

CHAPTER 1

INTRODUCTION

1.1 ENERGY SCENARIO

Since 1973, the word "energy" has been continuously in the news [1]. The increasing demand of energy has greatly stimulated the research into new sources of energy during the last few years. Solar energy holds a great promise from this point of view. The conversion of solar energy into electrical energy was first realized via p-n junction and schottky type photovoltaic devices [2]. This photovoltaic effect was observed in all solid state system in 1876 for the case of selenium. Further work in the 1930's on this material and on Cu-Cu₂O structures pioneered the way to the successful development of exposure meters for photography and no credence was given to the idea of utilizing the photovoltaic effect for producing electricity. Although a silicon cell was reported in 1941, it was not until 1954 that the forerunner of present silicon cells was announced and utilized as the source of electricity in space craft as early as 1958. By the early 1960, the design of the cells for the space use and stabilized and over the next decade, this was their major application.

The energy crisis in 1970's all over the world created the interest in terrestrial applications of solar

cells and this is the innovative period in the solar cell development with marked increase in realizable energy conversion efficiencies and newer device technologies. Several substantial break throughs in silicon solar cells have occurred in recent years. The conversion efficiency of silicon solar cell has been improved year by year. Recent research activities show that instead of using a p-n junction device, the solar energy conversion can be easily achieved by using an electrolytic photoelectrochemical (PEC) solar cell and it offers a relatively more attractive alternative. After the successful demonstration of the photoelectrolysis of water at n-TiO₂ electrodes by Honda and Fujishima [3], scientists thought of solving the problems associated with photovoltaic solar cells.

The photoelectrochemical cells have been widely studied for solar as well as non-solar applications. Recently, bibliography was published by Kalyanasundaran [4] giving a list of 1308 research papers published for the period of 1975-1983 on PEC cells. CdSe and Cd(Se, Te) in the form of a single crystal, sintered pellets and polycrystalline materials have been employed in PEC cells [5].

A large area polycrystalline films of CdSe and Cd(Se, Te) have been prepared by different techniques such as pressure sintered, evaporation, slurry painted, sprayed,

vacuum deposited, fused salt electrolysis, spray pyrolysis etc. [6-8].

Pawar and co-workers [9] have electrodeposited cd(Se, Te) films onto titanium substrates. Ecpv cells can be converted into electrochemical storage cells. There are different configurations of electrochemical storage cells. Sharon et al. [10, 11] developed a solar chargeable battery under the name of "Saur Viddyut Kosh".

Tien and Jockowska [12] have developed a semiconductor septum cell. Tien et al. [13] have made a semiconductor septum cell for photoelectrolysis of seawater. Pawar and Patil have further developed semiconductor septum cell as semiconductor redox storage cell [14, 15].

Recent investigations in the field of energy resources have been aiming at harnessing the solar energy to meet the challenges of diminishing fossil fuels.

1.2 ENERGY RESOURCES

Man has needed and used energy at an increasing rate for his sustenance and well being ever since he came on the earth a few million years ago. Today, every country draws its energy needs from a variety of sources. We can broadly categorize these sources as commercial and noncommercial. The commercial sources include the fossil fuels

(coal, oil and natural gas), hydroelectric power and nuclear power, while the noncommercial sources include wood, animal wastes & 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 particularly true for oil and natural gas [1].

It is worth noting that while man's large scale use of commercial energy has led to a better quality of life, it has also created many problems. Perhaps the most serious of these is the harmful effect on the environment. The combustion of fossil fuels has caused serious air pollution problems in many areas because of the localized release of large amounts of harmful gases into the atmosphere. Similarly, the release of large amounts of waste heat from power plants has caused thermal pollution in lakes and rivers leading to the destruction of many forms of plant and animal life. In the case of nuclear power plants, there is also concern over the possibility of radioactivity being released into the atmosphere in the event of an accident and over the long-term problems of disposal of radioactive wastes from these plants. The gravity of most of these environmental problems had not really been foreseen. Now, however, as man embarks on the search for alternative sources of energy, it is clear that he would do well to keep the environment in mind.

Solar energy is a very large, inexhaustible source of energy. The power from the Sun intercepted by the earth is approximately 1.8×10^{11} MW [1], which is many thousands of times larger than the present consumption rate on the earth of all commercial energy sources.

In addition to its size, solar energy has two other factors in its favour. Firstly, unlike fossil fuels and nuclear power, it is an environmentally clean source of energy. Secondly, it is free and available in adequate quantities in almost all parts of the world where people live.

The energy from the Sun can be used directly and indirectly. The direct means include thermal and photovoltaic conversion, while the indirect means include the use of water power, the winds, biomass and the temperature differences in the ocean.

Tar sands and oil shale : As supplies of crude oil are getting depleted, attention is increasingly being focussed on two naturally occurring sources in which the crude is found intimately mixed with either large proportions of sand or rock. These sources are called tar sand and oil shale.

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 the tidal wave as it moves up the narrowing channel of the estuary.

Basically, in 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. The first commercial tidal power station in the world was constructed in France in 1965 across the mouth of the La Rance estuary. It has a capacity of 240 MW.

Wave energy arises because of the interaction of the winds with the surface of the oceans. It could therefore be considered as one of the indirect ways of utilizing solar energy. The energy available varies with the size and frequency of the waves. However, on an average, it is estimated that about 10 KW are available for energy metre of wave front.

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 , while the radial temperature gradient which causes this heat flow is about 0.03°C per metre. Thus, on an average, the

temperature of the earth increases by 30°C per kilometre as one moves inwards. The first commercial geothermal power station was erected in Larderello in Italy in 1904. The capacity of the plant was increased in stages and was 406 MW in 1975.

Wind Energy : Winds are caused because of two factors (i) the absorption of solar energy on the earth's surface and in the atmosphere, and (ii) the rotation of earth about its axis and its motion around the Sun. Because of these factors, alternate heating and cooling cycles occur, differences in pressure are obtained, and the air is caused to move. The potential of wind energy as a source of power is large. This can be judged from the fact that the energy available in the winds over the earth's surface is estimated to be 1.6×10^7 MW, which is of the same order of magnitude as the present energy consumption on earth. Besides, the energy available is free and clean.

The function of a windmill is to extract energy from the wind and to produce mechanical energy which may be converted into other forms of energy like electrical energy.

Ocean Thermal Energy : Temperature differences exist naturally between the upper and lower levels of water in the ocean. Tropical oceans collect and store very large amounts

of solar energy. Utilization of this energy with its associated temperature difference and its conversion into work forms the basis of ocean thermal energy conversion (OTEC) systems.

In addition to the primary sources, there are many secondary alternatives. These sources are different in the sense that they require a primary source or one of the existing sources of energy for their production. A good example of a secondary source is hydrogen, which has to be produced from water. Hydrogen may well be the liquid fuel of the future for transportation purposes.

1.3 ELECTRICITY GENERATION

The major sources of electric energy, in India, are the fossil fuels and water. The present contribution by different types of plants [16] are :

Steam plants	57.92%
Hydro plants	36.61%
Nuclear plants	2.06%
Diesel and Gas plants	3.41%

There are no immediate prospects of large scale utilization of alternate sources of energy like Sun, Wind, Tides etc. for generation of electric energy.

Thermal Power Plants :

Thermal power plants convert the heat energy of coal into electrical energy. Coal is burnt in a boiler which converts water into steam. The expansion of steam in turbine produces mechanical power which drives the alternator. Thus the main equipment in a thermal plant consists of boiler, steam turbine and alternator. To achieve efficient conversion of heat energy into electric energy, a variety of auxiliary equipment is needed.

The coal consumption depends, in addition to plant efficiency, on quality of coal and load factor of the plant.

Hydro-Electric Plants :

Hydro-electric projects harness water power for generation of electric energy. When water drops through a height, its energy is able to rotate turbines which are coupled to alternators. The electric power P , is given by

$$P = \frac{736}{75} QH\eta \text{ Kilowatts}$$

Where Q = Discharge, m^3/sec

H = Water head, m

η = Efficiency of turbine and alternator

Hydro-electric plants offer many distinct advantages over other means of power generation.

Nuclear Plants :

The energy needs of a country cannot be met from a single source. Hydro electric stations produce cheap power but need a thermal backing to increase the firm capacity. The coal reserves of the world are fast depleting. The nuclear power is the only source which can supply the future energy demands of the world.

A nuclear plant consists of a nuclear reactor (for heat generation), heat exchanger (for converting water into steam by using the heat generated in reactor), steam turbine, alternator, condenser etc. Thus it is similar to a steam station except that the nuclear reactor and heat exchanger replace the boiler.

Nuclear energy is produced by the destruction of mass, according to Einstein's mass energy relation

$$E = mc^2$$

Where E = energy in Joules

m = mass in Kilogram

c = velocity of light (3×10^8 m/sec)

If one gram of matter is destroyed, the energy produced is 9×10^{13} joules or 25000 MW hours.

Diesel and Gas Plants :

The diesel engine, for a diesel electric plant, may be a four stroke or a two stroke engine. In 4 stroke

engine the cycle of operation is completed in 4 strokes (two revolutions), the four strokes being suction, compression, working and exhaust. In the two stroke engines all the four operations are completed in two strokes or one revolution, the backward stroke combining working and exhaust and forward stroke combining intake and compression.

Diesel electric plants have many advantages over other plants. Their design and installation is simple. They can quickly started and put on load without any stand-by losses and have good efficiency. They require less space for fuel storage and are free from ash-handling problem. Their operation is also simple.

A gas turbine plant consists of a compressor, combustion chamber, gas turbine and alternator. The compressor takes in atmospheric air, compresses it and supplies the pressurised air to the combustion chamber. Fuel is injected into the combustion chamber and burnt in the stream of air supplied by the compressor. The combustion raises the temperature of air and increases its volume under constant pressure. The hot pressurised gas expands in the turbine, produces mechanical power and turns the rotor of the turbine. Both the compressor and the alternator are coupled to the turbine shaft. Due to the high temperature of the products of combustion, the turbine output exceeds the

input to the compressor. The turbine, therefore, drives the compressor and the surplus power drives the alternator. The products of combustion, after expansion through the turbine, are finally exhausted to the atmosphere. Such plants are known as open cycle gas turbine plants. The efficiency of an open cycle plant is very low.

1.4 SEPTUM SOLAR CELL

One important alternative source of energy to overcome energy crisis is solar energy, which is, clean, renewable, abundant and widely distributed in a global sense. Six possible pathways for trapping solar energy can be examined.

1) Photovoltaic 2) Photogalvanic 3) Photothermic 4) Photosynthetic 5) Ocean and 6) Wind

The necessity of finding alternative fuel sources has rekindled interest in solar energy and the interest in using semiconductor liquid junctions grew to form almost a separate discipline which was named photo electrochemistry. The interest in energy resources through photo chemical route has stimulated since 1973. 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 conventional p-n junction or Schottky barrier cells [17-21].

When the semiconductor electrode had taken as a separator of two aqueous compartments in PEC cells, it is called as semiconductor septum (SC-SEP) solar cells. The idea of construction of a PEC cell with semiconductor separator is basically taken from the modelling of natural photosynthetic systems with a pigmented bilayer lipid membrane. The single-compartment construction limits the maximum photoelectrical response to the degree of band bending and is controlled, therefore, by the Fermi level for a given semiconductor and redox couple. This major drawback has been overcome in the so-called semiconductor septum electrochemical photovoltaic (SC-SEP) cell [22].

SC-SEP solar cell can be used for electricity generation as well as for Hydrogen production.

1.5 PURPOSE OF DISSERTATION

Photo electrochemical (PEC) cells employing semiconductor and redox system have been extensively studied since last decade because of their significant advantages over solid state photovoltaic cells [1-4]. A key element of PEC cells, is the semiconductor-electrolyte interface and the origin of photo-potentials and corresponding photocurrents. Several semiconductor materials are being tested for the conversion of solar energy [3, 4, 12]. It is well known that the semiconductor photo electrodes are now successfully

used in photo electrochemical conversion of solar energy to electrical energy [13].

Most of the research on PEC cells has been conducted in a small scale. However, the data for large scale are few to date. Here, we have tried to work on large size semiconductor septum solar cells.

In the present investigation we report on the preparative parameters of electrodeposited large area n-CdSe thin films on stainless steel substrates and their use as septum electrode in redox storage cells. The charging and discharging characteristics of different septum electrode size and at different concentrations of electrolyte in compartment II have been discussed. The mechanism of corrosion of septum cell with FeCl_3 electrolyte in compartment II is studied and reported. Modelling of SC-SEP solar cells has been discussed. SC-SEP solar cell can also be used for hydrogen production. New type of SC-SEP solar cell for H_2 production by using line concentrator has been designed and constructed and studied for H_2 production.

REFERENCES

1. Sukhatme, S.P., Solar Energy, (1984).
2. Becquerel, E., C.R. Acad. Sci., 9(1839) 561.
3. Fujishima, A. and Honda, K., Nature (London), 238,37, (1972).
4. Kalyanasundaran, K., Sol. Cells. 15(1985) 93.
5. Miller, B., Heller, A., Robbins, M. et. al. J. Electrochem. Soc. 124(1977) 1019.
6. Hodes, G., Nature 285(1980) 29.
7. Liu, C.J. and Wang, J.H., Appl. Phys. Lett. 36(1980) 852.
8. Russak, M.A. and Reichmann, J., J. Electrochem. Soc. 129(1982) 719.
9. Lokhande, C.D., Dhabade, R.V., Patil, P.S. and Pawar, S.H., Bull. of Electro. 7(1991) 319.
10. Sharon, M., Sharon, S.G., Prasad, B.M., Bholagir, A.P. and Pradhananga, R.R., International Solar Energy Conference, Delhi (1980) 814.
11. Sharon, M., Sharon, S.G., Kapoor, B.M. and Sinha, A., Development of photogalvanic cell, TERI, Delhi (1980) 14.
12. Tien, H.T. and Jockowska, K., Solar Cells 23(1988) 147.
13. Tien, H.T. and Chen, J.W., Photochem. Photobiol. 49(1989) 527.

14. Pawar, S.H. and Patil, P.S., Bull. of Electrochem. 6(1990) 618.
15. Patil, P.S. and Pawar, S.H., Bull. of Electrochem. 8(1989) 618.
16. Gupta, B.R., Generation of Electrical Energy, (1983).
17. Bard, A.J., J. Photochem. 10(1979) 59.
18. Fujishima, A. and Honda, K., Nature, 238(1972) 57.
19. Nozik, A.J., Ann. Rev. Phys. Chem., 29(1978) 189.
20. Wrighton, M.S., Acc. Chem. Res., 12(1979) 303.
21. Heller, A. and Miller, B., Electrochem. Acta., 25(1980) 29.
22. Tien, H.T., Bi, Z.-C. and Tripathy, A.K., Photochem. Photobiol., 44(1986) 779.