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HYDROGEN GENERATION FROM WATER USING SEMICONDUCTOR SEPTUM ELECTROCHEMICAL PHOTOVOLTAIC (SC-SEP) CELLS

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Using sunlight to extract hydrogen from water has been the dream of generations of scientists and engineers, and remains the goal of researchers in the 21st century. That dream may at last be realized in the semiconductor septum electrochemical photovoltaic (SC-SEP) cell, which is modeled after nature's photosynthetic thylakoid membrane. This novel SC-SEP cell arose from studies of pigmented bilayer lipid membranes (p-BLMs). The cell is easy to construct and simple to operate. It appears to offer a practical approach to the photochemical conversion and storage of solar energy. In principle, one may say hydrogen can and indeed has been generated from water via a number of schemes, including the SC-SEP cell. In practice, however, ways need to be devised so that the process is competitive with the current technologies. This paper describes how hydrogen is produced from seawater when the visible light of the solar spectrum irradiates a SC-SEP cell. Recent work from other laboratories is delineated.

INTRODUCTION

Current ways of producing hydrogen from water is expensive and requires large amount of energy. It seems in the long run, however, that the production cost could be drastically reduced with a method based on membrane biophysics and photoelectrochemistry. The method is grounded on the principle gleaned from natural photosynthesis, using the so-called SemiConductor-Septum Electrochemical Photovoltaic (SC-SEP) cell (Davison, 1989). First, it might be informative to recount how it all began.

Prior to the energy crisis of the 1970s, the best source book on solar energy utilization was the one by Daniels (1964), in which the whole field ranging from then recent history, the basic principles of photochemistry, to practical applications including photosynthesis *in vitro* (i.e., artificial photosynthesis) was examined. In particular, Daniels stated that green plant photosynthesis could be expressed as

$$CO_2 + H_2O \xrightarrow[\text{light}]{\text{chlorophylls}} [H_2CO] + O_2 \qquad (1)$$

where photons of light, mediated through chlorophylls, are used to drive the reduction of CO_2 to $[H_2CO]$ and the oxidation of water to oxygen. Through photosynthesis, as summarized in Eq. (1), our food and fuel are created. The byproduct, O_2, makes life possible via respiration. On the mechanism of photosynthesis, Daniels discussed the work of Rabinowitch (1961a, 1961b), who had pointed out that the chloroplasts 'have alternate layers of materials that are wet by water and that repel water and the chlorophyll molecules are probably located at the interfaces in such a way that the products of the photochemical reactions can be kept separate'. Further, research efforts should be directed toward the photochemical behavior of chlorophyll outside the chloroplast under radically different conditions, and this might lead to a method of artificial photosynthesis. Clearly, what Rabinowitch and Daniels had in mind was that a study of natural photosynthesis might point the way toward research in the quest for new photochemical reactions that can use and store solar energy. Since these prophetic remarks of Daniels and Rabinowitch, our understanding of green plant photosynthesis has greatly increased. Concurrently, advances in solid state physics, photoelectrochemistry, and membrane biophysics have made crucial contributions to the understanding of the phenomena at the interfaces, we shall discuss presently. It is informative, perhaps, to have a brief overview of photosynthesis.

In plant photosynthesis the conversion and storage of solar energy is conceptually quite simple. The process consists essentially of two coupled, light-driven redox reactions that take place on opposite sides of the thylakoid membrane of the chloroplast. Pigment molecules embedded in the thylakoid membrane mediate the reactions. Structurally, the principal construct of the thylakoid membrane is a lipid bilayer. On one side of the membrane/solution interface, water is oxidized to its basic components (electron, proton and oxygen). On the other side, light-generated electrons and protons reduce carbon dioxide to energy-rich products such as carbohydrates. These reactions take place in plants, algae and some types of bacteria. Through photosynthesis, the trapped free energy is then used to drive the formation of organic compounds. In green plants and algae, the photosynthetic process depends on complex protein molecules embedded in the lipid bilayer of thylakoid membrane. The protein complexes embedded in the lipid bilayer, separating two aqueous phases, have a unique orientation with respect to the inner and outer phase (stroma). The asymmetrical arrangement of the protein complexes allows some of the energy released during electron transport to create an electrochemical gradient of protons across the thylakoid membrane. In photosynthesis, there are the so-called ‘light reactions’, which consist of electron and proton transfer reactions and the ‘dark reactions’, which consist of the biosynthesis of carbohydrates from CO_2 (Barber, 1979).

More specifically, the light reactions occur in a complex bilayer lipid membrane system. The first step is the conversion of a photon to an excited electronic state of a pigment molecule located in the antenna system. The antenna system consists of hundreds of pigment molecules (mainly chlorophyll and carotenoids) that are anchored to proteins within the thylakoid membrane and serve a specialized protein complex known as a reaction center. The electronic excited state is transferred over the antenna molecules as an exciton. Some excitons are converted back into photons and emitted as fluorescence, some are converted to heat, and some are trapped by a reaction center protein. Excitons trapped by a reaction center provide the energy for the primary photochemical reaction of photosynthesis: the transfer of an electron from a donor molecule to an acceptor molecule. In terms of time scale, the photosynthetic process is initiated by the absorption of a photon by a pigment molecule, which occurs in about a femtosecond (10^{-15} s) and causes a transition from the electronic ground state to an excited state. Within 10^{-13} s the excited state decays by vibrational relaxation to the first excited singlet state. The fate of the excited state energy is guided by the structure of the protein. Exciton energy transfer between antenna molecules is due to the interaction of the transition dipole moment of the molecules. The probability of transfer is dependent on the distance between the transition dipoles of the donor and acceptor molecules ($1/R^6$), the relative orientation of the transition dipoles, and the overlap of the emission spectrum of the donor molecule with the absorption spectrum of the acceptor molecule. These molecules are located in the so-called photosystem I (PS I) and photosystem II (PS II) reaction centers. In more details, PS-II, made of more than fifteen polypeptides and at least nine different redox components, uses the photon energy to drive two chemical reactions: the reduction of plastoquinone and the oxidation of water. Further, the PS-II complex undergoes a light-induced electron transfer and is initiated by charge separation between P_{680} and pheophytin (Pheo), creating $P_{680}^+/\mathrm{Pheo}^-$. Primary charge separation occurs in a few picoseconds (10^{-12} s). The presence of the lipid bilayer prevents the primary charge separation from recombining. PS-II contains the only known protein complex that can oxidize water, resulting in the release of O_2 into the atmosphere. At present, however, little is known concerning the molecular events resulting in water oxidation, despite years of research.

Energetically, water is an indigent electron donor. The oxidation-reduction midpoint potential of water is +0.82 V (pH 7). In PS-II, this reaction is driven by the oxidized reaction center, P_{680}^+ (the midpoint potential of P_{680}/P_{680}^+ is estimated to be +1.2 V at pH 7). How electrons are transferred from water to P_{680}^+ is still obscure. It is known that P_{680}^+ oxidizes a tyrosine on a certain membrane protein and that Mn plays a key role in water oxidation. Four Mn ions are present in the water-oxidizing complex. X-ray absorption spectroscopy shows that Mn undergoes light-induced oxidation. Water oxidation requires two molecules of water and entails four sequential turnovers of the reaction center as evidenced by flash excitation experiments. Each photochemical reaction creates an oxidant that removes one electron. The net reaction results in the release of one O_2 molecule, the deposition of four H^+ into the inner water phase, and the transfer of four electrons (producing two reduced plastoquinone molecules). The PS-I complex catalyzes the oxidation of plastocyanin (a Cu-protein), and the reduction of Ferredoxin (a FeS protein). PS-I is composed of a heterodimer of proteins, where primary photochemistry is initiated by a chlorophyll-*a* dimer, P_{700}. The reaction center is served by an antenna system that consists of about 200 chlorophyll molecules (mainly chlorophyll *a*). In contrast to PS-II, many of the antenna

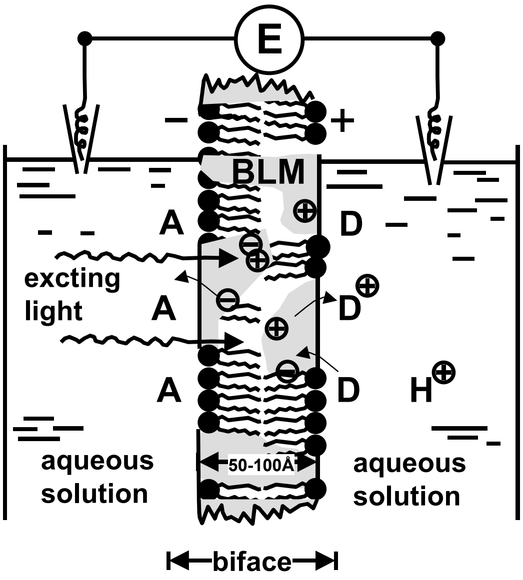

Fig. 1. Schematic illustration of the basic electronic processes in photoactive BLM separating two aqueous solutions. A — Electron acceptor; D — electron donor; D^+ and D_{ox} are oxidized forms of D; D; circles with minus — electron; circles with plus — positive hole. It is postulated that electrons and holes are generated in the BLM via exciton dissociation on illumination.

chlorophyll molecules in PS-I are bound to the reaction center proteins. Also, FeS centers serve as electron carriers in PS-I. Insofar as is known, PS-I electron transfer is not coupled to H^+ translocation.

Electron transfer from water to $NADP^+$ requires three lipid bilayer-bound protein complexes operating in series: PS-II, the cytochrome (bf) complex and photosystem I. Electrons are transferred between these large protein complexes by small mobile molecules (plastoquinone = PQ and plastocyanin). Because these small molecules carry electrons (or hydrogen atoms) over relatively long distances, they play a unique role in photosynthetic energy conversion. Because PQ is hydrophobic, its movement is restricted to the lipid bilayer core of the thylakoid membrane. PQ operates by diffusing through the membrane until, due to random collisions, it becomes bound to a specific site on the PS-II complex.

Thus, as a result of electron transfer and proton translocation, a proton electrochemical potential gradient is created, which results from two types of reactions: (a) the release of protons during the oxidation of water by PS-II and the translocation of protons from the outer aqueous phase to the inner aqueous phase by the coupled reactions of PS-II and the cytochrome bf complex in reducing and oxidizing PQ on opposite sides of the bilayer lipid membrane, and (b) the primary charge separation at the reaction center drives an electron across the lipid bilayer, which creates an electric potential across the thylakoid membrane. Although under normal conditions the value of E_m (membrane potential diffierence) across the thylakoid membrane in chloroplasts can be as large as 100 mV, it is mainly due to the proton concentration gradient. For example, during photosynthesis, the outer pH is typically near 8 and the inner pH is typically near 6, giving a pH difference of 2 (~120 mV) across the membrane. Finally, this pH gradient is utilized to drive the ATP synthesis as summarized in the following:

$$ADP^{-3} + P_i^{-2} + H^+ \xrightarrow[\text{ATP synthase}]{\text{lipid bilayer bound}} ATP^{-4} + H_2O \quad (2)$$

where P_i - inorganic phosphate. All plants and algae remove CO_2 from the environment and reduce it to carbohydrate. The process is a sequence of biochemical reactions that reduce carbon and rearrange bonds to produce carbohydrate from CO_2 molecules. It should be noted that photosynthetic quantum yield and energy conversion efficiency are rather low (free energy stored as carbohydrate/photon absorbed). The theoretical minimum quantum requirement for photosynthesis is 8 quanta for each molecule of oxygen evolved (4 quanta required by each PS-II and PS-I). Under optimal conditions, plants can achieve energy conversion efficiencies within 90% of the theoretical maximum. However, under normal field conditions the actual performance of the plant is far below the theoretical values. One of the most efficient crop plants is sugar cane, which stores up to 1%/year of the incident sunlight radiation. However, most crops are less productive, typically ranging from 0.1 to 0.4 %. per year.

Until recently, little was known about the structure of the thylakoid membrane and how it worked at the molecular level. Now, our knowledge about the process has emerged in physicochemical terms through membrane reconstitution and *in vivo* studies. In the membrane reconstitution studies, reaction centers of PS-I and PS-II have been incorporated into experimental BLMs (planar lipid bilayers), *see* Wardak, Brodowski, Krupa and Gruszecki (2000). The insights gained from such studies led to the development of solar conversion devices modeled after natural photosynthesis. This paper describes a conversion system, known as the semiconductor septum electrochemical photovoltaic cell (SC-SEP cell for short), using only the visible light of the solar spectrum and without externally applied voltage (Tien, Bi and Tripathy, 1986; Kalyanasundaram, 1987; Davison, 1989;

Tien, 1990; Tien and Chen, 1990; Ginley, Catalano, Schock, Eberspacher, Peterson and Wada, 1996; Volkov, Deamer, Tanelian and Markin, 1998). The simplicity of the SC-SEP cell, as described in some details below, makes it suitable for the generation of electricity, for the process-scale photoelectrolysis of water to hydrogen, and possibly for pollution control.

Background of the SC-SEP cell

Hydrogen can be and has been produced directly from aqueous solutions, including seawater, in a SC-SEP cell. The origin of the SC-SEP cell is traceable to early studies of membrane biophysics aspects of photosynthesis, which goes back more than 30 years to the time when it was found that an illuminated chlorophyll-containing bilayer lipid membrane (BLM) less than 6 nanometers thick, separating two aqueous solutions, generated a voltage and a current (Tien, 1968; Tien, 1974; Tien and Higgins, 1982; Tripathy and Tien, 1987; Tien 1990; De Silva and Tien, 1990; Ottova, Otto and Cerhata, 1991; Tan, Luo, Ren, Sun, Tien and Ottova, 1994; Bi, Qian, Zhao, Shen, Yu, Xu and Tien, 1994). The presence of this ultrathin lipid bilayer is crucial in minimizing the thermodynamically favorable back electron transfer reaction, thus mimicking the function of the natural photosynthetic membrane (Fig. 1). In the years since those early studies, pigmented BLMs (p-BLM) have been extensively investigated as models of photoactive biomembranes (Davison, 1989). The heart of this novel solar or SC-SEP cell is a semiconductor septum bipolar electrode, taking the place of the pigmented BLM, separating two aqueous solutions. An example of this type of electrode is a n-type polycrystalline cadmium selenide (CdSe) deposited on metal (e.g., nickel foil) separating two compartments filled with electrolytes. Shining light on the CdSe septum induces electron and hole separation within the semiconductor depletion layer. The contacting electrodes immersed in the front and back compartments complete the circuit. For a workable SC-SEP cell, light induced voltage and current over 1 V and tens of mA/cm^2, respectively, have been obtained. This is in sharp contrast with conventional photoelectrochemical cells (PECs) whose reported photovoltage rarely exceed 800 mV and photocurrent density 20 mA cm^{-2} (Gerischer, 1979). Additionally, SC-SEP cells possess their own redox potentials and can therefore operate as a battery in the dark.

Semiconductor model of photosynthesis

After photoelectric effects were observed in BLMs containing chlorophyll, specific models based on solid physics were suggested, *see* Fig. 2 (Tien and Verma, 1970; Tien and Karvaly, 1977). The interpretation of light induced phenomena is based on the theory of photochemical reactions and the quantum theory of radiation and matter. In this connection, photoelectric effects from dye-modified bilayer lipid membranes (BLMs) and related systems have been widely studied for the purpose of elucidating details of light-induced processes in photosynthesis (Frackowiak, Erokhina, Jadzyn., Shubin and Shkuropatov, 1981; Naser, Planner and Frackowiak 1998; Tien and Karvaly, 1977; Tien and Ottova, 2000). For example, Amao, Kamachi and Okura (1998) reported in a series of papers on the preparation and characterization of water-soluble viologen-linked zinc porphyrin and bisviologen-linked zinc porphyrin, and observed photoinduced hydrogen evolution in the system containing nicotinamide-adenine dinucleotide phosphate, trisulfonatophenylporphyrin, and hydrogenase under steady state irradiation. A useful model for the thylakoid membrane of green plant photosynthesis may be best discussed in terms of the theories of p-n junctions and Schottkey barriers. Figure 3 shows the thylakoid membrane as a p-n junction (or two Schottky barriers) separating two aqueous solutions.

The energy levels in aqueous solutions containing redox couples are governed by their standard redox potentials. The Fermi level in a membrane is determined by its so-called flatband potential (E_{fb}), which is the potential at which band-bending is zero. Absorption of photons by pigments embedded in the lipid bilayer at the two interfaces results in the generation of electron-hole pairs (excitons) that separate at the respective interfaces. For reduction to occur on the left membrane/solution interface and oxidation on the right, the redox couple in the bathing solution must possess redox potential values such that the acceptor of a p-type interface is equal to or below the conduction band of the membrane photocathode and the redox potential of the donor in an n-type interface is equal to or above the valence band of the membrane photoanode. For the photoelectrolysis of water, the interfacial electron transfer (redox) reactions may written as

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2 \ h\nu \qquad (3)$$

Thermodynamically, the overall reaction for water decomposition, as summarized in Eq. (3), requires a minimum of 1.23 eV or 284 Kcal as the overall

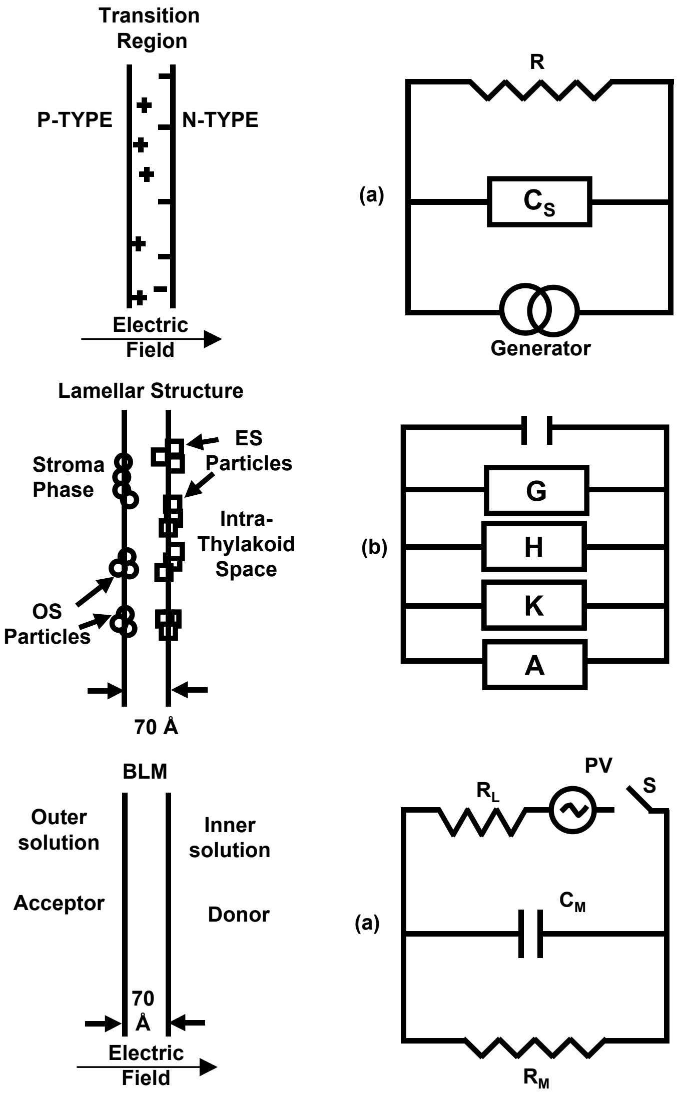

Fig. 2 Diagrammatic illustration of ultrathin barrier and conversion of light into electrical/chemical energy in three different systems: (a) the p-n junction of the silicon solar cell; (b) the thylakoid membrane of chloroplasts; (c) the pigmented BLM system. Electrical equivalent circuits are shown at right (*see* Bolton, 1977, p. 170).

dissociation energy per mole. In natural photosynthesis this is accomplished by having two photosystems arranged in series in the lipid bilayer of the membrane. Thus, for each electron transferred, the absorption of at least two photons is necessary. This elemental insight from green plant photosynthesis is of crucial importance in devising a model of artificial photosynthesis that is capable of splitting water (Bolton, 1977; Gerischer, 1979; Seta and Bienvenue, 1985; Delarosa, Navarro and Roncel 1991).

Pigmented BLMs in filters

A BLM formed in the conventional manner is a fragile structure and difficult to work with; it is not suitable for practical applications. A decision was made in the mid-1970s during the energy crisis to develop a model membrane system with a longer lifetime, a larger surface area, and greater stability in the face of chemical and mechanical disturbances. The resulting membrane system was achieved by filling the smooth circular pores of a microporous polycarbonate film (known commercially as Nuclepore filter) with a standard BLM-forming solution (Mountz and Tien, 1978). The pigmented lipid bilayer was supported in such a manner that an aqueous solution could be easily added to both sides. In an ideal situation this lipid-coated Nuclepore filter may be visualized as tens of thousands of micro BLMs simultaneously generated *in situ*. Photoelectrochemical cells (PECs) based on Nuclepore-supported BLMs were constructed and tested using 1% TPP (meso-tetraphenylporphrin), 1% phosphatidylcholine in a 1:1 (volume) solution of n-octane and chloroform. The most suitable pore size was found to be 3 μm. With this type of PEC, V_{oc} up to 400 mV and I_{sc} of 21 μA cm^{-2} could be obtained.

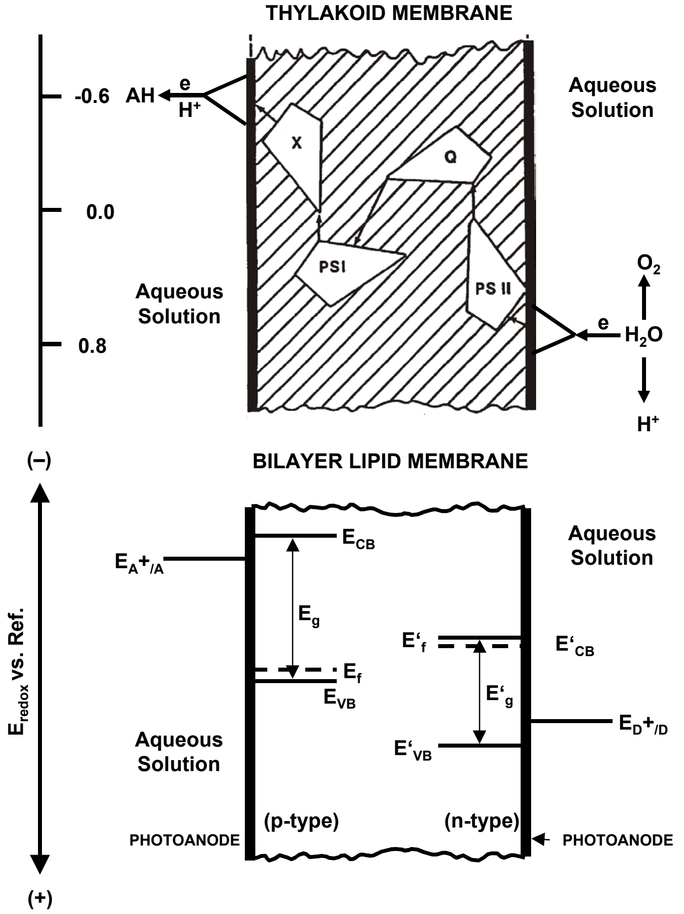

Fig. 3 Semiconductor model of photosynthesis. *Upper*: PS I and PS II denote Photosystem I and II, respectively. *Lower*: Pigmented (BLM) as an experimental model of the thylakoid membrane (adapted from Metzner, 1978; Barber, 1979; Davison, 1989).

Polycarborate semiconductor electrochemical photocells

In the proceeding sections the photoactive compounds in the membrane phase were either natural products (chlorophylls, carotenes) or organic pigments (tetraphenylporphyrins, dyes), whose long-term stability is limited. In the interest of constructing devices for practical applications, we initiated a project in 1982 that used inorganic pigments. Specifically, we used a Nuclepore membrane filter, as described in the preceding paragraph. It was placed between two thin Teflon sheets. There were holes in the Teflon to allow contact with the bathing solution. $Cs(NO_3)_2$ was placed in the bathing solution on one side and Na_2S in the solution on the other side. This resulted in the *in situ* formation of semiconductor crystallites such as CdS in the pores of the Nuclepore membrane. The CdS crystallites thus formed, blocked the pores of the supported membrane. Upon illumination, an open-circuit photovoltage V_{OC} of 500 mV and a short-circuit photocurrent density I_{SC} of 30 μA cm^{-2} were observed. It should be noticed in passing that the CdS-Nuclepore membrane septum electrochemical photocell can be further sensitized by pigments and dyes such as tetraphenylporphyrin (TPP) and Victoria Blue B (VBB) (Tien *et al.*, 1986). In this connection, Wrobel, Hanyz, Bartkowiak and Ion, (1998) recently reported ion porphyrin dyes fulfill an essential function in photosynthesis and are important in photodynamic therapy (PDT) and in a range of electronic devices. Their spectroscopic characteristics may play a crucial role in these processes. Concerning PDT, mention should be made that some of these photosensitizers have been used in BLM systems (Rokitskaya, Antonenko and Kotova, 1998). It is worth mentioning that a most unique group of compounds, namely fullerenes are of great interest in materials science. Fullerene C_{60}, for instance, is an excellent electron mediator and behaves as a n-type semiconductor, which might be useful in SC-SEP cells (Kureishi, Tamiaki, Shiraishi and Kazuhiro, 1999; Jiang, Li, Diao, Jia, Tong, Tien and Ottova, 2000).

SC-SEP cells

Having described the essential principles of green plant photosynthesis and the photoelectronic processes in pigmented bilayer lipid membranes (p-BLMs), we will now discuss the construction of practical "membrane-based" PECs for artificial photosynthesis. A convential PEC consists of a photoactive semiconductor electrode, such as CdSe, a counter electrode, and an electrolyte, all contained in one compartment (Hautala, King and Kutal, 1979; Gerischer, 1979; Davison, 1989, Dhumure and Lokhande, 1993). This single-compartment construction limits the maximum photoelectrical response to the degree of band bending. Therefore, the photoelectrical response is controlled by the Fermi level for a given semiconductor and redox couple. This major drawback is overcome in a novel semiconductor/liquid junction PEC, the SC-SEP cell. The basic idea of the SC-SEP cell is that photoactive compounds (e.g., pigments, semiconductors), in the form of a "membrane" or pellet, act as a bipolar electrode between two redox solutions. The progress to date in this area, along with some recent ideas from our laboratory, are summarized in the following paragraphs.

Description of the SC-SEP Cell

The principal components of a SC-SEP cell are a semiconductor septum (bipolar electrode) in place of the pigmented BLM, two contacting electrodes and two aqueous solutions containing redox couples of either like or unlike materials. The semiconductor septum serves as the photoactive bipolar electrode through which light-generated electrons and holes are translocated under the influence of an electrical field. As shown in Fig. 2, an ultrathin barrier exists in the SC-SEP cell. The exposure of CdSe to light induces electron/hole separation within the SC depletion layer.

The holes thus created are driven and used for polysulfide oxidation at the left electrolyte/CdSe interface, while the electrons move through the bulk of the SC to the other side of the CdSe septum to effect a reduction. Reactions complementary to those just described take place at the respective contacting electrodes. Additionally, the SC-SEP cell possesses its own redox potential and can, therefore, operate as a battery in the dark, with storage capability. Our initial findings, beyond offering a novel design for a photovoltaic cell, also indicate a photo-to-electrical energy conversion efficiency of more than 10%.

Water photolysis via SC-SEP cells

At a membrane technology symposium in 1983 (see Davison, 1989), it was pointed out that the photolysis of water according to the principles of green plant photosynthesis is one of the most significant experiments in the field of photochemical conversion and storage of solar energy for the future. The overall reaction requires a minimum redox potential of 1.23 V. Various energy losses such as electrode overpotentials and backward reactions must also be considered, as they are inherent in the process of quantum conversion. Backward reactions (i.e., charge recombination) can be prevented by creating an electrical field to facilitate the charge separation and collection. The charge separation and collection can be further enhanced by the presence of suitable redox couples. Moreover, to put the reaction indicated in Eq. (3) to work, the hydrogen and oxygen produced should be separated from each other by a membrane, for example, as a first step. Since a minimum of two photons is required for each molecule of H_2 generated and four photons are required for each molecule of O_2, a scheme using two coupled photosystems, as observed in natural photosynthesis, is a logical choice (Barber, 1979). The system shown in Fig. 4 has been suggested since 1970 by various authors (Gerischer, 1979; Davison, 1989). With the development of SC-SEP cells, we are now in a position to explore the feasibility of water photoelectrolysis via a variety of semiconductor septum electrodes covered with suitable catalysis. The following paragraphs describe the details of our experimental findings when the SC-SEP cell was used to produce hydrogen from aqueous solutions, including seawater.

MATERIALS AND METHODS

An example of this bipolar electrode is n-type polycrystalline cadmium selenide (CdSe) deposited on a nickel foil separating two compartments filled with electrolytes, *see* Fig. 4 (Jackowska and Tien, 1988). The arrangements of the cell may be represented as shown in Eq. (4).

Glassy carbone electrode
↓
0.2 M $K_3Fe(CN)_6$
0.01 M $K_3Fe(CN)_6$
↓
n-CDSe film
↓
Nickel foil
↓
Artificial seawater
↓
Lead electrode
(4)

Chemicals

Polycrystalline CdSe and other semiconductor materials used for thin film preparations were purchased commercially (Johnson Matthey, N. H. and Atomergic Chemical Corp., N. Y.). The metal foils (Pt, Ni, Ti, brass) of various thicknesses (0.008 to 0.24 mm) as substrates and electrodes were obtained from MatalsMart (N. J.) and Aldrich Chem. Co. (WI). Artificial sea water (Sigma Chemical Co., St. Louis, MO) and other chemicals of high purity were obtained from commercial sources and were used as received without further purification. Double-distilled water was used throughout.

Cell arrangement and septum electrode preparation

The cell consisted of two compartments made of transparent plastic (e.g. Lucite) with holes drilled on their sides. The CdSe-coated metal (M) foil was cut into an appropriate size so that it covered the drilled holes in the plastic compartments. The semiconductor/metal (SC/M) septum, which served as the bipolar electrode, was glued over the holes between the plastic compartments with epoxy resin and was allowed to cure for 24 h at room temperature. The compartment adjacent to the lamp was usually filled with 3-S solution (sodium hydroxide, sodium sulfide and sulfur, all at 1 M) or ferro-/ferri-cyanide in 0.1 M KOH solution [0.2 M $K_4Fe(CN)_6$, 0.01 M $K_3Fe(CN)_6$ and 0.1 M KOH] in contact with the CdSe film. The other compartment, not irradiated but having the metallic surface exposed, was filled with various solutions (sulfuric acid, 5 M; Na_2SO_4, 0.5 M; or artificial seawater). A contacting electrode (Pt, C, SnO_2, saturated calomel, Ag or brass) was placed in each compartment. For gas collection experiments, an inverted calibrated tube was attached to one of the compartments.

Setup and methods of study

The experimental set-up used is shown in Fig. 4. The voltage between the contacting electrodes was measured with an electrometer (Model 616, Keithley). Another electrometer (Model 160, Keithley) was used for current measurements. It was connected in series with a voltage source (B) and a variable resistor box (R) (0 to 10^3 MΩ to open circuit). The gas evolved was collected via a calibrated tube, which permitted the measuring of gas volume as a function of time. Voltammograms were recorded with an IBM Electroanalyser (Model 225, IBM Instruments Co.) and an x-y recorder (Model 2424M, IBM). A two-pen x-t recorder (Houston Instruments Co.) was also included in the set-up. The light intensity at the SC/M septum electrode was 80 mW cm^{-2} as measured with a light meter (Model 214, General Electric Co.).

Different Depositions of the Cdse-Film onto a Metal Surface of Ni or Ti

In further progress of our experiments different methods for the deposition of semiconductor films have been tried out. They can be divided into the following four types.

Painting method. A slurry of 50 mg CdSe and 1 mg of zinc chloride was prepared and 50 ml of 5% aqueous , Triton X-100 was added. This slurry was painted onto a carefully degreased foil of either nickel or titanium (usually 25 cm^2)

Chemical deposition. Based on results published (Hodes, Fonash, Heller, and Miller, 1983; Ginley *et al.*, 1996), the following mixture was used throughout, which was considered to be optimal for solution growth of CdSe on a metallic substrate; cadmium acetate (final concentration 0.05 M), ammonia solution (2 M), sodium selenosulfate, i.e. nickel or titanium foil (about 2×3 cm^2) was fixed and the solution was slowly heated (about 0.25°C min^{-1}) in the range from 63 to 85°C. In some experiments, stirring was done by means of a magnetic stirrer. In other experiments, a weak electric field was applied. In these cases, two foils (2×3 cm^2) of nickel at a distance of 4 cm were immersed into the beaker which were used as electrodes. A low-voltage constant current was provided by an electrophoresis apparatus. The field was switched on as soon as the temperature reached 46°C. Deposition was continued for 30 min after reaching a temperature of 85°C. The foils were taken out from the beaker and were carefully rinsed with distilled water to remove loosely attached CdSe. The foil was then dried in an oven for 10 min at 80°C.

Suspension method. In this method, powder like CdSe, and in some experiments also CdTe, was suspended in distilled water to obtain a final concentration of 8% (w/v). Zinc chloride was added to achieve a final concentration of 0.16% (w/v). The carefully degreased metal foil was attached to a mechanical stirrer. Mechanical stirring at 200 rpm was carried out for different durations. the foil was taken out and dried at 80°C as described above. The film formation is rather irregular and irreproducible. The film obtained by the suspension method is not always uniform at it could be judged by the visual inspection under the microscope. The order of the thickness obtained through this method is much less as compared with other methods.

Ultrasound method. In this method, the solution was made from 4% CdSe and 0.16% $ZnCl_2$. A beaker of a total volume of 250 ml filled by two-thirds with this solution was placed into a bath type ultrasound apparatus (Tesla, Czechoslovakia). The device was set to full power. A metal foil (about 2×3 cm^2) was horizontally fixed between the two arms of a pinzette and was immersed about 1 cm below the surface of the CdSe solution. The foil was taken out holding it horizontally and transferred into an oven for drying at 80°C for 10 min.

Preparation of the SC-SEP cell

The foils prepared by the above methods were annealed at 410°C in air for 1 hour. A strip of suitable size was cut, which was then glued over the holes (diameter 7 mm, area 0.38 cm^2) of two translucent plastic chambers. The chambers were filled with solutions in a cell arrangement as described (Tien and Chen, 1992).

Compositions of the solutions: A: 0.2 M $K_4Fe(CN)_6$ + 0.01M $K_3Fe(CN)_6$ + 0.1 M KOH; B: 1 M Na_2S + 1 M sulphur + 1M KOH; C: 1M Na_2SO_3; D: 2M Na_2SO_4 + 2M H_2SO_4; E: saturated solution of $(NH_4)_2SO_4$ + 1M H_2SO_4.

The CdSe/Ni or CdTe/Ni septum electrode was illuminated by means of a halogen lamp (55 W). Light was focused through a magnifying lens and was filtered through a 2% $CuSO_4$ solution (thickness 4 cm). The open-circuit photovoltage $V^*_{OC} = (V_{light} - V_{dark})$ and the short-circuit photocurrent $I^*_{sc} = (I_{light} - I_{dark})$ were calculated from the voltage- and current-measurements under light and dark conditions. One comment has still to be made concerning the treatment of the SC-SEP cell prior to measurements.

Treatments. Chemical etching and photo etching

Chemical etching. The chamber containing the CdSe film deposited on the metal substrate was filled with 2% nitric acid. After 10 sec the acid was poured out and the chamber was rinsed with distilled water.

Photo etching. The chamber mentioned above was filled with 0.1M sulphuric acid and then exposed to white light (sunlight) for 60 sec.

Further Experimental Testing. Procedures with different combinations of the semiconductor/metal layer (SC/M layer).

The scheme of the electrochemical cell, as well as the arrangement used for photopotential and photocurrent measurements, is shown in Fig. 4. The mechanism responsible for photopotential and photocurrent generation is presented in Fig. 4. Such a mechanism has been proposed previously (Davison, 1989). The equivalent electrical scheme of the system used is shown (*see* Figs. 2 and 4). The general scheme of the cell can be described as

$$\text{(light) CE-1} \mid \text{S1} \mid \text{SC} \mid \text{MS} \mid \text{S2} \mid \text{CE-2} \qquad (5)$$

where CE-1 and CE-2 are counter electrodes in illuminated and dark compartments, respectively, whereas S1 and S2 are the electrolytes in these compartments, SC is a semiconductor layer deposited on MS-the metal substrate separating the compartments. In our experiments, various combinations of semiconducting layers CdSe, CdS and CdTe with metal substrates (Ni, Mo, and Cu) were investigated.

The semiconducting layers on the substrate were prepared using two different methods:

a. painting and annealing and
b. vacuum evaporation

In the first method, CdSe/Ni electrodes were prepared by slurry painting according to the procedure of Hodes *et al.* 1983; *see* also Xiao and Tien, 1983. Electrodes were heated in air at 80^{o} for 1 h, then at 450°C (also for 1 h) and then slowly cooled over 12 h to room temperature. The thickness of these layers in most cases was larger than 20 μm. In the second method, CdS, CdSe and CdTe were deposited on Ni, Mo and Cu foil substrates by vacuum evaporation at a pressure below 2×10^{-6} torr. The rate of film deposition, as well as the temperature of the source of the evaporating material and substrate, were fully controlled. The obtained n-type CdSe, CdS and CdTe layers have electron concentrations of about 5×10^{16}, 4×10^{17} and 6×10^{17} cm^{-3}, respectively.

There has been an attempt made, in which In and Cu doping of these semiconducting films by diffusion during layer heating was used. However, such a procedure was unsuccessful, because of peeling off of the obtained layers. The cell dimensions were 10×10×45 mm^3. The illuminated area of the semiconductor was 0.38 cm^2. The illuminated compartment of the cell was always filled with 3S solution (NaDH, Na_2S and S - all at 1 M), which was in contact with the semiconducting electrode. The S^{2-}/S_2^{2-} ions made, in this case, a redox couple, whereas the chamber not illuminated, with the metal part of the separating layer, was filled by 1-5 M H_2SO_4 or 0.5 M Na_2SO_4. The face of the semiconducting layer and CE-electrodes were etched and prepared by the procedure described above.

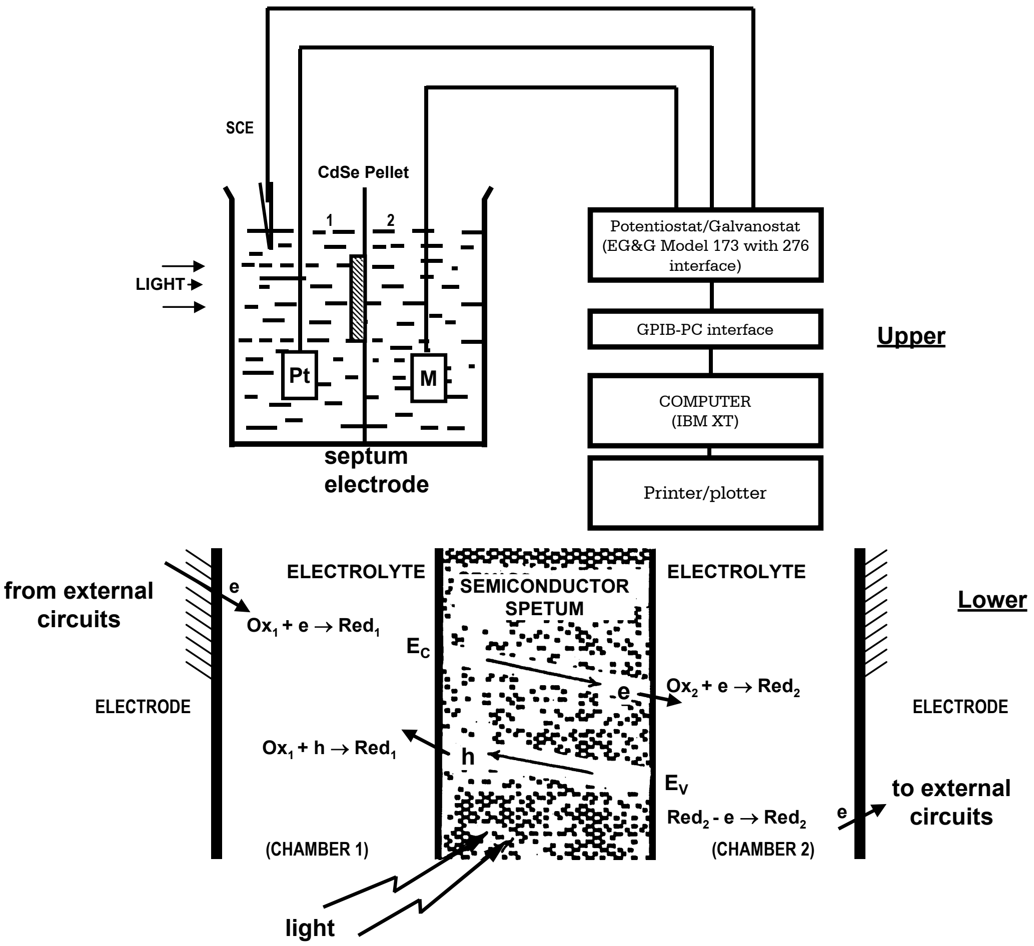

Fig. 4. *Upper*: Diagrammatic representation of a semiconductor septum electrochemical photovoltaic (SC-SEP) cell. *Lower*: Mechanism of operation.

Preparation of a SC-SEP cell for hydrogen evolution

A typical experiment for preparing a SC-SEP cell that is capable of hydrogen gas evolution as well as exhibiting photoelectric effects is given below.

Materials.

1. Items:1. 50 mg CdSe powder.
2. 0.01 g. $ZnCl_2$.
3. Five drops of Triton X-100 or any common household liquid detergent.
4. A piece of 5 cm × 5 cm foil of Ti or Ni.
5. Epoxy glue.
6. Transparent plastic containers with flat surface areas.
7. A 1 cm × 8 cm sheet of lead (Pb) for the contacting electrode in the chamber not exposed to light.
8. A piece of glassy carbon rod (size not critical) as a contacting electrode in the illuminated chamber.
9. 100 ml of 0.2 M $K_4Fe(CN)_6$, 0.01 M $K_3Fe(CN)_6$, and 0.1M KOH.
10. 200 ml solution saturated with NH_4HSO_4 ($NaHSO_4$ or $KHSO_4$) or 200 ml sea water or 0.5 M Na_2SO_4 + 10 ml H_2SO_4.

Equipment. Items:

11. An oven capable of reaching 600 °C.
12. A multimeter for measuring potential difference (mV), current (mA to μA range).
13. A light source (halogen lamp) or sunlight with a magnifying glass to concentrate the light.

Procedure. Steps:

1. Mix items 1-3 together with enough water to form a thick paste.
2. Paint it on Ti or Ni foil, this will be made into a septum electrode.
3. Bake item from step 2 in the oven at 450°C for 1 hour, cool to room temperature (Xiao and Tien, 1983).

4. Take one plastic bottle and drill a hole, the size of which should be a bit smaller than the painted, baked foil (septum), see step 2.
5. Do the same as in Step 4 to the other plastic container.
6. Prepare Epoxy glue, glue the septum electrode to one plastic container.
7. Align the second plastic container and glue it to the first one so that the septum electrode (from Step 3) separate the two containers.
8. Fill the container with the CdSe painted surface with solution from item 9 (*see* under **Materials**).
9. Fill the other container (dark chamber) with sea water or other solution - item 10 (*see* under **Materials**).
10. Insert the carbon electrode into the container filled with item 9 solution (*see* under **Materials**).
11. Insert the Pb electrode into the container filled with item 10 solution (*see* under **Materials**).

Action. Steps:

1. Connect the SC-SEP cell to the multimeter.
2. Shine the light onto the septum electrode via the item 9 solution (*see* under **Materials**).
3. Record the voltage and current both in the dark and under the light.
4. If everything is right, hydrogen gas bubbles from the dark side of the septum electrode (on the surface of Ti or Ni foil) should be visible.

RESULTS AND DISCUSSION

The crucial component of a SE-SEP cell is that the photoactive compounds (e.g., pigments, semiconductors) in the form of a "membrane" or pellet should serve as a bipolar septum electrode between two redox solutions. When the CdSe/Ni septum electrode of the cell was illuminated with light from a 650 W halogen-tungsten lamp at 80 mW cm^{-2}, open-circuit photovoltage ($V_{OC}^{*} = V_{light} - V_{dark}$), respectively, were obtained. When the cell was irradiated under open-circuit conditions, no bubbles were observed at the Ni surface. As the load between the contacting electrodes (CE) was reduced, gas bubbles were seen leaving the Ni surface. The gas evolution reached a maximum under short-circuit conditions. Figure 5c shows the volume of hydrogen produced as a function of time. All these results are based on the CdSe thin film preparation on metal (SC/M) by the painting method.

The mechanism of operation of this kind SC-SEP cell is illustrated in Fig. 4. Upon illumination with visible light (2 > 400 nm > E_g), photogenerated excitons (electron-hole pairs) are produced and separated under the influence of the electric field in the space charge region (Gerischer, 1979). At the left side of the SC-septum, the electrons migrate through the bulk of the SC to the metal and to the metal/electrolyte interface and the holes move to the opposite interface. There are four solid/liquid junctions (from right to left: CE/electrolyte, electrolyte/M, SC/electrolyte, electrolyte/CE). The following redox reactions are believed to take place at these respective junctions.

At the left glassy carbon (GC) electrode/electrolyte junction

$$\mathrm{Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_6^{4-}} \qquad (6)$$

The electrons for the reaction (Eq. 6) originate from the right contacting electrode (Pb)

$$\mathrm{Pb \rightarrow Pb^{2+} + 2e} \qquad (7)$$

The photogenerated holes at the left SC-septum/electrolyte interface oxidize where

$$\mathrm{Fe(CN)_6^{4-}} + h \rightarrow \mathrm{Fe(CN)_6^{3-}} \qquad (8)$$

Concurrently, the photogenerated electrons at the nickel surface reduce absorbed H^+ (or $H_3{}^+O$), from aqueous solution to hydrogen atoms, which upon combination are released from the surface as molecular hydrogen. In the case of artificial sea water

$$\mathrm{2e + 2H_2O \rightarrow H_2 + 2OH^-} \qquad (9)$$

The pH of the solution in the right chamber (i.e., the chamber containing sea water) was measured before and after hydrogen gas collection (see Fig. 4) and was found to change from 8.52 to 8.87. This finding is in accord with Eq. (9) and is also consistent with later experiments using acidified seawater at pH 1 (the equilibrium is shifted towards the right with a greater amount of hydrogen produced). Thus, the overall reactions may be summarized as follows. In the left chamber no net chemical change should take place in the bathing solution, whereas in the right chamber containing Pb electrode and artificial seawater, H_2O is decomposed to hydrogen and OH^- ions. The Pb^{2+} from the Pb electrode thus produced may exist either as $PbSO_4$, PbO, or as $Pb(OH)_2$ in equilibrium with their dissociated ions. Alternately, hydrogen peroxide could conceivably be formed.

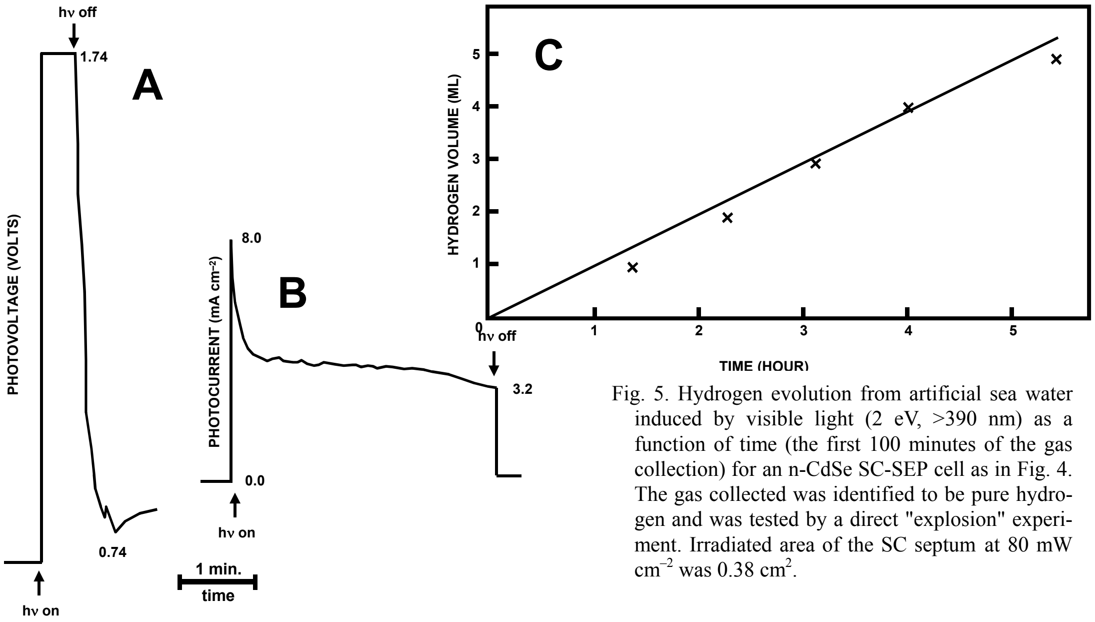

Fig. 5. Hydrogen evolution from artificial sea water induced by visible light (2 eV, >390 nm) as a function of time (the first 100 minutes of the gas collection) for an n-CdSe SC-SEP cell as in Fig. 4. The gas collected was identified to be pure hydrogen and was tested by a direct "explosion" experiment. Irradiated area of the SC septum at 80 mW cm^{-2} was 0.38 cm^2.

BASIC PRINCIPLE OF THE SC-SEP CELL OPERATION

All the results reported here were obtained in cells of a common design shown in Fig. 4. The cell, termed the semiconductor septum electrochemical photovoltaic (SC-SEP) cell, consisted of two compartments, one of which was fitted with a calibrated tube for gas collection. The SC/M septum, which separates two compartments, is the key element together with its two interfaces where light-driven charge generation, separation, transport and redox reactions take place. Since the design and mode of operation of a SC-SEP cell is quite different from those of conventional PECs, a brief description of the two types of photocells is appropriate. A conventional PEC consists of a photoactive semiconductor electrode and a metal counterelectrode, both of which are immersed in an aqueous electrolyte. However, such a PEC does not have proper energetics to photolyse water directly when illuminated with visible light, unless an additional voltage is applied. Alternatively, PECs employing two photoactive semiconductor electrodes have been reported to yield hydrogen and oxygen from water with low efficiency. A variation of PEC with two photoactive electrodes for water splitting are colloidal platinized semiconductor particles. Apart from the reported low efficiencies, the gaseous products generated in the aforementioned one-compartment system preclude their separation.

The system is analogous to that of the pigmented bilayer lipid membrane separating two redox solutions (Tien and Verma, 1970; *see* also Fig. 1). Proof of concept experiments have demonstrated that these SC-SEP cells are capable of generating open-circuit photovoltage V_{oc}^{*} and short-circuit photocurrent I_{sc}^{*}, when irradiated with visible light from a tungsten - halogen lamp at 80 mW cm^{-2}. The results of typical photovoltage/time and photocurrent/time curves of an SC-SEP cell are shown in Fig. 5. Over a period of more than 5 h, the measured values remained unchanged indicating the cell's remarkable stability. By varying the load resistor between the cell terminals, from open to short-circuit conditions, the photocurrent - photovoltage characteristics of the cell were obtained; from these the fill factor (FF) was calculated. The FF for the SC-SEP cells thus far studied ranged from about 0.25 to 0.4. Few or no gas bubbles were observed under open-circuit conditions. When the load resistor was about 300 Ω, bubbles were observed to leave the metal surface. The intensity of gas evolution was seen to increase in intensity as the load was reduced to zero (short-circuit conditions). Figure 5c shows the results of hydrogen production obtained with an n-CdSe SC-SEP cell using visible light. The findings clearly demonstrate that the SC-SEP cell can be used to transduce light directly either to electricity or/and stored chemical energy of hydrogen.

The electrical parameters and hydrogen production of SC-SEP cells were highly dependent on the nature of contacting electrodes. Glassy carbon (GC) electrodes were the most effective contacting electrodes used in producing hydrogen. When Pt was used (as) the contacting electrode in the dark chamber, no bubbles were seen in any of the cases studied.

The following notation is used to represent a semiconductor septum electrochemical photovoltaic (SC-SEP) cell

CE/Redox solution/SC/M/Redox solution/CD (10)

where CE denotes the contacting electrode, SC is the semiconductor, M is the metal. A slash represents a junction. As a specific example, the polycrystalline CdSe-based SC-SEP cell used in this study (see Fig. 4) may be represented as

GC/3-S/CdSe/Ni/Sea water/GC, (11)

where 3-S is a solution of sodium hydroxide (1M), sodium sulfide (1M), and sulphur (1M). GC is the glassy (vitreous) carbon electrode, CdSe/Ni stands for the septum electrode. The simplified energy band diagram of an n-type SC-SEP cell under illumination is shown in Fig. 3. At equilibrium, the thermodynamics of the n-SC/M septum require that the Fermi level (E_f), which represents the average energy of the carrier be constant throughout the junction (Bolton, 1977; Gerischer, 1979). The upward band bendings both at the n-CdSe/electrolyte interface and at the n-CdSe/metal interface are produced by the choice of the electrolyte and metal, respectively. The redox potential is more positive than the flatband potential and work function is much greater than that of the SC. Thus, a depletion layer and hence a strong electric field are produced below the CdSe surface (Davison, 1989). Analogously, one can also describe a case for a p-type SC-SEP cell. In this case a depletion layer and a strong electric field of the opposite direction to that of Fig. 3 are produced below the SC surface.

Upon illumination of the SC-SEP cell with a photom energy ($h\nu$) greater than E_g (band gap of the SC), an electron - hole pair will be produced within the SC. Those holes and electrons which are generated near or within the depletion layer are separated immediately by the electric field and driven toward opposite sides of the septum as shown in Fig. 4. For n-CdSe SC-SEP cell, the SC becomes positively charged with respect to the metal. This charge separation results in the so-called photoelectric effect. The electromotive force (EMF) thus generated may be used to dissipate power in an external load or to produce chemicals via redox reactions as will be discussed later after a brief consideration of the efficiency of the SC-SEP cell.

The electrical characteristics of the n-CdSe SC-SEP cell under illumination in terms of the open-circuit photovoltage V_{oc}^* and short-circuit photocurrent I_{sc}^* are defined as follows:

$$V_{oc}^* = (V_{h\nu} - V_d)_{oc} \tag{12}$$

and

$$I_{sc}^* = (I_{h\nu} - I_d)_{sc} \tag{13}$$

where superscripts $h\nu$ and d refer to light and dark, respectively. From the voltammogram (I-V curve) the maximum power output of the cell is given by

$$P_{\max} = V_p I_p \tag{14}$$

where V_p and I_p are the voltage and current, respectively, at the maximum power point. Using standard equations (Hautala *et al.*, 1979; Gerischer, 1979; Davison, 1989), the conversion efficiency of the cell is given by

$$n = \frac{FF\, V_{cc} I_{sc}}{E} \tag{15}$$

where *FF* lis the so-called fill factor (from the voltammogram) and is defined by ($V_p I_p / V_{oc}^*$), and *E* is the incident light. It is worth noting that up to now no attempts have been made to improve the efficiency of the cell by treatments such as chemical etching and photoetching. However, this comment is valid so far only for the n-CdSe SC-SEP cell, where the CdSe thin film on metal (SC/M) was made by the slurry painting method of Hodes *et al.* (1983) followed by annealing in air at 450 ^{o}C for 1 h.

Due to the presence of heterojunctions in the SC-SEP cell (*see* Fig. 3), a depletion region is formed in the n-CdSe (SC) which causes an electric field to be generated below the SC surface. Those photons absorbed within the CdSe produce electron-hole pairs which are separated into electrons and holes under the influence of the electric field and migrate to opposite sides of the SC/M layer. The separated holes tend to move to the n-CdSe/electrolyte interface causing sulfide (S^{2-}). Meanwhile, the separated electrons are driven to the metal/electrolyte interface to reduce absorbed protons (or H_3^+0) to hydrogen or to reduce other reducible species in the bathing solution. Concurrently, a photocurrent is observed in an external load connected between the contacting electrodes

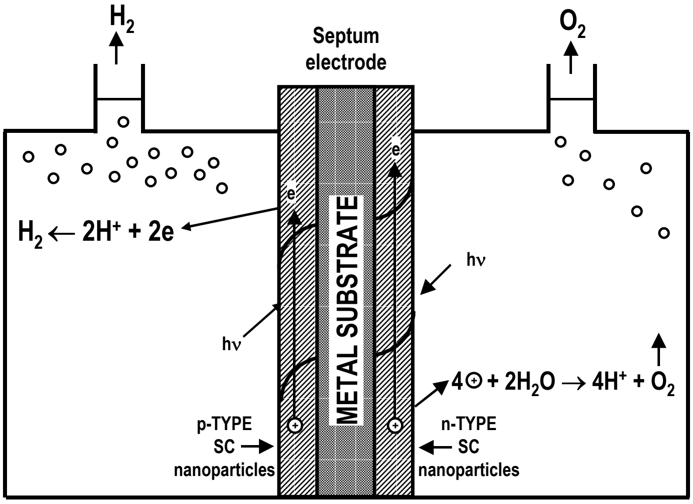

Fig. 6. The proposed SC-SEP cell for water photolysis using solar energy (Tien and Ottova, 2000).

(CE), where appropriate redox reactions occur. For the n-CdSe SC-SEP cell separating 3-S solution and sea water in which hydrogen is produced, S_2^{2-} ions are reduced to $2S^{2-}$ on the left-hand side of the CE (see Fig. 4). The hydrogen evolution reaction of the cell in the dark compartment (right-hand side) can be written as follows:

$$H_2O \rightarrow H_{ads} + OH^- \qquad (16)$$

$$2H_{ads} \rightarrow H_2(gas) \qquad (17)$$

where H_{ads} denotes an absorbed hydrogen atom.

As already mentioned, hydrogen evolution was at a maximum under short-circuit conditions. That this is so can be understood from Figs. 3 and 4, since the total amount of light converted is equal to the sum of electrical energy and stored chemical energy. For example, during the measurement of photogeneration of hydrogen, we recorded a current density of 0.14 mA cm^{-2} for the system: GC / 3-S / CdSe / Ni / Seawater / GC, which corresponds to 0.57 liter H_2 h^{-1} m^{-2}. This rate calculated from current measurements is in good agreement with that measured directly, namely, 0.50 liter H_2 h^{-1} m^{-2}. This is a further evidence that the gas evolved was pure hydrogen (*see* Fig. 5).

The mechanism of operation of the SC-SEP cell was illustrated in more details elsewhere (Ginley *et al.*, 1996). Thus, the overall reactions may be summarized as follows. In the left compartment, no net chemical change should take place in the bathing solution. In the right compartment containing Pb electrode and one of the solutions D and E (*see* **Compositions of the solutions**), respectively, the separated electrons will be driven to the metal/solution into face to reduce absorbed protons (or H_3^+O) to hydrogen or to reduce other reducible species in the bathing solution. The possible products of Pb^{2+} from the Pb electrode in the cathodic compartment are discussed in (Goc and Tien, 1993; Tien and Ottova, 2000). Further improvements in efficiency and in design of the SC-SEP cell as well as of the whole experimental set-up (all four methods: A = painting methods, B = chemical deposition without or with a weak external electrical field - estimated field strength between 1 to 5 V cm^{-1}, C = suspension method and D = ultrasound method) are anticipated, for example by using other SC materials like CdTe or mixtures of $CdSe_x$ $CdTe_{1-x}$.

SUMMARY OF OWN WORK

The fundamental process of natural photosynthesis involves the light-driven charge separation and translocation across an ultra-thin pigmented lipid membrane separating two aqueous phases, in which oxidation and reduction take place on opposite sides of the membrane. Through the redox reactions water is split into its basic components (electron, proton and oxygen), which allow the green plant to convert solar energy into stored chemical energy. This insight is the main idea of the SC-SEP cells which have been taken from the modeling of the photosynthetic thylakoid membrane using pigmented BLMs. In the SC-SEP cells, a septum of polycrystalline CdSe plays the role of pigmented BLM.

From the photocurrent denisty-photovoltage characteristics of the cell and from the collection of hydrogen gas from the dark chamber, these findings demonstrate conclusively that the SC-SEP cell reported in our work can be used not only to convert visible light (2 eV >390 nm) of the solar spectrum to electricity but into stored chemical energy in the form of hydrogen as well.

Thus far, although the performance of the SC-SEP cell based on polycrystalline n-CdSe has not been optimized, efficiencies of the cell could be greatly improved by using catalytic surfaces for hydrogen evolution, using other or mixed semiconductor materials such as GaAs, InP, Fe_2O_3, $CdSe_xCdTe_{1-x}$ and CdSe-CdS of nanoparticle sizes, and by using more suitable redox couples. To further enhance light absorption, the nanoparticles may be sensitized by dyes.

Finally, we summarize in Fig. 6 the concept, the goal, and the overall experimental system (i.e. the SC-SEP cell), as well as the expected results, of our long-term project. This novel SC-SEP cell, inspired by, and modelled after Nature's photosynthetic membrane, will be used to produce hydrogen from aqueous solution, in particular seawater for storing solar energy.

Related experiments from other laboratories

At the beginning of the 1990s there have been a number of publications dealing with semiconductor septum electrochemical photovoltaic (SC-SEP) cells. In this review we shall concentrate on scientific achievements reached with SC-SEP cells in other laboratories.

Todkar, Lawangar, Pawar, Awana, Agarwal and Narlikar (1990) published their results achieved with SC-SEP cells. They have tested different metallic counter electrodes like Cd, Cu, Ag etc. in electrolytic solutions like $Cd(NO_3)_2$, $Cu(NO_3)_2$, $AgNO_3$, etc. in the "dark" compartment of the septum cell. Such a cell can store energy above some threshold, the highest value of which depends on the position of the band edges of the septum electrode relative to the Fermi levels of the redox systems. For the semiconductor septum fabrication, different techniques have been used like electrodeposition, coprecipitation, spray pyrolysis, etc. For achieving effective charging of the SC-SEP redox storage cell, Pawar and coworkers had to use acceptor redox couples in the dark compartment, having standard potentials within 500 mV negative of it.

However, the SC-SEP solar cell shows promise not only for generating electricity but also for producing chemicals. In their work, Pawar, Patil, Madhale and Lokhande (1989) describe a semiconductor septum electrochemical photovoltaic cell (SC-SEP) in which storage of electricity and hydrogen production are possible. Their paper reports also the performance of sprayed Fe_2O_3 semiconductor as a septum electrode in redox storage cells. In 1991, there have been two publications of Cai, Li, Dong and Jian (1991a), Cai, Jiang, Dong and Jian (1991b) dealing with performance of the $TiO_2/Ti/TiO_2$ semiconductor septum photoelectrochemical cell. In their first paper (Cai *et al.*, 1991a), these authors describe the open circuit voltage, photovoltage, short circuit photocurrent and photovoltage-photocurrent character of the $TiO_2/Ti/TiO_2$ septum cell, all of which are influenced by the pH of solution in the light compartment (I), the redox couple in the dark compartment (II) and the kind of dark electrodes in both compartments. The mechanism of these influences has been discussed. For certain system, according to conclusion of authors (Cai *et al.*, 1991a), the performance of semiconductor septum electrochemical photocell (SC-SEP) could be superior to that of the photoelectrochemical cell (PEC) of a single-compartment construction.

In their second publication Cai *et al.* (1991b) have studied the influence of material property of metal modified on dark Ti surface on the cell performance. Their investigation was based on previous experiences with the $TiO_2/Ti/TiO_2$ SC-SEP cell and with the $TiO_2/Ti/Pt$ SC-SEP cell. The present experimental system is represented as

$$O_2/H_2SO_4(pH=1)/TiO_2/Ti/M/H_2SO_4(pH=1)/Zn \qquad (18)$$

where M = Cu, Zn, Pt. These systems were compared with the $TiO_2/Ti/TiO_2$ SC-SEP cell. Main results can be summarized as follows:

Open-circuit photopotential, short-circuit photocurrent density and fill factor under illumination are

1.46V, 0.72 mA cm^{-2}, 0.68 for $TiO_2/Ti/Cu$ septum;
1.16V, 0.45 mA cm^{-2}, 0.63 for $TiO_2/Ti/Pt$ septum;
0.57V, 0.36 mA cm^{-2}, 0.47 for $TiO_2/Ti/Zn$ septum;
1.37V, 0.39 mA cm^{-2}, 0.51 for TiO_2 septum, respectively.

The dark short-circuit current density of above systems are 0.32 mA cm^{-2} (for $TiO_2/Ti/Cu$ septum), 0.03 mA cm^{-2} (for $TiO_2/Ti/Pt$ septum), 0.14 mA cm^{-2} (for $TiO_2/Ti/Zn$ septum) and 0.06 $mA\cdot cm^{-2}$ (for $TiO_2/Ti/TiO_2$ septum). The interfacial potential of the dark side of the above septum are 0.03V (for $TiO_2/Ti/Cu$ septum), –0.10 V (for $TiO_2/Ti/Pt$ septum), –1.10 V (for $TiO_2/Ti/Zn$ septum) and –0.01 V (for TiO_2 septum) - vs. saturated calomel electrode (SCE). The septum cell was constructed as follows: the semiconductor septum was mounted on a PVC partition with PVC solution. After drying, the chambers of the cell were filled with 1M polysulphide (photoexposed side) and different electrolytes like $CdCl_2$, $CuSO_4$, $CuCl_2$ and $Cu(NO_3)_2$ in the second compartment.

Graphite was used as a counter electrode in the photoexposed side and either graphite, Pt, Cu or Cd was the electrode in the other compartment. According to Murali, Subramahian, Rangarajan N., Lakshmanan and Rangarajan S. K. (1991), X-ray diffraction studies indicated polycrystalline CdSe corresponding to hexagonal structure. Scanning electron microscopy (SEM) studies on annealed layers revealed agglomeration of crystallites. A band gap of 1.65 eV was obtained from optical observation studies. The septum cell of the following configuration

C/Polysulphide/CdSe film/Ti/Electrolyte solution 2/Electrode 2 (19)

was studied under an illumination of 80 mW cm^{-2}. Among all combinations, the highest photovoltage and photocurrent were achieved when Cd/$CdCl_2$ was used in the dark compartment. The noteworthy features of experiments done by Murali *et al.* (1991) are the large area (25 cm^2) CdSe electrodes, novel plating technique, higher output parameters of the fill factor (0.59), open-circuit voltage (1.54V) and efficiency (~ 9 %), as against those reported for cells even with small area (1.0 cm^2) slurry coated and electrodeposited septums. The improvement observed may partly be due to the postdeposition argon treatment that has not been hitherto used. The rate of cooling in argon atmosphere has a profound influence on the output parameters. Improvements in efficiency are expected by changing the deposition conditions, suitable doping and modifying and further optimizing heat treatment procedures.

The same group represented by Murali, Subramanian, Rangarajan N., Lakshmanan and Rangarajan S. K. (1992) published another paper dealing with Cd(SeTe) septum photoelectrochemical cells. Septum cells based on electrodeposited Cd(SeTe) films were reported in their work for the first time. Their films used for the septum were prepared by a selective plating technique from an electrolyte containing 0.1M $CdSO_4$, 0.066M SeO_2 and 0.033 M TeO_2 on conducting SnO_2 and titanium substrates. The films were adherent and had a thickness around 5.0 mm. They were annealed in argon for 20 min. at 550°C and were further annealed at 300°C under a vacuum of 10^{-6} torr for 30 min. Diffuse reflectance measurements on the films were performed. The films were characterized by X-ray diffraction studies and surface morphology was examined by a scanning electron microscope. The septum of Cd(SeTe) film on titanium substrate (5 cm^2) was positioned firmly in a groove in the PVC cell with PVC solution. The solvent was allowed to evaporate. After drying, 1 M alkaline polysulphide was added to one compartment (photoexposed side) and different electrolytes $CdCl_2$, $CuSO_4$, $CuCl_2$ and Cu $(NO_3)_2$ to the other. Graphite was used as the counter electrode on the photoexposed side and either graphite, platinum, copper or cadmium was used as electrode on the other. Among the film compositions prepared that one corresponding to hexagonal polycrystalline $CdSe_{0.21}Te_{0.79}$ having a band gap of 1.45 eV, gave the best output in the conventional PEC cell. Hence a composition of $CdSe_{0.21}Te_{0.79}$ was used throughout for the fabrication of septums. The SEM of $CdSe_{0.21}Te_{0.79}$ film showed a smooth and uniform surface with a grain size distribution around 1.0 mm. The resistivity of the deposited films was found to be around 120 Ω cm. When the Cd(SeTe) film-electrolyte interface has been illuminated, electron-hole pairs were generated. The electrons moved through the bulk of the n-type semiconductor and the titanium substrate and reached the other compartment. There the electrons reduced metal ions to the metal. This process could be used to recover precious metals from industrial wastes. The hole, on the other hand, travelled to the surface of the semiconductor and oxidized the sulphide ions. A photovoltage as high as 1.03V and a photocurrent density of 1.80 mA cm^{-2} were obtained when Cd/$CdCl_2$ was used in the second (dark) compartment. It was observed (Murali *et al.*, 1991) that the photovoltage obtained with platinum, graphite or the respective metal electrodes contacting the electrolyte in the second compartment does not follow a systematic variation. However, the photocurrent was found to be the highest when the electrode was reversible to the cation in solution. Concerning graphite and platinum electrodes, the former yielded a higher photocurrent output. When Cu/$CuCl_2$ was used in the second compartment, copper deposition was observed on the Ti surface facing the $CuCl_2$ solution and it was found that the copper electrode had turned slightly greyish, indicating the probable formation of copper oxide. The load characteristics of the cell with the following configuration

C/polysulphide/Ce(SeTe)/$CuCl_2$/Cu (20)

with a fill factor of 0.32, V_{oc} of 0.83 V, I_{sc} of 2.53 mA cm^{-2} and efficiency of 1.49% were obtained under illumination of 45 mW cm^{-2}. Both V_{oc} and I_{sc} increase gradually with increase in photoetching time. A 60s photoetching yielded a 24% increase in photocurrent and a 26% increase in photovoltage. This increase may be attributed to the increase in photoresponse of the semiconductor electrode with increase in photoetching time. The septum cell of the configuration mentioned earlier was tested under sunlight for 15 days. Negligible variation in the approximate photo-output for daylight hours for the length of period studied was noticed indicating good electrode stability. Long term stability studies are planned by Murali *et al.* (1992). In concluding remarks of this work, new promising semiconductor septum electrodes based on electrodeposited $CdSe_xTe_{1-x}$ films are presented (Murali *et al.*, 1991). However, further work to improve the efficiency of the light conversion capability of the system is still needed.

Another important publication dealing with the TiO_2 - Ti semiconductor septum based electrochemical photovoltaic cell appeared (Kondapaneni, Singh and Srivastava, 1992). In their work they have described the fabrication as well as the structural and photo electrochemical characterization of a semiconductor-septum based photoelectrochemical (SC-SEP, PEC) solar cell, with a TiO_2-Ti septum electrode connecting the illuminated and dark compartments, containing different redox electrolytes. In the SC-SEP, PEC cell the septum acts as a transducer electrode through which electrons can pass from one compartment to the other under illumination, and the opposite reaction occurs at the auxiliary electrode in the illuminated compartment. The photovoltage of the SC-SEP, PEC cell arises predominantly from the difference between the flat-band potential (V_{Fb}) of the semiconductor in the illuminated compartment (compartment A) and redox potential (E_{redox}) of the oxidizing electrolyte in the dark compartment (compartment B). In comparison to cadmium chalcogenides, oxide semiconductors (e.g. TiO_2) are known to be more stable photoelectrodes. In view of this fact, Kondapaneni *et al.* (1992) have employed TiO_2 deposited over Ti (TiO_2-Ti) as a new SC-SEP photoelectrode in the following arrangement: Pt , 1M NaOH , TiO_2-Ti , redox electrolyte , contacting electrode. All the measurements were carried out after keeping the cell short circuited for 1 h in dark to establish equilibrium. The photoelectrochemical characteristics, i.e. open-circuit photovoltage $V_{oc}^{*} = (V_l - V_d)_{oc}$ and short-circuit photocurrent $I_{sc}^{*} = (I_l - I_d)_{sc}$ of various SC-SEP cells having different electrolytes in the dark compartment, were measured under dark and illuminated conditions. The output power values reported by Kondapaneni *et al.* (1992) will therefore represent the changes brought about only by the illumination. The individual potentials at the electrode/solution interfaces under dark and illumination were measured with reference to SCE.

SC-SEP cell under dark conditions

The auxiliary electrode in the illuminated compartment shows a negative polarity while the auxiliary electrode in the dark compartment has a positive polarity. After the SC-SEP cell is kept short circuited for 1 h in the dark, some silver (1%) gets deposited on the Ti surface and the auxiliary electrode in the dark compartment. The presence of silver was confirmed through chemical analysis and energy-dispersive analysis of X-ray (EDAX). This slight deposition of silver is probably due to the potential difference between the redox potential (E_{redox}) of the two half-cells (OH^- /O_2 and Ag^+/Ag) of the SC-SEP solar cell (Pandey, Chandra and Srivastava, 1996). The deposition of silver affects the dark I-V characteristics of the SC-SEP cell. The most significant effect is the shifting of the dark equilibrium potential and current . The output power values (V_{oc}^{*} and I_{sc}^{*}) of the SC-SEP cell reported in the present study are the differential values between the respective V_{oc} and I_{sc} under light-illumination (*l*) and dark (*d*). Therefore, the output power characteristics of the SC-SEP cell owe their origin to illumination.

The results discussed above suggest that the present SC-SEP cell may correspond to a rechargeable type of electrochemical photovoltaic cell. This cell can convert both the light and chemical energy into electrical power with better output than the conventional PEC cell. Further studies aimed at uncovering the details of individual electrode potential and capacitance at the five interfaces, the potential-dependent half-cell reactions at each electrode, and the chemical land electrochemical reversibility of the reactions at the four electrodes in the SC-SEP cell are in progress.

Murali *et al.* (1991; 1992) described the fabrication and the structural and photoelectrochemical characterization of a semiconductor-septum based photoelectrochemical (SC-SEP, PEC) solar cell, with a TiO_2-Ti septum electrode connecting the illuminated and dark compartments, containing different redox electrolytes. The output power characteristics (V_{oc} and I_{sc}) of the semiconductor-septum based photoelectrochemical (SC-SEP, PEC) solar cell having various redox couples such as Sn_4^+/Sn_2^+, Cu_2^+/Cu^+, Cu_2^+/Cu, Cu^+/Cu, $Fe(CN)_6^{3+}/Fe(CN)_6^{4-}$, I^-/I_2, Fe^{3+}/Fe^{2+}, Ag^+, Ag/Pt, Pd^{2+}/Pd and Pt^{2+}/Pt in the dark compartment have been studied. When redox couples of higher redox potential (E_{redox}) are added into the dark compartment, keeping ingredients of the illuminated compartment unchanged, there is an increase in the photovoltage of the semiconductor-septum based photoelectrochemical (SC-SEP, PEC) solar cell. For example, a conventional Pt, 1 M NaOH parallel to TiO_2-Ti PEC cell yields V_{oc} and I_{sc} of 0.7 V and 5 mA cm^{-2}, whereas Pt, 1 M NaOH parallel to TiO_2-Ti parallel to 0.1 M $AgNO_3$, Pt SC-SEP cell yields reproducible V_{oc} and I_{sc} values of 1.2 V and 15 mA cm^{-2}. When an external bias of +0.2 V vs. SCE is applied to this SC-SEP cell, the V_{oc} and I_{sc} values of this cell have been found to increase to 1.9 V and 9 mA cm^{-2}. The short-circuit photocurrent characteristics of this SC-SEP cell monitored for a long time revealed that the cell is quite stable. The structural and compositional analysis of septum electrode carried out through X-ray diffractometry, scanning electron microscopy, and EDAX confirmed that the TiO_2-Ti electrode shows a negligible change in its gross and surface structure with no discernible change in its elemental composition, even after prolonged operation. Goc and Tien (1993) investigated several combinations of electrodes in semiconductor septum electrochemical photovoltaic (SC-SEP) cells. Semiconductor layers on metal, separating two aqueous solutions were prepared using two methods, either by painting and annealing or by vacuum evaporation. The most stable and efficient of all the investigated cells seem to be the system in the following schematic configuration: GC/3-S/CdSe/CdS/Mo/H_2SO_4/GC. It was established that for hydrogen production applications, a vacuum deposited layer seems to be more promising than a painted one. The mechanism of ion transport in the investigated cells was explained in terms of their energy band scheme and the equivalent electrical circuit model. Concerning these, Wrobel *et al.* (1998) reported ion porphyrin dyes fulfill an essential function in photosynthesis and are important in photodynamic therapy and in a range of electronic devices. Their spectroscopic characteristics may play a crucial role in these processes. The spectral properties of two porphyrin dyes: tetraphenylporphyrin and tetraphenylsulfporphyrin in organic solvents (acetone, chloroform, methyl alcohol, and dimethylsulfoxide) and in polyvinyl alcohol and polymethylmethacrylate films have been investigated. Absorption, fluorescence and microsecond time-resolved delayed luminescence spectra have been measured at room temperature. The existence of different aggregated dye forms in the ground and excited states has been demonstrated. The manifold of dye species depends on the solvent/polymer. In the case of the polymers, it also depends on the solvent used to coat the polymer film. Delayed luminescence spectra and decay times of the two porphyrins in the different solutions and in polymeric matrices suggest that different mechanisms of deexcitation of the singlet excited states may be responsible for their generation in these and other porphyrin dyes.

Morales, Sebastian and Solorza (1998) reported preparation and characterization of CdSe/Ti and CdS/Ti photoelectrodes for their application in photoelectrochemical hydrogen production using a semiconductor septum solar cell configuration. The septum electrodes were characterized structurally, optoelectronically and photoelectrochemically for their use in septum solar cells for hydrogen production. Both these septum electrodes exhibited high photosensitive current in the solid-state and the photoelectrochemical solar cell configuration. The *i* - *E* (current density - potential) characteristics of the semiconductors in the photoelectrochemical cell configuration indicated promising photochemical energy conversion current (photocurrent). Pawar and Pawar (1996) reported preparative parameters of electrodeposited n-CdSe thin films on stainless steel pipe substrate and their use as septum electrode in semiconductor septum solar cells for hydrogen production are reported. For hydrogen production high intensity of light is required. In this note the authors report the design and construction of the cell for which line concentrator has been used for getting high intensity. Pandey, Babu and Srivastava (1996) reviewed the prospectives and perspectives of high conversion efficiency photoelectrochemical (PEC) solar cells. The PEC solar cells score over their solid state counterparts on several points. Some of these are ease of fabrication and inbuilt storage capability. In order to make PEC solar cells viable, their conversion efficiencies need to be enhanced so as to reach optimum values. Several feasible efficiency enhancement processes for PEC cells such as electrode surface modification, photoetching, electrolyte modification etc. have been described and discussed in this article. The case of efficiency enhancement of n-GaAs based PEC solar cell through the modification of GaAs by Os^{3+} or Ru^{3+} ions leading to efficiency enhancement from 9 to 15 % has been described and discussed. In regard to efficiency enhancement through electrolyte modification, the example of n-CdSe based PEC cell where the electrolyte $K_3Fe(CN)_6/K_4Fe(CN)_6$ is modified through KCN, has been dealt with. The efficiency obtained in this cell is up to similar to 16%. For the PEC solar cells embodying the d-d phototransition, MX(2) type layered materials, the most dramatic conversion efficiency enhancements come through photoetching of electrode surfaces. The authors have described and discussed in detail the efficiency enhancements in n-WSe_2/ I_3^- I^-/Pt solar cells through photoetching of n-WSe_2 photoelectrodes in 0.1 M aquaregia. High efficiencies up to similar to 17% have been obtained for those solar cells. Yet another route of fabricating viable PEC solar cells giving high power output corresponds to the development of newer PEC cell designs. One example of the newer cell designs, which has been described and discussed in this article, corresponds to semiconductor-septum (SC-SEP) PEC solar cell. The SC-SEP, PEC solar cells have been found to yield higher power outputs (V_{oc} and I_{sc}) than the conventional single compartment PEC cells. For example, n-CdSe/Ti septum based PEC solar cell with configuration: Pt , 1 M 3S/n-CdSe/Ti/0.1 M $AgNO_3$, Pt has been found to give higher power output (1.42 V and 20 mA cm^{-2}), as compared to n-CdSe based conventional PEC cell (0.64 V and 6 mA cm^{-2}). Similarly, n-TiO_2/Ti septum electrode based SC-SEP cell: Pt , 1 M NaOH/n-TiO_2/Ti/0.1 M $AgNO_3$, Pt also gives higher power output (1.2 V and 15 mA cm^{-2}). The case of another new PEC cell design incorporating nanostructured TiO_2 photoelectrode overlaid with special dye - Ruthenium trinuclear cyanide complex and exhibiting efficiencies of 7% (under usual solar illumination) and 12% (in diffuse solar light) has also been outlined. Yao and Cachet (1998) recently reported that the effects of electrolyte composition (solvent, redox species) are analyzed with respect to the charge transfer process at a semiconductor /electrolyte interface (SC/EL). A correlation between charge transfer and stabilization is established for gallium arsenide (GaAs) in contact with different solvents according to the redox couple reducing ability. It is shown that the charge transfer kinetics at n-GaAs/electrolyte junctions mainly depends on the redox couple position in the gap of the semiconductor, in agreement with the Marcus-Gerischer theory (Gerisher, 1979). The experimental study takes benefit of the redox properties of the heteropolyanion P2W18O626. In another study, Pandey, Misra and Srivastava (1998) reported photoelectrochemical and hydrogen evolution characteristics of CdSe/Ti and TiO_2/Ti based semiconductor-septum photoelectrochemical (SC-SEP, PEC) solar cell have been studied. The SC-SEP cell in the configuration: 1 M 3S//CdSe/Ti//5 M H_2SO_4, Pt(W) , Pt(C) gave power output of 0.62 V and 11 mA cm^{-2}, whereas the conventional PEC cell in the configuration: Pt , 1 M 3S//CdSe/Ti gives power output of 0.64 V and 6 mA cm^{-2}. The hydrogen evolution characteristics of the CdSe/Ti septum based SC-SEP cell in the following configuration: 1 M 3S//CdSe/Ti//5 M H_2SO_4 , Pt(W) , Pt(C) exhibited a rate of 1.0 to 1.5 l h^{-1} m^{-2} under an illumination intensity of 80 mW cm^{-2}. The TiO_2/Ti septum based SC-SEP solar cell in the configuration: 1 M NaOH//TiO_2/Ti//5 M H_2SO_4 , Pt(W) , Pt(C) gives power output of 0.74 V and 14.5 mA cm^{-2}, whereas the conventional PEC solar cell in the configuration: Pt , 1 M NaOH//TiO_2/Ti gives power output of 0.7 V and 5 mA cm^{-2}. The hydrogen evolution characteristics of TiO_2/Ti based SC-SEP cell measured in the configuration: 1 M NaOH//TiO_2/Ti//5 M H_2SO_4 , Pt(W) , Pt(C) gave a hydrogen evolution rate of 10-15 l h^{-1} m^{-2} under an illumination intensity of 450 mW cm^{-2}. It has been shown in the present investigation that TiO_2/Ti based SC-SEP solar cell is more stable and gives higher rate of hydrogen production compared to the CdSe/Ti based SC-SEP cell. Further studies to optimize the stability and other conditions for the production of solar hydrogen using these SC-SEP solar cells have been outlined. Misra, Pandey and Srivastava (1997) reported a SC-SEP cell with the configuration:

SCE/1 M NaOH/TiO_2/Ti/H_2SO_4+K_2SO_4/Pt-CE, Pt-WE (21)

The current-voltage characteristics of the above SC-SEP cell revealed an enhancement in short-circuit current I_{sc} up to three times (from 5 to 15 mA cm^{-2}) that of its single compartment PEC cell counterpart based on the n-TiO_2 photoelectrode. The rate of hydrogen production was found to change with variation in the concentration of the electrolyte in the dark compartment, e.g. for 1 M H_2SO_4 it is 6.31 1 h^{-1} m^{-2} and for 5 M it is 13.15 1 h^{-1} m^{-2}. The optimum hydrogen production rate was found to be 13.15 1 h^{-1} m^{-2} for 5 M H_2SO_4. With a further increase in H_2SO_4 concentration, the hydrogen production rate was found to be invariant. The hydrogen production rate of TiO_2/Ti based SC-SEP cells when compared with the only other known SC-SEP cell based on n-CdSe/Ti and corresponding to the configuration: SCE/polysulfide + 0.1M selenium solute/n-CdSe/Ti/5 M H_2SO_4/Pt-CE , Pt-WE exhibits a hydrogen production rate higher by about 10 times. In summary, chemical nature of surface of the dark side of septum plays according to this work an important role in performance of the cell. Desirable surface should provide excellent catalytic activity and more positive interfacial potential. A more efficient material modified on the dark side of septum and a mechanism of the influence of interfacial potential on the current and on the potential under dark and illumination conditions have been studied in publications of Murali *et al.* (1991). Murali and associates stressed in their work the potential appliction of metal recovery from industrial waste for SC-SEP cells, where the septum enables oxidation and reduction reactions in separate compartments. What limits a full realization of these concepts to practical utilization is the need to fabricate large area electrodes with higher efficiencies. They have electrodeposited CdSe films (5 mm thick) on Ti substrates (25 cm^2 for 20 min at room temperature from a bath containing 0.5 M $CdSO_4$ and 0.1 M $NaSeO_2$ (pH=4). The films were sensitized at 823 K = 550°C in argon atmosphere and cooled at different rates. In a recent study Srivastava, Karn and Misra, (2000) reported photoelectrochemical and hydrogen evolution characteristics of a new type of SC-SEP cell in the configuration: *Ref. electrode/1 M NaOH/*TiO_2*(ns)/Ti/*H_2SO_4*+*K_2SO_4*/Pt-Contacting electrode , Pt-Working electrode*. It showed the photovoltage and photocurrent of 0.72 V and 8.6 mA cm^{-2}, whereas the SC-SEP cell employing In_2O_3 mixed TiO_2(ns) photoelectrode and having the configuration: *SCE/1 M NaOH/*TiO_2*(ns)-*In_2O_3*/Ti/*H_2SO_4*+*K_2SO_4*/Pt-CE , Pt-WE* showed the photovoltage and photocurrent of 0.92 V and 14.6 mA cm^{-2}, respectively. The hydrogen gas evolution for the SC-SEP cell based on TiO_2(ns)/Ti photoelectrode was found to be 8.2 1 h^{-1} m^{-2}. On the other hand the In_2O_3 modified TiO_2(ns) exhibited a higher hydrogen gas evolution rate of 11.8 1 h^{-1} m^{-2} (*cf.* Tien and Chen, 1989). The better performance of the new septum electrode is thought to be due to improved spectral response and catalytic activity of In_2O_3 in regard to the hydrogen gas evolution kinetics. Evidence and arguments have been put forward to show that the presence of In_2O_3 over TiO_2 makes the system having the advantages of a colloidal photochemical system (Ginley *et al.*, 1996). Finally, mention should be made of papers by Subramanian, Mahalingam, Sanjeeviraja, Jayachandran M. and Chockalingam, (1998) and by Rajpure and Bhosale (2000) who fabricated a SC-SEP storage cell with the configuration: *C/0.5 M Polyiodide/n-*Sb_2S_3*/Ti parallel to 0.1 M* $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$*/C*. The charging and discharging modes were studied and found that the storage of chemical energy in the semiconductor-septum cell is possible by using Sb_2S_3 electrode.

Concluding Remarks

In concluding, many semiconductor materials can be used to construct SC-SEP cells with a variety of redox electrolytes and contacting electrodes. In analogy with the photosynthetic membrane, the light-generated electrons and holes may be utilized to react not only with water but other related species such as H_2S, isopropanol, etc. Extension of the SC-SEP cells for the photoxidation of halides and photoreduction of CO_2 and nitrogen as well as other compounds is of evident interest and should be carried out. The present work describes a SC-SEP in which electricity and/or hydrogen can be produced. The SC-SEP cell is simple in construction and operates under visible light illumination without any externally applied bias voltage. When operated under short-circuit conditions, the cell may be used for the inexpensive process-scale photolysis of seawater to hydrogen, using solar energy.

Currently, experiments increasing the efficiency of the SC-SEP cell by improving the design and by using SC materials, metal substrates, catalysts, other electrolytes as well as different deposition techniques of semiconductors onto metal foils (Xia,. Xiao, Yuan H. Y., Chen, Yuan, F. C. and Yu, 1999). From a purely technical viewpoint, hydrogen is almost an environmentalist's dream come true. The combustion of hydrogen in air generates no pollutants such as carbon monoxide, volatile organic compounds, sulfur dioxide, and carbon dioxide. It is well known that these pollutants are associated with urban air quality, acid rain and the greenhouse effect. When hydrogen burns in air, the main product is water with minor by-product of nitrogen oxide. Thus, with the oil shocks of the 1970s, the prospect of hydrogen fuel produced with solar energy is exciting. In this publication a novel two-compartment photocell, termed the semiconductor septum electrochemical photovoltaic (SC-SEP) cell, that is capable of generating hydrogen from water without externally applied voltage and using only the visible light of the solar spectrum. It is anticipated that, with more developmental work, improvements in the efficiency of the SC-SEP cell for hydrogen production can be made through better designing of the SC-SEP cell and by using other polycrystalline semiconductor materials of nano-dimensions, metal substrates, catalysts, and electrolytes in the illuminated compartment. Some experiments detailed and reviewed in this paper are currently in progress.

REFERENCES

Amao Y., Kamachi T. & Okura I. (1998). Preparation and characterization of water-soluble viologen-linked zinc porphyrin and bisviologen-linked zinc porphyrin. *Inorganica Chimica Acta*, **267**, 257-263.

Barber J. (Ed.) (1979). *Photosynthesis in Relation to Model Systems* (Vol. 3). New York: Elsevier/North Holland.

Bhardwaj R. C. & Tien H. T. (1990). Nickel based CdSe, CdS, and $CdSe_{1-x}$ semiconductor separator in 2-

compartment electrochemical photocells. *Int. J. Energ. Res.*, **14**, 1-7.

Bi Z.-C., Qian Y.-Y., Zhao X.-L., Shen S.-Y., Yu J.-Y., Xu H.-J. & Tien H. T. (1994). Photosensitization systems of covalently linked phthalocyanine complexes in both BLMs and tin oxide photovoltaic cell. *Photochem. Photobiol.*, **59,** 111-115.

Bolton J. R. (Ed.) (1977). *Solar energy and fuels*. New York: Academic Press.

Cai N. X., Li Q., Dong Q. & Jian C. (1991a). SC-SEP cells I. *Chinese J. Appl. Chem.*, **8**, 1-5.

Cai N. X., Jiang M., Dong Q. & Jian C. (1991b). SC-SEP cells II. *Aeta Energiae Solaris Sinica*, **12**, 155-160.

Daniels F. (1964). *Direct use of the sun's energy*. New Haven: Yale University Press.

Davison S. G. (Ed.) (1989). *Photobiophysics and photobiology. Progress in surface science.* New York: Pergamon Press.

Delarosa M. A., Navarro J. A. & Roncel M. (1991). Solar-energy conversion from water photolysis by biological and chemical-systems. *Appl. Biochem. Biotech.*, **30,** 61-81.

De Silva K. T. L. & Tien H. T. (1990). Semiconductor septum electrochemical photovoltaic cell with electrodeposited CdSe thin-films. *Int. J. Energy Research*, **14**, 209-213.

Dhumure S. S. & Lokhande C. D. (1993). Studies on photoelectrochemical storage-cells formed with chemically deposited CdSe and Ag_2S electrodes. *Sol. Energ. Mat. Sol. C*, **29**, 183-194.

Frackowiak D., Erokhina L. G., Jadzyn Cz., Shubin L. M. & Shkuropatov A. Y. (1981). Photo-voltaic effect of biliproteins, their subunits and aggregates. *Photosynthetica*, **15**, 36-48.

Gerischer H. (1979). Solar photoelectrolysis with semiconductor electrodes. [In:] Seraphin B. O. (Ed.), *Solar energy conversion* (pp. 115-143). Berlin: Springer-Verlag.

Ginley D. T., Catalano H. W., Schock C., Eberspacher T., Peterson, M. & Wada T. (Eds.) (1996). *Thin films for photovoltaic and related device applications, materials research society* (Vol. 426). Warrendale, PA.

Goc J. & Tien H. T. (1993). Electron and ion transport in SC-SEP cells with semiconductor thin film electrodes. *Int. J. Hydrogen Energy*, **18**, 5-12.

Hautala R. R., King R. B. & Kutal C. (Eds.) (1979). *Solar energy: Chemical conversion and storage* (pp. 419-420). New Jersey: Humana Press.

Hodes J. S. J., Fonash A., Heller B. & Miller J. (1983). [In:] Gerischer H. (Ed.), *Advances electrochemistry and electrochemical engineering* (pp. 113B-158B). New York: Wiley.

Jackowska K. & Tien H.T. (1988). Photoelectrochemical cell with semiconductor septum electrode. *Solar cells*, **23,** 147-157.

Jiang D. L., Li J. X., Diao P., Jia Z. B., Tong R. T., Tien H. T. & Ottova A. L. (2000). Photoinduced electron transfer across a gold supported octadecanethiol/phosphatidylcholine hybrid bilayer membrane mediated by C-60 in different redox species solution. *J. Photochem. Photobiol. A-Chem.*, **132,** 219-224.

Kalyanasundaram K. (1987). *Photochemistry in microheterogeneous systems*. New York and Tokyo: Academic Press, .

Kondapaneni S. Ch., Singh D. & Srivastava O. N. (1992). TiO_2-Ti semiconductor septum based electrochemical photovoltaic cell. *J. Phys. Chem.*, **96**, 8094-8099.

Kureishi Y., Tamiaki H., Shiraishi H. & Maruyama, K. (1999). Photoinduced electron transfer from synthetic chlorophyll analogue to fullerene C_{60} on carbon paste electrode. Preparation of a novel solar cell. *Bioelectrochemistry and Bioenergetics*, **48**, 95-100.

Metzner H. (Ed.) (1978). *Photosynthetic Oxygen Evolution*. New York: Academic Press.

Misra M., Pandey R. N. & Srivastava O. N. (1997). Solar hydrogen production employing n-TiO_2/Ti SC-SEP photoelectrochemical solar cell. *Int. J. Hydrogen Energy*, **22**, 501-508.

Morales M., Sebastian P. J. & Solorza O. (1998). Characterization of screen printed Ti/CdS and Ti/CdSe photoelectrodes for photoelectrochemical hydrogen production. *Sol. Energ. Mat. Sol. C*, **55**, 51-58.

Murali K. R., Subramahian V., Rangarajan N., Lakshmanan A. S. & Rangarajan S. K. (1991). Photoelectrochemical studies on pulse plated CdSe films. *Journal of Electroanalytical Chemistry*, **303**, 261-266.

Murali K. R., Subramanian V., Rangarajan N., Lakshmanan A. S. & Rangarajan S. K. (1992). Cd(SeTe) Septum Photoelectrochemical Cells. *J. Appl. Electrochem.*, **22**, 87-89.

Mountz J. M. & Tien H. T. (1978). The photogalvanovoltaic cell: A new approach to the use of solar energy. *Solar Energy*, **21**, 291-294.

Naser N. S., Planner A. & Frackowiak D. (1998). Action spectra of the photopotential generation for pigment and dye solutions in nematic liquid crystals located in the electrochemical cell. *J. Photoch. Photobiol. A*, **113,** 279-282.

Ottova A., Otto M. & Cerhata D. (1991). Semiconductor septum electrochemical photovoltaic cells with CdSe, CdTe and $CdSe_xTe_{1-x}$ for water photolysis. *Bulletin of Electrochemistry*, **7**, 232-234.

Pandey R. N., Babu K. S. C. & Srivastava O. N. (1996). High conversion efficiency photoelectrochemical solar cells. *Prog. Surf. Sci.*, **52**, 125-192.

Pandey R. N., Chandra K. S. & Srivastava O. N. (1996). High conversion efficiency photoelectrical solar cells. *Prog. Surf. Sci.*, **52**, 125-192.

Pandey R. N., Misra M. & Srivastava O. N. (1998). Solar hydrogen production using semiconductor septum (n-CdSe/Ti and n-TiO_2/Ti) electrode based photoelectrochemical solar cells. *Int. J. Hydrogen Energy*, **23**, 861-865.

Pawar S. H., Patil P. S., Madhale R. D. & Lokhande C. D. (1989). Preparative parameters and dependent properties of Fe_2O_3 films formed by spray pyrolysis technique. *Indian Journal of Pure & Applied Physics*, **27**, 227-230.

Pawar S. H. & Pawar P. D. (1996). Line septum solar cell for hydrogen production. *Indian Journal of Pure & Applied Physics*, **34**, 504-505.

Rabinowitch E. (1961a). *Photosynthesis and Related Processes*.New York: Interscience.

Rabinowitch E. (1961b). Photosynthesis and related processes. *Proc. Natl. Acad. Sci.*, **47**, 1296-1306.

Rajpure K. Y. & Bhosale C. H. (2000). Sb_2S_3 Semiconductor-septum rechargeable storage cell. *Materials Chemistry Physics*, **64**, 70-74.

Rokitskaya T. I., Antonenko Y. U. & Kotova E. A. (1998). The interaction of phthalocyanine with planar lipid bilayers – photodynamic inactivation of gramicidin channels. *FEBS Lett.*, **29**, 32-335.

Seta P. & Bienvenue E. (1985). Solar energy. *Images Chimie, Suppl. CNRS*, **65**, 1-10.

Srivastava O. N., Karn R. K. & Misra M. (2000). Semiconductor-septum photoelectrochemical solar cell for hydrogen production. *Int. J. Hydrogen Energy*, **25**, 495-503.

Subramanian B., Mahalingam T., Sanjeeviraja C., Jayachandran M. & Chockalingam M. J. (1998). Electrodeposition of SnS thin films from aqueous medium. *Bull. Electrochem.*, **14**, 398-401.

Tan Z., Luo W., Ren P., Sun X., Tien H. T. & Ottova A. (1994). Improved studies of septum electrode in semiconductor septum electrochemical photovoltaic (SC-SEP) cells. *Proc. Hydrogen '94*, Cocoa Beach, FL, pp. 1-6.

Tien H. T. (1968). Light-induced phenomena in black lipid membranes constituted from photosynthetic pigments. *Nature*, **219**, 272-275.

Tien H. T. & Verma S. P. (1970). Electronic processes in bilayer lipid membranes. *Nature*, **227**, 1232-1235.

Tien H. T. (1974). *Biology and Semiconduction in Solid-state Physics and Chemistry* (Ch. 14.). Weller P. F. (Ed.), New York: Dekker, Inc.

Tien H. T. & Karvaly B. (1977). *Ultrathin barriers and solar energy conversion in solar power and fuels* (pp. 167-225). Bolton J. R. (Ed.), New York: Academic Press.

Tien H. T. & Higgins J. (1982). Electrochemical solar cells with two photoactive electrodes. *Chem. Phys. Lett.*, **93**, 276-278.

Tien H. T., Bi Z.-C. & Tripathy A. K. (1986). Photoresponses of semicoductor polycrystallites separating two aqueous solutions. *Photochem. Photobiol.*, **44**, 779-783.

Tien H. T. & Chen J. W. (1989). Hydrogen generation from artificial seawater in a semiconductor septum electrochemical photovoltaic cell. *Photochem. Photobiol.*, **49**, 527-530.

Tien.H.T. (1990). Solar induced hydrogen production in a semiconductor septum electro-chemical photovoltaic (SC-SEP) cell. *Advanced Materials*, **2**, 263-266.

Tien H. T. & Chen J. W. (1990). Hydrogen production from water by SC-SEP cell using visible light. *Int. J. Hydrogen Energy*, **15**, 563-568.

Tien H. T. & Chen J. W. (1992). Photoelectrolysis of water in semiconductor septum electrochemical photovoltaic cells. *Solar Energy*, **48**, 199-204.

Tien H. T. & Ottova A. L. (2000). *Membrane Biophysics: As viewed from experimental bilayer lipid lipid membranes (planar lipid bilayers and spherical liposomes)* (Ch. 9 and 10). Amsterdam and New York: Elsevier.

Todkar B. M., Lawangar R. D., Pawar S. H., Awana V. P. S., Agarwal S. K. & Narlikar A. V. (1990). Electroluminescence of Gd-doped Y-Ba-Cu-O superconductors. *Materials Letters*, **9**, 421-424.

Tripathy A.K. & Tien H. T. (1987). Dual electrolyte semicondutor contact CdSe electrochemical photocells. *J. Appl. Electrochem.*, **17**, 569-573.

Volkov A. G., Deamer D. W., Tanelian D. L. & Markin S. V. (1998). *Liquid Interfaces in Chemistry and Biology* (pp. 406-451). New York: Wiley, Inc.

Wardak A., Brodowski R., Krupa Z. & Gruszecki W. I. (2000). Effect of light-harvesting complex II on ion transport across model lipid membranes. *J. Photochem. Photobiol., B*, in press.

Wrobel D., Hanyz I., Bartkowiak R. & Ion R. M. (1998). Fluorescence and time-resolved delayed luminescence of porphyrins in organic solvents and polymer matrices. *J. Fluorescence*, **8**, 191-198.

Xiao X.-R. & Tien H. T. (1983). Electrochemical solar cells using CdSe thin film electrodes. *J. Electrochem. Soc.*, **130**, 55-61.

Xia S. X,. Xiao D., Yuan H. Y., Chen B. J., Yuan F. C. & Yu R. Q. (1999). Copper(II) ion-sensitive electrode using chemical vapor deposited Nb-Ge superconducting films. *Analytica Chimica Acta*, **382**, 151-156.

Yao N. A. & Cachet H. (1998). Charge transfer kinetics and stabilization at the n-GaAs/aqueous and non aqueous electrolyte interface. *Journal de Chimie Physique et de Physico-Chimie Biologique*, **95**, 1118-1133.