



FABRICATION AND CHARACTERIZATION OF A NANO CRYSTALLINE NATURAL DYE-SENSITIZED SOLAR CELL AND DESIGN OF AN ARTIFICIAL SOLAR SIMULATOR

A dissertation submitted in partial fulfillment of requirement for the degree of Bachelor of Science in Electrical and Electronic Engineering

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DONE IN COLLABORATION WITH

INSTITUTE OF RADIATION AND POLYMER TECHNOLOGY (IRPT)

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We hereby declare that this thesis is from the students' own work and effort, and all other sources of information used have been acknowledged. This thesis has been submitted with our approval and it meets all academic criteria for the award of an academic degree.

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ABSTRACT

The present thesis investigates the performance of a dye-sensitized solar cell (DSC) under both idealized and outdoor conditions. Different electrical behavior under varying compositions of TiO_2 is found. An understanding of the cell behavior with respect to the change in different compositions of TiO_2 paste has been sought by experimental investigations and following data analysis. The efficiency, behavior of the cell with different molarity of acid, effect of using industrial grade TiO_2 instead of laboratory grade TiO_2 , life time of the cell with variation of the film thickness of electrolyte are also carried out in this chapter. The performance of Red Spinach (*Amaranthus cruentus*) has been investigated for the first time ever. The experimental investigations have been carried out in the laboratory under controlled conditions and the influence of one performance parameter could be determined. The cells investigated show very different electrical behavior under varying conditions.

An artificial solar simulator has been built using a 450W Xenon lamp that produces a light of intensity from $200W/m^2$ to $1200W/m^2$. It has been made using all the cheap materials available in Bangladesh. The system can produce AM 1.5G which is the standard to measure the solar cell performance in a condition with no sunlight. The main purpose of making this solar simulator is to measure cell performance under AM 1.5G as most of the time around the year it is very difficult to get continuous solar radiation of $1000W/m^2$ in Bangladesh.

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LIST OF ABBREVIATIONS

Abbreviation Full form

DSSC	Dye-sensitized Solar Cell
ITO	Indium doped Tin Oxide
SEM	Scanning Electron Micrograph

CHAPTER 1

THE NEED FOR SOLAR POWER

Introduction

With increasing demand for electrical energy worldwide, it is of utmost importance to produce energy from renewable and unconventional energy sources like solar energy. The fossil fuel reserve is limited and will run out. The challenge is to find an alternative that would be beneficial in the sense of solving the energy crisis and in this regard, solar energy can play a vital role. Though solar cells may be expensive at present but it is estimated that the manufacturing cost as well as installation cost will be lowered to a great extent in the near future.

1.1 Background

Fossil fuels such as coal, oil and gas are energy sources formed that as produced as a result of decomposition of animals and plant remnants which are contain carbon. The formation of fossil fuels which mainly consist of hydrocarbons takes about hundreds of millions of years and necessitates the availability of intense heat and pressure.

Fossil fuels are extremely essential for the survival of human beings for the fact that they supply 85% of our energy needs. Electricity is an integral part of our life and it is impossible to imagine a world without electricity and vast portion of this electrical energy is generated from fossil fuels, which are non-renewable. This is illustrated in figure 1 which shows the annual electricity production from different sources. In this ever advancing world where new technological advancements are made every day, the need for electricity becomes inevitable which implies that the use of fossil fuels would increase.

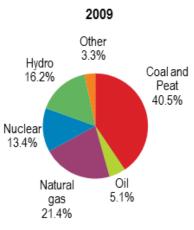


Fig.1. Annual electricity production from different energy sources worldwide in 2009 [1]

As the world population increases, so does the demand for electrical energy. With global population expected to reach almost 10 billion by midcentury and China and India (together comprising over a third of the world's population) expected to increase their per capita energy usage by three to five times over the next thirty years, it becomes clear that the global energy usage would grow at an ever increasing rate. [2] In fact the rapid modernization and urbanization are causing the fossil fuels to deplete at a rate greater than any time in history.

Fossil fuels are non-renewable, i.e. they can't be replenished and one has to rely on other sources from where fossil fuels can be extracted once they are used up. It is not surprising that an overwhelming energy crisis is imminent. Fossil fuels are being used up at a rate greater than any time in history and this is primarily due to increase in global population and rapid modernization and urbanization as mentioned previously. If this continues, fossil fuels may become scarce and mankind has to rely on other sources of energy. The graph shown below gives an insight into how long the fossil fuels may last. It can be easily understood that the day is not long when there won't be enough fossil fuels left for generation of electricity. Thus the quest for finding clean, renewable sources of energy becomes a great challenge.

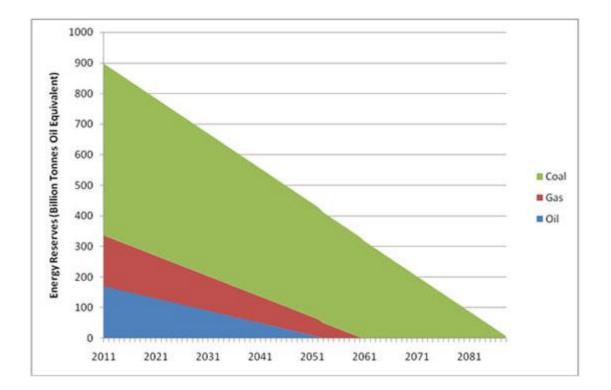


Fig.2. The variation of energy reserves of the Earth with time [3]

In addition to being limited in amount coal, oil and gas contribute largely to pollution and play a major role in emitting carbon dioxide and thus causing greenhouse effect and in turn global warming which is detrimental to this planet. In addition to causing global warming, burning of fossil fuels releases by products that can cause several respiratory diseases in humans. Moreover, these electrical energy power sources require large capital investments and scheduled maintenance. For instance in coal-fired power plants, there are problems of high capital investment, transportation cost, and delivery delay under adverse climatic conditions.

Thus with increasing demand for electricity all over the world and limitation of fossil fuels, it becomes essentially crucial to look for alternative energy sources due to the fact that fossil fuels or conventional sources of energy will deplete and thus won't last forever. In other words there must be a solution to the energy crisis that the world will be confronted with in the near future.

Nuclear power may be cited as one of the best possible solutions to future energy crisis but there are several problems associated with it. These are explained as follows.

- Nuclear energy is that it is expensive to establish and to maintain
- There's always a risk of accidents which might cause radiation hazard, e.g. Fukushima Nuclear power plant in Japan in 2011.
- Nuclear waste generated has to be treated and dumped with careful control. A typical reactor generates 20 to 30 tonnes of high-level of nuclear waste annually. If this waste is not disposed of easily, it remains potentially dangerous until it decays. [4]
- Nuclear reactors consistently release millions of curies of radioactive isotopes into the air and water each year. These unregulated by products include the noble gases krypton, xenon and argon, which if inhaled by people living near a nuclear reactor, are absorbed through the lungs and finally migrate to the fatty tissues of the body even near the reproductive organs. Radiation from these elements can cause mutation of genes in the ova and sperms. Tritium, another by product from nuclear reactor, is incorporated into the DNA molecule, where it may again cause mutation. **[5]**

No wonder the research for finding new energy sources or harnessing energy from renewable sources have gained popularity in the past decades. In fact renewable energy (including solar energy) will become an integral part of our energy sources. Although currently renewable energy sources only contribute to more or less 5% of the annual electricity production worldwide, it can be said without doubt that they will play a major role in fulfilling our energy needs.

The annual consumption worldwide of different renewable energy sources are shown in the following table:

	Electricity (GW)	Heating (GW)	Total (GW)
Hydropower	816	_	816
Biomass energy	44	220	264
Solar energy	5.4	88	93.4
Wind energy	59	-	59
Geothermal energy	9.3	28	37.3
Ocean energy	0.3	_	0.3
Total	934	336	1270

Table-1: The current use of renewable energy sources as electricity and heating where applicable in figures of continuous energy consumption (1 GW = 10^9 J/s) [6]

	Current use (TW)	Technical potential (TW) ^a	Theoretical potential $(TW)^a$
Undropomer	0.816	1.6	
Hydropower			4.8
Biomass energy	0.264	>7.9	92
Solar energy	0.0934	>51	124000
Wind energy	0.059	19	$190(370^{b})$
Geothermal energy	0.0373	158	4440000
Ocean energy	0.0003	6^c	235
Total	0.934	>238	>4560000

Table-2: The renewable energy resources in terawatt (1 TW = 10^{12} W).Global use in 2004 = 15 TW [6]

1.2 Solar energy

Solar energy is the energy from sun whose energy comes from internal fusion of hydrogen atoms into Helium atoms. It is estimated that solar energy will be one of the means through which electricity will be harnessed and contribute substantially to energy used in the transportation infrastructure. The advantages and disadvantages of solar cells are enumerated below:

Advantages	Disadvantages
Fuel source is vast and essentially infinite	Fuel source is diffuse (sunlight is a relatively
	low-density energy)
No emissions, combustion or radioactive fuel	
disposal (does not contribute perceptibly to	
global climate change or pollution)	
Low operating costs (no fuel)	High installation costs
No moving parts (no wear)	
Ambient temperature operation (no high	
temperature corrosion or safety issues)	
High reliability in modules (>20 years)	Poorer reliability of auxiliary (balance of
	system) elements including storage
Modular (small or large increments)	
Quick installation	
Can be integrated into new or existing building	
structures	
Can be installed at nearly any point-of-use	Lack of commercially available system
	integration and installation so far
Daily output peak may match local demand	Lack of economical efficient energy storage
High public acceptance	
Excellent safety record	

Table-3: The advantages and disadvantages of solar cells [7]

Though one of the main barriers in implementing solar cells is their high cost, it is expected that the cost of solar cells will decrease dramatically in the coming years due to technological advances as presented in the following table. This is illustrated in Fig 3 and 4.

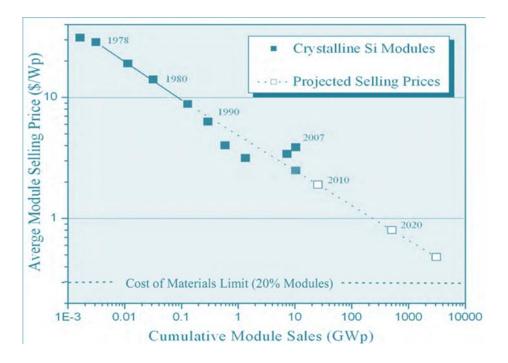


Fig.3. Price experience curve of solar module over 30 years [8]

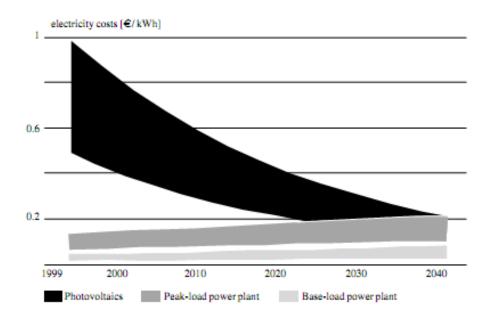


Fig.4. Estimation of cost of electricity from 1999 to 2040 [9]

1.3 Working principle of a silicon/ solid state solar cell

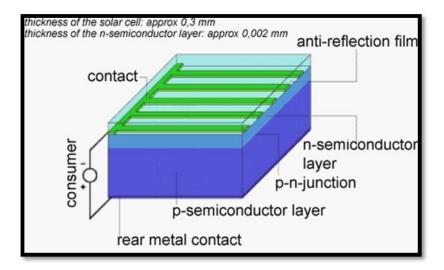


Fig.5. Structure of a silicon solar cell [10]

Electricity is generated in solar cells by means of photovoltaic effect where absorption of photons from light by semiconducting material produces electrons and holes. Usually a solar cell consists of a p-n junction as shown in the figure above. The p-n junction consists of two semiconducting material e.g. silicon of different doping levels joined together. p-type semconductor has excess postive charges, i.e. holes while n-type has excess negative charges, i.e electrons. When p-type and n-type materials are brought in close contact with each other, a p-n junction is formed.

When the junction is illuminated, photons having energy equal to or higher than the width of the forbidden band, or band gap, transfer their energy to atoms, causing the electron to move from the valence band to the conduction band, leaving behind it in turn a hole and finally creating an electron-hole pair. If a load is poitioned at the cell's terminals, electrons from the n region will migrate back to the holes in the p region, by way of outside connection, giving rise to a potential difference called photovoltage. **[11]**

1.4 Classification of solar cells

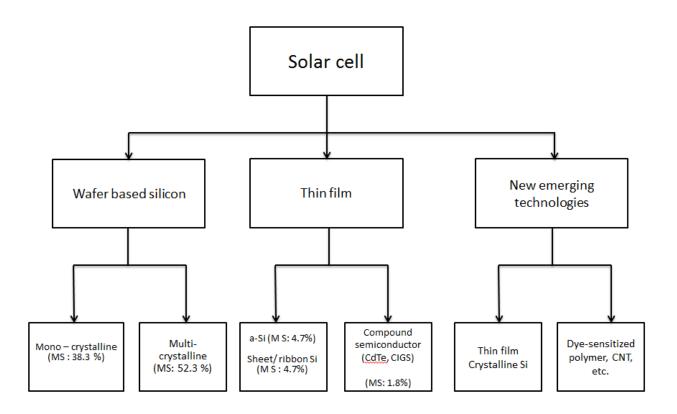


Fig. 6. Classification of solar cells [12]

Solar cells can be classified into the following groups: [12]

- Wafer based crystalline silicon solar cells
- Thin-film solar cells, which includes, Copper Indium Gallium Diselenide (CIGS), Cadmium Telluride, Amorphous silicon (a-Si) etc.
- Emerging technologies such as thin-film silicon, dye-sensitized solar cells; polymer organic solar cells etc.

1.4.1 <u>Wafer-based crystalline silicon solar cell technology</u> [12]

The technology used to make most of the solar cells is further classified into two categories as:

- Single- / Mono-crystalline silicon solar cell and
- Polycrystalline silicon solar cell

Single/mono-crystalline silicon solar cell [12]

This is the most established and efficient solar cell technologies till date, which have module efficiency of 15-18%. The name single/mono comes from the fact that a single silicon crystal is used to fabricate them and the process involved is called Czochralski process. During manufacturing, c-Si crystals are cut from cylindrical ingots and thus they do not completely cover a square solar cell module.

Polycrystalline silicon solar cell (poly-Si or mc-Si) [12]

These cells have module efficiency of around 12-14%. The fabrication of polycrystalline cells is more cost-efficient as they are manufactured by cooling a graphite mould filled with molten silicon. Liquid silicon is poured into blocks that are subsequently cut into plates. During solidification of the material, crystal structures of varying sizes are formed, with defects appearing at the borders.

1.4.2 Thin film solar cell technology [12]

In case of thin film solar cells, thin layers of semiconductor material are deposited onto a supporting substrate, such as a large sheet of glass. The thickness of semiconductor material is used is less than a micron, i.e. 100-1000 times less than the thickness of Silicon wafer. Some of the thin film solar cells in use are as follows;

- a Si
- CdTe (Cadmium Telluride)
- CIS, CIGS (copper indium gallium di-selenide)
- Thin film crystalline silicon

Amorphous silicon thin film (a-Si) solar cell [12]

Amorphous Silicon (a-Si) modules are the first thin film solar module to be commercially produced. Amorphous Silicon (a-Si) solar can be fabricated at a lower deposition temperature hence permits the use of various low cost flexible substrates by easier processing technique. The overall efficiency drops inevitably at module level and at present the efficiencies of commercial modules are in the range of 4-8%.

Cadmium telluride (CdTe) thin film solar cell [12]

In this technology, Cadmium Telluride is sandwiched with cadmium sulfide to form a p-n junction PV solar cell. CdTe with laboratory efficiency as high as 16% have been developed. Multitudes of manufacturing techniques are main advantage of these solar cells which are suitable for large scale production. Limited availability of cadmium and pollution problem associated with Cadmium is main concerns with this technology.

Copper Indium Gallium Diselenide (CIGS) solar cells [12]

This is a new semiconductor material comprising copper, indium, gallium and selenium in a specific order, which is used for solar cell manufacturing. It is one of the most promising thin film technologies due to their high-attained efficiency and low material costs. The advantage of CIGS solar cell is its extended operational lifetime without significant degradation. The inherent properties of CIGS also provide an opportunity for maximizing the efficiency.

The maximum efficiency that can be obtained under the best conditions from a single junction solar cell is in the range of 40%. The best efficiency so far obtained for single-junction solar cells is 27.6%, with GaAs research-type cells under concentrated sunlight of 255 suns, that is, of 255 times the concentrated standard power density (i.e. at 255 kW/m2). **[13]**

Cells	Efficiency [%] Global AM1.5	Efficiency [%] AM0	Area [cm ²]	Manufacturer
c-Si	22.3	21.1	21.45	Sunpower [17]
Poly-Si	18.6	17.1^{a}	1.0	Georgia Tech/HEM [18]
c-Si film	16.6	14.8^{a}	0.98	Astropower [19]
GaAs	25.1	22.1^{a}	3.91	Kopin [19]
InP	21.9	19.3 ^a	4.02	Spire [19]
GaInP (1.88 ev)	14.7	13.5	1.0	ISE [18]
GaInP/GaAs/Ge	31.0	29.3	0.25	Spectrolab [20]
Cu(Ga,In)Se ₂	18.8	16.4 ^a	1.04	NREL [19]
CdTe	16.4	14.7^{a}	1.131	NREL [19]
a-Si/a-Si/a-SiGe	13.5	12.0	0.27	USSC [19]
Dye-sensitized	10.6	9.8 ^a	0.25	EPFL [19]

The following table summarizes the efficiency of different solar cells:

Table-4: Measured global AM 1.5 and measured or estimated AM 0 efficiencies for small-area cells [13]

1.5 Dye-sensitized solar cells

The dye-sensitized solar cells are one of the new emerging technologies and are known as the third generation of solar cells [14]. It differs from the inorganic solid state junction solar cells in the sense that the optical absorption and the charge separation processes are achieved by means of a sensitizer which acts as light-absorbing material and a wide band gap semiconductor of mesoporous or nano crystalline morphology [14]. The sensitizer is usually a photosensitive dye and hence the name dye-sensitized solar cell has been coined.

A lot of research is going on dye-sensitized solar cells and it is expected that in the coming days it will compete strongly with conventional solid state solar cells though dye-sensitized solar cells have not been widely commercialized yet.

1.6 Advantages of Dye-sensitized solar cells (DSSC)

The advantages can be summed up as follows: [15]

Good Price/Performance Ratio

The overall peak power-production efficiency of dye-sensitized solar cells is about 11% and thus they are best suited to low-density applications. Though the efficiency of DSSCs is less than many of the best thin-film cells, the price-to-performance ratio obtained through these solar cells is superior to others.

Low Cost

The main advantage of DSSCs is that they are made of cheap materials and these solar cells do not require any apparatus and can be printed on any flexible surface. Due to the reduced manufacturing costs, DSSCs are less expensive when compared to other semiconductor cells.

The balance of system payback (BOSP) is 3.7 years for silicon compared to 0.8 years for DSSC. Projected reductions in BOSP will see silicon reduce to 2.1 years and DSSC reduce to 0.5 years. [16]

Ability to Work at Wider Angles and in Low Light

The dye used in dye-sensitized solar cells can absorb diffused sunlight and fluorescent light. Moreover, they are able to work in cloudy weather and low-light conditions without much impact on efficiency, while the other traditional cells would fail at illumination below a threshold level. DSSCs have a very low cutoff and also work at wider angles, a fact which makes the cells absorb most of the available sunlight.

Long Life

The performance of dye-sensitized solar cells does not deteriorate in sunlight over time and thus last much longer.

Mechanical Robustness

DSSCs are mechanically robust. They are made of lightweight materials and require no special protection from rains or trees or any other harsh objects, enabling easy maintenance.

Temperature change

The performance of a DSSC is quite insensitive to temperature change. Thus, raising the temperature from 20 to 60 °C has practically no effect on the power conversion efficiency. **[13]**

Ability to Operate at Lower Internal Temperatures

As the temperature rises, some electrons in semiconductors are pushed to conduction band mechanically. Hence the silicon cells require protection by covering in a glass box and efficiency decreases with rise in temperature. In DSSCs heat radiates away easily to reduce the internal temperature as it consists of only a thin layer of plastic.

1.7 Natural Dye-sensitized Solar cells

A natural dye-sensitized solar cell is no different from a normal dye-sensitized solar cell except that it uses photosensitive dyes which are found in nature. The advantage of natural dye-sensitized solar cell is that dyes obtained naturally are very cheap while artificial dyes are very expensive. Research is going on worldwide to obtain a substitute for artificial dye and in this regard, natural dyes are showing prospect though there's still a long way to go. Our thesis focuses on performance of dye-sensitized solar cells using natural dyes that are found in Bangladesh. For the first time the dye of red spinach (*Amaranthus cruentus*) has been used. The whole process and details of dye-sensitized solar cells has been elaborated in chapter 2.

1.8 Problem statement

Dye-sensitized solar cells have been invented since the 90's and there has a vast improvement in its efficiency over these years using dyes which contain Polypyridyl complexes of ruthenium and osmium [14] and the best artificial dye found to give the best performance so far is N3 dye. The main impediment in using artificial dyes is the fact that they are extremely expensive and this raises the manufacturing cost of the solar cell.

We focused on using natural dyes which contain "Anthocyanin" group and exhibits photosensitivity in the visible region of the electromagnetic spectrum. Natural dyes are easy to extract and readily available and thus makes solar cell cost effective. Natural dyes can be a good substitute for artificial dyes but yet a lot of research has to be done to increase its efficiency which is still low compared to solid state solar cells.

1.9 <u>Scope of the thesis</u>

This experimental work done for writing this thesis opens up new avenues for working with different natural dyes and in particular those dyes that are cheap, easy to obtain and more importantly locally available in Bangladesh.

1.10 Objectives

- To find a good substitute for artificial dye with appropriate natural dye with optimum output.
- To investigate the effects of increasing acid concentration used in preparing the Titanium dioxide paste on the solar cell output.
- To increase the efficiency of the solar cell.

1.11 Contribution of the thesis

This thesis aims to present the investigation carried into natural dyes such as those extracted from Red spinach (*Amaranthus cruentus*) and Malabar spinach (*Basella alba*), with special focus on Red spinach and thus find a dye that fulfills all the conditions to be used in a dye-sensitized solar cell and be a substitute for artificial dye.

1.12 Organization of the thesis

The dissertation has been divided into 4 chapters in total. The first chapter explains the need and advantages of solar power with a comparison between silicon and dye-sensitized solar cells.

The second chapter contains precise description of structure of Nano crystalline dye-sensitized solar cell, Degussa P-25, Sensitizer, working principle of Nano crystalline dye-sensitized solar cell, Natural Dye-sensitized Solar Cell, Fabrication of a dye-sensitized solar cell, Characterization, calibration and performance analysis of the Cell using red spinach were illustrated in this chapter.

In Chapter three we developed simulation codes using MATLAB and Simulink software to analyze different performance parameters for any generalized cell with pre-assumed inputs. Here we used various MATLAB built in functions and simulation blocks to design program that can calculate desired performance parameters. Simulation of Efficiency calculations of a cell, Simulation of cell efficiency with varying corresponding irradiance, graphical plot of Efficiency vs. Irradiance etc. were discussed elaborately.

Finally the last chapter is about design of an artificial solar simulator which has been designed using materials available in Bangladesh. Design procedure, working principle, materials used and circuit diagrams have been described.

Summary

The field of dye-sensitized solar cells has a bright prospect and the work done for this thesis shows that there's a great possibility of using natural dyes as dyes for DSSC and the chances are increasing day by day as more and more in-depth analysis is being performed. The next chapters go into extensive details of the work done in order to try and find a substitute for artificial dye and replace it with natural dye for dye-sensitized solar cells.

References:

[1] OECD Factbook 2011: Economic, Environmental and Social Statistics - ISBN 978-92-64-11150-9 - © OECD 2011

[2] Bradford, T. "Solar Revolution-The Economic Transformation of the Global Energy Industry", ISBN 0-262-02604-X—ISBN 978-0-262-02604-8

[3] http://www.ecotricity.co.uk/our-green-energy/energy-independence/the-end-of-fossil-fuels

[4] http://www.wagingpeace.org/menu/issues/nuclear-energy-&-waste/nuclear-energy-fact-sheet.php

[5] http://www.commondreams.org/views05/0415-23.htm

[6] Krebs, F. Polymer photovoltaics: a practical approach, ISBN 978-0-8194-6781-2

[7] Luque, A.; Hegedus, S., "Handbook of photovoltaic science and engineering", ISBN 0-471-49196-9

[8] "Photovoltaics, Past present and future": Ryne. P. Raffaelle (ceramics.org/wp-content/uploads/mcare/solar_raffaelle.pdf)

[9] Luque, A.; Hegedus, S., "Handbook of photovoltaic science and engineering", ISBN 0-471-49196-9

[10] http://www.solarserver.com/knowledge/basic-knowledge/photovoltaics.html

[11] www.cea.fr/var/cea/storage/static/gb/library/.../pdf/encadred.pdf

[12] http://sovoxglobal.com/cell_classification.html

[13] Luque, A.; Hegedus, S., "Handbook of photovoltaic science and engineering", ISBN 0-471-49196-9 [14] Grätzel, M., "Conversion of sunlight to electric power by nano crystalline dye-sensitized solar cells", Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 3–14, Elsevier

[15] http://www.doityourself.com/stry/6-advantages-of-using-dyesensitized-solar-

cells#.UHBkG6CUNQI

[16] http://www.csiro.au/en/Outcomes/Energy/Renewables-and-Smart-Systems/dye-sensitised-solar-cells.aspx

CHAPTER 2

DYE-SENSITIZED SOLAR CELLS

Introduction

The dye-sensitized solar cell (DSSC) was invented by Michael Grätzel and co-workers in the early 90s **[1]**, and is known as a third generation solar cell. This type of solar cell differs greatly from the conventional silicon solar cell, as no silicon is needed in the manufacturing. The working principle of the DSSC is like the plant photosynthesis, where a dye converts the solar energy to electricity.

Production prices are expected to be very favorable as there are possibilities to make the production very effective without high-tech facilities needed. The focus of this thesis has been to gain an overall understanding of the electrical behavior of the DSSC with respect to different fabrication parameters, variation in compositions in chemicals, incident irradiance intensity, life time of the cell etc. A wide range of both internal and external parameters is varied to show their influences on the performance of the DSSC. For the first time Red Spinach (*Amaranthus cruentus*) extract has been used as the dye. The performance of Malabar spinach (*Basella alba*) has also been investigated. Degussa P25 has been used as the TiO₂ paste to make mesoporous oxide layer, Γ / Γ^{3-} (Iodide/tri-Iodide) solution as the electrolyte and carbon layer deposited on Indium doped Tin Oxide (ITO) glass has been used as the counter electrode. The performance of the cell in these conditions has been discussed in this paper and also a comparison has been shown between the cell performance using Degussa P25 and that of using industrial grade TiO₂ as oxide layer.

2.1 Structure of a Nano crystalline dye-sensitized solar cell

A dye-sensitized solar cell consists of a wide band semiconductor which is placed in between two electrodes and stays in contact with en electrolyte consisting of a redox couple. The dye molecules (sensitizer) are chemically bonded to the wide band gap semiconductor and they cause injection of an electron into the conduction band of the semiconductor as a result of photon absorption. **[1]**

A detailed structure of a dye-sensitized solar cell is shown in the following figure:

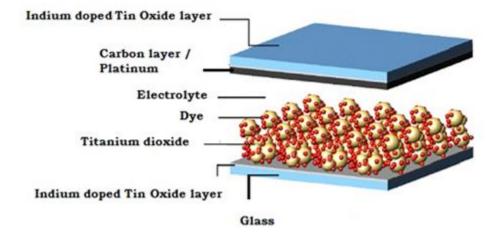


Fig.1. Structure of a DSSC [2]

The wide band gap semiconductor used is Titanium Dioxide which forms a mesoporous structure and behaves like a photonic crystal. The Titanium dioxide used is of laboratory grade and in particular the Degussa P25 can be used.

As shown in the figure, the bottom of a dye-sensitized solar cell is the Indium doped Tin oxide (ITO) coated glass on which the nano crystalline film of Titanium dioxide is coated, the latter forming the second layer. ITO coating is used as Tin Oxide (SnO₂) is transparent as well as electrically conductive. The dye molecules are distributed throughout the TiO₂ crystal, bonded to Titanium atoms.

At the top of Titanium oxide layer is the electrolyte layer which consists of a redox couple [1] and finally the cell is completed by a counter electrode which conducts electrons to the external circuit. The counter electrode can be ITO glass with a graphite layer from a pencil, carbon soot from candle / Carbon from carbon rod of an alkaline battery / Carbon from an artist's charcoal pencil or just Platinum.

2.1.1 Degussa P-25

Titanium dioxide occurs in nature as minerals such as rutile, anatase and brookite. [3] Degussa P-25 is a special brand of Titanium dioxide powder which contains anatase and rutile particles in the ratio of about 3:1 and is regarded as a standard material for photocatalytic reactions. The average sizes of the anatase and rutile particles are 25 and 85 nm respectively and they form their agglomerates separately in Degussa P-25 as revealed by Transmission Electron Micrograph (TEM) images. [4]

Degussa P-25 is manufactured by the Aerosil process, where Titanium tetrachloride (TiCl4) undergoes hydrolysis in the vapor phase at an elevated temperature (19, 20). During this process, the growth of particles is quenched when the particles (or the agglomerates) reach a certain size. [4]

We have used Degussa P-25 in all our works to form the nano crystalline film to hold the sensitizer (dye) molecules and it forms the necessary mesoporous structure. The advantage of a mesoporous structure is that they have a greater surface area to volume ratio [23] and thus when light passes through the Titanium Dioxide crystal, huge number of dye molecules can be stimulated by light which wouldn't be the case if it were only a single layered crystal. In addition to holding the dye molecules, it also conducts the electrons to the counter electrode generated from photon excitation. **[5]**

On contrary, had we used a single layer of dye molecules on a flat surface, it would have been able to absorb up to only 1 % of the incident light. Using Nano porous TiO_2 electrodes with a roughness factor of ca. 1000 dramatically increases the light harvesting efficiency. [6]

An advantage of mesoporous TiO_2 structure is that the high surface roughness does not pro-mote charge carrier loss by recombination as electrons and the positive charges are found on the opposite sides of the liquid–solid interface within picoseconds of photo excitation [1].

2.1.2 Sensitizer (Dye)

The sensitizer (dye) used should fulfill the following conditions [1]:

- It should be able to absorb all wavelengths below a threshold wavelength of about 920 nm which means it should be able to absorb wavelengths in the visible range of electromagnetic spectrum.
- Moreover, it must also contain groups such as carboxylate or phosphonate or anthocyanin to firmly bind to the semiconductor oxide surface. These groups ensure that it spontaneously assembles as a molecular layer upon the Titanium dioxide film to a dye solution and this advantageous as soon as a photon is absorbed, the excited state of the dye molecule will relax by electron injection to the semiconductor conduction band.
- Upon excitation it should inject electrons into the solid with a quantum yield of unity. In other words there should be little or no mismatch between the energy level of the excited dye and lower bound of the conduction band of the oxide so that energetic losses during the electron transfer reaction are minimized. Moreover, its redox potential should be sufficiently positive that it can be regenerated via electron donation from the redox electrolyte.
- It should be stable enough to sustain about 108 turnover cycles or in other words it should be able to work efficiently for at least 20 years of exposure to sunlight.

The best photovoltaic performance has so far been achieved with polypyridyl complexes of ruthenium and osmium. Sensitizers having the general structureML2(X)2 where L stands forbipyridyl-4,4-dicarboxylic acid M is Ru or Os and X presents a halide, cyanide, thiocyanate, acetyl acetonate, thiacarbamate or water substituent, are good options. All these dyes have anchoring groups e.g. carboxylate, phosphonate or hydroxamate for chemically binding onto the surface Titanium atoms by means of dative covalent bond. The ruthenium complex cis-RuL2 (NCS) 2, known as N3 dye, shown in Fig. surpasses all other artificial dyes with a conversion efficiency of 10%. **[1]**

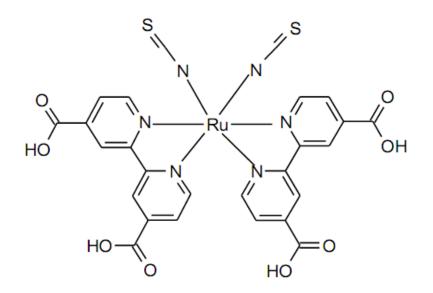


Fig.2. Chemical structure of N3 dye [6]

The fully protonated N3 has absorption maxima at 518 and 380 nm, i.e. in the visible spectrum. It emits at 750 nm the lifetime being 60 ns. As soon as the dye is excited, an electron is transferred from the metal to the orbital of the surface holding carboxylated bipyridyl ligand from where it is released into the conduction band of TiO_2 within picoseconds [1].

Conducting Cathode glass TiO₂ Dye Electrolyte Injectio -0.5 Maximum Voltage 0 E vs Mediator Ox NHE Red 0.5 (V) Diffusion 1.0 e', е

2.2 Working principle of a Nano crystalline dye-sensitized solar cell

Fig.3. Outline of a dye-sensitized solar cell constructed with a working electrode consisting of dye-sensitized semiconducting oxide film, a carbon counter electrode deposited on glass substrate, and electrolyte filled between the working and counter electrodes. **[1]**

As mentioned earlier, that photo-excitation of the wide band gap semiconductor results in the injection of an electron into the conduction band of the Titanium dioxide and this photo excitation is done by the dye itself when it absorbs photons from light. As a result the electrons get excited, i.e. their energy increases and thus they travel out of dye molecules into the mesoporous structure of Titanium dioxide where they travel through the crystal to the counter electrode (which could be platinum or simply carbon cathode) to the external circuit. Since the TiO₂ nano particles are too small for a macroscopic electric field to build up, the main transport mechanism for electrons in the TiO₂ layer is diffusion. **[6]**

As for any cell there must be an electrolyte and the electrolyte for dye-sensitized solar cells is usually a redox couple such as Iodide/ tri- Iodide couple [I_3^- (aq)]. The electrolyte acts as the donor during electron flow which means they fill up the deficiency of electron caused by photo-

excitation of the dye. The Iodide Ion (I⁻) in the electrolyte donates an electron to the excited dye molecule which lost an electron, causing it to get oxidized and form tri Iodide ion (I₃⁻)

This Tri Iodide ion finally gains an electron from the counter electrode and regains back its original state and thus the process continues. This is how one complete cycle of production of photocurrent in a nano crystalline dye-sensitized solar cell.

The photovoltage generated corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. [1]

"Fig. 1" shows the schematic diagram of a dye-sensitized solar cell and also the electron flow mechanism.

$D + light \rightarrow D^*$ (i)
$D^* + TiO_2 \rightarrow e^- (TiO_2) + D^+ \dots (ii)$
$e^{-}(TiO_2) + C.E. \rightarrow e^{-}(C.E.) + electrical energy \dots(iii)$
$2 I + D^+ \rightarrow I_2 + D$ (iv)
$2 I_2 \rightarrow I + I_3$ (v)

Reaction steps (iv) and (v) can be combined to form

 $2 D^+ + 3 I^- \rightarrow 2D + I_3^-$ (vi)

 $I_3 + 2e^{-}(C.E.) \rightarrow 3I^{-} + C.E.$ (vii)

N.B. D* represents excited state of the dye and C.E. = Counter Electrode, D= Dye

The efficiency of a DSSC is based on different rate constants for iodine reduction at the frontand counter electrode. The iodine reduction at the counter electrode (reaction vii) has to be orders of magnitudes faster than the recombination at the TiO_2 / electrolyte interface otherwise efficiency will be low. [6]

The carbon layer at the counter electrode acts as a catalyst for reaction (vii)

It takes nanoseconds for the dye to get back to its original state (reaction vi) and is typically 100 times faster than any recombination reaction and about 108 times faster than the intrinsic lifetime of the oxidized dye. It is a two step (reaction iv and v) electron transfer with a large driving force (0.6 V). **[6]**

It is a two step (reaction iv and v) electron transfer with a large driving force (0.6 V). [6]

The open circuit voltage of dye-sensitized solar cells is usually low due to the discrepancy between the energy levels of the dye and the redox couple For efficient charge injection the energy level of the exited dye molecule should be about 0.2 - 0.3 eV above the conduction band of the TiO₂. [6]

2.3 Natural Dye-sensitized Solar Cell

As the name suggests, a natural dye-sensitized solar cell is no different from a normal dyesensitized solar cell except that it uses natural dyes instead of artificial dyes. As mentioned previously that the sensitizer used must exhibit photosensitivity below a threshold wavelength of 920 nm, so only those natural dyes fulfilling this condition can be used. Moreover, the sensitizer must have attachment groups for it to graft to the Titanium dioxide surface molecules and thus the natural dye must also have some attachment groups in order to do this.

These properties are found only in those natural dyes containing the "Anthocyanin" group.

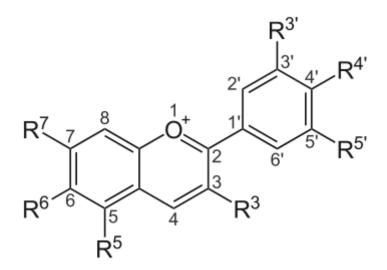


Fig.4. Structure of Anthocyanin [7]

Anthocyanins are water-soluble vacuolar pigments that may appear red, purple, or blue depending on the pH and fall into the category of flavonoids synthesized through the phenylpropanoid pathway. Anthocyanins are derivatives of anthocyanidins, which include pendant sugars. **[8]**

Anthocyanins occur in all tissues of higher plants, including leaves, stems, roots, flowers, and fruits. In these parts, they are found predominantly in outer cell layers such as the epidermis and

peripheral mesophyll cells. Most frequently occurring anthocyanin in nature are the glycosides of cyanidin, delphinidin, malvidin, pelargonidin, peonidin, and petunidin. Roughly 2% of all hydrocarbons fixed in photosynthesis are converted into flavonoids and their derivatives such as the anthocyanins.

Anthocyanin is found in *Vaccinium* species, such as blueberry, cranberry, and bilberry and also in *Rubus* berries, including black raspberry, blackberry red raspberry, and blackberry. B, cherry, eggplant peel, black rice, Concord grape, muscadine grape, red cabbage, pomegranate and violet petals are also rich in anthocyanin. **[8]**

The advantage of natural dye-sensitized solar cells is that natural dyes can be extracted by simple procedures and extremely cost effective. Artificial dyes are pretty expensive while natural dyes are cheap and readily available in nature. Moreover, natural dyes are non-toxic and completely biodegradable and thus so much research is going on in this field.

In general, natural dyes suffer from low open circuit voltage, which is at best 100 mV lower than an equivalent N719 / N3 sensitized cell. This is due both to possible efficient electron / dye cation recombination pathways and to the acidic dye adsorption environment. Hydrogen ions are potential determining ions for TiO_2 and proton adsorption causes a positive shift of the Fermi level of the TiO_2 , thus limiting the maximum photovoltage that could be delivered by the cells. [9]

Among the best results so far are the anthocyanins extracted from Jaboticaba and Calafate yielding ISC = 9 mAcm-2, VOC=0.59 V and 6 mAcm-2, 0.47 V respectively and that from blackberries gave a conversion efficiency of 0.56 %. Tannins and other polyphenols extracted from Ceylon black tea produced photocurrents of up to 8 mAcm⁻². **[6]**

This thesis aims to investigate the effects of natural dyes such as those extracted from Red spinach (*Amaranthus cruentus*) and Malabar spinach (*Basella alba*), with special focus on Red spinach and the effect of increasing acid concentration in the preparation of Titanium Dioxide paste. The results obtained from such experiments will be presented later in the thesis.

2.4 Literature review

The dye-sensitized solar cell was invented by Michael Grätzel and co-workers in the 90's [10]

As far as artificial dye is concerned, numerous researches have been done on it. The best photovoltaic performance has so far been achieved with polypyridyl complexes of ruthenium and osmium and the ruthenium complex cis-RuL2(NCS)2, known as N3 dye, stands out as the best artificial dye for dye-sensitized solar cells with an efficiency of 10%. **[1]**

The "black dye"tri (cyanato)-2,2- 2-terpyridyl 4,4-4--tricarboxylate) Ru(II) achieved a 10.4% efficiency in full sunlight back in 2001 but then again the N3 dye in used with guanidinium thiocyanate, performs better than this black dye. Recently sensitizers, efficiencies reaching up to 7.7% in full sunlight have been achieved with sensitizers of coumarine or polyene type. **[1]**

Rigorous research has been done and being done on artificial dyes improve the efficiency of solar cells but we concentrated on natural dyes. Recently natural dyes are receiving a lot of attention as they are cheap and readily available. Some of the works on natural dye has been summarized below:

Natural dye source	Jsc / mAcm ⁻²	Voc /V	FF / %	η / %	Ref .no.
Indian Almond plant	0.402	0.508	60.3	0.14	[11]
Cashew leaf	0.2	0.49	61.7	0.06	
Dragon fruit			30	0.22	[12]
Red turnip	9.5			1.7	[13]
Sicilian prickly pear	9.4			1.26	
Rosella	1.63	0.404	0.57	0.37	[14]
Blue pea	0.37	0.372	0.33	0.05	
Mixed rosella-blue pea	0.82	0.382	0.47	0.15	

Natural dye source	Jsc / mAcm ⁻²	Voc /V	FF / %	η / %	Ref. no.
Authurium flowers	2.9 - 3.2	0.440 - 0.480			
Black rice	1.1	0.00055	0.52		[14]
Fruit of Calafate	0.96	0.00052	0.56		
Skin of Jaboticaba	2.1	0.00057	0.58		
Begonia	0.63	0.537	72.2	0.24	-
Tangerine peel	0.74	0.592	63.1	0.28	
Rhododendron	1.61	0.585	60.9	0.57	-
Fructus lycii	0.53	0.689	46.6	0.17	-
Marigold	0.51	0.542	83.1	0.23	[15]
Perilla	1.36	0.522	69.6	0.5	
Herba artemisiae scopariae	1.03	0.484	68.2	0.34	
China Ioropetal	0.84	0.518	62.6	0.27	
Yellow rose	0.74	0.609	57.1	0.26	
Flowery knotweed	0.6	0.554	62.7	0.21	
Bauhinia tree	0.96	0.572	66	0.36	
Petunia	0.85	0.616	60.5	0.32	-
Lithospermum	0.14	0.337	58.5	0.03	
Violet	1.02	0.498	64.5	0.33	
Chinese rose	0.9	0.483	61.9	0.27	
Mangosteen pericarp	2.69	0.686	63.3	1.17	
Rose	0.97	0.595	65.9	0.38	
Lily	0.51	0.498	66.7	0.17	
Coffee	0.85	0.559	68.7	0.33	
Broadleaf holly leaf	1.19	0.607	65.4	0.47	

Table-1: The performance of various natural dyes

2.5 Fabrication of a dye-sensitized solar cell:

2.5.1 Preparation of TiO₂ Paste

Titanium dioxide powder is used for forming the mesoporous structure which holds the dye molecules. At first it must be made into a paste form so that it can be applied to the ITO glass. Moreover, the paste must contain a binding agent so that it can attach to the glass surface without getting scraped off.

Materials used for making the TiO₂ paste are as follows:

- i) TiO₂ (Degussa P25)
- ii) Citric Acid
- iii) Titanium isopropoxide
- iv) Triton X-100

One gram of TiO_2 powder (Degussa P25 which contains Anatase as well as Rutile in different proportions) is mixed with 1 ml of Citric acid and 0.5 ml of Titanium isopropoxide and then 0.5 ml Triton X-100 is added to the mixture and the total mixture was sonicated using a Sonicator for 10 minutes so that TiO_2 paste formed becomes uniform. The paste formed with the specified amounts of different chemicals can be used to coat several ITO glasses.

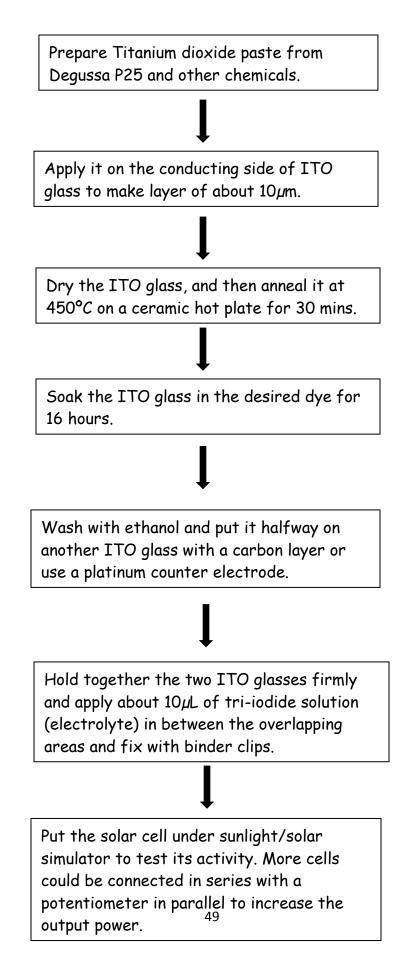
To investigate the effect of increasing Citric acid molarity on the output of the solar cell, different molarities of Citric Acid is used to make different types of TiO_2 paste keeping the others same. Molarities used for Citric acid are 1M, 0.75M, 0.50M, 0.3M, 0.2M, 0.1M, 0.075M and 0.05M. The results obtained will be presented later in this thesis.

2.5.2 Preparation of Dye

The natural dye was made from leaves of Red Spinach (*Amaranthus cruentus*) in a simple and cost-effective procedure. The leaves were smashed in a ceramic mortar and then soaked in acetone for 3.5 hours in a sealed black bottle in a dark place so that the dye from the leaves diffused into the acetone. The final solution was filtered and used as dye which would act as the sensitizer for the solar cell.

2.5.3 <u>Cell Assembly</u>

Indium-doped Tin Oxide (ITO) coated transparent glasses are used to make a full DSSC. Two glasses were cut at a size of 2.5 cm X 2.5 cm each. The resistance of each of the glass is around 15 ohm. The glasses are then washed with ethanol to remove any impurities present on the surface. TiO₂ paste prepared using Degussa P25 is uniformly coated on the conducting surface of one of the ITO glasses using Doctor's Blade Technique and the thickness of the layer is made around 10 micrometer. The TiO₂ coated ITO glass is then exposed in the air for some time and then heated at 450°C on a hot ceramic plate for 30 minutes for annealing Titanium dioxide crystal. During the period of heating, the Titanium oxide layer turns light brown and then finally becomes white again. After the glass has been cooled down, it is soaked in a container containing the natural dye. The ITO glass is placed so the Titanium dioxide coated layer faces the bottom of the container. The container is wrapped with aluminium foil and left for 16 hours. Thus the dye molecules get enough time to diffuse into the mesoporous structure and bind to Titanium atoms. The ITO glass is finally taken out of the container and washed with fresh ethanol again to remove any impurities on the surface. The white colour of the Titanium dioxide should now look purple. For the counter electrode, carbon layer is coated on the conducting surface of another ITO glass using soot from candle flame. The carbon coated glass is kept in the air to cool down. Then finally the two ITO glasses are assembled together keeping TiO₂ paste coated surface and the carbon coated surface face to face halfway along each ITO glass. Before fixing the glasses with binder clips, 10 microlitre of Iodide solution is slowly injected between the overlapping areas of the two ITO glasses. Iodine solution would move through capillary action and diffuse throughout the Titanium dioxide nano crystals. The natural dye-sensitized solar cell is now finally complete. Its output can be checked by placing it under sunlight or under a solar simulator.



2.6 Equivalent circuit models:

2.6.1 Silicon solar cells:

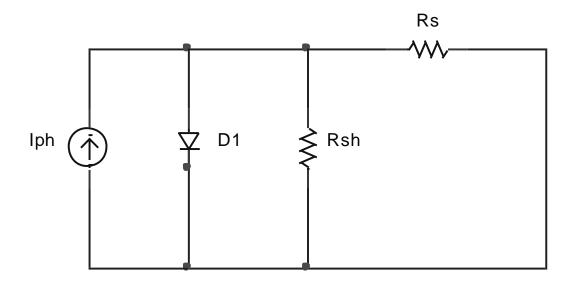


Fig.5. Equivalent circuit of a silicon solar cell

The different components in the equivalent circuit are as follows: [16]

- Iph Excitation of excess carriers by solar radiation
- D1 p-n junction
- Rs Bulk resistance of semiconductor materials, metallic contacts, interconnections, contact resistance between metallic contacts and semiconductor
- Rsh Resistance due to leakage across the p-n junction, around the edge of the cell, presence of crystal defects and impurities in junction region

2.6.2 Dye-sensitized solar cells:

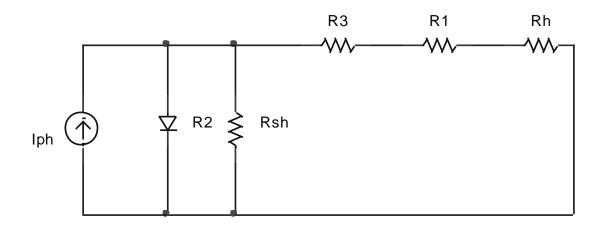


Fig.6. Equivalent circuit of a DSSC

The different components in the equivalent circuit are as follows: [16]

- Iph Excitation of excess carriers by solar radiation
- R1 = Resistance due to charge transport at counter electrode
- R2 = Resistance due to charge transport at TiO_2 / dye / electrolyte interface
- R3 = Resistance due to charge transport by ions within the electrolyte
- Rh = Sheet resistance of ITO glass and contact resistance between ITO glass and TiO₂ crystal
- Rsh = Resistance due to back transfer of electrons across the $TiO_2 / dye / electrolyte$ junction mainly in dye free regions of electrodes.

2.7 Characterization of the Cell

After the cell is prepared, it is kept under the sunlight to measure the cell performance. At the month of April in Dhaka under full sunshine, the performance was measured. We have measured the performance of the cells made using different molarities of the citric acid. We have varied the molarity of the citric acid from 0.05M to 1.00M.

As shown in the figure, the solar cell is illuminated under sunlight with the film coated ITO glass facing light and the two ends are connected to the two ends of a multi meter and readings taken. The results are show in Table-1.

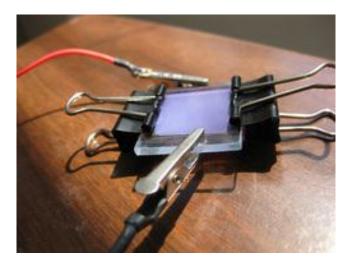


Fig. 7 Assembling a solar cell and measuring its output [17]

Molority of Aoid (M)	Voltage	Current density
Molarity of Acid (M)	(mV)	(mA/cm^2)
1	347	0.1
0.75	430	0.31
0.5	440	0.5
0.3	457	0.52
0.2	514	0.6
0.1	505	1
0.075	450	0.4
0.05	400	0.39

Table-2 The variation of Voltage and current density with the molarity of acid

It is found that the voltage and current increases with decrease in the molarity from 1M to 0.1M, after 0.10M they start decreasing. The optimum voltage and current is found using 0.10 M citric acid. The measured data using different molarities of citric acid is shown in Table-1. At 0.10M the measured voltage is 505 mV and the current is 1 mA/cm^2 .

"Fig. 8" shows the relationship of voltage and current with the molarity change.

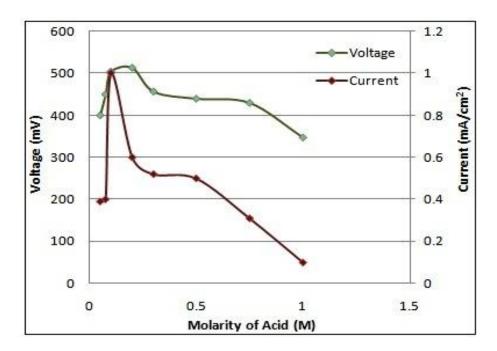


Fig. 8: Relationship of voltage and current with the molarity of Citric acid.

As seen from the graph that as the molarity of citric acid increases the cell performance increases and the optimum result is found when open circuit voltage is 505 mV and short circuit current density is 1 mA/cm^2 .

2.8 Calibration of the Cell under Sunlight

Bangladesh is situated at 24° 00' North latitude and 90° 00' East longitude [18]. At this position the maximum hours of sunlight each day is approximately 11 -12 hours a day in the month of April [19].

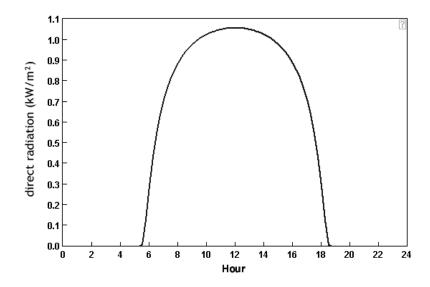


Fig. 9. The maximum intensity of direct radiation in kW/m² throughout the day in month of June in Bangladesh. **[19]**

From "Fig. 5" it is seen that intensity of solar radiation remains at 1000 W/m² for 2-3 hours when the sunlight is maximum in the month of June. At other times sunlight varies. But the real life scenario is not the same as the theoretical measurement mentioned in the figure. Even in the month of June, it is not possible to get 1000W/m² in Dhaka. We have measured the sunlight of 650 W/m² with our pyranometer on that particular day of April. It is not possible to get a sunlight of 1000W/m² which is the global standard, AM 1.5G in the months of April in Bangladesh. So, we have measured the cell performance under 650 W/m² instead of AM 1.5G. Under this condition the DSSC is calibrated under the sunlight and an efficiency of 0.39% is achieved.

2.9 Current-Voltage Characteristics

As the optimum cell performance is achieved using 0.1 M, the I-V characteristics of the solar cell are found using this molarity. The open circuit voltage (Voc) for the DSSC and short circuit current (Isc) has been found to be 505 mV and 1 mA/cm² respectively. On that particular day the intensity of the solar radiation was 650 mW/cm². The voltage and current are varied with a potentiometer connected in series with the cell to find out the I-V characteristics of the DSSC.

"Fig. 3" shows the I-V characteristics of the DSSC. Voltage across the cell (in mV) is plotted along the X-axis and photocurrent produced by the cell (in mA/cm^2) is plotted along the Y-axis. The x intercept represents the open circuit voltage (Voc) of the DSSC and the y intercept represents the short circuit current (Isc).

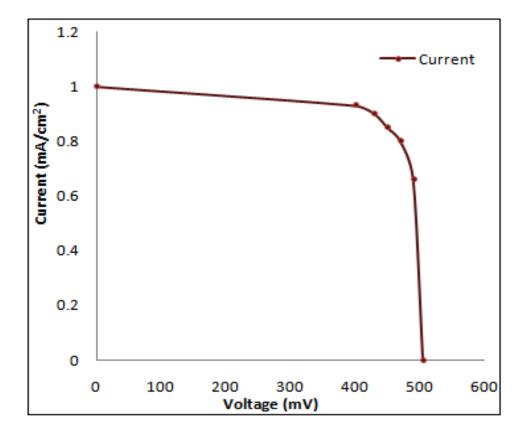


Fig. 10: The I-V curve of DSSC based on carbon counter electrode and Red Spinach Dye.

The Fill Factor (FF) **[20]** and the efficiency of the cell can be calculated from the "Fig. 3". The maximum power point on the I-V curve is that point that gives maximum power, i.e the point where the product of voltage and current is maximum.

$$FF = \frac{Vmp \times Imp}{Voc \times Isc}$$

The efficiency [21] of a solar cell is

$$\eta = \frac{Voc \times Isc \times FF}{Pin}$$

where

FF = Fill factor $\eta = Efficiency$ Vmp = voltage that gives maximum output power of the cell Imp = current that gives maximum output power of the cell Voc = Open circuit voltage of the DSSCIsc = Short circuit current of the DSSC

P_{in}= Input Power

(Vmp, Imp) is the maximum power point which is (430, 0.9) in the figure 3.

So, Fill Factor is **0.77** and the efficiency of the cell is calculated to be **0.39%**.

2.10 Observation of the Performance of the Cell using Industrial Grade TiO₂:

2.10.1 Preparation of Titanium dioxide Paste

We have used two different formula to make TiO_2 paste: one with HNO_3 and another without HNO_3 . All the other materials are same in both cases. The following formula has been followed for making Titanium (IV) Oxide (TiO₂) paste which is common for both the pastes (with or without HNO_3):

- 1. Anatase (80% TiO₂) 1.6 g
- 2. Rutile (20% TiO_2) 0.4g
- 3. 0.2M Nitric acid $(HNO_3) 1$ ml
- 4. PEG (Poly Ethylene Glycol) 1.4 ml
- 5. Triton X100 $(C_{34}H_{62}O_{11}) 0.5$ ml
- 6. Titanium Tetra Isoproxide 0.5 ml
- 7. 1N Sodium hydroxide (NaOH) 12µl

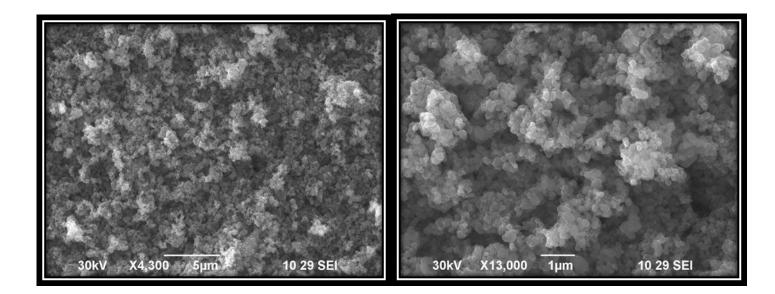
All other methods of preparation, e.g. dye extraction, heating, etc. are same as with Degussa P25 (shown previously)

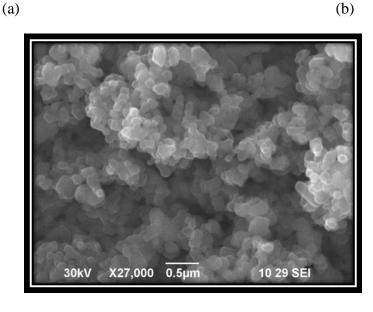
2.10.2 Results of the Cell Performance

After keeping the cell for several minutes under the sunlight, photoionization starts occurring. We have achieved a voltage of 704 mV from a single cell, but an extremely low current of 50 μ A. Moreover, the resistance of the cell was found to be 970 kilo ohms. We have got this result under full sunlight of April in Bangladesh which is 650 W/m². Pyranometer has been used to measure the light intensity of that particular time like before.

2.10.3 Discussion of the Result

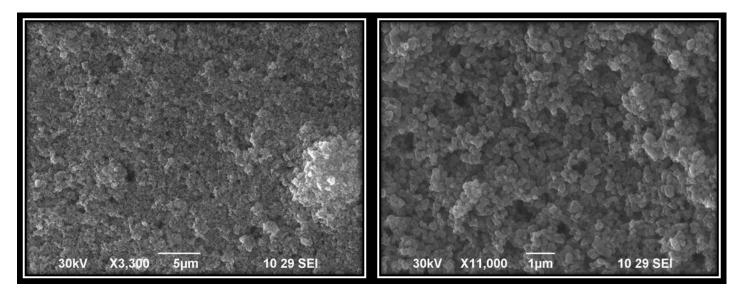
Fig. 1 and Fig. 2 show the scanning electron micrograph of TiO_2 mesoscopic layer which are made from pastes using HNO₃ and without HNO₃ respectively. If Degussa P-25 (laboratory grade TiO_2) is used it has seen that the TiO_2 nanoparticle distribution along the film is uniform.



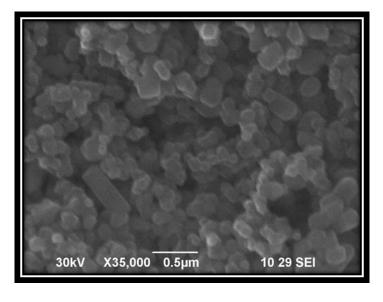


(c)

Fig.11. Scanning electron micrograph (SEM) of mesoporous TiO_2 film (HNO₃ used in making the films) supported on ITO glass (a) 5µm (b) 1 µm (c) 0.5 µm. The exposed facets of the anatase nano crystal are mainly oriented in (101) direction. [done in University of Dhaka]



(a) (b)



(c)

Fig.12. Scanning electron micrograph of mesoscopic TiO_2 film (HNO₃ not used in making the films) supported on ITO glass (a) 5µm (b) 1 µm (c) 0.5 µm. The exposed facets of the anatase nanocrystal are mainly oriented in (101) direction. [done in University of Dhaka]

2.10.4 Limitations

• The reason for getting extremely low amount of current can be attributed to the purity of the industrial grade TiO2 which is quite impure in terms of its chemical constituents. The impurity atoms contribute to the high resistance of the crystal, hindering efficient electron conduction by acting as an insulator. Thus electrons cannot pass through the insulated parts of the film resulting in low current.

If we look at the SEM (Fig. 1 and Fig. 2) of each sample from the range of 5μ m to 0.5μ m we can see that the nanoparticle distribution of the TiO₂ film is not uniform; it has little or no resemblance to the crystal formed using Degussa P-25 (Laboratory grade TiO₂). In fact, in some places it has created multiple crystals other than creating single crystal. Moreover, the impurities act as insulator as explained earlier. This implies that majority of the dye molecules could not bind to the Titanium atoms, causing much less photoionization. As a result low photoionization leads to very little amount of current.

- In case of counter electrode (cathode) number of options are available for using with ITO glass with graphite layer from pencil, carbon soot from candle / Carbon from carbon rod of an alkaline battery / Carbon from an artist's charcoal pencil or just platinum (usually recommended). Platinum would be a very good electrode had it been not for the fact that it is expensive while our goal is to make the cell cost effective. Thus we used carbon cathode. The graphite/ carbon layers from aforementioned sources do not produce a uniform layer and can get scraped off very easily.
- In open condition under sunlight the life-time stability of the cell is observed. It is found that the life time of DSSC varies with different thickness of the iodide electrolyte film. The cell made with 0.1 M citric acid has an electrolyte film thickness of 15 µm gives stable performance under sunlight for one hour and after that the short circuit current and open circuit voltage starts decreasing and after 15 minutes it reaches zero. This is due to the

electrolyte getting oxidized. Increasing the iodide film thickness increases the life time of the cell, but decreased the amount of short circuit current as the electrolyte film has high resistivity above 20 μ m. Keeping all the cell configurations same, we have increased the iodide solution thickness to 30 μ m which increases the life time of the cell when we have got open circuit voltage of 650mV-700mV for one and a half hour, but the short circuit was almost zero due to the fact that at this film thickness the resistance of the cell becomes 4.3 MΩ.

2.10.5 Ways to Increase Efficiency

- It is possible to increase the efficiency of the dye-sensitized solar cell using materials which are cheap and can bring down the fabrication cost of the cell. Besides using Red Spinach dye, some other natural resources such as dye from Malabar Spinach, River Ebony fruit, Black Berry and those containing anthocyanin can be introduced. These resources can be potential sensitizers for DSSC. The main goal of our future research was to make cheap efficient DSSC which can replace the presently used silicon based solar cell and thus we concentrate on sensitizers (dyes).
- Multiwall carbon nanotubes can be a very good cathode to increase the efficiency of the DSSC.
- Nickel cathode can be used by attaching Nickel to ITO glass by Chemical Vapour Deposition Method [22] and this can act as a good substitute for carbon while being less expensive than platinum.
- Replacing the tri-iodide solution (electrolyte) with a new cobalt complex [1] or reduce the thickness of electrolyte layer. [16]

Summary

We have discussed some new findings such as performance dependence of DSSC on molarity of citric acid, life time stability and have also showed an analysis that why DSSC made from industrial grade TiO_2 does not give good cell performance. We have also showed the detailed work and result of the cell made with TiO_2 (Degussa P25), carbon cathode, Red Spinach dye and iodide electrolyte which has given an efficiency of 0.39%. The performance of our cell is quite good and also the new findings of ours will give a new edge in the dye-sensitized solar cell research. The results we have shown in this thesis have been done by multiple experiments to ensure the quality of the work. Though 0.39% efficiency of the natural DSSC is still quite low compared to the silicon based solar cells, it is very much cost effective. With further research it is possible to improve the efficiency of the cell keeping the fabrication cost lower.

References:

[1] Grätzel, M., "Conversion of sunlight to electric power by nano crystalline dye-sensitized solar cells", Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 3–14, Elsevier

[2] http://www.solarnenergy.com/eng/info/show.php?c_id=3830

[3] http://en.wikipedia.org/wiki/Titanium_dioxide

[4] Ohno, T.; Sarukawa, K.; Tokieda,K.; Matsumura,M., "Morphology of a TiO₂ Photocatalyst (Degussa, P-25) Consisting of Anatase and Rutile Crystalline Phases", Journal of Catalysis 203, 82–86 (2001)

[5] Gratzel, M., "Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells", Inorganic Chemistry. 2005, 44, 6841–6851

[6] https://docs.google.com/viewer?a=v&q=cache:Kg3KPTc-tVwJ:www.diss.fuberlin.de/diss/servlets/MCRFileNodeServlet/FUDISS_derivate_000000002568/02_2.pdf%3Fhos ts%3D+&hl=en&pid=bl&srcid=ADGEESi_8AjHPZxXJG_-6u6n9Hrbe1UkpMdx3uLxs5I94jNm28IP4AuM6xAMyYq3IYgguxBf8p63IIo_q1g1rUTldcJvp8k RYN0NI_SFcPM2c8EoE6E4_SwcqcxYuEO3eE5hA03uho5p&sig=AHIEtbRAxRun9DAZkg6FuIeDPrCuhv5dw

[7] http://en.wikipedia.org/wiki/Anthocyanin

[8] http://en.wikipedia.org/wiki/Anthocyanin

[9] Calogero, G.; Marco, G.D.; Cazzanti,S.; Caramori, S.; Argazzi, R.; Carlo, A.D.; Bignozzi, C.A., "Efficient Dye-Sensitized Solar Cells Using Red Turnip and Purple Wild Sicilian Prickly Pear Fruits", International Journal of Molecular sciences, V.11(1); Jan 2010

[10] O' Regan, B. Grätzel, M., "A low cost, high efficiency solar cell based on dye-sensitized colloidal TiO₂ films", Nature, Vol. 353, 1991, p. 737-739

[11] Isah, K.U.; Kimpa, M.I.; Chidi, E.E.; Baba-Kutigi, A.N., "Dye-sensitized solar cell with natural dyes extracted from Indian almond plant andCashew leaf", The Third International Renewable Energy Congress December 20-22, 2011 – Hammamet, Tunisia.

[12] Ali, R.A.M.; Nayan, N., "Fabrication and analysis of dye-sensitized solar cell using natural dye extracted from dragon fruit", International Journal of Integrated Engineering (Issue on Electrical and Electronic Engineering)

[13] Calogero, G.; Marco, G.D.; Cazzanti,S.; Caramori, S.; Argazzi, R.; Carlo, A.D.; Bignozzi, C.A., "Efficient Dye-Sensitized Solar Cells Using Red Turnip and Purple Wild Sicilian Prickly Pear Fruits", International Journal of Molecular sciences, V.11(1); Jan 2010

[14] Wongcharee, K.; Meeyooa, V.; Chavadej, S., "Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers" Department of Chemical Engineering, Mahanakorn University of Technology, Nong Chok, Bangkok 10530, Thailand and The Petroleum and Petrochemical College, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand.

[15] Zhou, H.; Wu, L.; Gao, Y.; Ma, T."Dye-sensitized solar cells using 20 natural dyes as sensitizers", Journal of Photochemistry and Photobiology A:Chemistry, Elsevier.

[16] Koide, N.; Islam, A.; Chiba, Y.; Han, L.," Improvement of efficiency of dye-sensitized solar cellsbased on analysis of equivalent circuit", Journal of Photochemistry and Photobiology A: Chemistry 182 (2006) 296–305, Elsevier.

[17] http://dyesensitizedsolarcell.weebly.com/

[18] Bilkis A. Begum, Eugene Kim, Swapan K. Biswas, Philip K. Hopke, "Investigation of sources of atmospheric aerosol at urban and semi-urban areas in Bangladesh", Atmospheric Environment, Elsevier, Volume 38, Issue 19, June 2004, Pages 3025-3038.

[19] http://pveducation.org/pvcdrom/properties-of-sunlight/calculation-for-solar-insolation.

[20] http://www.pveducation.org/pvcdrom/solar-cell-operation/fill-factor

[21] http://www.pveducation.org/pvcdrom/solar-cell-operation/efficiency

[22] T. Maruyama, T. Tago, "Nickel thin films prepared by chemical vapour deposition from nickel acetylacetonate", Journal of Material Science, Volume 28 Number 19 (1993), 5345-5348, DOI: 10.1007/BF00570088.

[23] Grätzel, M., "Dye-sensitized Solar Cells", Journal of Photochemistry and Photobiology C:Photochemistry Reviews 4 (2003), p 145-153.

Chapter 3

MATLAB Simulations

Introduction

Simulation is a way of observing the performance of any system by varying different performance parameters under various conditions. There is various kind of simulation software present for simulation purposes. In this chapter we will use MATLAB and Simulink to observe different performance parameters of any generalized solar cell. Here we performed the simulations with assumed input values so that the simulations are applicable to all kinds of solar cells. Using the codes developed here we can calculate the efficiency, irradiance vs. efficiency plots of any type of general cells.

3.1 Functions used

In MATLAB there are various built in functions which perform different tasks. Functions [1] which we used for simulation are discussed below-

- **Input** (): This function requests data input from the user in the workspace. The general syntax for this function is user_entry=input ('prompt'). The string 'prompt' will appear in the workspace and prompt the user for any data input, which will be returned to the variable 'user_entry'
- **Display** (): It displays any text or array which we want as results of our simulation. The generalized syntax of this function is 'display(x)'; which displays the value contained in variable x in the workspace.
- **Zeros** (): This function creates an array of zeros. Therefore we can declare an array where data value at different times can be stored. The generalized syntax for this function is

'zeros (m, n)'. Here an array of m rows and n columns are created which is more like a matrix. Thus we can store different values at different positions.

- **Figure** (): This function opens a figure in workspace where necessary plots or graphical results can be shown. The generalized syntax of this function is 'figure (n)'; where n is the number of the figure declared.
- **Plot** (): This function is used to plot any data in our general x-y graphical format. Therefore we can compare the performance of a parameter against another one. The generalized syntax being 'plot (x, y)'; the data value of x and y are plotted graphically in a two dimensional fashion.
- **Surfc** (): This function helps us to plot variable data values in three dimensional shaded spaces. The generalized syntax being 'surfc (x, y, z)'. Therefore the data values of different parameters are depicted by x, y, z in a three dimensional space.
- **Xlabel** (): This function gives a label to the x-axis in a two dimensional or three dimensional plots.
- **Ylabel** (): This function gives a label to the y-axis in a two dimensional or three dimensional plots.
- **Title** (): This function gives a title to the two dimensional or three dimensional plots in the figure.

Besides the above mentioned functions there are some other functions used like 'clear all', 'close all', 'clc' etc. which clears any previous data value from the workspace and resets the software for debugging of the codes.

3.2 Familiarization with some parameters used

There are some parameters **[2]** used as variables which have different function and operations. They are discussed below:

I=incident sunlight intensity in Watt/square meter
A=area of cell in square meter
Voc=open circuit voltage in volts
Isc=short circuit current in amperes
FF=fill factor
Pout=maximum power output in watt
Pin=input power in watt
n=number of readings taken

3.3 Simulation of Efficiency calculations of a cell

In this simulation we coded a MATLAB program to calculate the efficiency of any generalized solar cell. The efficiency calculations [3] are performed using the equation:-

Efficiency, $\eta = \frac{output \ power}{Input \ power}$

$$= \frac{Voc*Isc*FF}{(area of the cell)*(incident sunlight intensity)}$$
[5]

3.3.1 MATLAB codes

```
%% Efficiency calculations of a general cell
   Pout=maximum power output in watt
8
8
  Pin=input power in watt
  Voc=open circuit voltage in volts
8
  Isc=short circuit current in amperes
00
  FF=fill factor
8
9
 A=area of cell in square meter
 I=incident sunlight intensity in Watt/square meter
00
clear all;
close all;
A=input('please input area of cell in square meter');
I=input('please input incident sunlight intensity in Watt/square
meter');
Pin=I*A;
Voc=input('please input open circuit voltage in volts');
Isc=input('please input short circuit current in ampere');
FF=input('please input fill factor');
Pout=Voc*Isc*FF;
n=100*(Pout/Pin);
display(Pin)
display (Pout)
display(n)
```

This program can calculate efficiency of a cell for different input parameters. For some general cases we consider following parameter values (values are assumed for checking the operation of the program):-

3.3.2 <u>Case 1</u>

Incident sunlight intensity, I= 650 watt/square meter

Area of cell, A=0.000625 square meter

Open circuit voltage, Voc=1.5 volts

Short circuit current, Isc=0.04 amperes

Fill factor, FF=0.7

3.3.3 Results in MATLAB Workspace

```
please input area of cell in square meter.000625
please input incident sunlight intensity in Watt/square meter650
please input open circuit voltage in volts1.5
please input short circuit current in ampere.04
please input fill factor.7
Pin =
        0.4063
Pout =
        0.0420
n =
        10.3385
fx >> |
```

Fig.1. Results	s in MATLAB	Workspace
----------------	-------------	-----------

Efficiency of the general cell with assumed values is calculated as 10.3385%

3.3.4 <u>Case 2</u>

Incident sunlight intensity, I= 550 watt/square meter

Area of cell, A=0.000625square meter

Open circuit voltage, Voc=2.5 volts

Short circuit current, Isc=0.03 amperes

Fill factor, FF=0.7

3.3.5 Results in MATLAB Workspace

```
please input area of cell in square meter.000625
please input incident sunlight intensity in Watt/square meter550
please input open circuit voltage in volts2.5
please input short circuit current in ampere.03
please input fill factor.7
Pin =
        0.3438
Pout =
        0.0525
n =
        15.2727
```



Efficiency of the general cell with assumed values is calculated as 15.2727%

3.3.6 Discussions

For any generalized cell we calculated efficiency 10.3385% and 15.2727% respectively in case 1 and case 2. (Input values are assumed). Therefore the functionality of the program is variifed.

3.4 Simulation of Solar irradiance vs. corresponding efficiency

In this simulation we coded a MATLAB program to plot graphically Solar incident irradiance vs. corresponding efficiency in a two dimensional graphical plot. Therefore the change in efficiency of any cell with change in corresponding irradiance can be observed with the help of this program (with assumed values).

3.4.1 MATLAB codes

- %% Plotting Solar Irradiance vs corresponding Efficiency (fig-1)
- % Pout=maximum power output
- % Pin=input power
- % Voc=open circuit voltage
- % Isc=short circuit current
- % FF=fill factor
- % A=area of cell in square meter
- % I=incident sunlight intensity in Watt/square meter
- % n=number of readings taken

```
%% COPYRIGHT : OMAR ASIF, RADIF RILDAD HAQUE, KHAIRUL ANAM
```

```
% Islamic University of Technology
```

```
clear all;
```

close all;

```
n=input('input number of readings taken');
```

```
Voc=zeros(1,n);
```

```
Isc=zeros(1,n);
```

```
FF=zeros(1,n);
A=zeros(1,n);
I=zeros(1,n);
Pout=zeros(1,n);
Pin=zeros(1,n);
E = zeros(1, n);
for m=1:n
    Voc(m)=input('input open circuit voltage in volts');
    Isc(m)=input('input short circuit current in ampere');
    FF(m)=input('input fill factor');
    A(m)=input('input area of cell in sq.m');
    I(m)=input('input solar irradiance in W/sq.m');
    Pout (m) = Voc(m) * Isc(m) * FF(m);
    Pin(m) = I(m) * A(m);
    E(m) = 100 * (Pout(m) / Pin(m));
end
display(I);
display(Voc);
display(Isc);
display(E);
figure(1);
plot(I,E,'--*');
xlabel('Irradiance in W/sq.m');
ylabel('Efficiency');
title('Efficiency vs Irradiance');
```

This program can calculate Solar incident irradiance vs. corresponding efficiency for different input parameters. For some general cases we consider following parameter values (assumed):-

3.4.2 <u>Case 1</u>

number of readings taken= 5

Incident sunlight intensities, I=[300 400 500 600 700] watt/square meter

Area of cell, A=0.000625 square meter

Open circuit voltages, Voc=[1.5 2.0 2.25 2.37 2.461] volts

Short circuit currents, Isc=[0.02 0.03 0.035 0.04 0.045] amperes

Fill factors ,FF=0.7

3.4.3 <u>Results in MATLAB Workspace</u>

	I =				
	300 400	500 á	500 <mark>7</mark> 00		
	Voc =				
	1.5000	2.0000	2.2500	2.3700	2.4610
	Isc =				
	0.0200	0.0300	0.0350	0.0400	0.0450
	E =				
	11.2000	16.8000	17.6400	17.6960	17.7192
fx,	>>				

Fig.3.Results in MATLAB Workspace

3.4.4 Plot of Efficiency vs. Irradiance [6]

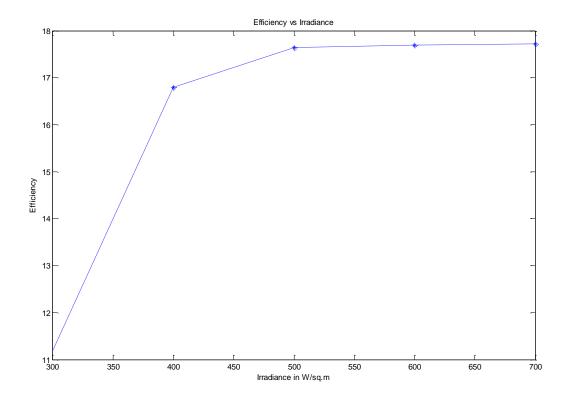


Fig.4.Plot of Efficiency vs. Irradiance [6]

3.4.5 <u>Case 2</u>

number of readings taken= 6

Incident sunlight intensities, I=[300 400 500 600 700 800] watt/square meter

Area of cell, A=0.000625 square meter

Open circuit voltages, Voc=[1.289 1.666 1.964 2.08 2.1875 2.2625] volts

Short circuit currents, Isc= [0.02 0.03 0.035 0.04 0.045 0.05] amperes

Fill factors ,FF=0.8

3.4.6 Results in MATLAB Workspace

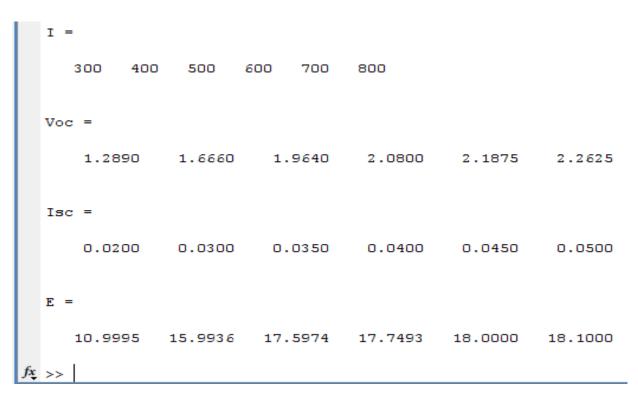


Fig.5.Results in MATLAB Workspace

3.4.7 Plot of Efficiency vs. Irradiance [6]

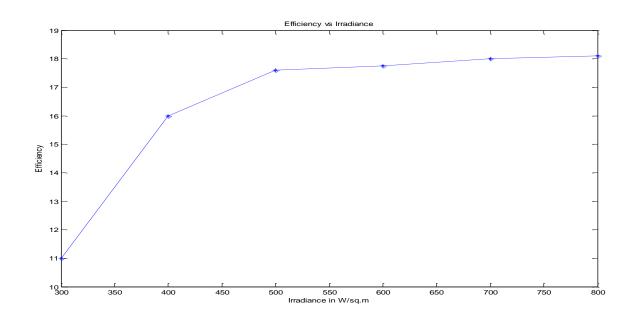


Fig.6.Plot of Efficiency vs. Irradiance [6]

3.4.8 Discussions

In above cases we considered taking five and six readings for case 1 and case 2 respectively. The number of readings taken can be increased if the user wishes. The codes developed here perform simulation based on the input parameters given and graphically plots Efficiency for corresponding varying Solar Irradiance. The plot shows that with increase of irradiance the efficiency of the cell also increases. Therefore the efficiencies have almost linear relations with incident irradiance at lower values. But efficiencies gradually reach constant values for higher irradiances

3.5 Simulation of Efficiency calculations using Simulink

Simulink is an important and effective tool of MATLAB. Simulink helps us to perform simulations using various blocks present in Simulink library. Here we do not need to write lengthy codes. Therefore it is an efficient approach for simulations.

3.5.1 <u>Functional blocks used</u> [4]

Constant: This block outputs the constant value specified as an input. It is represented by-



Product: This block can perform element wise or matrix multiplications. It is represented by-



Divide: This block can perform element wise or matrix divisions. It is represented by-



Display: This block is used to numerically display output data value. It is represented by-



3.5.2 Simulink blocks representation

We will perform the same cases as described in section **3.4.2**, **3.4.4** and observe if the results are similar or not. (Input values are assumed to check functionality of the Simulink blocks).

3.5.3 Case 1

Incident sunlight intensity, I= 650 watt/square meter

Area of cell, A=.000625 square meter

Open circuit voltage, Voc=1.5 volts

Short circuit current, Isc=.04 amperes

Fill factor, FF=0.7

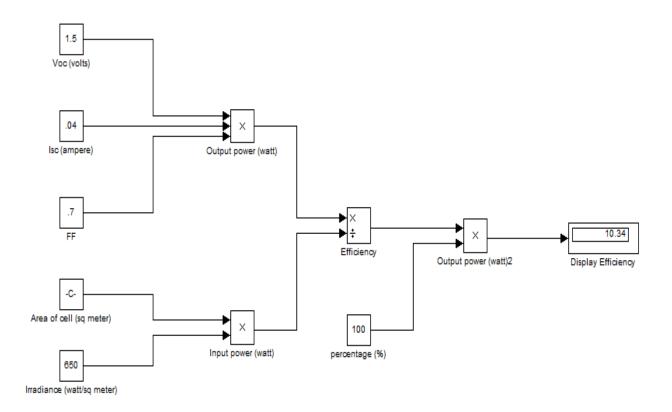


Fig.7. Simulink blocks representation

Efficiency of the general cell with assumed values is calculated as 10.34% which is very close to the one calculated in section **3.4.3** (10.3385%).

3.5.4 <u>Case 2</u>

Incident sunlight intensity, I= 550 watt/square meter

Area of cell, A=0.000625square meter

Open circuit voltage, Voc=2.5 volts

Short circuit current, Isc=0.03 amperes

Fill factor, FF=0.7

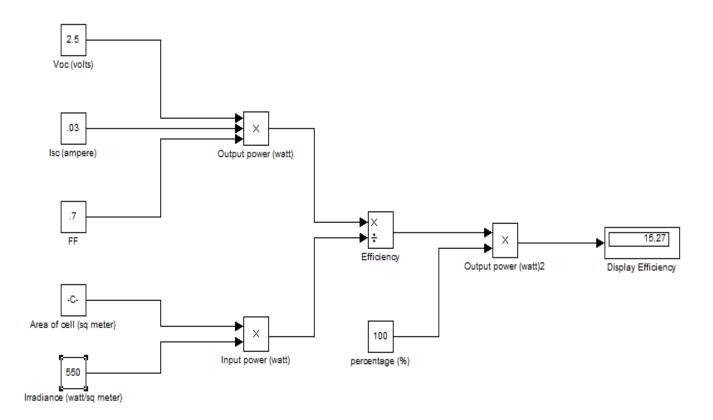


Fig.8. Simulink blocks representation

Efficiency of the general cell with assumed values is calculated as 15.27% which is very close to the one calculated in section **3.4.5** (15.2727%).

Therefore we see that efficiencies found by MATLAB codes in section 3.4 are same as efficiencies calculated by Simulink blocks. Also using Simulink blocks are advantageous because we did not need to write codes.

3.5.5 Discussion

In this Simulink block representation for efficiency calculations we start with giving input values as constants. Thus we input values of Open circuit voltages, Voc; Short circuit currents, Isc; Fill factors, FF; Area of cell, A ; Incident sunlight intensities, I etc. After inputting values we perform multiplication and calculate input power and output power. Later by division efficiency

is calculated. We multiply the calculated efficiency by 100 to express the result as percentage (%). Here we interpreted the following equation (discussed earlier) using Simulink blocks.

Efficiency, $\eta = \frac{output power}{Input power}$

 $= \frac{Voc*Isc*FF}{(area of the cell)*(incident sunlight intensity)}$ [5]

Summary

The simulations done can help to predict the nature of solar cells and make a thorough analysis of its characteristics. The simulated outputs can help us predict what the actual results would be and thus make a comparison with real outputs.

References:

[1] MATLAB version 7.8.0.347 (R2009a), License number: 161051, Copyright 1984-2009, The MathWorks, Inc.

[2] http://pveducation.org

[3] http://pveducation.org/pvcdrom/solar-cell-operation/efficiency

[4] Simulink tool, MATLAB version 7.8.0.347 (R2009a), License number: 161051, Copyright 1984-2009, The MathWorks, Inc.

[5] http://pveducation.org/pvcdrom/solar-cell-operation/efficiency

[6] Donovan, M.; Bourne, B.; Roche, J. "Efficiency vs. Irradiance characterization of PV modules requires angle-of-incidence and spectral corrections", SunPower Corp., Richmond, CA, USA, Photovoltaic Specialists Conference (PVSC), 2010 35th IEEE.

CHAPTER 4

COST EFFECTIVE ARTIFICIAL HIGH FLUX SOLAR SIMULATOR BASED ON 450W XENON LAMP

Introduction

A Solar Simulator is a device consisting of a light source which imitates the action of sunlight by providing light whose spectrum is close to that of sunlight. The reason for using such a device is to illuminate solar cells for testing purposes in the lab when sunlight is not available as in the case of cloudy days or during nightfall when it might become necessary to test a solar cell.

With the increasing popularity of solar energy, scientists are working to build efficient solar cell. Efficiency measurement of solar cells is an important factor and it has to be measured under certain condition. As the solar radiance and intensity are different in different places on earth, a global standard has been set to consider the full sunshine which is $1000W/m^2$ which is called AM 1.5G [1]. As during night or in the cloudy and rainy days, it is not possible to get AM 1.5G,

An artificial system is made so that we can measure the efficiency of the solar cells made in the laboratory at any conditions. The system is build using 23kV bulb type capacitor, a 450W Xenon HID bulb and an AC to DC converter. This paper describes the design procedure, system description, working principle and whole mechanical structure of the simulator box.

4.1 Background Study

For measuring the solar cell performance in the absence of sunlight solar simulator is necessary. Some previous research has been done on this by many researchers in which different

types of solar simulator are designed and most of these solar simulators use Halogen and Xenon lamp to produce desired solar intensity, but these facilities are large and expensive [2]. Moreover, halogen lamps increase the temperature of the solar cell in significant amount due to presence of higher portion of infra-red spectrum. Temperature increase is undesirable as solar cell performance degrade with increase in temperature. In some cases, solar simulator is designed using LEDs which compensate for the problem associated with temperature, but light intensity is not sufficient with LEDs [2]. Therefore, to reduce the design cost, size of the facility and to increase the intensity of the light to a sufficient level we have designed a new solar simulator which produces sufficient light intensity to generate AM 1.5 spectrum.

4.2 Basic Design

The basic design includes a Xenon lamp source, a wooden structure to hold the lamp source and creating an environment so that the solar cell kept inside gets the desired light intensity and light spectrum from outside cannot interfere the Xenon light spectrum changing the intensity level. At the top of the wooden box there should be a water bath which acts as an Infra-red filter. It absorbs the infra-red portion of the light spectrum created from Xenon light source.

4.3 Light Source Simulating Artificial Sunlight

For the light source, a 450W Xenon HID bulb has been used because spectral irradiance of the sunlight has almost the same behavior as Xenon lamp. HID xenon lamp is brighter, more energy efficient and longer lasting than any other available incandescent lights [3]. The efficiency of the incandescent light varies from 8-14%, while the efficiency of HID metal halide bulb such as Xenon can reach up to 36% [4]. "Fig. 1"shows the spectral irradiance of artificial light sources compared to the spectral irradiance from the sun which clearly indicates among the artificial sources available Xenon lamp has the closest behavior as sunlight. One more benefit of using Xenon lamp is its capacity of producing less infra-red light. One disadvantage of infra-red light is that it produces heat which increases the temperature of the internal environment of the total

structure. Some important characteristics of HID bulb are: Source-Arc Discharge type light, colour temperature of 4,100° K and life duration is nearly 3000 hours.

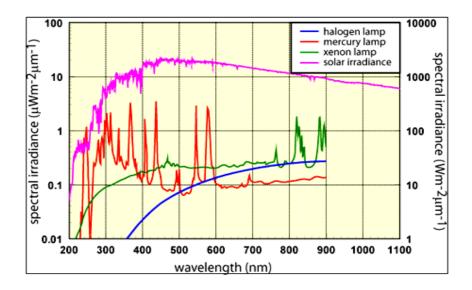


Fig.1. The spectral irradiance of artificial light sources (left axis) compared to the spectral irradiance from the sun (right axis) [4]

This Xenon bulb is connected to a 23kV bulb type discharging capacitor. The capacitor is connected to an AC-DC converter which converts 220V AC current from the supply into 12V DC voltage. The capacitor gets charges first and then discharges to illuminate the Xenon lamp. Basic block diagram of the light source is given in "Fig. 2" below.

Moreover, the price of the HID Xenon bulb is very cheap. It usually varies from approximately \$22 to \$50 depending upon the type and system [6]. In our case the HID Xenon bulb with the buck-boost convertor system costs \$25.

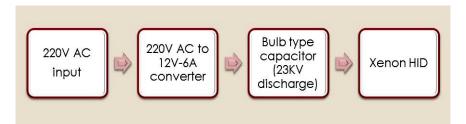


Fig. 2. Block Diagram of the 450W Xenon Lamp based Light Source.

"Fig. 3" shows the circuit diagram of the Xenon Lamp source. A 220V AC power is supplied to centre- taped transformer.

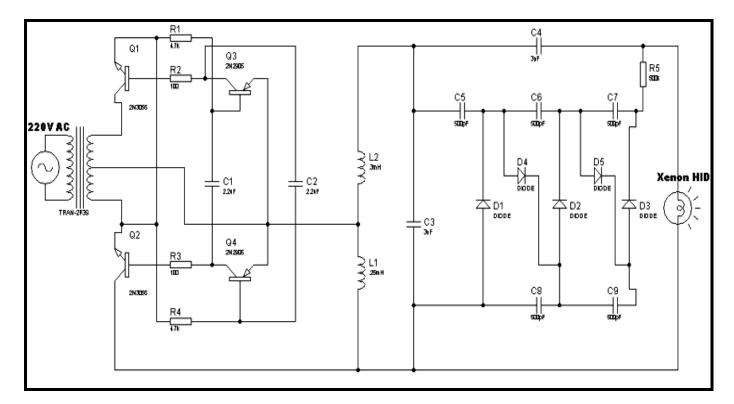


Fig. 3. Schematic Diagram of a Xenon lamp based artificial Solar Simulator

Here the transformer step downs the AC voltage level to 12 V. This voltage is stepped down but current rises to 6 A as the power remains same in both sides. Now, the BJTs (Q1, Q2, Q3, and Q4) simply act as switching devices to rectify the alternating current to direct current (same as rectifier function). Capacitors are used to reduce ripple in DC current so that we can maintain a steady and nearly constant current flow. The capacitor block is used to discharge a voltage of

23kV instantly. It generates a high pulse voltage of very short duration and supplies it to the HID lamp. DC voltage is higher than the breakdown voltage of the HID lamp and the capacitor block supplies the DC voltage to the HID lamp. To boost the voltage across the capacitor C3, capacitor C4, five capacitors (C5, C6, C7, C8, and C9), five diodes (D1, D2, D3, D4, D5) and one resistor R5 are used. The inductors work as reactors to create resonant circuit. HID lamps need high voltage pulse to illuminate. A high current (about 6A) turns the electrodes of the HID bulb into arc discharge state (HID lamps are arc discharge type lamps).

4.4 Mechanical Structure Of The Box Creating Internal Sunlight Environment

When it comes to the mechanical structure, it is one of the most cost-effective designs which serve the purpose of usual solar simulators. The structure of the simulator has been constructed using plywood and is 4 feet tall and with an area of 12 inches X 8 inches. The whole structure is closed except at the front where a flexible door is present. Solar cell can be put inside using this door and the latter prevents light from external source interfering with the spectrum of the internal light source and changing the intensity level. The interior consists of a Xenon HID lamp source suspended from the top, a thin wooden plate to hold the solar cell and associated circuitry. The internal walls of the box is colored with reflective white paint so that the light from the Xenon HID lamp gets reflected from the surrounding walls and falls upon the solar cell kept on the surface inside the box. Moreover, nails have been hammered into two opposite walls at 1 inch interval starting 6 inches from the bottom of the Xenon HID lamp source until the bottom of the simulator. This enables measuring the output of the solar cell at different light intensities as intensity of light depends on the distance from the source.

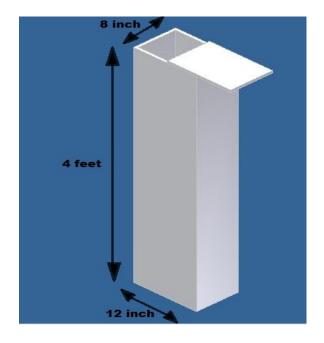


Fig. 4. Three dimensional view of the mechanical structure of the wooden box creating the internal solar environment

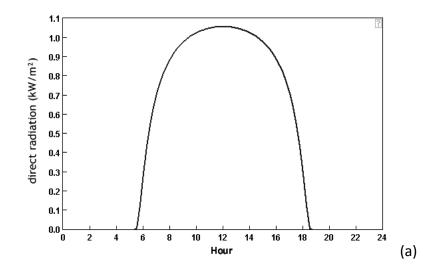
"Fig. 4" shows the 3D view of the mechanical structure of the wooden box. At the top of the box, there is a water bath chamber which acts as the Infra-red filter. As Xenon light spectrum has some portion of infra-red wavelength, water bath absorbs it and helps to keep the internal temperature of the box less.

4.5 Irradiance Measurement

The artificial solar simulator that's been built using a "450W Xenon lamp produces light of intensity from 200W/m² to 1200W/m². The irradiance of light generated by Xenon lamp is measured using a pyranometer for every point on the wall. The first point which is under 6 inch from the light source has an intensity of 1200W/m². The second to tenth point which are at a distance of 1 inch from one another have intensities of 1150W/m², 1100W/m², 1000W/m², 940W/m², 500W/m², 350W/m², 270W/m², 200W/m² respectively. At these points, the characteristics and performances of a solar cell can be measured in different intensities.

4.6 <u>Calculation Based On Solar Insolation And Comparison Between Sunlight and Solar</u> <u>Simulator</u>

Bangladesh is situated at 24°00' North latitude and 90°00' East longitude. At this position the maximum hours of sunlight each day is from June-July (approximately 12 -13 hours a day). "Fig. 5a" and "Fig. 5b" are generated analyzing the location of Bangladesh and solar insolation during the month of June-July using the tools from reference [7]. "Fig. 5b" shows the amount of hours of sunlight in Bangladesh. So, for the remaining hours of the day we are getting no sunlight at all. For other ten months the maximum hours of sunlight each day is less and sometimes fall down to 10 hours/day. Our experiment was carried out in the month of April, when the sunlight approximately stays available for about 11-12 hours/day. In these rest of the hours when sunlight is absent, our simulator can be a great supplement for solar cell performance testing.



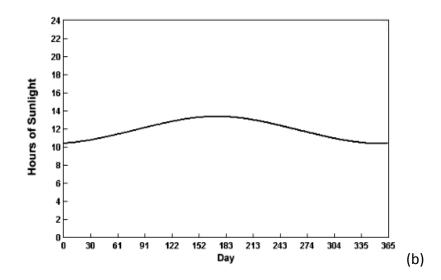


Fig. 5. (a) The maximum intensity of direct radiation in kW/m² throughout the day in month of June; (b) The amount of hours of sunlight in Bangladesh. [7]

From "Fig. 5a" it is also clear that intensity of solar radiation remain at 1000W/m² for 2-3 hours, i.e. at other times we cannot get this intensity from sunlight which is the global standard for measuring the solar cell performance. For the rest of the hours of the day the artificial solar simulator can be a good solution to generate AM 1.5G (1000W/m²) whenever needed.

Summary

The solar simulator and the box are very simple design made by us. The components used are not very costly which made the system very much cost-effective as well. The system is being used in the laboratory to measure the cell performance regularly and it has been performing efficiently. We are working on other light source besides Xenon lamp as even though we are using water bath chamber a sufficient amount of infra-red still remains in the box environment raising the temperature. The system is a great relief to work with at night and cloudy environment. Our further research is going on to make the system more effective so that the no water bath chamber has to be used which will give the system more transportable advantage.

References

[1]Safa O. Kasap, Optoelectronics And Photonics: Principles and Practices, First Impression 2009, ISBN 978-81-317-2468-2, pg. 254-261.

[2] Shogo Kohraku, Kosuke Kurokawa, "New methods for solar cells measurement by LED solar simulator", Proceedings of 3rd World Conference on Photovoltaic Energy Conversion, 2003. IEEE Xplore, Vol. 2, pages:1977-1980

[3] M A Mainster, G T Timberlake, "Why HID headlights bother older drivers", Br J Ophthalmol 2003;87:113-117 doi:10.1136/bjo.87.1.113

[4] Y.K. Cheng, K.W.E. Cheng, "General Study for using LED to replace traditional lighting devices", 2nd International Conference ofn Power Electronic Systems and Applications 2006, pg- 173- 177

[5] http://pveducation.org/pvcdrom/properties-of-sunlight/spectral-irradiance

[6] http://kenuo88.en.made-in-china.com/

[7] http://pveducation.org/pvcdrom/properties-of-sunlight/calculation-fo-solar-insolation

Conclusion

In this thesis we are privileged to illustrate our work on "Fabrication and Characterization of a Nano crystalline Natural Dye-Sensitized Solar Cell and Design of an Artificial Solar Simulator". The thesis has been depicted in four chapters which covered background research, discussions on Dye-Sensitized Solar Cells, Simulations done using MATLAB, Artificial Solar Simulator etc.

Our main goal was to investigate the effect of natural dyes on dye-sensitized solar cells and hence find a substitute for artificial dyes which are expensive. Various ongoing researches suggest a viable option could be using Natural dyes in place of artificial dyes. In our work we projected a way to use locally available natural dyes to fabricate DSSC cells and characterize its functionality. Results obtained from using Red spinach (*Amaranthus cruentus*) dye are quite satisfactory and shows that natural dyes will play a significant role in the coming days and a lot of research work needs to be done.

The Solar Simulator that has been built using a 450W Xenon lamp produces a light of intensity from $200W/m^2$ to $1200W/m^2$. The purpose of making this solar simulator was to measure cell performance under AM 1.5G as most of the time around the year it is not possible to get continuous solar irradiance of $1000W/m^2$ in Bangladesh. The interesting part is that this solar simulator has been constructed using cheap materials available in Bangladesh for the first time. Hopefully this simulator would serve the purpose of expensive hi-tech solar simulators that are available in the market.