

CONVERSION OF LIGHT ENERGY TO CHEMICAL ENERGY

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- (a) Energy is the 'thing' that is required to do work. It is also the entity needed to change disorder into order. The evolution of living organisms and subsequent human civilization has made biosphere more and more orderly. This has happened at the expense of energy from the sun. Most of mankind's present energy requirements are met by the consumption of past products of photosynthesis i.e. fossil fuels such as coal and oil and by the combustion of firewood. Even hydro-electricity and wind power are finally derived from the energy of the sun. The energy of the fossil fuel deposits on Earth is currently estimated to be equivalent to 40×10^{21} J while the present annual consumption of these deposits is about 3×10^{20} J. Thus it is inevitable that a major energy crisis is going to affect the world in the next century. The ability to synthesize fuels and chemicals from abundant renewable resources could have a significant impact on the energy budget of the entire world. Thus transformation of solar energy to usable forms by photochemical mechanisms is one of the great social as well as scientific challenges of today. Our dependance on fossil fuel reserves combined with political unrest in major oil producing areas such as the middle-east have affected the economics of developing and developed countries alike. Nevertheless the use of our most abundant resource, the sun, has increased only marginally over the last several decades. The Earth receives at its surface about 6×10^{24} J per year and it can be seen that the sun delivers to the earth in roughly four days, the proven energy reserves of fossil and nuclear fuels combined.
- (b) Furthermore it can be seen that the total energy from the sun falling on the earth during an year is 30,000 times more than the present global consumption of energy. It has been estimated that if only 0.1% of the earth's surface were covered with solar collectors operating at an average efficiency of 10%, all of world's annual energy needs could be supplied by the sun.
- (c) Undoubtedly solar energy is plentiful, clean and non-polluting. However it is so diluted that direct

economical harnessing becomes exceedingly difficult. A solar power generator of capacity equivalent to Victoria will have to cover an area of several square kilometers. The construction of such a facility using silicon solar cells would cost more than Rs.5000 billion. The current research in solar energy is geared towards development of cheaper solar cells and photochemical systems capable of conversion and storage of solar energy.

All our energy requirements, in theory, can also be met by growing biomass via natural photosynthesis. However, there are practical limitations in achieving this goal. The efficiency of solar energy conversion by plant photosynthesis is very low and seldom exceeds 1% on an annual basis, except in the case of a few plants such as sugarcane.

However, plants can also be used to produce other useful chemicals that can be used as fuel, perfumes, drugs and food. These, combined with the rapidly advancing science of biotechnology may provide new avenues for tackling the impending energy crisis. For example, a tree belonging to the leguminosae family of the genus *Copaifera* can be tapped to produce about 25L of a diesellike material in a 24h period. Production of such materials from plants is also a way of solar energy conversion to produce desirable chemicals.

Alcohol produced by the microbial fermentation of sugars from sugar cane is also an important by-product from plants. Alcohol mixed with gasoline under the trade name 'gasohol' is commonly used in countries such as Brazil and also to a limited extent in the USA.

Biomimetic Photosynthetic systems aimed at solar energy conversion may be completely synthetic or may be a combination of synthetic and biological molecules. The objective here may be the photolysis of water or generation of a reduced redox species which can be coupled to a catalyst to produce H^2 or reduce CO_2 . Assemblies of porphyrins, quinones and carotenoids have been recently studied as possible model systems. Even combinations of semiconductors and biological molecules have been studied as components of artificial photosynthetic devices.

Photosynthesis is the secret of life. Understanding this marvellous process may significantly contribute to the survival of mankind.

Biological photosynthesis has the advantage of some three billion years of evolutionary development of elegant molecules which carry out highly specific reactions. Purely synthetic systems on the other hand are more flexible with higher solar efficiencies. They can be employed for the production of specific fuels and chemicals. Some processes of interest are photochemical water splitting to produce hydrogen, photofixation of molecular nitrogen and photoreduction of carbon dioxide to useful fuels such as methanol.

Chemical approaches to harnessing solar energy :

There are various physical approaches of using solar energy. Solar drying, solar cookers are some of these. However, here we shall discuss only the chemical approaches of solar energy conversion.

1. Solar cell Technology :

Photovoltaic solar cells convert light directly to electricity. Most of present day solar cells employ silicon metal doped with other impurities. Here silicon acts as a semiconductor where absorbed energy causes the excitation of an electron from the valence band to the conduction band of the semiconductor (appendix 1). The photogenerated electron can go through an external circuit where the absorbed energy is given out as electrical energy.

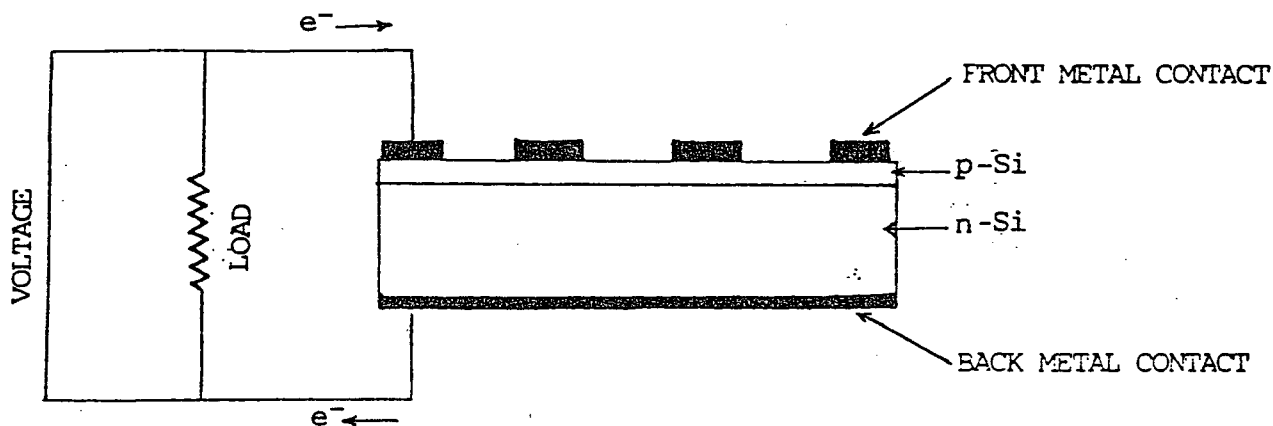


Fig. 1. A photovoltaic Cell

These systems although simple are however costly to fabricate. It is essential to produce single crystals of silicon which are 100% pure. Such advanced technology is only available in the most developed countries of the world. Storage of electricity is also a problem in this method. At the present time batteries similar to those used in cars are used for this purpose.

- (d) Hydrogen can be used as a fuel and if an efficient way of photosplitting water can be found the energy problem can be solved. This method has several advantages.
- (a) The raw material is water which is readily available anywhere.
 - (b) The combustion product is water which is non polluting when compared to burning fossil fuel.
 - (c) Solar energy is embargo-proof. ie, no one can reserve solar energy which falls everywhere on our planet.

Semiconductor based catalysts in principle can decompose water to hydrogen and oxygen. However the observed yields of hydrogen are quite small. Scientists throughout the globe are working on improving the efficiency of this process. An interesting discovery in this area of research is the generation of hydrogen from organic compounds such as alcohols, lignin, cellulose etc. when irradiated in the presence of a semiconductor catalyst. Scientists have shown that even ordinary garbage can be used. If these processes can be developed they will definitely have economic as well as social advantages for producing much needed energy. However, considering the fact that certain remote villages in Sri Lanka are still not connected to the national grid, solar cell technology shows excellent promise for the rural electrification schemes for such villages.

2. Photochemical splitting of water :

Fujishima and Honda in Japan first showed that water can be split into H_2 and O_2 using solar irradiation of TiO_2 titanium dioxide is a semiconductor which produces electron-hole pairs upon irradiation. The electrons are used for the reduction of water to give $H_2O \rightarrow H_2 + 1/2O_2$ while the holes oxidize water to O_2 . However, the yields obtained with these systems

are exceedingly small and have no commercial value. Attempts have been made in several laboratories to improve on the yields of H_2 by various chemical modifications. However, even to date there are no practically viable systems even on a laboratory scale.

3. Photochemical nitrogen fixation :

The conversion of nitrogen to fixed forms such as ammonia and nitrate is essential for Agriculture and hence for sustaining life on Earth. With the current fertilizer prices pathways leading to alternative nitrogen fixation pathways have assumed great economic and sociological importance. The use of sunlight to convert nitrogen to fixed forms is an attractive method especially for the developing countries. Semiconductor catalysts are widely used for this purpose. Upon irradiation, such catalysts generate electron-hole pairs and the excited electron can be utilized for reducing nitrogen to ammonia. However, even here the yields of ammonia produced are far too small to be of any practical value.

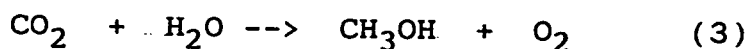


A large number of semiconductor catalysts have been investigated as possible catalysts for the photosynthesis of ammonia. These include metal doped TiO_2 catalysts, metal titanates and hydrous ferric oxides and their modifications. Research carried out at the Institute of Fundamental Studies and the Universities of Ruhuna and Peradeniya have identified several superior catalysts based on hydrous ferric oxides for this purpose. Several factors that lead to catalyst poisoning and also valuable information concerning the mechanism of this interesting reaction have been discovered.

If a nitrogen-fixing solar cell can be developed its advantages are numerous especially for a developing country such as Sri Lanka. Even if the yields of ammonia are small the enrichment of soil nitrogen may be significant over a long period of time.

4. Photofixation of carbon dioxide :

The reduction of CO_2 via multi-electron transfer reactions could produce formic acid, carbon monoxide, formaldehyde, methanol or methane. The exact products depend on the particular system used. It has been shown that CO_2 reduction takes place on illuminated semiconductors such as TiO_2 , ZnO , CdS , GaP and SiC .



There are several other reactions which can be similarly carried out on semiconductor catalysts using solar energy. Some examples are; depollution of water, decarboxylation of carboxylic acids, Amino acid synthesis, Photooxidation of alkenes, alkanes and alcohols, photosynthesis of hydrogen peroxides, hydrogen photoproduction from organic materials.

- (e) If methods are found for carrying out reactions (1), (2) and (3) using sunlight, almost all human problems can be solved. The first reaction would provide a clean plentiful supply of storable energy. Ammonia from the second reaction can be used to manufacture fertilizer. Methyl alcohol and other reduction products of carbon dioxide are readily utilizable fuels.

Economic development has resulted in pollution of the environment. The pollution which endangers life is an increase of disorder on the surface of the planet. To overcome pollution, energy is again necessary. There are indications that here too solar energy can be adopted. In the ultimate analysis all social evils originate from insufficiency in energy. If the supply of energy is ample, the disorder can be put into order and all material needs can be made from cheap and inert matter.

A breakthrough in harnessing solar energy, especially photochemical conversion would come from the global research effort in this direction. Apart from the practical necessity, investigations in this field present challenging fundamental problems. Difficult problems always attract scientists. It is more difficult to photo-split a water molecule and store energy than to split a uranium nucleus and release stored potential energy.