

Outlook for Chemtrapse

Balu Venkataraman

A4/1 Century Enclave, 54, Kalakshetra Road, Madras 600 041, India

Eleven years have elapsed since a group of Indian scientists met in March 1983, under the auspices of the Tata Energy Research Institute (TERI) and assessed the status of the International effort on designing and developing *Chemical Routes for Trapping Solar Energy* (Chemtrapse). The group recommended three areas for research and development in India: 1. Photoelectrochemistry, 2. Photocatalysis and 3. Biomimetism. It also identified in these three areas, tasks and broad research strategies to be detailed out by appropriate subcommittees. With the support of TERI, the subcommittees held several workshops and evolved by April 1985, a work plan involving several Indian scientists and Indian institutions. What was initiated by TERI was adopted by the Department of Nonconventional Sources of Energy of the Government of India (DNES) and the total work plan in the area of photoelectrochemistry was approved for funding by DNES by April 1986. Two coordinated projects, involving five institutions were also sanctioned in the area of Biomimetism. In 1988 a few projects in the area of photocatalysis were initiated. However, the level of support from DNES has decreased considerably over the past few years on account of the resource crunch. DNES is hopeful of finding adequate support for 'Chemtrapse' during the current plan period.

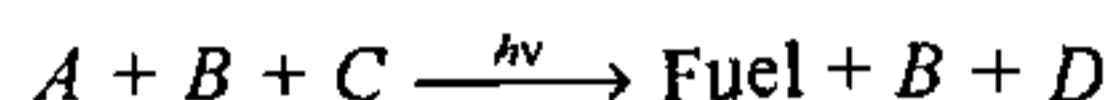
It is appropriate that *Current Science* is publishing at this time a special section on 'Chemtrapse' since it provides us an opportunity to assess the results of the Indian effort spread over a decade. The current status of the Indian effort in the three main areas is discussed in detail elsewhere in this issue. The main goals and achievements of this Indian programme would be mentioned in brief here. This presentation will also discuss the general scientific principles involved in 'Chemtrapse strategy' and assess the outlook for this area in the near future.

General scientific principles

The basic objective in light to chemical energy conversions is to deposit light energy in low-energy materials and thereby convert them into higher energy substances (fuels) which are thermodynamically unstable but kinetically stable. Alternatively, the energy of the solar photons can initiate separation of charges in electrode/electrolytes (as in a solid photovoltaic cell), leading to the operation of a photovoltaic cell or

performing electrochemical conversions. Such photo-initiated electrochemical changes can produce value-added products.

In most cases, a photochemical fuel generation scheme can be represented as



where *A* is the low energy substance(s) and *B* is the photosensitizer. *C* and *D* may not be present in certain cases. In certain cases *A* itself could absorb photons and be converted into a fuel. *B* in the photoexcited state could also catalyse exergonic reactions; this scheme would be photocatalysis.

In fuel generation schemes (as in natural photosynthesis), which are endergonic, the required energy is supplied by the solar photons and the general requirements are:

- (a) *A* should be an abundant, easily available and inexpensive raw material.
- (b) In cases where *A* itself absorbs photons, the fuel generation and the fuel consumption sequences should be cyclic to ensure high turnover.
- (c) Irreversible degradation of the photosensitizer *B* by side reactions, should be almost totally absent.
- (d) The kinetic barrier for the fuel consumption reaction must be high to permit long-term storage of the fuel under ambient conditions; however, the same reaction should proceed rapidly under special conditions such as the presence of a catalyst, elevated temperatures, etc.
- (e) It would be desirable to have the threshold wavelength for the fuel formation reaction towards the red or near infrared region so that the wide bandwidth of the visible and ultraviolet photons of the solar spectrum can be profitably used.
- (f) The quantum yield for the production of *F* should be as high as possible.
- (g) The fuel should be capable of easy storage and transportation.
- (h) It is necessary that the raw materials, container materials, etc. should be inexpensive and non-toxic.

In a photoelectrochemical system, the distinct advantage in a liquid (electrolyte) – solid (semiconductor or metal electrode) junction is the possibility of avoiding single crystal electrodes leading to simplicity in fabrication technology, as compared to photovoltaic cells. While it is obvious that many of the requirements

listed above would apply to photoelectrochemical systems, the most important of these would be high efficiency, inexpensive and non-toxic electrodes and electrolytes, and stability of the entire system. Stability has been the main hurdle of this route of trapping solar energy. In addition, packaging might pose considerable difficulties, especially if liquids are involved; a solution may be to replace liquids with conducting gels.

The general problems associated with the utilization of solar energy through chemical routes are:

(i) The diffusive nature of solar energy – this is a drawback for all methods of utilization of solar energy. One needs about 35 hectares of collection area for a 100 MW solar energy power station assuming that we can collect and store all the energy needed for 24 hours during daytime. Off-shore installations may provide a solution to this problem.

(ii) Loss of efficiency due to back reactions – since the solar photons are trapped by driving reactions uphill the tendency for back reactions always exist. The two commonly used principles to minimize losses are (i) removal of the products formed from the site of the reaction as in the case of photoelectrochemical cells, where charges are separated instantaneously; (ii) the existence of an energy barrier for the reverse reaction as in fuels. Both the methods necessitate a decrease in the overall efficiency of conversion and the ideal maximum efficiency (solar engineering efficiency) is calculated to be 39%.

The current status

During the past decade and a half, there has been globally a vigorous attempt to find new ways to use sunlight for the production of chemical fuels from abundant cheap materials such as nitrogen, carbon-dioxide, water and even sand (SiO_2). Methods such as photoinduced isomerization of compounds (like norbornadiene) to their energy rich tautomers (quadri-cyclene), and the reverse process to extract the energy stored have been studied in great depth but found to be very inefficient for commercial exploitation. At present, there is no efficient, commercially viable process available for the utilization of solar photons to generate fuels which could be stored and used at a later time. Man has not achieved what nature has been doing through photosynthesis for millions of years. However, from the effort to achieve this goal, some fascinating chemistry (especially, supramolecular chemistry) has emerged. Again, no viable success has been achieved in utilizing the solar photons for the production of value added compounds by photocatalysis (homogeneous or heterogeneous); but the prospects of utilizing solar energy for pollution abatement through photocatalytic conversions of toxic substances such as H_2S , organics,

etc. in industrial effluents, with particulate catalysts (especially TiO_2), appear to be bright. This is one area where some commercial investment has been forthcoming in recent years. The effect of the size of the particulates, especially in the nanometre range is being studied in depth and quantum size effects are believed to be observed.

A sustained effort has been in progress to understand the elementary initial steps in photosynthesis, with the hope of designing an artificial photosynthetic system which would perform better than the natural one. We now have the crystal structure of two bacterial photosynthetic reaction centres and the recent emergence of ultrafast spectroscopic techniques has enabled the delineation of the initial elementary steps with femtosecond and picosecond resolution. There are still many questions remaining to be answered on several aspects of bacterial photosynthesis, which is much simpler than the plant system. Spectacular success has been achieved in synthesizing covalently linked compounds that mimic the natural photosynthetic systems in sustaining photoinduced charge separation for a time long enough to carry out useful redox reactions. These 'designer' compounds usually have a porphyrin (as in chlorophyll) which absorbs a photon and effects an electron transfer to a quinone moiety which is covalently linked to it through chosen spacer molecules. The efficiency of the electron transfer depends upon the relative orientation of the molecules and the distance between them, and the lifetime of the charge separated state depends upon the distance between the porphyrin and the final electron acceptor. A discussion of this aspect of biomimeticism would be found in this issue. We are far from realizing molecular photosynthetic systems which would ape nature with high efficiency and high turnover.

At present, the most promising chemical route for trapping solar energy seems to be the electrochemical route. The significant achievements in this area would find a place elsewhere in this issue. Efficiencies have been improving over the years and commercially viable efficiencies have been attained; however, the problem has been the poor stability of such systems, leading to unacceptably low lives for the devices. A group in Switzerland claims to have designed a system with electrodes made of particulate TiO_2 , sensitized by a trinuclear ruthenium complex, with high efficiency and reasonably good stability. As far as photoelectrochemical synthesis of value added products is concerned, one is far from achieving desirable efficiencies and stability of the electrodes. However, intense search is on, trying out various combinations and configurations of electrodes, electrolytes, methods of sensitization of electrodes, dressing electrodes to improve stability, different electrode-electrolyte combinations, etc. In the eighties, expectations ran high; at present serious intensive fundamental investigations to understand the

basic principles of the various electrochemical processes that follow photoexcitation, are in progress.

The future

From the papers presented and the discussions that followed at the last international conference on photochemical conversion and storage of solar energy held in Beijing in August 1992, it is clear that the optimism that was present in the eighties is currently subdued. Except for the Swiss claim, there is no clear case of a photoelectrochemical cell, which is anywhere near commercial viability at this time. Photoelectrosynthesis of fuels or value-added products also, has not reached the cherished goal. Photocatalysis, especially in the area of environment-oriented applications, seems to be attracting commercial investment. Photosynthesis and biomimeticism are subjects of intense basic research attracting considerably sophisticated measurement and synthetic techniques. We are far from creating a 'leaf' that would improve upon nature. However, all this effort, especially over the past decade and half has contributed towards developments in basic science or technology:

A. Science:

1. Measurement of electron transfer rates (in the fs and ps time domain)
2. Size quantization effects (1 dimension = superlattices; 2 dimension = quantum wires; 3 dimension = quantum particles)
3. Extremely novel chemical reactions
4. Supra molecular chemistry
5. Heterogeneous photocatalysis

B. Technology:

1. New type of photoactive materials
2. Stabilization of photoelectrodes by preferential kinetic control
3. New conducting polymers and their preparation by photoelectrochemical methods
4. Chemical sensors
5. Preparation and characterization of nano particles
6. Pollution abatement
7. Semiconductor device fabrication.

Three of the recent Nobel prizes in Chemistry have been awarded to work in areas closely related to 'Chem-trap'.

This area has to meet the challenges posed by development in other areas of solar energy utilization, especially from the silicon photovoltaic cell. To compete with it the photoelectrochemical devices should be not only cheaper to fabricate, but also very stable. Though claims are made that the devices proposed by

the Swiss group possess efficiency and stability comparable to those of the amorphous silicon photovoltaic cells, this point has to be firmly established. There is one great inherent advantage in photoelectrochemical systems – that is, they are capable of inherent *in situ* storage of energy. A photoelectrochemical cell, capable of storage and being rechargeable by sunlight would be the ideal goal for this area. Even if it turns out to be as expensive as or even slightly more expensive than a regular dry cell, it would have tremendous application potential – especially in remote areas, defence, etc.

As far as India is concerned, we started in 1985 with research workers claiming device efficiencies or process efficiencies far below the international achievements. It is gratifying to note that we have now caught up and our scientists have reported fabrication of photoelectrochemical devices that compete with the rest of the world. Many novel techniques of producing electrodes have also been tried out. There has been limited success in producing rechargeable storage photoelectrochemical cells. However, as with the rest of the world, we do not yet have any viable device, capable of being tried out even on a pilot scale.

There always has been talk of solar electricity eventually answering all the needs of humanity. This is far from reality and one can foresee its future, only in terms of a supplement to other technologies. Among the other technologies, the future seems to be heavily dependent on nuclear power, especially when the fossil fuels get depleted. Even though there is a great reluctance to pursue the nuclear energy option, risk analysis definitely projects nuclear energy as one of the safest and economically viable alternatives to fossil fuel. In fact, the development of nuclear energy is an unique example of a technology being progressively developed with great stress on safety factors. It is expected that in the later half of the twenty first century nuclear energy would provide a high percentage of the base load, while solar and other similar technologies are ideally suitable to provide the peak load. In addition, one could utilize solar energy for power production at remote places where coal, gas and oil are expensive to transport or where there is a deliberate need to protect the local environment from pollution accompanying the use of fossil fuels.

It is apparent that there remains a considerable amount of research and development to be carried out before solar energy can be claimed to be used to provide some percentage of the power needs of the world. Power generation based on the solid state photovoltaic cell is even now quite expensive, more than twice as expensive as nuclear power. The scenario might improve with further development; but there is an environmental price to pay for the photovoltaic solar energy power plant also. Besides the huge land needs for producing adequate power, due to the diffusive nature of the solar insolation, the fabrication of photovoltaic cells involves

the usage of poisonous chemicals such as hydrofluoric acid, boron trifluoride, arsenic, cadmium, tellurium and selenium compounds. The photoelectrochemical cell has not yet provided an answer to these problems in utilization of solar energy for power needs. There is hope that a solution may be eventually found through the photoelectrochemical route.

It is abundantly clear that India can ill afford to neglect effort in this area of Chemtrapese, if it wishes to

avoid the danger of being in a pitiable position to borrow or buy the technology, when it is available. Just as in nuclear energy, where we got in at the beginning of the game, it would be visionary if we support effort at a viable level so that we contribute to the development of this futuristic area and keep abreast with the developments and hence be able to absorb and adapt quickly any significant developments, to our needs.

Artificial photosynthesis: Efficient dye-sensitized photoelectrochemical cells for direct conversion of visible light to electricity

M. Grätzel and K. Kalyanasundaram

Institute of Physical Chemistry, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland

Significant advances have been made in recent years on the design of dye-sensitized photoelectrochemical cells for the direct conversion of visible light to electricity. One approach extensively developed in Lausanne involves textured, nanocrystalline TiO_2 membrane films as the charge separation/collection device and polypyridyl complexes of Ru as photosensitizers. Efficient solar cells have been made that give short-circuit photocurrents exceeding 17 mA/cm^2 , open-circuit photovoltage of 700 mV and sunlight to electrical conversion efficiencies of 10%. Herein the principles and recent advances in this area are reviewed.

GROWING energy requirements of the modern society, dwindling fossil fuel reserves and the energy crisis of the seventies forced a number of research groups around the world to reassess their research priorities and orient them towards search for alternate energy resources. In this context, direct conversion of sunlight to electricity is a very attractive goal to pursue. Indeed considerable effort has been devoted to this area in the last three decades. Commercially available solar cells based on silicon¹ as the light-absorbing material are clear-cut examples of how one can harness sunlight.

In Lausanne, for many years, we have been interested in photochemical approaches for the conversion and storage of solar energy²⁻⁵. This goal led us to look at a

variety of photochemical systems such as photoredox reactions of organic and inorganic dyes in the presence of finely divided redox catalyst, photochemical processes in organized media and photoredox reactions of semiconductor electrodes, dispersions and colloids. The topic of this review article is the outcome of cross-fertilization of our experience in these areas. It involves the design of an efficient photoelectrochemical cell for the direct conversion of light to electricity, one that is based on the concept of 'dye sensitization'⁶⁻⁸. It is the outcome of coordinated efforts of chemists of different interests and backgrounds – organic, inorganic, electrochemistry, colloids and interfaces, photochemistry and material science – a true interdisciplinary effort. The principles of dye-sensitized photoelectrochemical cells are outlined first followed by description of the features and performance characteristics of the solar cells.

Photoelectrochemical cells

A conventional photovoltaic/solar cell consists of two layers of a semiconducting material, usually Si. One is chemically treated to have an excess of electrons (*n*-type) and the other carries an excess of positively charged holes (*p*-type). When the two layers are brought into contact, electrons flow from the *n* to the *p* side, producing an electric field at the interface. The resulting