CHAPTER I - INTRODUCTION

1.1 GENERAL

Energy is a fundamental issue to all people, permeates the fabric of human life. Guaranteeing a long term energy supply is one of the most important pre-requisities for maintenance and further development of every national economy. In recent years, energy has acquired significant importance due to what has been called, the world's energy crisis. The growing demand of energy through the world has caused great importance to the exploration of new source of energy.

The energy crisis in 1970's stimulated research in energy related areas, perticularly those useful for utilization of solar energy [1]. Solar energy available on the surface of the earth constitutes clean, abundant and relatively cheap energy sources. Nearly, all the sources of energy in the world, derive directly or indirectly from solar energy. The number of possible path ways for trapping solar energy can be examined, such as,

1)	Photovoltaic	2)	photogalvanic
3)	Photothermic	4)	Photosynthetic
5)	Ocean	6)	Wind etc.

The interest in energy resources through photochemical routes has stimulated since 1973. Fujishima and Honda [2] demonstrated first time the decomposition of water into hydrogen and oxygen by using photoelectrochemical (PEC) cell.

In recent years, semiconductor electrolyte junction solar cells have been attracting a great deal of interest in the field of solar energy conversion, as they may have many advantages over the convensional p-n junction or Schottky barrier cells [3]. Reviews of extensive investigation of the electrochemistry of semiconductor materials and their photo effects have appeared in literature [4-7].

A large area polycrystalline film of n-CdSe and Cd(Se,Te) have been prepared by different techniques such as pressure sintered, evaporation, slurry painted, sprayed. Vacuum deposited, spray pyrolysis etc. [8-9]. Pawar and his co-workers [10] have electrodeposited Cd(Se,Te) films on titanium substrates. ECPV cells can be converted into electrochemical storage cells. Tien and Jockowska have developed a semiconductor septum cell. Tien et al [11] have made a semiconductor septum cell for photoelectrolysis of sea water. Pawar and Patil have further developed semiconductor septum solar cell as a semiconductor redox storage cell [12]. Recent investigations in the field of energy resources have been aiming at harnessing the solar energy to meet the challenges of diminishing fossil fuels.

If solar energy to be then one should convert this into fuel such as hydrogen, which can be easily transportable.

1.2 ENERGY RESOURCES

Primitive man required energy in the form of food. He discovered fire and his energy needs increased as he started to make use of wood and other biomass to supply the energy needs for cooking as well as keeping himself warm. With further demand for energy, man began to use the wind for sailing ships and for driving wind mills and the force of falling water to turn water wheels.

Industrial revolution (1700 A.D.) which began with the discovery of the steam engine brought about many changes. For the first time, man began to use a new source of energy viz. coal, in large quantities. A little later (1870 A.D.) the internal combustion engine was invented and the other fossil fuels, oil and natural gas began to use extensively.

The demand of energy depends on actual need for usable energy and, therefore, foremost on the living standards, the range of products, life style and consuming habits of an economy, and the climate of the regions concerned. Today, evrey country draws its energy needs from a variety of sources. We can broadly categorize these sources as commercial and non-commercial.

The commercial sources include the fossil fuels (coal, oil and natural gas), hydropower and nuclear power, while the non commercial sources include wood, animal wastes and agricultural wastes. In the past few years, it has become obvious that fossil fuel resources are fast depleting and that the fossil fuel era is gradually coming to an end. This is perticularly true for oil and natural gas.

The combusion of fossil fuels has caused serious air pollution problems in many areas because of the localised release of large amounts of harmful gases into the atmosphere. In the case of nuclear power plants, there is also concern over the possibility of radio-activity being released into the atmosphere in the events of an accident and over the long term problems of disposal of radio-active wastes from these plants.

Solar energy is an essentially inexhaustible source, potentially capable of meeting a significant portion of world is future energy needs with minimum of adverse environmental consequences. Solar energy is renewable because the Sun is an enormous fusion reactor, provided with such large amounts of hydrogen gas for combustion that a steady power input to the earth's surface is ensured for millions of years to come.

The power from the Sun intercepted by the earth is approximately 1.8×10^{11} MW, which is many thousands of times larger than present consumsion rate on the earth of all commercial energy sources. The energy from the Sun can be used directly and indirectly. The direct means, it includes thermal and photo-voltaic conversion while, indirect solar energy includes use of water power, biomass etc. Other sources of energy are [13],

1) Tidal and Wave Energy
2) Geothermal Energy
3) Tar Sands and Oil Shale
4) Wind Energy
5) Ocean Thermal Energy

1) Tidal and Wave Energy

Tides are generated primarily by the gravitational attraction between the earth and the moon. They arise twice a day. In mid-ocean the tidal range is only a metre or less but in some coastal estuaries, it is much greater. This is due to the amplification of tidal wave as it moves up the narrowing channel of the estuary.

Basically, in a tidal power station, water at high tide is first trapped in an artificial basin and then allowed to escape at low tide. The escaping water is used to drive water turbines which in turn drive electrical generators Jeffreys [14] has estimated that the rate of tidal energy dissipation for the world is about 3×10^6 MW. However, only small fraction of this can be exploited since, for practical purposes, one needs a certain minimum difference level between the high and low tides. Hubbert has compiled the available information on favourable locations and tidal power which can be generated at each of them, and estimates that a maximum capacity of 63800 MW can be harnessed [15].

Wave energy arises because of the interaction of the winds with the surface of oceans.

2) Geothermal Energy

Geothermal energy is energy coming out of the molten interior of the earth towards the surface. The average rate at which this heat emerges is about 0.05 W/m^2. Ground water comes into contact with the hot rocks in some of these locations and as a result, either dry steam or wet steam and water are formed. A well drilled to these locations causes the dry or wet steam to emerge at the surface where it's energy can be utilized either for generating electricity or for space heating. The first commercial geothermal power was erected in Italy. An estimate of the amount of electricity which could be generated from geothermal dry or wet steam sources all over the world has been made by white [16]. This estimate indicates that about 62500 MW, could be generated for period of 50 years. The Gothermal resource, which is really large, is the heat stored locally at depth of 1 or 2 km in the earth's mantle in hot dry rocks with which water has not come into contact.

3) Tar Sands and Oil Shale

As supplies of crude oils are getting depleted, attension is increasingly being focussed on two or naturally occuring sources in which the crude is found intimately mixed with either large proportions of sand or rock. These sources are called tar sands and oil shale. The tar is first separated from the sand. In order to do this, the mixture of sand and tar is transported to an extraction plant where, it is treated with hot water and steam in a slurry vessel. The sand separates and is discarded. Subsequently, the water and oil are separated.

4) Wind Energy

Wind energy is usually converted into mechanical or electrical power by wind mill-type systems. In Netherlands, for instance, about 20,000 wind mills of 20 KW each were in operation at the end of 18th century, most of them for polder drying.

5) **Ocean Thermal Energy**

The oceans cover 70% of surface of the globe and are particularly extensive in the tropical zones, therefore most of the Sun's radiation is absorbed by sea water; while, at the Ocean surface warm water flows from tropics towards the pole, along the ocean floor cold water circulates from thepole to tropics. Hence, in the tropics, the water temperature is 5°C at a depth of 1000 Km, where as at the surface it remains almost constant at 25°C. To extract power from this temperature gradient by means of carnot-type process such as a turbine-driven generator, the two currents must be found close together.

1.3 SEPTUM SOLAR CELLS

Most of the research of PEC has been conducted in a single compartment cell where the semiconductor is dipped in an electrolyte coupled with a counter electrode. In recent years, photoelectrochemical (PEC) solar cells have been attracting a great deal of interest in the field of solar energy conversion, as they may have many advantages over the convensional p-n junction or Schottky barrier cells. However several groups, have attempted the use of a membrane based PEC system for solar energy storage device and reviews of earlier work are available [17-18].

When the semiconductor electrode had taken as a separator of two aqueous compartments in PEC cell. It is called as a semiconductor septum (SC-SEP) solar cell. The single compartment construction limits the maximum, photoelectrical response to the degree of band bending and is controlled; therefore by fermi level for a given semiconductor and redox couple. This major drawback has been overcome in the so called semiconductor septum electro-chemical photo-voltaic (SC-SEP) cell. The idea for constructing such type of redox storage cell has taken from the work reported by Pawar et al [19].

The solar energy storage cells can be classified as follows.

Solar Energy Storage Cells

Redox storage electrode	Redox storage electrolyte	Semiconductor septum

The first two types of redox storage cells are well known, however, the solar energy storage with help of semiconductor septum cells is most promising due to its inherent properties. In this cell, under illumination, one side of the membrane solution interface reduction occurs while on the otherside oxidation takes place. SC-SEP cell can be used both for hydrogen production as well as electricity generation.

1.4 HYDROGEN PRODUCTION

In addition to the primary energy sources, there are many secondary alternatives. A good example of a secondary source is hydrogen, which has to be produced from water. Over the past few years much attention has been given to systems capable of the storage of solar energy in one form to another [20].

At present, there is considerable interest, from both academic institutions and industry, in the development and construction of a practical device capable of the collection and storage of solar energy in the form of chemical potential. Although by no means the only way of achieving this goal, the photogeneration of hydrogen from water offers a perticularly promising route and it is being actively pursued using photoelectrochemical, photochemical and photobiological approaches. One of the most attractive subjects until now, has been the photodissociation of water in H_2 and O_2 upon excitation with visible light, since this provides a means of storing sunlight in the form of a fuel hydorgen. This achievement would be rather a cheap way of collecting and storing water and so far at least, sunlight is freely available. In doing so we copy the natural photosynthetic process of green plants.

The production of hydrogen by water splitting is possible as follows.

1. Photoelectrochemical water splitting

It is based on the absorption of photons and generation of electron-hole pairs in a semiconductor in contact with an aqueous electrolyte.

2. Photochemical water splitting

This method requires just like photoelectrochemical methods, a suitable absorber in which radiation is transformed initially into potential energy of an excited state, which in turn initiate subsequent processes that trigger chemical reactions by electron transfer from an excited absorber system to redox system [21].

3) Photo-biological water splitting

In photobiological method, at the evolationary stage of bacteria and blue alge prokaryotes and among some green algae eukaryotes exists the capability to release hydrogen and oxygen with the aid of solar energy.

A key step for the biochemical formation of H_2 consists of the transfer of two electrons to protons for their reduction.

$$2H^+ + 2e^- \longrightarrow H_2 \uparrow$$

4) Thermal steam water splitting

In this method water splitting occurs at temperature above 200°K without requiring any other auxillary redox systems. However, the temperature required for thermal steam splitting are so high that resulting technical problems appear tomake thermal water splitting impossible.

5) Thermo chemical cyclic process

The thermo-chemical cyclic process, in contrast to direct chemical water splitting, the coupling of several equilibrium reactions which in separate process steps and different temperature level permit the separate release of hydrogen and oxygen at temperature less than 1200°K.

As an example the high temperature dissociation of metal oxide to oxygen and metal is coupled to the low temperature reaction of the same metal with water releasing hydrogen

$$MeO_2 \xrightarrow{\text{high temp.}} 2Me + \tfrac{1}{2}O_2$$

$$2Me + H_2O \xrightarrow{\text{low temp.}} MeO_2 + H_2 \uparrow$$

6) Water splitting by Electrolysis

For water electrolysis in general the minimum amount of electrical energy required is determined by the free enthalpy of the reaction.

At Cathode : $2H_2O + 2\bar{e} \longrightarrow H_2 + 2O\bar{H}$

At Anode : $2OH^- \longrightarrow \tfrac{1}{2}O_2 + H_2O + 2\bar{e}$

$$H_2O \xrightarrow{2F} H_2 + \tfrac{1}{2}O_2$$

$$\Delta \overset{\circ}{G} = 2F\overset{\circ}{U}$$

The theoretical decomposition voltage of water electrolysis at 25°C and 1 bar pressure is Uo = 1.23 V.

A number of methods exists for producing hydrogen by electrolysis. Water electrolysis using hydropower as the primary energy source is effective method of producing hydrogen. Energy from a nuclear power plant can be used to produce hydrogen indirectly via electrical power.

7) Hydrogen production from sea water

A novel two-compartment solar cell, termed the semiconductor septum electrochemical photovoltaic (SC-SEP) cell and modeled after natural photosynthesis has been used to generate hydrogen from sea water without externally applied voltage and using only visible light of solar spectrum.

1.5 HYDROGEN ENERGY APPLICATIONS

Hydrogen offers specieal advantages over existing energy technologies.

1) Large Scale Firing with Hydrogen

Asides from hydrogen|oxygen rocket engines which have contributed considerably to technical advances in this field hydrogen is burned in large amounts in the chemical industry to produce heat, especitlaly when it is not economical to purify it.

2) Gas Turbines

Gas turbines can be used as heat engines or jet engines even with hydrogen. They have the advantage of low maintenance and long life. Hydrogen completely avoids the problems of sediments and corrosion on turbine blades caused by residues and ash particles from liquid fossil fuels that, together with compressed air, get in to the turbines.

3) Internal Combustion Engines

Internal combustion engines are basically suited to hydrogen operation and they represent a very good compromise between manufacturing costs and durability. Hydrogen thus enables an extensive reduction of harmful engine emissions as compared to convensional fuels [22].

4) Hydrogen as Fuel

As one of the candidate among various alternatives fuel possibilities, hydrogen offers gradually increasing uses.

5) Hydrogen for Vehicles

It can be stored in motor vehicles as high pressure gas or in chemical form as NH_3 or CH_3OH. Internal combustion engines, gas turbines as well as fuel cells linked to electric motors can all be powered by hydrogen.

1.6 PURPOSE OF DISSERTATION

Recent publications indicate that pigmented bilayer lipid membranes are also of interest in the field of solar energy conversion.

Photoelectrochemical cells employing semiconductor and redox system have been extensively studied since last decade, because of their significant advantages over solid state photo-voltaic cells [23]. The concept of semiconductor septum (SC-SEP) solar cells is based on modeling of natural photo-synthesis system with a [BLM] pigmented bilayer lipid membrane [24-27].

Thus in developing systems for practical applications Tien et al [28] have replaced pigmented BLM with inorganic semiconductor in a novel type of photoelectrochemical cells. The semiconductor septum can be produced by using different techniques like spray pyrolysis, slurry painting, electrodeposition.

But, electrodeposition is an attractive method of preparation of thin films, the main advantage being the easy to control growth rate trough electrical quantities. The large band gap materials do not respond to visible light, while relatively low band gap materials like CdSe (1.7 eV) respond to major fraction.

Most of research on PEC cell has been conducted in small scale. However, few reports are available on large scale. Here we have tried to work on large size semiconductor septum solar cells.

In present investigation, we report on the preparative parameters of electrodeposited large area n-CdSe thin film on stainless steel substrate. The deposition potential is fixed from polarization curve. After annealing n-CdSe films their micrographs and X-R-D patterns are recorded and thickness is measured. The semiconductor septum cells are constructed by employing these n-CdSe films as separator of two different redox electrolytes in two compartments.

An attempt has been made to study hydrogen production at static electrolytic conditions from artificial sea water by changing different parameters like semiconductor septum area, volume of electrolytes and intensity of illumination. The hydrogen production at electrolytic dynamic conditions for continuous and interrupted flow of electrolytes has been studied. The charging and discharging mode upon illumination and in dark are also studied.

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