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Preface—An overview

This issue contains the invited lectures given at the Fifth International Conference on Photochemical Conversion and Storage of Solar Energy (IPS-5) held at Osaka Science and Technology Center, Osaka, Japan, on August 26 - 31, 1984. About 330 delegates attended the conference, 230 of whom were from Japan, 40 from the U.S.A. and 60 from 18 other countries. This number of delegates, as well as the number of contributed papers (190), is the highest of this conference series, indicating the continued growth of interest and research activity in the area of photochemical and photoelectrochemical conversion of solar energy.

The first of this conference series was held in London, Ontario, Canada, in 1976, when public concern in the development of new energy was heightened by the oil crisis which started in 1973. Now that eight years have elapsed and the supply of oil and other fuels is conducted in an orderly manner, the attention of the public to new energy seems to be somewhat lessened. The importance of research into solar energy utilization, however, never declines. It is encouraging in this respect that the present conference gathered so many attendants and was very active.

The research in the photochemical conversion and storage of solar energy, as seen from the previous conferences, can be divided into two categories. The first category includes the work on photoelectrochemical cells using semiconductor electrodes and on semiconductor powder photocatalysts. The latter may be regarded as microphotoelectrodes and therefore research on the semiconductor powder photocatalysts has much in common with that on the photoelectrochemical cells. The second category includes work on photochemical reactions of organic substances or metal complexes in solutions as well as in organized assemblies. Most of the work in the second category deals with photoredox reactions, simulating the processes in the photosynthetic systems in biological cells.

The conference consisted of six plenary lectures, twelve invited lectures, poster sessions in which about 190 papers were presented and four panel discussions. Dr. Melvin Calvin gave the opening lecture and Dr. Sir George Porter presided over the closing discussions. The present issue contains the opening address by Dr. Calvin, the papers presented as the plenary and invited lectures, and an article on Japanese solar technology by Dr. Takashi Horigome who gave a special lecture on this subject. The abstracts of the contributed papers, as well as those of plenary and invited lectures, have been published in the Book of Abstracts of IPS-5 which was distributed to the attendants of the conference.

I should like to make a brief survey of the state of the art as manifested in the work presented and in the discussions made at the conference.

Photoelectrochemistry at semiconductor electrodes (52 papers)

Photoelectrochemical cells containing semiconductor electrodes have two different functions: one to produce electrical power and another to induce energy-storing chemical reactions. In the former function, photoelectrochemical cells should compete with the solid photovoltaic systems. Some photoelectrochemical cell systems have been proposed which have high conversion efficiencies (12% - 13%) and durabilities comparable with those of solid photovoltaic systems. It is argued that photoelectrochemical cells have some merits in simplicity of design and economic feasibility when compared with solid photovoltaic systems. The design is simple because no conducting overlayers are necessary for photoelectrochemical cells. The economic feasibility is a result of the fact that in certain cases surface impurities and defects do not greatly deteriorate the photovoltaic capacity of the cells.

As for the second function of photoelectrochemical cells, namely chemical conversion, a difficulty has been pointed out in the fact that the known semiconductor materials having proper band gaps, *e.g.* CdS, silicon and GaAs, are corrosive in aqueous solution. To overcome this difficulty, coatings with conductive organic layers or with precious metals have been proposed and studied. Metal coating is also important for its catalytic activity in many systems. It has now been demonstrated that the decomposition of hydrogen halides (HI or HBr) can be done with fairly high conversion efficiencies (8% - 12%) and with good durability. The efficient decomposition of water, however, has been unsuccessful. It has been proposed that multilayer amorphous silicon electrodes might produce sufficiently high voltages and become stable enough to undergo efficient photoelectrolysis of water.

Investigations on entirely new semiconductor materials for photoelectrochemical conversion are continued by some groups. This approach is also important in view of the fact that there are many inorganic materials whose properties still remain unknown. Although this approach is not easy and will need a huge project of systematic research, such work will undoubtedly profit a wide variety of technologies.

Research into organic semiconductors is also an interesting approach which is being developed in some groups (9 papers).

The reduction of CO, CO_2 and N_2 is pursued by several researchers. Although the efficiencies of these reactions still remain low, such reactions are attracting much attention because of their technological importance. It is noteworthy that reactions of different types occur sometimes with different semiconductors. It might be possible to obtain specific products which cannot be derived from simple electrolysis in the dark cell.

Heterogeneous photocatalytic reactions

Research into photoreactions using semiconductor powder photocatalysts is also very active (39 papers). The possibility of splitting water using this approach was much disputed for a certain period of time. It is now clear that with our present techniques hydrogen evolution occurs with high efficiency only if sacrificial electron donors are present in the solution. The organic electron donors involved in the reactions are either ultimately decomposed into CO_2 or partially oxidized to aldehydes, ketones or acids.

It has been shown that some organic synthetic reactions can take place with semiconductor photocatalysts, *e.g.* the formation of amino acids, peptides, amines and phenols as well as several other reactions forming C—C bonds. Many workers now believe that useful syntheses or removal of polluting materials can be performed by photocatalytic reactions under sunlight.

Photoredox reactions, energy transfer and simulation of photosynthesis (79 papers)

The essential feature of natural photosynthesis is frequently characterized as a combination of quantum harvesting processes and photo-induced electron transfer processes (photoredox reactions) in the reaction centre as emphasized by Calvin in the opening lecture. Photo-induced electron transfer reactions using various dyes and electron-donating and electron-accepting substances have been widely investigated to simulate photoredox processes in the reaction centre. Some new dyes and electron-relay compounds have been proposed. Hydrogen evolution from such systems, using a platinum catalyst for example, was successfully realized in the presence of certain sacrificial electron donors as in the case of heterogeneous photocatalysts. Oxygen evolution from water was also observed in the presence of appropriate electron acceptors. Thus, in systems of simple homogeneous solutions, efficient electron transfer reactions occur only if substances which undergo either irreversible oxidation or irreversible reduction are present. In other words, the reaction can proceed only by the aid of the free energy supplied from exoenergetic reactions which prevent the back electron transfer processes between photochemically produced active species; endoenergetic reactions such as the water-splitting reactions are difficult in simple aqueous solutions.

Success now depends on whether we can devise a system which makes the electron transfer, or charge separation, through the reversible mediators more efficient. This has been pursued by many workers using polymer electrolytes, micelles, vesicles or other membrane systems or synthetic compounds, including dyes, donors and acceptors. To date, many interesting findings have been accumulated. However, it will take more time for us to obtain real success towards this very attractive goal. Research into the molecular structure and physical properties of natural photosynthetic apparatuses is also progressing, and in some years the information gained from this approach will aid us to accomplish efficient reactions simulating photosynthesis.

The science and technology of chemical conversion and the storage of solar energy in various ways as described above will hopefully be developed further before the next conference, which is scheduled to be held in Paris in 1986.

Finally, I should like to express thanks to the International Organizing Committee and the Japanese Local Organizing Committee to which I was much indebted for the organization and management of the IPS-5 conference. On behalf of both committees, I wish to express thanks to the Commemorative Association for the Japan World Exposition and to about 100 Japanese companies for their generous donations on which the management of the conference entirely depended.

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