrane potential. This stored energy is utilised by the cell for synthesising ATP and to drive other transport processes, such as uptake of nutrients or ejection of Na' ions. Even though it is a much simpler photosynthetic pigment, still the relation between the structure and proton pumping mechanism is posing a challenge to membrane biologists.

In this paper we have described the possibility of utilising photosynthetic pigments in general and bacteriorhodopsin in particular for light energy transduction. This can be done either to produce fuel (biophotolysis of water) or to generate electric current directly (photoelectrochemical cell). The fuels are materials which can be generated and stored indefinitely and from which energy can be recovered on demand *e.g.* H_2, O_2, CH_4, CH_3OH, etc.

Production of Fuels

The production of fuels is based on the photodecomposition of water (Biophotolysis) using photosynthetic pigments and can be described by the following equation:

$$2H_2O \xrightarrow[\text{Pigment}]{h\nu} 4H^+ + 4e^- + O_2$$

$$4H^+ + 4e \xrightarrow{\text{Catalyst}} 2H_2$$

In chlorphyll-based photosynthesis, the pigment decomposes water into protons, electrons and oxygen which is liberated as a byproduct of the reaction. The liberated electrons are transported through electron carrier chain upto the stage where they can combine with protons in the presence of catalysts to produce H_2 gas which can be used as fuel in the fuel cell (figure 1). The formation of hydrogen atoms itself, before they combine to form molecular hydrogen should in

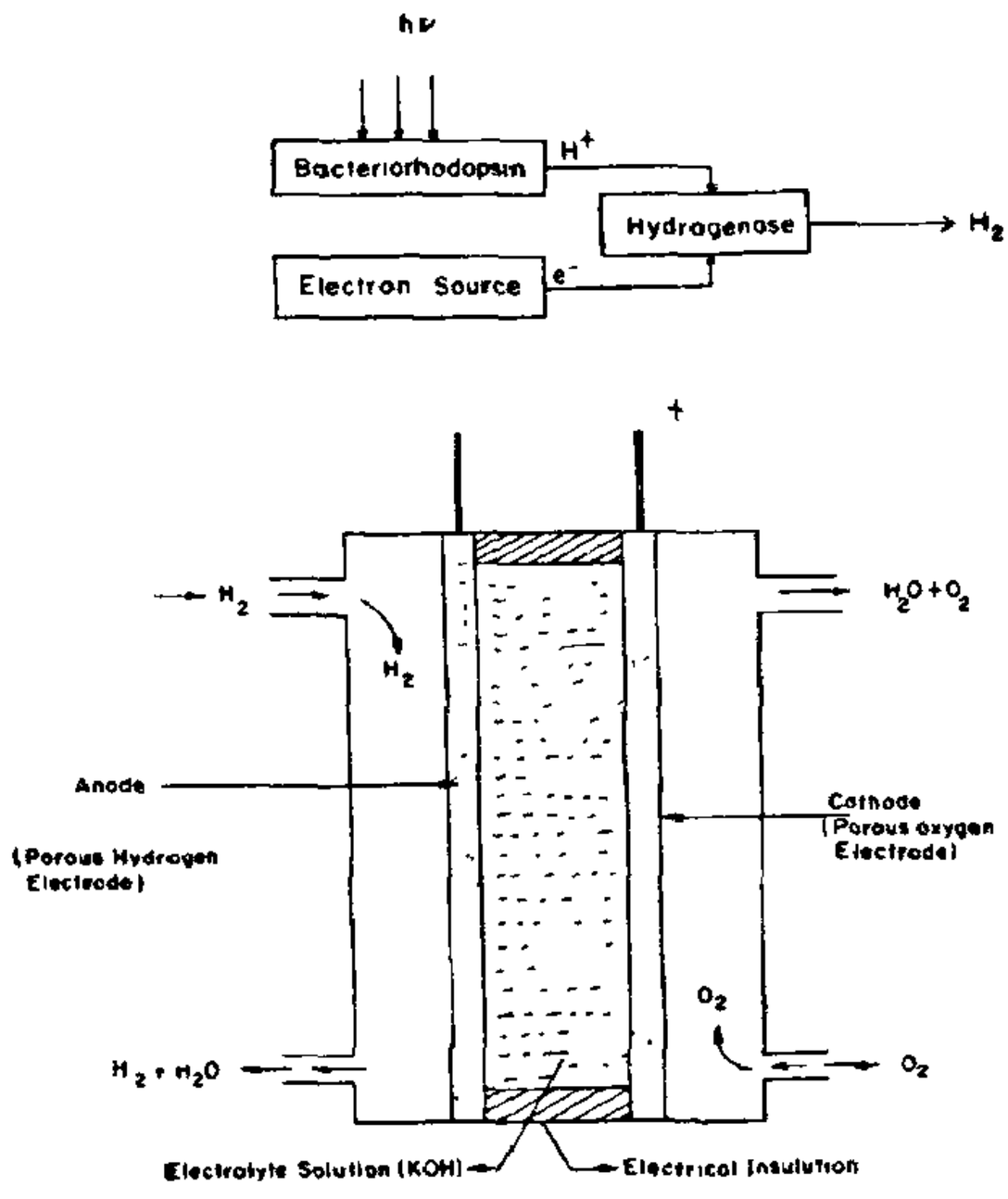

Figure 1. H_2 - O_2 Fuel cell.

fact generate about 13.5 eV of energy (equivalent to the ionization potential of hydrogen atom). This will be true only if the reaction takes place in the gaseous phase and will also be dependent on other factors such as electron capture cross section, volume and the kinetic energies of proton and electron.

The efficiency of the light energy conversion for the biophotolysis of water based on chlorophyll pigments can be determined by the following relationship:

$$\epsilon = \epsilon_0 \frac{\Delta G}{nE} \times 100\%$$

where ϵ is the efficiency in percent of conversion, ϵ_0 is the fraction of solar energy absorbed and is about 0.4, ΔG is the free energy change involved in 'the conversion of 1 mole of CO_2 to carbohydrate or the free energy of hydrogen oxidation ($\simeq$ 112 K cal/mole), n is the number of quanta absorbed for the formation of 1 mole of oxygen and E is the energy per quantum ($\simeq$ 40 K cal/mole) at λ_{max} of chlorophyll pigment. This gives a theoretical efficiency of 14%. This has been estimated assuming that all the four protons upon photolysis will be available for the formation of H_2 gas. If this efficiency can be achieved in practice, then this could possible be one of the most economical methods of light energy conversion. However, the actual efficiency for a system using chloroplast, ferredoxin and bacterial hydrogenase[3] is found to be only 1%. This means that the laboratory efficiency is almost the same as that obtained in natural plant photosynthesis (1%), where the main purpose is synthesis of carbohydrates. That means the aim of light conversion into useful form of energy have not been achieved. What could be the factors for such a low efficiency? Such a low efficiency is probably due to cumulative effect of the following factors:

(1) Insufficient compatibility of plant chloroplast and ferredoxin with bacterial hydrogenase.
(2) Inactivation of catalyst due to poisoning of hydrogenase with oxygen.
(3) It could be due to nonavailability of all the four protons. This may be possible in the wake of the recent findings of the role of plastocyanine as proton translocater[8].

Unless these problems are solved the chlorophyll systems for transduction of light energy into fuel will not be a viable proposition. A recent report[9] indicates that using chloroplasts, methylviologen and hydrogenase, the conversion efficiency of 5% can be achieved.

Can we use the new photosynthetic pigment, bacteriorhodopsin for light energy transduction (*i.e.* fuel generation)? The protons generated during the pumping can be made to combine with electrons from an electron source (figure 1) with a reducing power equivalent to—0.42 volts ($2H^+ + 2e \rightleftharpoons H_2 \simeq -0.42$ V). Such electrons can be produced from electron donor system. The efficiency of such a system would depend on the concentration of bacteriorhodopsin in the biological system, the number of protons ejected per cycle and the cycling time. The number of protons ejected will depend on the quantum yield of photocyclic reaction which has not been unequivocally determined. There are two values for the quantum yield[10] (0.79) and (0.3)[11]. Until the kinetics of the photoreaction cycle are fully delineated, it is not possible to say whether bacteriorhodopsin will be a better pigment than chloropnyll in terms of energy conversion, but it definitely widens the scope for the application of photosynthetic pigments in fuel generation.

Photoelectrochemical Cell

The objective in a photoelectrochemical cell is to generate charged species in the solution by photochemical means and to make them react through external circuit rather than in the solution. Since the proton pumping across the membrane generates the membrane potential[12], the bacteriorhodopsin also functions as a molecular electric generator *i.e.* equivalent to charge separation. This property of bacteriorhodopsin can be utilised to devise a photoelectrochemical cell (figure 2). The theoretical estimate of the photocurrent for an ideal case would be 10^{-9} A cm^{-2}, if the purple membrane fragment of 0.5 μm diameter, containing about 10^5 molecules of bacteriorhodopsin pumps one proton per cycle and the cycling time is 10 msec. The photoelectrochemical cells with purple membrane incorporated into planar lipid membranes, which are attached to bilayer lipid membranes, purple membrane incorporated into liposomes that are attached to lipid membrane, purple membrane bound to a cation selective ionic film and electrically oriented purple membranes in hydrogel have been designed[13] but the current density is still in the range of 10^{-6} A cm^{-2}. The lower current densities (as compared to theoretically calculated value) could be due to the random orientation of the purple membrane fragments, high internal resistance, and possibly due to some of the invalid assumptions. More systematic work is needed to understand the working of this potential photosynthetic pigment and its utilisation in the development of a photoelectrochemical cell.

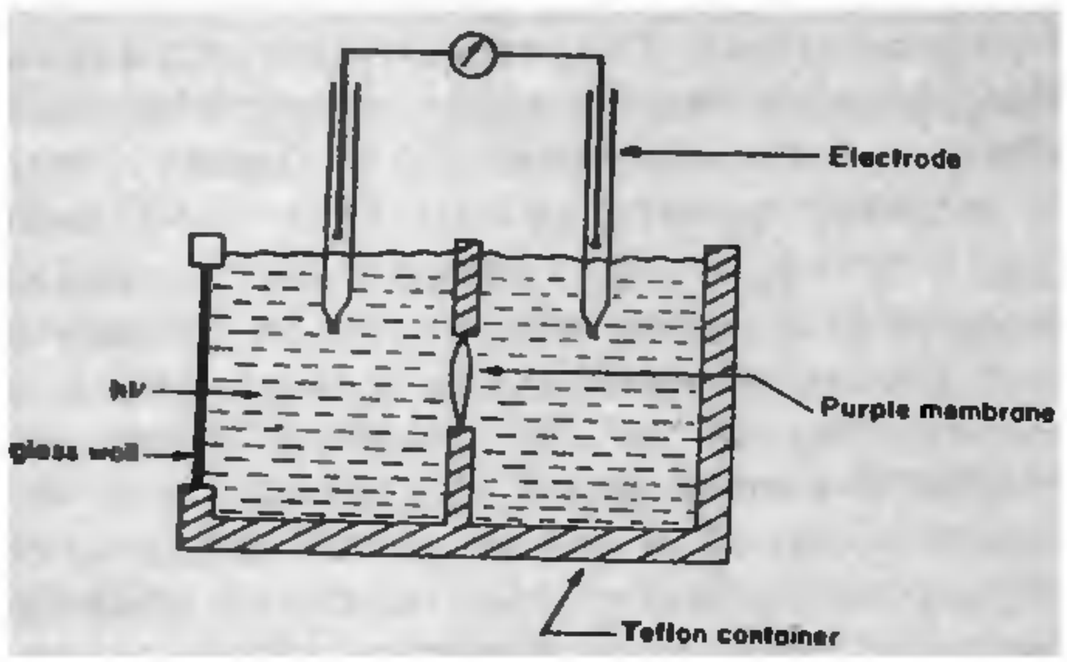

Figure. 2. Photoelectrochemical cell.

We have recently investigated the conformational states of the Schiff base of the retinal in the protein using PCILO (perturbation configuration interation of localized orbitals) method. We have proposed two models for the structure of the intermediate species of the photoreaction cycle[14, 15] of the purple complex. Further work on the isolation of the purple membrane from halobacteria and physico-chemical studies involving model systems are in progress. The development of a photoelectrochemical cell using isolated bacteriorhodopsin, after incorporating in synthetic membrane and attempts to improve the efficiency of the cell are contemplated. In addition, other applications of halophibic bacteria in biotechnology will be explored.

1. Wrighton, M. S., *Acct. Chem. Res.*, 1979, **12**, 303.
2. Benemann, J. R., Berenson, J., Kaplan, N. O. and Kamen, M. D., *Proc. Natl. Acad. Sci.*, USA, 1973, **70**, 2317.
3. Rao, K. K., Rosa, L. and Hall, D. O., *Biochem. Biophys. Res. Comm.*, 1976, **68**, 21.
4. Varfolomeev, S. D., Yaropolov, A. I., Berezin, I. V., Tarasevich, M. K. and Bogdanovskaya, V. A., *Bioelectrochem. Bioeng.*, 1977, **4**, 318.
5. Berezin, V. and Varfolomeev, S., D., *App. Biochem. Bioeng.*, 1979, **2**, 259.
6. Stoeckenius, W., *Acct. Chem. Res.*, 1980, **13**, 337.
7. Anderegg, R. J., Bayley, H., Biemann, K., Chang, S. H., Dunn, R. J., Gerber, G. E., Gray, C. P., Herlihy, W. C., Hojeberg, B., Huang, K. S., Joshi, V. C., Khorana, H. G., Kimura, K., Liao, M. J., Lind, C., London, E., Majumdar, A., Makabe, O., McCoy, J. M., Radhakrishnan. R., Rajbhandary, U. L., Ross, A. H., Simsek, M., Takagi, Y. and Wildenauer, D., in *Biomolecular stereodynamics*, (ed.) R. H. Sarma, Adenine Press, New York, 1981, Vol. 2, pp. 37.
8. Arnon, D. I., Tsujimoto, H. Y. and Tang, M., S. G., *Proc. Natl. Acad. Sci.*, USA, 1981, **78**, 2942.
9. Rao, K. K., Hogotov, I. N. and Hall, D. O., *Biochimie*, 1978, **60**, 291.
10. Oesterhelt, D. and Hess, B., *Eur. J. Biochem.*, 1973, **37**, 316.
11. Goldschmidt, C. R., Kalisky, O., Rosenfeld, T. and Ottolenghi, M., *Biophys. J.*, 1977, **17**, 179.
12. Drachev, L. A., Frolov, N. V., Kaulen, A. D., Liberman, E. A., Ostroumov, V. G., Plankunova, V. G., Semenov, A. U. and Skulachev, V. P., *J. Biol. Chem.*, 1976, **251**, 7059.
13. Singh, K., Korenstein, R., Lebedeva, H. and Roycaplan, S., *Biophys. J.*, 1980, **31**, 393.
14. Dhingra, M. M. and Saran, A., *Proc. Indian Acad. Sci.*, 1981, **A90**, 485.
15. Dhingra, M. M. and Saran, A., *Proc. Indian Acad. Sci.*, 1981, **A90**, 497.

ANNOUNCEMENT

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