PERFORMANCE OF NATURAL DYE SENSITIZED SOLAR CELLS FOR LOW POWER APPLICATIONS

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TERMS OF REFERENCE

This Report is made to fulfill the practical and academic requirements of the Doctor of Philosophy Research Degree in Electrochemical Engineering pertaining to the 3rd generation Solar Photovoltaic Cell Technology of Dye – Sensitized Solar Cells (DSSC's) of Renewable Energy Systems.

DECLARATION

This is a report of research work carried out at the Department of Chemical and Process Engineering and it's Laboratories of the University of Moratuwa, Katubedda, and Laboratories of the Solid State Chemistry Division of the Institute of Fundamental Studies (IFS), Hantana, Sri Lanka between November 2008 and November 2014. Except where the references are made to other work, the contents of this research work are original. This work has not been submitted in part or in whole to any other University.

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ABSTRACT

The need for renewable energy sources in Sri Lanka is assessed and solar photovoltaics (PVs) is identified to be the most technically suitable and economically viable power source for the conversion of solar energy to electricity in future. Three generations of solar PVs comprising 1st, 2nd and 3rd generations are dentified, and Dye – Sensitized Solar Cells (DSSCs) comprising the 3rd generation cutting – edge solar cell technology is identified being the low-cost easy to manufacture, durable, stable, long life time with reasonably high solar energy to power conversion efficiency (11% max with expensive , scarce, synthetic dyes like Ruthenium bipiridyl complex technology), or of about 1% with cheap, low-cost, abundant, non-toxic, environmentally friendly natural dyes of photosynthetic green plants. Natural dyes were selected to carry out further research and development work for practical applications.

Research done on DSSC's since inception in Sri Lanka were scrutinized and assessed at the Institute of Fundamental Studies (IFS), Hantana, Sri Lanka, and other Institutions in Sri Lanka. It has been observed that most of the research at the IFS has been done using very expensive synthetic Ruthenium metallic dyes and have achieved a high conversion efficiency of 10% in May 2001.

DSSCs sensitized with 145 natural dyes of plants growing in Sri Lanka were electrically and electronically tested and the ethanolic dye extracts of natural Mangoostein fruit rind (deep purple colour) exhibited the best conversion efficiency (of about 1%.) . It was also observed that other natural dyes such as Ekkiriya wood, Egg plant fruit peel, Karawalla kabilla fruit, Banana flower inflorescence, Beetroot tuber, Turmeric root and Fire fern leaf (not endemic to Sri Lanka) yield relatively good conversion efficiencies.

Natural dye-based DSSCs even though possess conversion efficiencies usually below 1%, may be improved by finding different additives. Such DSSCs are cost effective , easy to manufacture, environmentally friendly and stable . They are potential solar energy to electricity conversion devices for low power applications if further research is done to boost their conversion efficiencies to about 2% - 3%, and to increase their long term stability. The reasons why DSSC's have not been developed for commercial use in Sri Lanka have been identified, assessed and remedial measures proposed.

Research and development work were also initiated to develop practical DSSCs sensitized with low-cost abundant and environmentally friendly natural dyes of plants for low power applications such as battery charging of mobile telephones, iPod's, portable radio communications equipment, LED operated multi – coloured garden - night lights of hotels etc., construction of Building Integrated Photovoltaic (BIPV) systems to provide diffused lighting with multicoloured LED operated lighting systems, provision of propulsion power to small boats etc, in order to assist solve the impending energy crisis when all known sources of fossil fuel will be exhausted in a few decades.

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LIST OF ACRONYMS (ABBREVIATIONS)

Abbreviation	**Description**
AM	Air Mass Density
PV	Photovoltaic
DSSC’s	Dye –Sensitized Solar Cells
CB	Conduction Band
VB	Valance Band
WE	Working Electrode
FTO	Fluorine doped Tin oxide
CE	Counter Electrode
Pt	Platinum
IL	Ionic liquid
AN	Acetonitrile
I – V	Current – Voltage
Jsc	Short Circuit Current Density
Voc	Open Circuit Voltage
Io	Light intensity
ff	Fill Factor
η	Overall light to –electricity conversion efficiency
P_{in}	Intensity of incident light
P_{max}	Maximum Power
HOMO	Highest occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
HTM	Hole Transporting Material
LHE	Light Harvesting Efficiency
IPCE	Incident Photon to Current Converse
OPV	Organic Photovoltaic
N	Electron concentration
P	Hole concentration
R_S	Series Resistance
R_t	Electron Transport resistance
P	Power Density
K	Kinetic Constant
K_B	Boltzmann Constant
L	Length
L_D	Electron Diffusion Length
T	Temperature
W	Watt
eV	Electron Volts

LIST OF PUBLICATIONS

I. Design and development of Dye-Sensitized Organic Semiconductor Based Photoelectric System utilizing Nanotechnology for Low Cost and Efficient Conversion of Solar Energy to Electricity. 15th Engineering Research Unit Symposium 6 November 2009, Faculty of Engineering, University of Moratuwa, Sri Lanka . C.I.F. Attanayake, B.A.J.K. Premachandra, A.A.P.De Alwis, andG.K.R.Senadheera.

II. Solar Powered Naval Patrol Boat Operating on Dye Sensitized Solar Cells (DSSC's)utilizing Fruit and Spice Extracts. National Energy Symposium of Sri Lanka, Sustainable Energy Authority , 13 & 14 August 2011, Ministry of Power & Energy . C.I.F. Attanayake, B.A.J.K. Premachandra and A.A.P. De Alwis.

III. Study of Novel Dyes to Support DSSC Research. First National Nanotechnology Conference, 24 – 25 August 2012, National Science Foundation, Sri Lanka .C.I.F. Attanayake, B.A.J.KPremachandra, A.A.P De Alwis and G.K.R.Senadheera.

IV. Dye Sensitized Solar Cells : Using over 100 Natural Dyes as Sensitizers. American Institute of Chemical Engineers (AICHE), Annual Meeting 3 – 8 November 2013,Global Challenges for Engineering a Sustainable Future , Hilton San Fransisco Union Square, California, U.S.A. This invited research paper was accepted for oral presentation at the AICHE Annual Meeting , and published in the November 2013 Proceedings of the Annual Meeting .

V. Study of Novel Dyes for use in DSSC's . International Journal of Solar Energy Materials & Solar Cells submitted on 24 March 2014, being followed up and awaiting publication . **C.**I.F. Attanayake, B.A.J.K., Premachandra, A.A.P. de Alwis and G.K.R.Senadheera.

VI Review of Dye Sensitized Solar Cell Research in Sri Lanka. 01 November 2011. Department of Chemical and Process Engineering, University of Moratuwa, Katubedda, Sri Lanka**. C.**I.F. Attanayake, B.A.J.K., Premachandra, A.A.P. de Alwis and G.K.R.Senadheera.

VII Comparison of Characteristics and Properties of Rutin and Mangoostein Dye Sensitized Solar Cells. Submitted to the Chinese Chemical Society , Beijing, Peoples Republic of China , e-mail : wlhxxb@pku.edu.cn on 15 January 2016 for publication in the Solar Energy Materials and Solar Cells Journal and accepted for peer review process prior to publication . C.I.F.Attanayake, B.A.K.J. Premachandra, A.A.P.De Alwis and G.K.R.Senadheera.

CHAPTER 1

INTRODUCTION

1.1 The problem of energy sufficiency

The greatest challenge for human beings on the planet Earth at present is to find ways and means to replace the slowly, but inevitably vanishing fossil fuel supply with renewable energy resources, and at the same time to avoid the negative effects from current energy systems on climate, environment and health . Also the Indian Air Force stated that by 2030 the world will need 50% more energy than what is consumed right now. This is indeed a stray challenge.

1.2 Attempts made to solve the problem

Thus with oil, petrol, diesel, kerosene and furnace fuel oil prices increasing due to the dwindling of these scarce fossil fuel resources in the world market, vast amounts of renewable energy sources like wind, hydro,solar, geothermal, tidal and wave power have been identified as most suitable alternative energy sources for Sri Lanka as well.

Amongst renewable energy sources in Sri Lanka, Photovoltaic (PV's) have been identified to be a technically suitable and economically viable power source for solar energy to electricity conversion in future. Thus Photovoltaics would constitute the future of energy technology comprising following:

- PV Technology
- Thin Film PV Technology
- Organic PVs
- Dye Sensitized Solar Cells (DSSCs)
- Quantum Dot – Enhanced DSSCs

1.3 Literature Survey

Need for Renewal Energy

Fossil fuels which provided the backbone for power requirements of the industrial revolution in developed countries , contributed enormously to the development of modern society. It was of benefit only to some, not all of the world's population. It also pollutes the environment and increases the relative proportion of greenhouse gases in the atmosphere. Population growth coupled with climate change, mainly due to burning of fossil fuels, are presenting the human world with perhaps the most severe problem and challenge in living history. Fossil fuel is derived from organically generated carbon. i.e. former living organisms. It is a finite resource – not renewable. For the past 60 years these natural resources have been used at an increasing rate, with no thought for sustainability and future generations. Easily accessible fossil fuels are being used, and extraction costs are rising. Therefore the way forward is to use fossil fuels in an efficient and more controlled manner, while introducing renewable energy sources like Solar PV, Solar Thermal, Wind, Tidal and Wave. Of the renewable energy sources, solar power has the highest potential to develop and to reduce poverty or energy problems in the future. The photovoltic (PV) effect was first identified in 1839 by Edmond Becqueral, a French Physicist. The development of the Czochralski process for processing Silicon crystals for solar cells in early 1950 was the next major step towards the commercialization of the solar PV. As solar radiation is free, non-exhaustible and abundant source of energy for the whole world is technically able to provide Sri Lanka’s electrical energy needs. Thus photovoltaics would constitute the future of energy technology in the world. Therefore PV technologies especially DSSCs , should be manufactured and developed throughout Sri Lanka.

1.4 Background information

Technological achievements in the clean energy system infrastructure are a fundamental issue for worldwide economy and environmental improvements. Therefore in this 21st century, energy based non-renewable sources has to be converted into new energy systems by incorporating novel technologies derived from advancements in science [1], [2] .

Among several new energy technologies, Dye-Sensitized Solar Cells (DSSCs) are one of the most promising new generation energy systems for photovoltaic technology. It has emerged as one of the renewable energy sources as a result of exploiting new concepts such as nanotechnology and materials such as molecular devices. Even though the first dye sensitization of semiconductors was reported by Vogel in 1873, where Silver halide emulsions were sensitized by dyes to produce black and white photographic films, the use of dye sensitization in photovoltaics had achieved little noticeable results until a breakthrough was achieved at the early 1990’s, by Professor Michael Gratzel’s group. They developed a DSSC consisting of Titanium dioxide nanopowder semiconductor electrode sensitized with expensive, scarce ,synthetic Ruthenium bipiridyl complex dye, organic liquid electrolyte with iodine / iodide redox couple and expensive Platinum deposited counter electrode. The solar energy to electricity conversion efficiency reported was highest 7.1% in 1991 and 10% and 11% in 2015 . In these devices a monolayer of the dye is directly attached to the semiconductor surface via carboxyl groups,through which an efficient injection of charge carriers from photo excited dye to semiconductor. However reallized sensitization of TiO_2 for solar applications requires not only efficient but also stable and inexpensive sensitizers. So far, several organic dyes and organic metal complexes have been used to sensitize nanocrystalline TiO_2 semiconductors and one of the most efficient sensitizer is transition metal coordination compound (Ruthenium bipiridyl complex). This is because the complex has efficient charge- transfer (CT) absorption in the whole visible range, long excited lifetime and highly efficient metal to ligand charge transfer (MLCT).

However, other organic dyes, such as phythalocyanines, cyanine dyes, xanthalene dyes, coumarin dyes etc usually perform poorly in DSSC's because of weak bonding with TiO_2 film and low charge transfer absorption in the whole visible range, but these dyes are very cheap and can be prepared easily, compared with Ruthenium bipiridyl complexes [3 – 4], [6-- 8] .

On the other hand, in nature, the fruits, flowers, roots, stems and leaves of plants show various colours from red to purple and contain various natural dyes which can be extracted by following simple procedures. Therefore, it has been emphasized by many researchers to extract dyes as photo sensitizers for DSSC's from natural products, because of the simple preparation technique, widely available sources, and low cost . Due to these reasons the importance of work done to develop low cost solar energy to electricity conversion units in principle is emphasized [14] , [114 – 115] , [119] , [166 – 167] , [171 – 173] , [175 – 179] , [182] , [188] ,[198] , [209– 210],[213].

1.5 Objectives

The three generations of solar PV's constituting crystalline and amorphous Silicon solar cells, thin film solar cells, organic/polymer and dye – sensitized solar cells (DSSC's) being 1st, 2nd and 3rd generation respectively were assessed and analyzed . DSSC's comprising the latest cutting edge solar cell technology being of low cost, easy to manufacture, durable, stable and long lasting with reasonable energy conversion efficiency (12% maximum using expensive, scarce, synthetic Ruthenium dye complexes, and about 1% using low cost, abundant , environmentally friendly natural dyes) . Hence DSSC's utilizing natural dyes was selected to carry out further research and development work for practical implementation.

1.6 Thesis structure

In Chapter 1 , under 'Introduction' addresses the main problems of fast - depleting fossil supplies confronting mankind at present. Thereafter suggestions are made to identifyvarious options available to solve the problem with renewable energy sources like wind, hydro, solar , geothermal , tidal, and wave power . Background information pertinent to this issue is presented, and the objectives of the research to be done on solar photovoltaics as the best option highlighted .

Chapter 2 provides the 'Literature Review' on the energy crisis confronting the world at present , and identifies various options available with solar photovoltaics with emerging technologies such as PV Crystalline and amorphous Silicon Solar Cells, various Thin Film Technologies such as cadmium telluride , copper indium gallium selenide , gallium arsenide multi junction, Organic Polymer and Dye Sensitized Solar Cells (DSSC's). It also identifies the research carried out in Sri Lanka and in the World on these technologies since inception in the early 1990' s.

GAP and SWOT analysis of Solar PV's / DSSC's based on Nanotechnology , the Market Analysis and Technology Trends and Market Forecast for period 2010 to 2015 examined . It also notes the main research organizations and established companies in the world involved in DSSC's .

Chapter 3 highlights the experimental methodology of research work carried out on DSSC's comprising Natural Dyes of Plants and Trees growing in Sri Lanka utilizing Nanotechnology at the University of Moratuwa, Moratuwa, Sri Lanka , the Institute of Fundamental Studies , Hantana, Sri Lanka and the Sri Lanka Institute of Nanotechnology at Biyagama and subsequently at Pitipana, Sri Lanka .

Chapter 4 provides the results obtained on the research work done on DSSC's , their assessments, analysis and interpretation of results obtained , and incorporates the deductions in solving the problems presented . Chapter 5 incorporates the conclusions of the research work effected to solve the problems encountered .Chapter 6 enumurates the recommendations , and future research work to be carried out.

CHAPTER 2

LITERATURE REVIEW

2.1 Energy Crisis

It is apparent that the quality of human life on Earth depends to a large degree on the availability of clean energy sources. It is expected that the worldwide power consumption is expected to double in the next four decades due to the increase in world population, and the rising demand of energy, especially in developing countries. This implies the enhanced depletion of fossil fuel reserves, leading to further aggravation of environmental pollution. As a result of the dwindling of these scare resources, a huge power supply gap of about 14 TW is expected by 2050. This equals today's entire consumption, thus would cause acute shortage in power supplies throughout the entire planet. It is expected that Solar energy will play a crucial role as a future energy source. The Sun provides about 120,000 TW of power per hour to the Earth's surface, which amounts to 6,000 times the present rate of world's energy consumption. However, capturing solar energy and converting it to electricity at low cost, and using abundantly available raw materials remains a huge challenge.

2.2 Solar Energy Conversion to Electricity

2.2.1 Solar Radiation

Radiant energy from the Sun is vital for all life on our planet Earth. It determines the surface temperature of the Earth as well as supplying virtually all the energy for natural processes both on its surface, on ground , at sea and in the atmosphere. Every second the Sun emits the energy of 3.90 x 10^{26}J into space. Considering that the mean distance from Earth to Sun is 150 x 10^{9} metres our planet receives the energy of 1395 J / m^{2} every second. The Sun is essentially a sphere of gas heated by a nuclear fusion reaction at its centre with estimated temperature of up to 20,000 K .

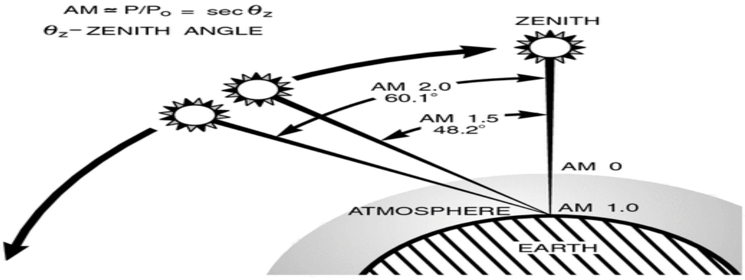

Figure 2.1 The path length of the solar radiation through the Earth's atmosphere in units of Air Mass (AM) increases with the angle from the Zenith. It increases from unity for 0 degrees (Zenith) to 1.5 for 48.2 degrees and 2.0 for 60.1 degrees 9AM 1.5 spectrum is the preferred standard spectrum for solar cell measurements.

However, this is not the temperature that determines the characteristic electromagnetic emission from the Sun since most of the intense radiation in absorbed after a few metres (near the centre) and by a layer of negative hydrogen ions near the surface. (These ions can exist because single electrons of the neutral hydrogen does not completely screen the positive protons).

The accumulation of heat in this layer sets up convection currents that transports the excess energy through the optical barrier into the so called photosphere. The temperature within the photosphere is 5,800 K and emits an essentially a continuous spectrum of electromagnetic radiation closely approximating to that expected from a black body at this temperature. This is the solar spectrum we receive outside the Earth's atmosphere which is also known as extraterrestrial or Air Mass zero (AMO) spectrum.

About 70% of the solar radiation in space can reach the surface after penetrating Earth's atmosphere. Apart from the reflection from clouds the reasons for such attenuation are:

- Scattering by molecules in the atmosphere (Rayleigh scattering) which is most effective at short wavelengths)
- Scattering by aerosols and dust particles.
- Absorption by the atmosphere and its constituent gases mainly oxygen, ozone and water vapour .

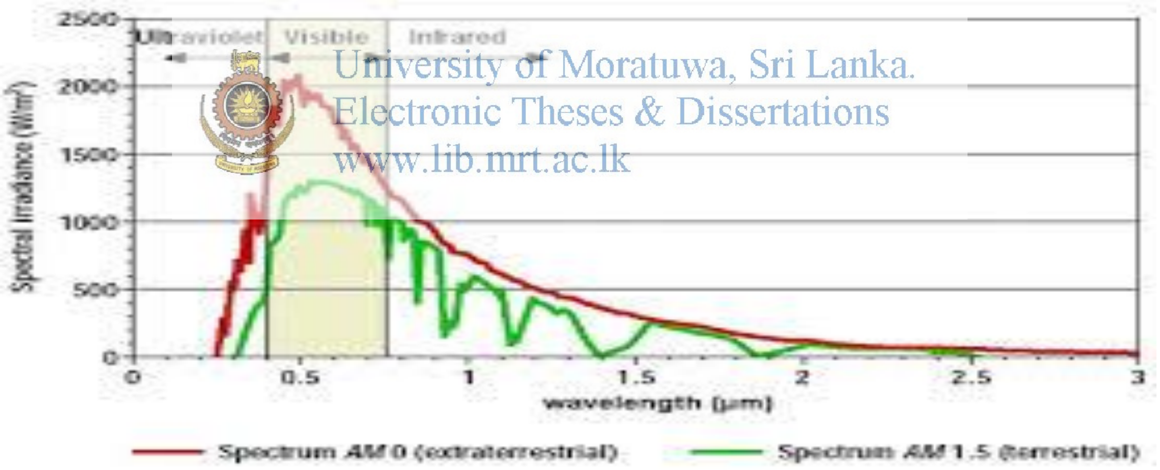

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Figure 2.2 The two most commonly used standard spectra, AM 1.5 direct and AM 1.5 global.

The global spectrum comprises the direct plus the diffuse sunlight. Thedifference is mainly in the shorter wavelength region since molecular scattering scales with Water vapour (H_2O) and Ozone (O_3) solar radiation in Earth's atmosphere.

AM is unity when the Sun is directly overhead , or larger according to

$$AM = \frac{1}{\cos\theta} \qquad (2.1)$$

where θ is the angle measured from the zenith.

Hence, when the sun is 48° off overhead, the radiation is AM 1.5. The easiest way to estimate the AM in practice is to measure S the length of the shadow cast by a vertical structure of height h using :

$$AM = \sqrt{1+\left(\frac{S}{h}\right)^2} \qquad (2.2)$$

Consequently, as opposed to the situation outside the Earth's atmosphere, terrestrial sunlight varies both in intensity and spectral composition. In order to allow meaningful comparison between the performances of different solar cells tested at different locations -- (preferably terrestrial) standard has to be defined , and measurement referred to this standard. The most widely used terrestrial standard is the AM 1.5 direct and AM 1.5 global spectrum as shown at Fig. 2.2.

2.2.2 Technologies available – Classical Systems

Solar energy is widely available in the world and is the the ultimate source of all our sustainable energy forms, with the exception of tidal and geothermal, driving the winds, ocean waves , currents and photosynthetic plant growth. Solar energy is the Sun's electromagnetic radiation and could be directly captured by solar thermal techniques into heat, and by solar photovoltaic cells to generate voltages and currents. All the types of presently available photovoltaic solar cells is depicted below at Table 2.1.

Table 2

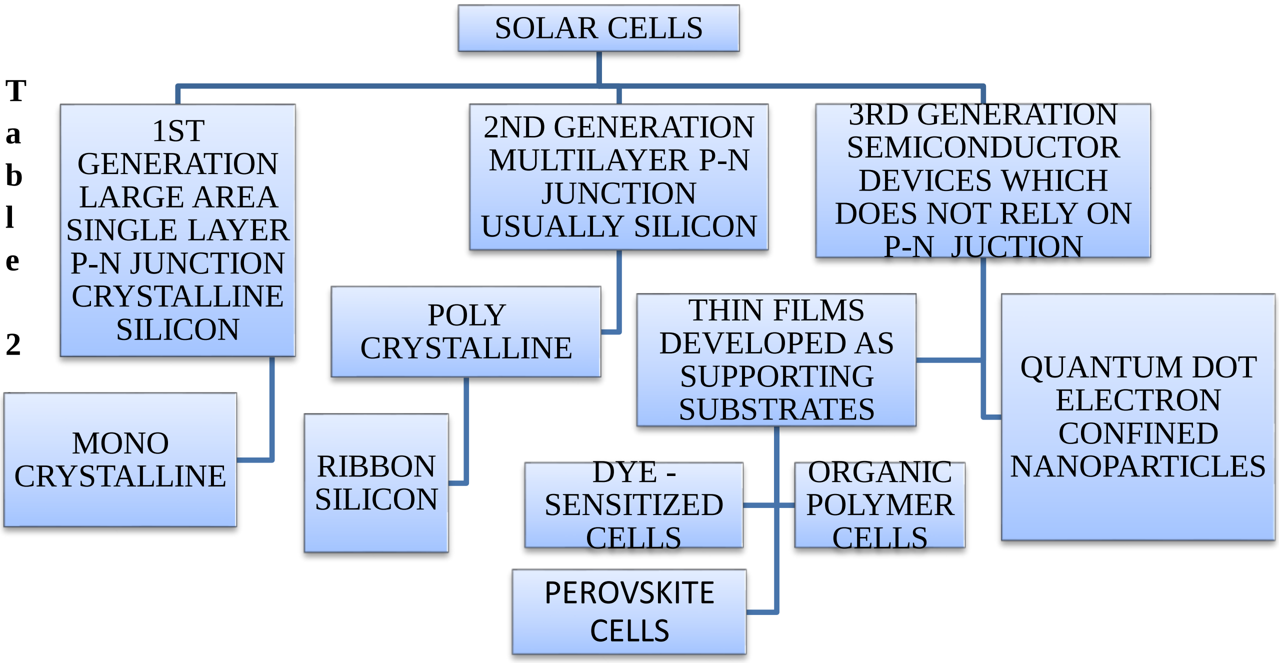


Table 2.1 Classification of all types of Photovoltaic Solar Cells

A solar photovoltaic cell needs to accomplish two fundamental tasks: firstly, the quantum mechanical absorption of photons to free electrons from their host atoms, resulting in pairs of mobile electrons and holes (electron vacancies) and secondly, the separation of the electrons and holes and their transport to electrical contacts. Some pairs recombine between these two steps and minimization of such recombination is an important research and engineering task. The first function requires a semiconductor material to be used and the most important semiconductor property is its bandgap – the wavelength at which it changes from being transparent at larger wavelengths to absorbing at shorter wavelengths. It is desirable to maximize electrical power, the product of current and voltage, so the ideal bandgap depends on a compromise between absorbing as much of the available spectrum as possible, which improves the electrical current output, and retaining as high as possible energy separation between electrons and holes, which improves electrical voltage output. A number of semiconductors such as p - Silicon, n – Silicon,Titanium dioxide, Zinc oxide, Zinc selenide, Cadmium sulphide, Cadmium telluride, Indium tin oxide, Indium phosphide, Gallium arsenide , Cadmium indium Gallium selenide etc have approximate suitable bandgaps and these are used in commercial solar PV cell production. The second function is commonly implemented by the built-in electric field formed by a doped junction of p-type and n-type semiconductor, but other separation techniques also exist, including metal-semiconductor junctions, and semiconductor wafer junctions .

2.2.2.1 PV Crystalline Solar Cells

The most prevalent bulk material available for solar cells is crystalline Silicon (c-Si). Bulk Silicon is separated into multiple categories according to crystallinity and crystal size in the resulting ingot, ribbon or wafer. Their manufacturing procedure is complicated and expensive.

a. Monocrystalline Silicon (c-Si)
b. Poly – or multicrystalline Silicon (Poly-Si or mc – Si)
c. Ribbon Silicon

These crystalline solar cells constitute the 1st generation of solar cell technology [7] ,[13] , [143], [148] , [151] , [153] , [230] , [233] .

2.2.3 Emerging Technologies of Solar PV's

(a) Thin Film Solar Cells

A thin- film solar cell is a second generation solar cell that is made by depositing one or more thin layers or thin films or PV material on substrate such as glass, plastic or metal. Thin film technologies reduce the amount of material required in creating solar cells. Though this reduces the material cost, it may also reduces energy conversion efficiency. Thin film Silicon solar cells have become popular due to low cost, flexibility, light weight and ease of integration compared to wafer Silicon solar cells. These thin film solar cells constitute the 2nd generation of solar cell technology and comprise following:

(i) Cadmium telluride solar cells

In Cadmium telluride solar cells (Cd Te), a thin film semiconductor layer is used to convert sunlight into electricity [219] , [222 -- 224] .

(ii) Copper indium Gallium selenide Solar Cells

Copper indium Gallium selenide solar cells (GIGS) is a direct bandgap material. It has the highest conversion efficiency (approx. 20% amongst thin film materials) [219] , [222] , [226] .

(iii) Gallium arsenide multi junction Solar Cells

These multi junction cells constitute multiple thin films produced by metal organic vapour phase epitaxy. A triple function cell for example, may consist of semiconductors: Ga, As, Ge and $GaInP_2$. Each type of semiconductor will have a characteristic band gap energy which causes it to absorb light most efficiently at a certain colour, or absorb electromagnetic radiation over a portion of the spectrum. The semiconductors are carefully chosen to absorb nearly all of the solar spectrum [219 -- 222].

(iv) Organic Polymer Solar Cells

Organic / Polymer Solar Cells constitute the 3rd generation of solar cell technology and research is underway around the world, but devices are not commercial. They are built from thin film of organic molecules including polymers. Their best conversion efficiency is around 4% --5%. Attractive aspects are flexibility, low weight, toughness, and low cost, but low efficiency and stability are serious concerns [23] ,[46], [53], [63], [84 --85], [89], [91], [97] ,[227--229] .

(v) Dye Sensitized Solar Cells (DSSCs)

These photo electrochemical solar cells which use light absorbing natural dyes of green plants also constitute 3rd generation of solar cell technology pathway. DSSC's are a major area of current research in the world, but the technology remains pre-commercial. They are a fundamentally different photovoltaic technology, being electrochemical devices with charge transport through a liquid electrolyte following a charge transfer from a dye in which initial absorption occurs. Efficiency as high as 11% has been reported. DSSC' s are made of low cost materials and do not need elaborate equipment to manufacture. DSSC's can be engineered into flexible sheets and through their efficiency is less than best thin film cells, its price / performance ratio should be high enough to allow them to compete with fossil fuel electricity generation.. These 3rd generation of solar cells also include Copper Tin sulfide , nano crystal , quantum dot, micromorgraph and perovskite solar cells. A perovskite solar cell is a type which includes a perovskite structured compound , most commonly a hybrid organic or inorganic lead or tin halide – based material , as light harvesting active layer .

(a) Dye Sensitized Solar Cells (DSSC's) – Structure

In the case of the original Gratzel design, the cell has three primary parts . On the top is a transparent anode made of Fluorine doped Tin Oxide (Sn O_2 ./ F) deposited on the back of the conductive glass plate which has a thin layer of Titanium dioxide (T_iO_2) which forms into a highly porous structure with an extremely high surface area. The plate in then immersed in a mixture of a photosensitive natural dye and a solvent. After soaking the film in the dye solution, a thin layer of the dye is left covalently bonded to the surface of the T_iO_2. A separate backing is made with a layer of potassium tri-iodide / iodide electrolyte spread over a conducting sheet, typically platinum metal (or graphite). The front and back parts are then joined and sealed to prevent the electrolyte from leakage. Figure 2.3.

(b) General Operating Principles

Conventional solar cells convert sunlight into electricity by exploiting the photovoltaic effect that exists at semiconductor junctions. They are closely related to transistors and integrated circuits. The semiconductor performs two processes simultaneously: absorption of light, and the separation of the electric charges (electrons and holes) which are formed as a consequence of that absorption.

The dye sensitized solar cells work on a different principle, where by the process of light absorption and charge separation are differentiated. Due to their simple construction, the cell offers hope of significant reduction in the cost of solar electricity.

(c) Principle's of Operation of Dye-Sensitized Solar Cells

In operation, sunlight enter the cell through the transparent SnO_2 : F top contact, striking the dye on the surface of the T_iO_2. Photons striking the dye with enough energy to be absorbed will create an excited state of the dye, from which an electron canbe 'injected' directly into the conduction band of the T_iO_2 and from there it moves by a chemical diffusion gradient to the clear anode on top. Meanwhile, the dye molecule will decompose if another electron is not provided. The dye strips one electron from iodide in electrolyte below the T_iO_2, oxidizing it into tri-iodide. This reaction occurs quickly compared to the time that it takes for the injected electron to recombine with the oxidized dye molecule, preventing this recombination reaction that would effectively short circuit the solar cell. The tri-iodide then recovers it mixing electron by mechanically diffusing to the bottom of the cell, where the counter electrode re-introduces the electron, after flowing through the external circuit. Figure 2.3 below depicts the present generation of Dye-Sensitized Solar Cell based on Nanocrystalline film of T_iO_2.

Energy conversion in a DSSC is based as the injection of an electron from a photoexcited state of a sensitizer dye into the conduction band of the T_iO_2 nanocrystalline semiconductor -- Equations (1) and (2). These cells also employ a liquid electrolyte (Iodine / Potassium tri iodidle redox – active couple dissolved in an organic solvent like Ethanol) to reduce the dye cation (viz., regenerate the ground state of the dye) -– Equation (3). Regeneration of the iodide ions, which are oxidised in this reaction to tri iodide is achieved at a Platinum (or Graphite) counter (+ve) electrode – Equation (4). Equations (1) --(6) depict this process as follows:

At Anode:

$TiO_2/S + hv \longrightarrow T_iO_2/S^*$ --------- (1)

$TiO_2/S^* \longrightarrow T_iO_2/S^+ + e^-$ --------- (2)

$TiO_2/S^+ + e^- \longrightarrow T_iO_2/S$ --------- (3)

$TiO_2/S^+ + 3/2\, I \longrightarrow T_iO_2/S + \frac{1}{2} I_3$ --------- (4)

At Cathode

$½\, I_3^- + e^- \longrightarrow 3/2\, I^-$ --------- (5)

Cell: $I_3 + 2e^- \longrightarrow 3\, I^-$ --------- (6)

Where S = ground state of dye, S* = dye when excited by light , S+ = oxidized state of dye.

(a)

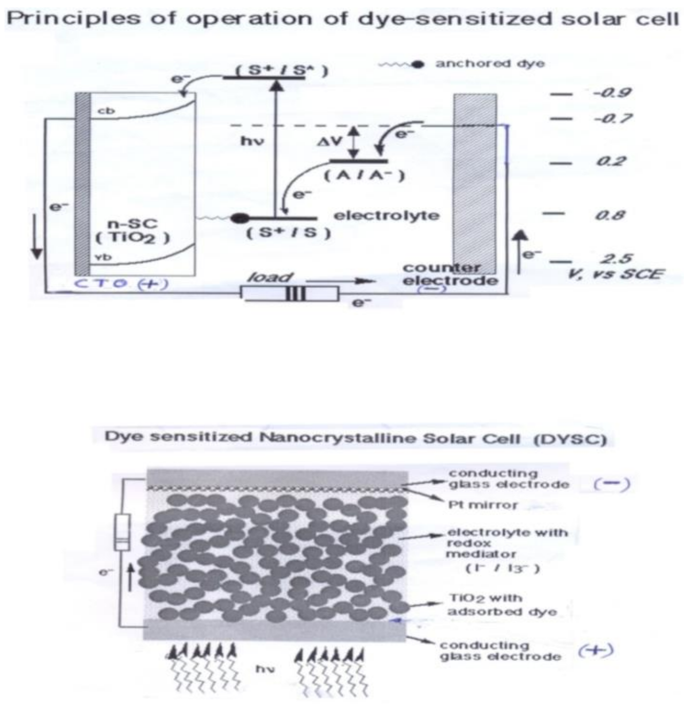


Figure 2.3 (a) Principles of operation of a DSSC and (b) Schematic Diagram of component structure

When the DSSC is illuminated with sunlight light absorption is performed by a monolayer of dye (S) absorbed chemically at the semiconductor surface . after having being excited (S*) by a photon of light , the dye usually a natural organi dye (or a transition metal complex) whose molecular properties are specifically engineered for the task, is able to transfer an electron to the semiconductor (TiO_2). The absorption of light by the dye is followed by injection of an electron from an excited state of the dye to the conduction band of the semiconductor whilst the holes remain on the sensitizers . The ground state of the dye (S^0) is then regenerated by electron doation from the redox system to the oxidized state of sensitizer

(S^+) . The electrons in the conduction band of the semiconductor are collected at the counter electrode and flow through the external circuit . Through these processes , the radient energy is converted into electricity .

The solar cell consists of the two conducting glass elecrodes in a sandwich configuration with a redox electrolyte separating the two . On one of these electrodes a few micron thick layer of TiO_2 is deposited using a colloidl preparation of mono – dispensed particles of TiO_2 . Thje compact layer is porous with a high surface area allowing mono molecular distribution of dye molecules . after apprpiate heat treatment to reduce the resistivity of the film , the electrode with the oxide layer is immersed in the dye solution of interest (typically 2 x 10^{-4}M in ethanol) for several hours . The porous layer acts like a sponge and there is very efficient uptake of the dye , leading to intense colouration of the film . Molar absorption of 3 and above are readily obtained with the micron – thick layer with a a number of natural dyes like Anthrocyanins . The dye coated electrode is then put together with another conducting glass electrode and the intervening space in filled with a redox electrolyte consisting of KI / I. (10:1 M).

(d) Degradation of natural dyes

DSSC's degrade when exposed to ultraviolet radiation. The barrier layer may include UV absorbing luminescent chromospheres (which emit at longer wavelengths) and antioxidants to protect and impose the efficiency of the cell.

(e) Advantages and drawbacks of natural dyes

DSSC's are currently fairly efficient 3rd generation solar technology available (11% max). Other thin film technologies are typically between 5% and 11%, and traditional low – cost commercial Silicon panels operate between 12% and 15%. This makes DSSC's attractive for large scale deployments where higher cost, higher efficiency cells are more viable, but even small increase in DSSC's conversion efficiency might make them suitable for some of these roles as well.

A practical advantage DSSC's share with most thin film technologies is the cell's mechanical robustness which indirectly leads to higher efficiencies at high temperatures. In any semiconductor, increasing temperature will promote some electrons into the conduction band "mechanically". The fragility of Silicon solar cells requires them to be protected from the elements, typically by encasing them in a glass box similar to a green house with a metal backing for strength. Such systems suffer noticeable decrease in efficiency as the cells heat up internally. DSSC's are normally built with only a thin layer of conductive glass/plastic on the front layer, allowing them to radiate away heat much easily, and therefore operate at lower internal temperatures.

The major disadvantage of the DSSC's design is the use of liquid electrolyte, which has temperature stability problems. At low temperatures the electrolyte can freeze ending power production and potentially leading to physical damage. Higher temperatures cause the liquid to expand, making sealing the panels a serious problem. Another major drawback is the electrolyte solution which contains volatile organic solvents and must be carefully sealed. This along with the fact that the solvents permeate plastics has precluded large scale outdoor applications and integration into flexible structures. Replacing the liquid electrolyte with a solid electrolyte has been a major ongoing field of research. Recent experiments using solidified molten salts have shown some promise, but currently suffer from higher degradation during continued operation, and are not flexible.

(f) Efficiency

Several important measures are used to characterize solar cells. The most obvious is the total electrical power produced for a given amount of solar power shining on the cell. Expressed as a percentage, this is known as the solar conversion efficiency. Electrical power is the product of current and voltage, so the maximum values for these measurements are important as well, Jsc and Voc respectively (Appendix H) .

(g) Characterization

The current – voltage characteristics of natural dyes with TiO_2 nonopowder incorporated in test DSSC's with an active surface area of 0.25 cm^2 (to obtain uniformity) could be measured with an Electronic Multimeter coupled to a programmed Computer for simulated sunlight of 100 mW/cm^2 intensity with a Halogen lamp. Graphs would be drawn automatically on computer screen with current density (mA/cm^2) open circuit voltage (mV)

The Fill Factor (*ff*) and Power connection efficiency (η) are calculated for following relationships.

Fill Factor (*ff*)

$$ff = \frac{Im \times Vm}{Isc \times Voc}$$

$$= \frac{Pm}{Isc \times Voc} \qquad \text{----(1)}$$

Power Conversion Efficiency

$$\eta = \frac{\text{Output power}}{\text{Input power}}$$

$$= \frac{Pm\left(\frac{mW}{Cm^2}\right) \times 100\%}{Light\ intensity\,(mW/Cm^2)}$$

$$= \frac{Isc \times Voc \times ff}{Light\ intensity} \times 100\% \qquad \text{--------(2)}$$

where,

I_m = Maximum current

V_m = Maximum Voltage

I_{SC} = Short circuit current

V_{OC} = Open circuit voltage

The effectiveness of DSSC to convert light of vrious wave lengths into electrical current is measured as the :

Incident Photon to Current Efficiency (IPCE) = Number of electrons generated by light per number of photons incident on the cell .

IPCE % = 1240 Jsc / λ W

Where, Jsc = Short Circuit Current Density (A/m^2)

λ = excitation wavelength (nm), W = photon flux (W/m^2)

2.2.4 Materials for Dye-Sensitized Solar Cells and their operational principle

The operational principle of the photoelectrochemical cells is based on several interfacial electron transfer and bulk charge carrier transport processes. A photon from sunlight absorbed by the sensitizing dye release an electron from a lower energy state to a higher energy state. The photo-excited electron which is also the carrier of the absorbed energy is injected into the meso-porous network of nanocrystalline T*i*O$_2$. The electron vacancy or the hole left on the dye molecule is reduced by I^- molecules from the electrolyte. The driving force for this regenerative electron transfer step is the more negative redox potential of the I- with respect to the oxidized dye molecule. The injected electrons are transported through the mesoporous TiO_2 network by a diffusion process until they reach the FTO substrate where they can be collected by the external circuit. The oxidized I^- molecule goes through several intermediate chemical transitions and finally forms the I_3^- molecule.This diffuses in the electrolyte until it reaches the Platinum (or Graphite) Counter electrode where it is reduced back to I^-.

(a) The working electrode

The working electrode material of commerecial DSSC's consists of transparent Fluorine –doped tin oxide (FTO) coated glass substrate. These substrates have high thermal stability, low haze and low sheet resistance (10-15 Ohm. cm^{-2}). The electrode material itself in usually on intrinsic N-type semiconductor such as Titanium dioxide (TiO_2), Zinc Oxide (ZnO), Tin dioxide (SnO_2) etc. These metal oxides are normally made froma sol-gel process yielding size tunable nano-particles. TiO_2. with Antase crystal structure the most commonly used metal oxide for DSSC's has a particle size of 15-20 nm in diameter, with an indirect band gap transition at 3.2 eV.

To form a high surface area scaffold of mesoporopus TiO_2. necessary for building efficient DSSC's, the nano-particles are dispersed in a viscous paste which could be doctor bladed or screen printed films of thickness up to 20 – 30 p.m. . TiO_2 films formed are then heated and sintered to temperatures between TiO_2 films formed are then heated and sintered to temperature between 400 and 500°C. This sintering ensures that all aditive of the paste such as solvent, binders and pore-forming agents decompose and evaporate and that the individual TiO_2.particles fuse together to form an electronically active meso-porous network.

The most important parameter of the mesoporous network is the surface area. For meso-porous films with TiO_2. particles the roughness factor is around 1000, which represents the real area or inner surface area of a sintered TiO_2. film is 1000 times larger than the geometric areas.

(b) TiO_2 blocking layers made by spray pyrolysis

One inherent propertyof a meso-porus network is that it does not completely coat the entire FTO substrate and thus leaves exposed FTO surface in contact with the electrolyte. For liquid electrolyte DSSC's based on the I_3^-/I^- redox couple the exchange current at this interface is negligible at short circuit conditions but significant at applied potentials. The most common method of creating these TiO_2. blocking layers is through spray pyrolysis . The spray pyrolysis method relies on spraying a solution containing the precursor of interest onto a hot surface. The droplets from the aerosol either reach the hot surface or turn to gaseous precursor which then react with the substrate due to elevated temperatures.

(c) The light absorbing material

The most important part of a DSSC is the light absorbing component. There are broadly three different categories of light absorbers for DSSC's – Metal –organic complexes, all organic dyes and quantum dots.

Beyond the need for the dye to absorb photon, they also have to transfer the molecules to the TiO_2. The proximity between the dye and the TiO_2 surface is controlled through the carbocyclic anchoring group on the dye molecule. In the simplest form, the anchoring group forms chelating bond between the hydroxyl groups of the TiO_2. surface with the carboxylic anchoring group of the dye. But proximity alone does not suffice for photo excited electron injection to occur. The energy level of the excited state has also to be sufficient high to allow for electron injection. Organic molecules have energy levels, in analogy with the valence and conduction band of inorganic semiconductors, which are called the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) respectively. The absorption spectra of a cross section of natural dyes suitable for use in DSSC's analyzed in this research work are depicted at Figures 4.5 , 4.6 & 4.7.

(d) Electrolyte / Hole transporting material

The function of the redox electrolyte with hole transporting material in a DSSC in to shuttle electrons from the counter electrode to the photo-oxidized dye molecule.A liquid electrolyte of I^- / I_3^- in the most efficient electrolyte system in DSSC's. Redox electrolytes are ionic conductors in which charges are transported via diffusion (concentration controlled) or by migration (electric field controlled). In a DSSC theionic conduction mainly takes place by diffusion. This occurs because the reduction - oxidation cycle at each electrode deplete and replenish the redox active species at each interface.

Holes are not a physical entity but rather a description of an electron vacancy in a system. A hole transporting material transfer charges by electronic conduction rather than through ionic mass transfer.

(e) Solar cell additives

Additives are usually molecules or materials which have been found to increase the performance of a DSSC when added to any step of the solar cell manufacturing process. Efficient additives are often found through screening of molecules and /or by extensive optimization of a DSSC. One of the most important additives or surface modification is the $TiCl_4$. Treatment of the TiO_2. mesoporous working electrode, a treatment which improves DSSC performance in liquid electrolyte solar cells. The effect of $TiCl_4$ treatment depends on the quality of the particles used for making the mesoporous TiO_2. Electrode but has in most cases been found to increase the short circuit photo current by reducing the interfacial electron-hole recombination. Other additives to DSSC; are traces of concentrated Hydrochloric acid or Acetic acid done to make the pH of dye solutions acidic (<5), and to chemically alter the molecular structure of the dye and to make it appear darker in colour and to increase its conversion efficiency.

(f) Counter electrode

The counter electrode is responsible for completing the internal electrical circuit by injecting electrons back into the electrolyte. In liquid electrolyte DSSC's based on the I^{-}/I_3^{-} system the counter electrode is built on TCO substrate on which Platinum metal electrocatalyst has been deposited. Carbon/Graphite coated electrocatalyst also has been found to be suitable for this purpose. The most important parameter for an efficient electrocatalyst in the rateof reduction of the redox mediator for the reduction of I_3^{-}. This influence the performance of DSSC's where a low catalytic activity, a high over potential add series resistance to the DSSC.

(g) Solar Cell preparation and assembly

The initial cleaning of Fluorine doped Tin oxide (FTO) coated glasses is done as follows:

The conducting glass slides are cut into dimensions of 2cm x 0.2cm x 0.25 cm with glass cutter. These glass slides are then cleared in a beaker filled with Teepol detergent by shaking the beaker with an Electronic Ultrasonic Cleaner (BRANSON 200) for about 5 min. Thereafter these slides were washed with clean tap water, dilute sulphuric acid and finally in distilled water. These slides were theen boiled in Propanol 20, removed with a Tweezer and kept on tissue paper with conducting side on top (using – multimeter).

2.2.5 Physical Factors which affect the Characteristics of DSSC's

This discussion provides an overview of purely physical parameters affecting current –voltage characteristics of DSSC's mainly from a device engineering point of view rather than from a materials and chemical point of view. Factors such as chemical composition of the dye with its absorption spectrum of the absorbed species, correct HOMO/LUMO matching with Titanium dioxide semiconductor conduction band, and the redox couple respectively, have a very direct impact on DSSC performance. Also the correct surface pH, TiO_2 particle size, chemistry, morphology and electrolyte additives are important in this regard.

The current voltage curves represent characterization method for DSSC's and solar cells in general. The open circuit voltage (Voc), short circuit current (I_{SC}) and the shape of the IV curve determine the conversion efficiency of DSSC's under any given light condition. There are three additional important prometers for IV curves of solar cells:

V_{mp} = Voltage at the maximum power point (Vmax)

I_{mp} = Current at the maximum power point (Imax)

ff = Fill Factor which describes how well the area under the IV curve "fills in" the maximum posible rectangle defined by I_{SC}x V_{OC} (i.e. the lightly shaded area in Fig.2.4). The Fill Factor can most easily be visualized by the ratio of the areas of the darkly shaded rectangle to the lightly shaded rectangle.

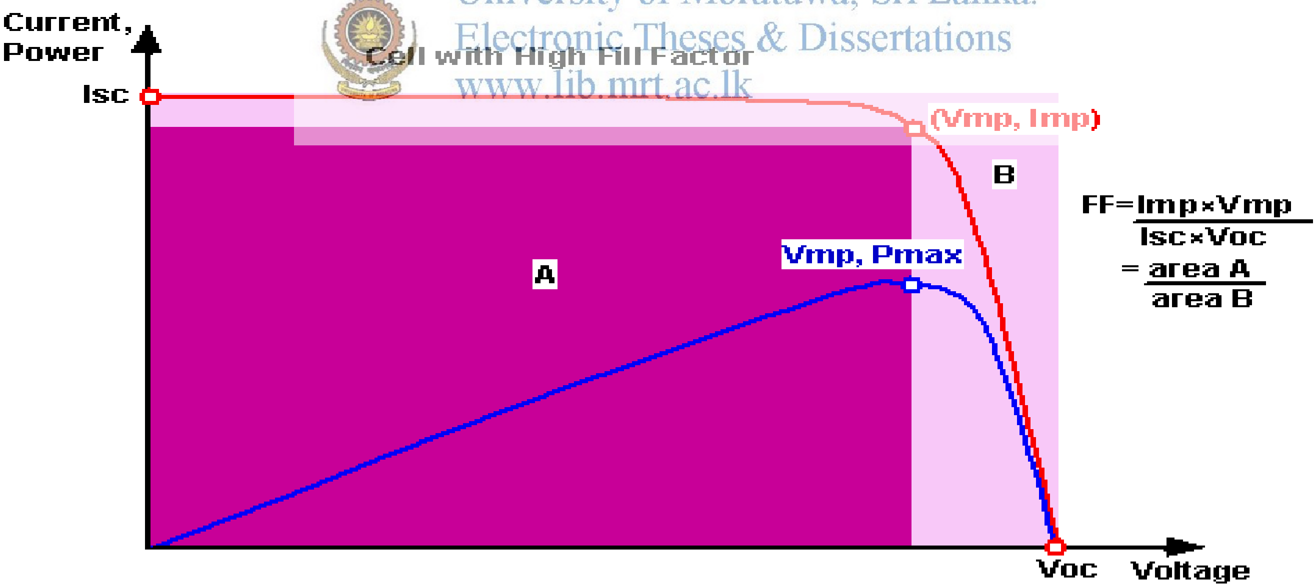


Figure 2.4 IV curve of a typical DSSC

In order to optimise DSSC performance it is important to fully understand the factors V_{OC}, I_{SC}, *ff* and η which affect the key features of DSSC IV characteristics.

(a) The ideal photodiode

Any photodiode can be described by the following equivalent circuit:

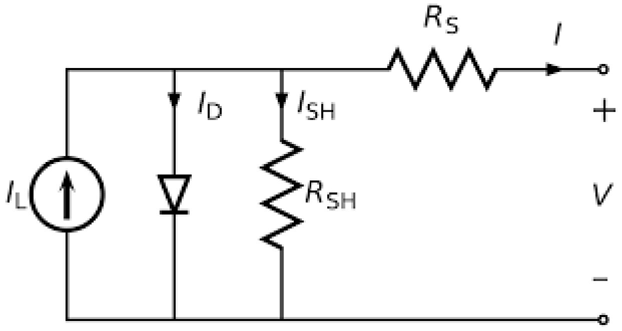


Figure 2.5 Equivalent circuit of a photodiode

The ideal solid-state photodiode has very low defects and thus low recombination, resulting in n being close to unit. n varies for different types of photodiodes or solar cells between 1 and 2 depending on the defect layer.

(c) Influence of temperature

Figure 2.6 shows IV curves for a typical commercial DSSC design at temperatures varying from 25^{O}C to 60^{o}C

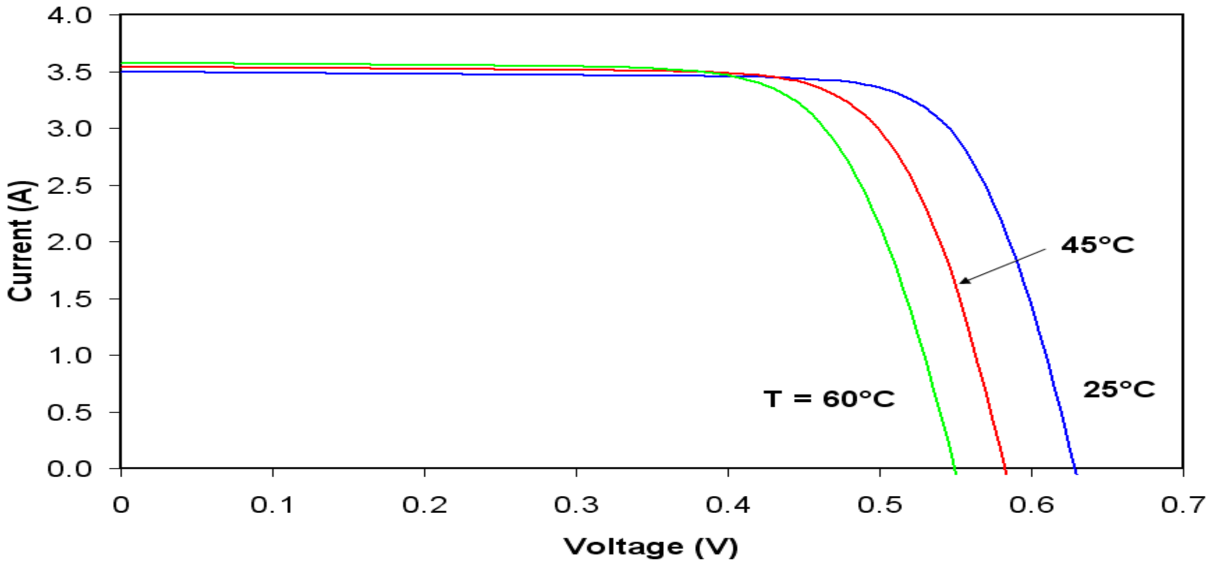


Figure 2.6 IV curves for a typical commercial DSSC.

While the open circuit voltage decreases linearly by approximately 2mV/decade, which is similar to Si photovoltaic cells, the maximum power point voltage of DSSC remains, in contract to Si cells, remarkably constant and only decreases slightly at temperatures above 45°C. Fill factors of DSSC; increase with temperature and only start to level off and then decrease above 45 – 60°C. The *ff* maximum as a function of temperature depends on the light level, on the electrolyte composition, specifically the I_3^-. Concentration, the electrolyte viscosity and other cell design parameters such as anode to cathode distance.

The V_{mpp} of a typical commercial synthetic dye sensitized DSSC is remarkably constant and varies only about ±20 mV over the temperature range from 25°C to 60°C. The exact voltage variation can be adjusted through a number of design parameters. Lowered VOC at higher temperatures is largely compensated by a corresponding increase in ff. SinceI_{SC} does not vary significantly with temperature the power P_{mmp} at the maximum power point is rather constant and varies at worst by only ± 12% over the entire temperature: range from 25°C to 60°C. Such a small influence of temperature on power output of DSSC is in sharp contrast to Si solar cells which show a much more pronounced decrease in performance at higher temperatures.

A power loss coefficient of 0.65% K at P_{mmp} has been for Si solar cells. Table 2.2 shows a comparism between typical DSSC's and Si Cells for two temperature ranges.

Table 2.2 Temperature increment effect for solar cells

Temperature increase	Pmpp drop for DSSC	P_{mmp} drop for C-Si cell
From 25^o to 45^{o}C	5%	19.5%
From 45^o to 60^{o}C	15%	32.5%

(d) Influence of electrolyte conductivity

The electrolyte resistance Re which represents part of the series resistance R_S depends according to Equation [4] on the electrolyte layer thickness, i.e. the distance d between the two electrodes the electrolyte conductivity σ and the electrode cross section. A.

$$R_e = \frac{d}{\sigma A} \qquad \text{———} \qquad [4]$$

In typical DSSC's with an electrode – to electrode distance of 40 μm and a conductivity of around 0.01 S/cm at 25^{o}C for a solvent – based electrolyte system, results in Re $\approx$ 0.4 Ohm for each cm^2 of cell area. This produces a voltage drop of 7 mV only at a photocurrent of 18 mA/cm^2. This is significant compared to the series resistance of the typical transparent conductive oxide (TCO) substrate. For solvent – free electrolyte systems such as ionic liquids the electrolyte conductivity may be lower and Re correspondingly higher.

While the electrolyte resistance has normally only a very slight direct impact on theIV characteristics the situation is complicated by concentration polarization. Often electrolyte systems with relatively low I_3^- diffusion coefficients can have a noticeable limiting effect on photocurrents.

(e) Influence of substrate conductivity, cell width and cell contacts

In contrast to standard photovoltaic cells which are based on solid – state PN junctions and light absorption by bulk semiconductor materials, thin layer DSSC's require at least one transparent conductive substrate. Since electronically highly conductive substrates generally display low light transmittance, the substrate sheet conductivity needs to be compromised for following.

- Best performance in a given application.
- Cost
- Availability of transparent conductive oxide (TCO) on a substrate such as glass.

Typical sheet resistances of commercially available TCO layers are in the order of 10 - 15 Ohm per sq.cm. This means that a 1 cm x 1 cm cell contacted on both sides by a bus bar displays a series resistance of10-15 Ohm. This value is much higher than the resistance of a typical electrolyte layer of Re $\approx$0.4 Ohm per sq.cm unit area.

For cells where the anode and cathode sheet resistances are equal, and where the cell electrical contacts are provided through two lateral bus bars just outside the real structure (one on anode and are on cathode side), the current lines are particularly uniform, and current density is the same over the entire cell area.

(f) Influence of the counter electrode

Electrochemical reactions are generally described by the Butler-Vollmer equation [7], which relates current a voltage through the "over potential" $n = E - E_0$ defined as the potential difference between the applied electrode potential and the electrode equilibrium potential E_0. E_0 is the I_3^-/I^- redox potential in the case of DSSC's. K_0 is the electron transfer constant at zero over potential, which is normally close to 0.5, n thenumber of exchanged electrons in thereto determining step and C_{red} and C_{ox} represent I^- and I_3^- concentrations.

$$J = k_0 \left[\mathbf{C_{red}} e^{(1-\alpha) n \eta F / RT} - \mathbf{C_{ox}} e^{-\alpha n \eta F / RT} \right] \quad \text{-----------------} \; [7]$$

(g) Influence of Iodine concentration

The influence of Iodine (I_3^-) concentration on DSSC's IV curves is a very complex one, including physical and chemical factors:

- Iodine absorbs violet and blue light and thus may significantly limit photocurrents with increasing concentration, particularly for reverse illuminated cells and for cells with relatively thick electrolyte layers (>40 micron).

- Low I_3^- Concentration can lead to mass transport limitations.

In a thin layer cell of internal thickness d, the mass transport (diffusion) limited current density is given by the following equations.

$$j_{\lim} = \frac{2n\ FD\left[I_3^-\right]}{d} \ldots .[11]$$

Where n represents the number of transferred electrons (n=2 for the I_3^-/I^- Redox couple), and D the diffusion coefficient of the limiting species (I_3^-). For $\left[I_3^-\right] \approx 0.1\ \mathrm{M}$, D is in the range 3 – 5 x 10^{-6} m^2/S, and for an internal cell thickness of 40 micros diffusion limited currents of 30 – 50 $mAcm^2$ can be achieved. Diffusion Coefficients increase with increasing temperature according to the Stokes – Einstein equation [12] where $\eta\kappa$ in the kinematic viscosity and *r* the hydrodynamic radius of the solvated ionic species. This D increases proportionately to the absolute temperature T and also because viscosity generally decreases with temperature.

$$D = \frac{kT}{6\pi\eta_k r} \qquad [12]$$

- Increasing I_3^- Concentration leads to lower V_{OC} because of the enhanced parasitic electron back transfer reaction [13] from T*i*O_2 conduction band (CB) electrons. It has been reported that V_{OC} at 82 $mWcm^{-2}$ decreases by around 65mV at 298°K per trifold increase in Iodine concentration.
- Low I_3^- Concentrations resulting, according to Equ[7], in lower currents at the counter electrode and consequently lead to lower DSSC fill Factors.

  Thus Iodine concentration exerts antagonistic effect on performance through V_{OC}, I_{SC} and *ff* and reach to be carefully tuned for given application and as a function of the chosen cell design.

(h) Influence of mass transport conditions.

Since the Iodide[I^-] concentration in a DSSC is generally significantly higher than for iodide [I_3^-], transport of the latter species from the porous from T*i*O_2network to the counter electrode is normally the major ion transport limitation. In thin layer cells linear concentration profiles are established across the cell relatively quickly. Under diffusion limitation the tri iodide concentration at the counter electrode surface drops to zero and the surface concentration at the from T*i*O_2 doubles with respect to the average tri iodide concentration of a cell in the dark. The increase in I_3^- concentration at the TiO_2 surface decreases its open Circuit Voltage (by approximately 20mV). On the CE side, the low steady-state I_3^- concentration slows the electron transfer reaction and lowers *ff* and V_{OC}because of the redox potential at the CE surface becoming more negative and thus closer to the TiO_2 Fermi level.

(i) TiO_2 layer thickness has to be avoided as well since it will –

Optimization TiO_2 layer thickness is very important for DSSC's, since insufficient TiO_2 would not absorb enough dye and thus the cell would not absorb sufficient light resulting in low photocurrents. On the otherhand too thick TiO_2 layer particularly

- Increase the length of the electron pathways, for reverse – illuminated cells, and thus decrease *ff* and V_{OC},and in extreme cases even I_{SC}.
- Unnecessarily increase the total TiO_2 surface area and therefore increase the extent of electron back transfer reaction and lower V_{OC}.
- Increase the diffusion length of I^-/I_3^- Species through the congested and tortuous mesoporus network which can increase d in Eqn [11] and lower I_{SC},
- Waste material TiO_2 and dye which cannot be utilized to their full 'potential'.

(j) Optical Engineering

None of the known dyes today absorb the entire solar spectrum. The most stable natural dyes do not collect and convert light at wavelengths longer than about 600 mm efficiently. Light management and optical engineering optimized for a given design can significantlyincrease light absorption. Particularly for the standard illumination geometry i.e. the light being directed into a cell from the TiO_2 side, light scattering layers on the electrolyte side or a balanced mixture of smaller and larger TiO_2 particles can significantly improve the light havesting efficiency. Mirror – like or white light diffusers as panel background and/or front – side antireflective layers can further improve cell efficiency.

(k) Additional physical factors influencing IV characteristics

There are quite a number of additional factors which influence DSSC output and which need to be considered in order to obtain meaningful and reliable IV data:

- Nature of the electrical contacts: Provision of a low electrical resistance contact to the measuring leads can be obtained through bus bars applied by screen printing or ultrasonic welding, followed by soldering the test leads to the bus bars.

- Lighting conditions: Care needs to be taken to avoid any diffuse or stay light hitting the device under test during IV curve measurements, which may artificially increase device output.
- Masking: Cell masking can be used to accurately define the illuminated cell area in the case of a well collimated light beam. With a more diffused light source, on the other hand, masking can be used to artificially boast measured currents due to internal light reflection and increased illumination of the masked area. Fill factor increases through masking due to lower absolute current resulting in less resistive losses. Used correctly, marking can provide more accurate cell performance data.

(l) Obstacles for increasing conversion efficiency of DSSC's

In liquid electrolyte-base DSSC's the existing limitations for increasing the device efficiency are two fold. The first one is relevant to the insufficient light harvesting in the near infrared region for sensitizers used. There exists near-infrared dyes which absorbs light in the higher wavelengths but these dyes are usually limited in conversion efficiency, mainly due to the low output photo voltage of these devices. The optimal band gap for a sensitizer dye follows the Shockley- Queisier limit which determines the theoretical optimal band gap of single absorbing material to 1.1 electron volt (eV). This theoretical limit predicts a maximum conversion efficiency just above 30% for a perfect absorber in an ideal solar cell. The DSSC has electronic losses which cannot be neglected in this analysis and will influence the optimum band gap energy of the sensitizing dye. Some of these losses are necessary for driving electron transport processes in the solar cell, while other are over potential losses which can be avoided in an optimized DSSC.

2.2.6 Natural Dyes for DSSC's

(a) Natural Dyes

Natural dyes of plants which are cheap, abundant and environmentally friendly alternative to very expensive and scarce synthetic organic dyes for dye sensitized solar cells (DSSC's). Various components of plants have been tested over the last two decades as suitable sensitizers.

Dyes may be natural (as present in plants), or may be synthetically created. The most precise and scientific classification of dyes is based upon their chemical structures. Natural dyes have very low toxicity which gives them advantages over synthetic dye colouring agents especially for food products.

Dyes impart colour to tissues of plants, and contain chromophores which is the part of a molecule responsible for its colour. The colour arises when a molecule absorbs certain wavelengths of visible light, and transmits or reflects the molecule where the energy difference between two different molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophores can they be absorbed by exciting an electron from its ground state into an excited state.

The variations on colour of dyes are due to slight alteration in the molecules which do not affect the fundamental chemical structure. They usually occurs as mixtures which vary from plant to plant.

The colour of the dyes and pigments can also be determined by the pH of the medium in which it is dissolved. The extracts of natural dyes from plant tissues such as leaves, stems, bark, root, seeds, flowers, fruits etc. could be made in polar and non-polar solvents like ethanol, acetone, acetonitrile, chloroform, ethyl acetate, diethyl ether and water, depending on their solubility.

As previously discussed, chromophores almost always arise in two forms: conjugated pi systems (also known as resonating systems), and metal complexes.

In conjugated chromophores, the electrons jump between energy levels that are extended pi orbitals, created by a series of alternating single or double bands, often in automatic systems. Various factors in a chromophore's structure go into determining at wavelength region in the spectrum the chromaphore will absorb light. Lengthening or extending a conjugated system with more unsaturated (multiple) bonds in a molecule will tend to shift absorption to longer wavelengths.

The metal complex chromophores arise from splitting of d-orbitals by binding of a transition metal to ligands. Examples of such chromophores can be seen in chlorophyll (used by plants for photosynthesis).

(b) Plant pigmentation

Plant pigmentation occurs due to the electronic structure of the pigment interacting with sunlight to alter the wavelengths that are either transmitted or reflected by the plant tissues. The specific colour will depend on the abilities of the observer. Humans without colour blindness can detect wavelengths between approximately 390 nm to 780 nm, representing the visible spectrum. The human eye "senses" six hues:

1. Red = 780 - 622 nm
2. Orange = 622 - 597 nm
3. Yellow = 597 – 577 nm
4. Green = 577 – 492 nm

5. Blue = 492 – 455 nm

6. Violet = 455 – 390 nm

The pigments can be described in two ways : the wavelength of maximum absorbance (λmax) and the colour perceived by humans. Table 2.3 illustrates the grouping of plant pigments based on the common structure and biosynthesis basis.

Table 2.3 Pigments in Plants

Pigment	Common type	Occurrence
Chlorophylls	Chlorophyll	All photosynthetic green plants
Carotenoids	Carotenes, Xanthophylls	Green plants, fruits like mangoes, roots like carrots
Flavanoids	Anthrocyanins, aurones, chalcones, flavanols	Flowers, fruits
Anthrocyanins	Anthrocyanins Anthrocyanodins	Green plants, flowers, fruits
Betalains	Betacyanins betaxanthones	Flowers, fruits, roots

(c) Chlorophylls

Chlorophylls present in chloroplasts is green and is responsible for the green colour of foliage and leaves. More importantly by enabling plants to produce oxygen from the leaves in the presence of carbon dioxide absorbed from the atmosphere, and water absorbed by the roots in the presence of sunlight to produce carbohydrates or sugars as food for all living beings and organisms and it is critical to sustain life on Earth.

(d) Carotenoids Carotenoid ($C_{40}H_{56}$) is a large conjugated molecule found in chloroplasts of many plants. It is a pigment that absorbs blue and indigo light energy and transfers it to chlorophyll molecules to appear yellow, orange and red coloured pigments. The distinctive colours of mango, carrots, and yams are due to various forms of carotene. Lycopene, canthoxanthones and astraxanthones share a similar molecular structure of carotene. The red tones of tomatoes, guava, red grapefruit, papaya and watermelon indicate the presence of lycopene.

(e) Flavanoids

Flavanoids are the yellow plant pigments seen mostly in lemons, oranges and grape fruit. The name stems from the Latin word "flavious" which means yellow. Flavanoids from flowers and fruits which provide visual cues for birds, bees and insect pollinators and animal seed dispenses to locate their targets. Flavanoids are located in the cytoplasm and plastids Many of the foods we eat including dark chocolate, strawberries, black currant, grapes, cashew nuts etc contain flavanoids. Flavanoids include red, purple or blue anthrocyanins, as well as white or pale yellow compounds such as kaempferol and quercetin.

Anthrocyanins and pro anthrocyanins, and reddish brown pigment rutin found in Mangoostin fruit rind act to create colour, which most of the flavanoids are visible only under UV light. The yellow colours of flavanoid pigments can also be found as chalones, aurones and flavanols in flowers, leaves, wood and bark.

Flavanoids also comprises anthrocyanins which absorb blue, blue-green, and green light. Leaves containing only anthrocyanins appear red. Anthrocyanins provide the scarlet, blue and purple hues of nature. Red cabbage leaves, black rice, eggplant fruit peel, cherries, promegranate, karawilla kabilla fruit, red and black grapes, raspberries, strawberries, mulberry, black current, plums, red apples contain anthrocyanins as part of their palette. Anthrocyanins play an important role in the colours of ripening fruit.

Anthrocyanins are found dissolved in cell sap, and are not attached to the cell membrane, as in carotenes and chlorophyll. The acidity (pH) of the cell sap determines the perceived hue of the pigment, with acidic sap producing a red colour and less acidic sap producing purple.

Anthrocyanins are formed when the sugar concentration reaches a level high enough to react with certain proteins in the cell, providing a signal that the fruit is ripe and sweet. Light is also required for this reaction, so that an apple growing with one side in the shade may be half green (on the shaded side) and half red.

Anthrocyanins announce to birds, insects and animals to entise them to eat them and enable seed distribution.

(f) Betalains

Like carotenoids and flavanoids, betalains also seem to play an important role in attracting animals to flowers and fruits, and to produce a similar range of colours. The betalains consists of two sub groups, red-violet (betacyanin) and yellow to orange (betaxanthin) pigments. They only occur in certain plant families, and always independently of anthrocyanins.

Betacyanins gave rise to the distinctive deep red of beetroot. The composition of different betalain pigments can vary, giving rice to breeds of beetroot that are yellow or other colours in addition to familiar deep red. Betalains in beet include betamin, isobetamin, probetamin and neobetamin (the red to violet ones are known collectively as betacyanin). Other pigments contained in beetroot are indicaxanthin and valgaxanthin (orange to yellow pigment known as betaxanthin).

(g) Anthrocyanins

Anthrocyanins belong to a large group of secondary plant metabolites collectively known as flavonoids. They are group of very efficient bioactive compounds that are widely distributed in plant food. Anthrocyanins occur in all plant tissues, including leaves, stems, flowers, roots and fruits.

Anthrocyanins have structures consisting of two aromatic rings linked by there Carbons in an oxygenated heterocyclic. The basic chromophone of anthrocyanins is the 7 – hydroxyflavylum ion. Anthrocyanins pigments consists of two or three chemical units : an aglyion base or flavylum ring (anthrocyanadin). Sugar and possibly acylating group. The Chromophore of eight double bonds carrying a positive change on the heterocyclic oxygen ring in responsible for the intensive red – orange to blue – violet colour produced by anthrocyanins under acidic conditions.

2.2.7 Effects of individual components of a DSSC on its overall performance

(a) Substrates

Fluorine – doped Tin oxide (SnO_2 : F) and Indium Tin oxide (In_2O_3 : Sn) are the most frequently used TCO's in thin films PV cells. The standard preparation procedure of nanostructured TiO_2 electrode includes syntering of the deposited TiO_2 film at 450^0C–550 ^{0}C. As the only TCO coating stable at these temperatures, SnO_2 : F has been the material choice for DSSC's.

The choice of sheet resistance of the SnO_2 coated glass plate is a compromise between conflicting beneficial properties of the TCO – coated glass, the higher the conductance the lower the transmittance, and vice versa.

(b) Nanoparticle electrodes

Oxide semiconductors are perfected in photoelectrochemistry because of their exceptional stability against photo corrosion on optical excitation in the bandgap (>3eV) of the oxide semiconductors is needed in DSSC's for the transparency of the semiconductor electrodes for large part of the solar spectrum.

In addition to TiO_2, semiconductors used in porous nanocrystalline electrodes in DSSC's include for example ZnO, Cd Se, Cd S, Fe_2O_3 and SnO_2. However Titanium dioxide has been and still is the commonly used semiconductor for DSSC's.

(c) Sensitizer dyes

These dye molecules play a very important part in injecting free electrons when TiO_2 nanoparticles are exposed to photons of sunlight in these cells. Also the structure of the pigment affects the performance – if the structure has a longer R group, this results in the steric hindrance for the pigment to form bond with the oxide surface of the TiO_2 and hence prevents the molecules from arranging on the TiO_2film effectively.

The absorption of the incident light is DSSC's is realized by specifically engineered dye molecules placed on the semiconductor electrode surface. To achieve a high light – to – energy conversion efficiency in DSSC's the properties of the semiconductor particle surface are essential. Such desirable properties can be summarized as :

- **Absorption :**
  The dye should absorb light at wavelengths upto about 920 nm, i.e. the energy of the excited state of the molecule should be about 1.35 eV above the electronic ground state corresponding to the ideal bandgap of a single bandgap solar cell.

- **Energetics :**
  To minimize energy losses and to maximize the photovoltage, the excited state of the absorbed dye molecules should be only slightly above the conduction band edge of the TiO_2, but yet above enough to present an energetic driving force for the electron injection process. For the same reason, the ground state of the molecule should be only slightly below the redox potential of the electrolyte.
- **Kinetics :**
  The process of electron injection from the excited state to the conduction band of the semiconductor should be fast enough to outrun competing unwanted relaxation and reaction pathways. The excitation of the molecule should be preferentially of the MLCT – type.

- **Stability :**
  The absorbed dye molecules should be stable enough in the working environment (at the semiconductor electrolyte interface) to sustain about 20 years of operation at exposure to natural daylight. i.e. at least 10^8 redox turn overs.

- **Interfacial properties :**
  Good absorption to the semiconductor surface.

- **Practical properties :**
  High solubility to the solvent used in the dye impregnation.

These can be considered as prerequisites for a proper photovoltaic sensitizer. However, the factors that actually make the dye-sensitization work efficiently and yield good photovoltaic performance in the practical cells are much more complicated with all details not even fully understood at the moment.

Absorption of light by other cell components such as TiO_2 and the electrolyte is undesirable because it on one hand does not lead to current generation and reduces thereby the efficiency and on the other hand may induce side reactions with possibly degrading effects on the cell performance in the long term.

(d) Electrolytes

The electrolyte used in DSSC's consists of Iodine (I^-) as a redox couple in a solvent with possible other substances added to improve the properties of the electrolyte and the performance of the operating DSSC I^- / I_3^- redox couple.

The ideal characteristics of the redox couple for DSSC electrolyte are :

a. Redox potential thermodynamically (energetically) favorable with respect to the redox potential of the dye to maximize cell voltage.

b. High solubility to the solvent to ensure high concentration of charge carriers in the electrolyte.

c. High diffusion coefficients in the used solvent to enable efficient mass transport.
d. Absence of significant spectral characteristics in the visible region to prevent absorption of incident light in the electrolyte.
e. High stability of both reduced and oxidised form of the couple to enable long operating life.

f. Highly reversible couple to facilitate fast electron transfer kinetics.

g. Chemically inert toward all other components in the DSSC.

Since the discovery of the DSSC about 24 years ago (Gratzel & O'Ragan in 1991), no redox couple proceeding the performance of the I^- / I_3^- couple in DSSC has been discovered. The I^- / I_3^- redox electrolyte is prepared by adding Iodine to the solvent (Ethanol) together with some Iodine salt like KI, Li I and Alkyl Methylimidazalism iodide.

The redox electrolyte of KI/I in the ratio of 10:1 by volume has been successfully used for about 24 months for the construction of practical DSSC's for the Catamaran Boat.

(e) Solvents

The following are the criteria for a suitable solvent for a high efficiency liquid electrolyte DSSC's :

- The solvent must be liquid with low volatility at operating temperatures (-40^{0}C to + 80^{0}C) to avoid freezing or expansion of the electrolyte, which would damage the cells.
- It should have low viscosity to permit rapid diffusion of charge carriers.
- The redox couple should be soluble in the solvent.
- It should have a high dielectric constant to facilitate dissolution of the redox couple.
- The sensitizing dye should not deabsorb into the solvent.
- It must be resistant to decomposition over long period of time.
- And finally from the point of view of commercial production, the solvent should be of low cost and low toxicity.

Examples of solvents used in the electrolytes of DSSC's are:- Ethanol, Acetonitrile, Methoxyacetonitrile, Ethylene carbonate and Propylene carbonate.

The solvent used in early DSSC's - Acetonitrile seems to be still the best choice when the cell efficiency is to be maximized. However, with respect to the preferred solvent properties listed above, Acetonitrile immediately fails at least in two points. Firstly, it is highly volatile with boiling point of 82^{0}C which is about the maximum temperature that of a roof-top solar cell can reach at full sunlight, and due to the high volatility it easily escapes from the cell through the sealing. Secondly, acetonitrile is highly toxic and carcinogenic chemical

The choice of solvent is thus always a trade-off between low viscosity with better ion diffusion properties and high viscosity with ease of manufacturing and less stringent sealing requirements.

(f) Additives

The performance and stability of DSSC's can be enhanced to some extract by adding specific compounds to the electrolyte.

One example is the optical properties of the electrolyte. Tri iodide absorbs light below 500nm, so the tri iodine concentration in the electrolyte must not be too high. This filtering effect can be avoided by using a base, e.g. tetra butylammonium hydroxide (TBA OH), which converts the light absorbing I_3^- complexes into colourless IO$^-$ ions, which are reduced to I$^-$ + OH$^-$ at the counter electrode.

The use of TBA OH often believed to lead to improved cell efficiencies.

Another important purpose of the modification of the electrolyte composition is to enhance the long-term stability of the cells under operation. All in all the chemical composition and properties of the electrolyte plays a significant role in the operation and performance of DSSC's.

In test DSSC's prepared trace amounts of conc.HCl and Acetic acid were used to alter the chemical structures of Fire fern leaf extract to further darken its colour and to increase the conversion efficiency of the dye molecules.

(g) Counter Electrode Catalysts

For sufficient fast reaction kinetics for the tri iodide reduction reaction at the TCO coated cathode, a catalyst coating is needed.

(h) Platinum

As a traditional and usually most efficient catalyst, Platinum (which is expensive) has been used almost exclusively in literature on DSSC's. However, the performance of the catalyst layer depends on the method by which the Pt is deposited onto the TCO surface. Pt catalyst coatings have been performed for example electrochemically by sputtering, pyrolytically or by spin coating. Electrochemical and vapour deposition of Pt has been found to be unstable in the presence of iodide electrolyte. However an alternative thermal Pt catalyst method seems to be a suitable technique. During the preparation of test DSSC's of the size of $0.25cm^{-2}$ area at the IFS, exclusively used commercial Platinum metal electrodes and were found to be satisfactory.

(I) Carbon

Whilst having excellent catalytic action, Platinum has the disadvantage of being very expensive. However, Graphite which is very cheap and abundant could be used instead for this purpose. Also a better proposition would be to use a porus carbon – counter electrode catalyst layer. This is done by using a mixture of carbon black, graphite powder and nanocrystalline TiO_2 particles. A high conductivity (sheet resistance of $5\Omega.cm^{-2}$) for a 50 μm thick layer) is obtained due to the carbon black particles connecting together separate graphite flakes, while TiO_2 particles are used as a binder to the structure.

(j) Electrical Contacts

Similar to Amorphous Silicon and other Thin Film Solar Cells deposited on TCO coated glass, the design of dye cells and modules is effected by the limited conductivity of the TCO layer. To keep the resistive losses in the TCO layer reasonably low, the longest distance from a photo active point to a current collector should not exceed about 1 cm. For example, Silver paint and adhesive Copper tape can be used to extend the contact area of the current collector to fulfill this geometric requirement.

A Iodine based electrolyte is highly corrosive attacking most metals such as Silver, Alumunium, Copper, Nickel and even Gold, and can be particularly problematic when it comes to designing as electrical contact of single cells in an integrated DSSC molecule.

(k) Sealing

Sealing the DSSC's has long been a difficult question because of the corrosive and volatile liquid iodine electrolyte used in the cells. Being directly related to the long term stability of the cells it seems to be one of the main technological challenges of the DSSC architecture. A suitable sealing material should be :

a. Leak proof to the electrolyte components and impermeable to both ambient oxygen and water vapour.

b. Chemically insert towards the electrolyte and the cell components.

c. Adhere well to the glass substrate and TCO coating.

Several sealing materials have been used such as Epoxyglue, water glass (Sodium silicate), Ionomer resin Sulyn from Du Pont, Aluminium foil laminated with polymer foil, a vacuum sealant from Torr Seal ®, Silicone resin glue etc.

One important question when selecting the sealant is the tolerance of the sealing material towards iodide and tri iodide in the electrolyte. Stable long term operation has been demonstrated for DSSC's utilizing Surlyn ® sealing with iodide electrolyte and also Silicone resin glue .

2.3 Research done in Sri Lanka on DSSC’s since 1994

All research done on DSSC’s in Sri Lanka since 1994 is listed at Appendix A and Appendix B.

2.3.1 All Research done in Sri Lanka on DSSC’s since 1994

Most of the research done on DSSC’s in Sri Lanka have been performed at the Institute of Fundamental Studies (IFS), Hantana, Kandy since 1994 by research teams led by Professor K. Tennakone. The full list of all research papers published in reputed local and international journals in Chemistry and Physics are shown at Table 1 of Appendix A.

It is observed that almost all these papers have analyzed the chemical, physical, electrical and electronic characteristics and/or molecular behavior of organic and inorganic chemicals, nanopowders, various dyes (almost all synthetic), solvents, catalysts and additives used in the composition of DSSC’s as appropriate. Those which affect their short circuit current, open circuit voltage, fill factor and solar energy to electricity conversion efficiency have also been evaluated as appropriate. Also when relevant the operation and functioning of these cells pertaining to their stability, deterioration/degradation, and useful lifetimes have been ascertained.

The research done at the IFS have also analysed, evaluated performance of DSSC’s and categorized them based on the nature of electrolytes they constitute:

a. Liquid type DSSC’s (with different dyes, different semiconductors, thin films)

b. Quasi solid (jelly) type (use of polymer electrolytes)

c. Solid state (use of different hole conductors like Cul, CuSCN, CuBr Complexes, Pentacene, PEDOT etc).

d. Use of conducting Polymers as dyes of hole collectors.
   (i) Use of thiophene and its derivatives.
   (ii) Use and payroel and its derivatives.
   (iii) Use of co-polymers.

e. Use of natural pigments as dyes.

2.3.2 International Recognition of research done on DSSC's at the IFS in Sri Lanka

During the past 18 years R & D in the fields of DSSC's some based on nanoscience have also been done at the IFS, Hantana, Sri Lanka.Sri Lanka has been ranked 10th in the world according to the number of research papers (51) published in reputed internationally recognized Chemistry, Physics and Technology Journals, according to the research article on "Profiling Research Patterns for a New and Emerging Science and Technology" , Beijing Institute of Technology, Beijing, Peoples, Republic of China and Georgia Institute of Technology, Georgia, U.S.A. [5].

All research done on DSSC's and allied fields at the institutes in Sri Lanka (other than at the IFS) are shown at at Appendix B.

It is observed that about 99% of the research done on DSSC's at the IFS (AppendixA) and other institutions in Sri Lanka. (Appendix B) have been done using expensive and scarce synthetic dyes. Hence the research on DSSC's exclusively utilizing cheap, abundantly available and environmentally friendly natural dyes of plants grown in Sri Lanka was done by mimicking the primary process of natural photosynthesis, which has been operating in green plants and organisms for over 3.5 billion years and hence is a well-established principle. In the green leaf, chlorophyll molecules absorb photon energy from sunlight and generate electric charges, which however are not collected as electric current. Instead they are converted by redox reactions at the membrane level to generate oxygen from water absorbed by the roots, and to reduce carbon dioxide absorbed by the leaves from the air to produce chemical energy in the form of carbohydrates.

By using the principle of natural photosynthesis, the DSSC Solar Cells being developed first achieves the separation of the two functionsof light absorption and charge carrier transport and finally produces electrical energy. In a conventional PV cell these tasks are actually assumed by the same material. Thus in Silicon solar cell semiconductor consisting of a sandwich of positively (p) and negatively (n) doped Silicon absorbs sunlight, resulting in the generation of electric charges. These need to be separated from each other first by the local electric field present at the p-n junction, which is followed by transport to the charge collectors. Thus Silicon has to absorb light, separate the positive from negative charges and conduct the charges to the two electric current collectors. Things get quite complicated and ultra – pure materials are required to accomplish the photo-electric conversion at high efficiency. Solar grade Silicon requires 99.9999% purity, which makes it expensive and energy-intensive to produce. The approach which the Author has taken is a radical one, even though it is not a new one, because the light energy conversion in photosynthesis uses a very similar principle.

2.4 History of Research done on DSSC's

Technological achievements in the clean energy system infrastructure are a fundamental issue for worldwide economy and environmental improvements. Therefore, in this 21st century, energy based non-renewable sources has to be converted into new energy systems by incorporating novel technologies derived from advancements in science. Among several new energy technologies, Die-Sensitized Solar Cell (DSSC's) are one of the most promising new energy generation systems for photovoltaic technology. It has emerged as one of renewable energy sources as a result of exploiting several new concepts and materials, such as nanotechnology and molecular devices. Even though the first dye sensitization of semiconductors was reported by Vogel in 1873, where Silver halide emulsions were sensitized by dyes to produce black and white photographic films, the use of dye sensitization in photovoltaic's had been achieved little noticeable result until a break though at the early 1990's by Gratzel's group. They developed a DSSC consisting of T_iO_2 electrode sensitized with Ruthenium (11) complex dye, organic liquid electrolyte with iodine/iodide redox couple and Platinum deposited counter electrode. The solar energy to electricity conversion efficiencies were reported on high as 7.1% in 1991 and 10% and 11% in 2008. In these devices a monolayer of the dye is directly attached to the semiconductor surface via carboxyl group, which could realize and efficient injection of charge carriers from photo excited dye to semiconductor. However this sensitization of T_iO_2 for solar applications requires efficient , stable and inexpensive sensitizers. So far, several organic dyes and organic metal complexes have been employed to sensitize nanocrystalline T_iO_2 semiconductors and one of the most efficient sensitizer is transition metal coordination compound (Ruthenium polypyridyl complex). This is because the complex has intense charge – transfer (CT) absorption in the whole visible range, long excited lifetime and highly efficient metal-to-ligand charge transfer (MLCT).

However, other organic dyes, such as phythalocyanine, cyanine dyes, xanthene dyes, coumarin dyes and so on usually perform poorly in DSSC's because of weak binding energy with T_iO_2 film and low charge transfer absorption in the whole visible range, but these dyes are very cheap and can be prepared easily, compared to Ruthenium polypyridyl complexes. On the other hand, in nature, the fruit, flower, root and leaf of plants show various colours from red to purple and contain various natural dyes which can be extracted by simple procedure. Therefore, it has been emphasized by many researchers to obtain useful dyes and photo sensitizers for DSSC's from natural products, because of the simple preparation techniques, widely available sources, and low cost.

2.4.1 Development of Conventional Solar PV's / DSSC's

2.4.2 Introduction

Since solar power is a clean energy source which has been around for decades,one might wonder why it was not use more. The answer to this lies partially in the cost of producing solar panels, as well as in the efficiency of the solar panels.

Presently research is being done on second generation of solar panel technology and verging on the third. A lot has changed since thefirst generation. Solar panels are becoming a viable source of clean energy. Please refer to the Best Research Cell Efficiencies Graph of the world of NREL at Appendix G.

The solar cells of earlier times were relatively large and bulky compared to current modules. In view of the amount of energy and material required to produce them, and the amount of energy they actually produced, it was more costly to use solar energy than to use fossil fuels. The only exception was in places where little or no fossil fuels were available, such as in space.

With second-generation solar cells, attempts were made to tackle this exact problem by improving manufacturing techniques to reduce the costs, materials and energy needed for the production of solar cells.

Recently, major advances have been made in the production of solar cells, which have reduced production costs.

Once contribution in this area was the development of techniques to coat glass or ceramic materials with very thin layers of semiconductor substances. This made it possible to produce solar panels using only a fraction of the semiconductor material that was required earlier. The production of solar panels using this second generation technology is referred to as 'Thin Film Technology'. Third generation solar energy technologies are currently being researched and developed. The objective is to improve the power of the solar cells even further (while keeping production costs to a minimum) in which case 30% to 60% of the sunlight hitting the panels will be converted into electricity (currently solar panels convert only about 20%).

But regardless of third generation solar technology, the second generation solar cell is efficient enough to make solar technology viable and a host of new solar powered products have hit the consumer market.Solar powered calculators have been in use for the while along with other novelty devices.But only in the last few years have solar devices come into serious practical use. The last five years in particular have seen a virtual explosion of solar devices hitting the market. Solar flashlights, solar powered radio's and, recently solar battery chargers.All of this is a result of the developments in solar technologies and the coming of the Solar Age .

2.4.3 DSSC Technology Trend and Market Forecast 2010 – 2015

As the overall PV industry were given with the goal of innovative saving in production cost, recently Dye-Sensitized Solar Cell (DSSC) has emerged as the 3rd generation semiconductor solar cell. Unlike traditional semiconductor solar cell the utilize wafer substrate, Dye-Sensitized Solar Cell became widely known as Prof. Michael Gratzel reported highly efficiency Photo-electrochemical solar cell basing as the principles of photosynthesis that showed 7.1% conversion efficiency to the 'Nature' magazine in 1991. The conversion efficiency of DSSC's were higher by using wide band semiconductor T_iO_2 (band gap 3.2eV) that currently shows over 11% energy conversion efficiency. Compared to the solar cells that utilize highly expensive poly-silicon and vacuum equipment, the production cost of DSSC's could be save from of the production costs of the solar cells that gathers much attention recently as many international companies announcing their plans of commercialization. However, there exist merits of savings in the manufacturing cost but commercialization had been delayed due to low photo conversion efficiency of the module, reliability in long hours, and problems in original patents.

Recently Companies that are developing DSSC's offer data resolving problems in reliability on long hours one by one and the original patent owned by Prof. Gratzel from Switzerland expired in October 2008, that interrupted international Companies centered in Japan, announced commercialization prototypes that anticipates earlier commercialization of DSSC's than expected.

The economic solution and in particular the upward trend in the price of fossil energies and political pressure on the markets induced in part by public opinion and in part by geopolitical aims to loosen theties of energy dependence has meant that considerable budgets have been allocated over many years to the development alternative energy sources. The productionof photovoltaic electricity is one promising avenue among these various types of 'Clean energies'. [199].

2.4.4 Market Analysis and Investment Opportunities in Start up Companies Active in the field of Solar PV

Experiencing one of the highest energy growth rates worldwide (over 30% in 2003) for the last five years, the photovoltaic industry could be expected to sustain this high growth rate (27% - 34%) for the next 20 years. The market is currently dominated by the first (crystalline silicon wafers) and second (thin-film) photovoltaic generations. The market share of the crystalline silicon – based technology (>80%) has already stated to erode because of the technological development of a cheaper alternative offered by thin films (especially the amorphous silicon, a-S). However, major technological improvements to increase efficiency willnot happen in the crystalline silicon –based technology.

However, the world solar PV industry growth rate of 30% in 2010 has dropped to 25% in the first quarter of 2011 mainly due to policy changes in the three leading manufacturing countries – Germany, Japan and United State. There will dramatically slow down theindustries growth rate this year and next year. The policy changes include tightening of incentive terms determined by cuts in unit tariff, policies,supply requirements vs. manufacturers plans, factory – gate prices and manufacturing costs and gross margins.

Bringing innovative features such as flexibility and low weight while offering relatively high efficiency (10%), thin-film should continue to conquer market shares. Since the technology still relies on Silicon, the prices remain to expensive to be profitable without the benefit of subsidies provided by governments for installation (Japan, Germany and USA). Prices should not be decreased significantly mid termbecause the price of silicon is increasing due to a relative scarcity and a growing demand. Additionally, this film manufacturing processes are very complex and require substantial capital investments.

The commercialization and market potential of Solar PV's indicating the yearly market price graph is attached at Appendix H. List of major solar PV cell manufacturing companies in the world is at Appendix J.

In this context, organic photovoltaic (OPV) technologies should be able to successfully enter the market. OPV is even cheaper than the thin-film and has unique feature. OPV modules are light flexible, transparent, and can use diffused light to produce energy. Among the different OPV technologies that have been developing, the Dye-sensitized Solar Cell (DSSC) technology is ready to be marketed. The two other technologies (polymer and small molecules) have a long way before becoming marketable. DSSC leakage problems are being solved by substituting liquid electrolyte by solid electrolyte, and this fact will bring it to the market threshold.

Currently themarket to be considered for DSSC application is not roofing because the lifetime of the DSSC is still too short for this application to be possible. This problem should be solved in the future but apparently probably not within the next five years. Most likely, the primary market applications will be for the military equipment and consumer goods. As it is often the case with technological developments, the military application market is expected to boost the OPV within the next two to four years. The worldwide market for the first application fields is expected to be around US$ 1.3 – 1.5 billion.

DSSC Companies are positioned in the research and manufacturing segments of the value chain the strategy is to start generating profit with the current marketable applications andcontinue their R & D efforts in order to propose modules for building integrated PV roofing (BIPV) and façade applications. The barriers inhibiting market development and expansion are :

- Technical barriers and standards.
- Legal and administrative barriers.
- Market barriers, different units of measurement.
- Perception barriers and acceptance DSSC's which was a little more than a curiosity a few years ago are positioned at the edge of the organic PV space. However, recent developments suggest that this approach to PV is rapidly commercializing offering a potential low-cost technology solution for Building Integrated PV's (BIPV), military applications (battery chargers for manpack radios, portable satnavetc), and consumer goods. Recent material – related innovations like new transparent electrolyte, replacing of expensive Platinum electrodes with less costly electrodes of Carbon /Graphite/Cobolt, development of low-cost transparent doped conducting Tin oxide coated glass electrodes by low temperature sputtering/ adhesive bonding, and re-thinking of DSSC cell architecture are now leading to their rapid commercialization.

The uses of Nanomaterials too are leading to new opportunities for production of cheaper and more efficient DSSC's. Quantum dots, metal oxide nanopowder, fullerenes, carbon nanotubes and graphite which are at the forefront of the PV applications also promise significant improvements to practical conversion efficiency of DSSC's.

2.4.5 Solar Photovoltaic Development in U.S.A as a Role Model

- PV installations totaled 832 MW in second quarter (Q_2) of 2013, up 15% over $Q_1$2013.
- Cumulative operating PV capacity in U.S.A. now stands at 8,858 MW.
- The residential market was flat quarter over quarter in Q_2, breaking its streak of incremental quarterly growth.

- The non residential market was down in Q_2 continuing a relatively light year for the segment.

- The utility segment completed 38 projects totaling 452 MW, currently there are an
` additional 4.1 GW of utility PV under construction.

- Anticipate that 4.4 GW of PV will be installed in 2013 up 30% over 2012.

- The average residential PV system price fell to US$ 4.81/W., while the average non-residential system price dropped to US$ 3.71/W.
[107], [199], {232].

Concentrating Solar Power (CSP)

- Despite zero CSP in installations in Q_2 2013, maintain bullish expectations for 2013 with over 900 MW ac slated to come on-line by the end of the year.

- Bright Source Energy's 392 MW ac Ivanpah CSP project is on schedule to deliver electricity to the grid in late 2013.

Current US Solar PV Projects

In 2013, the US Solar Market will achieve a number of significant milestones. Among them :

Over 100,000 individual solar system will be installed by year's end.

Cumulative installed solar photovoltaic capacity will surpass 100 GW.

The US sphere of global solar installations will reach a high of 13%, up from 5% in 2008.

A solar project will be installed, on average every four minutes in the US.

. All these achievements are a result of a continually growing market. It is forecast that 4.4 GW of PV and 912 MW of concentrating solar power (CSP) will be installed in 2013, up from 3.4 GW of PV and zero CSP in 2012. Still the market is not without uncertainty. Three key developments are identified that present risks for the market moving forward.

2.5 GAP / SWOT Analysis of DSSC's in Sri Lanka

GAP analysis involves the comparison of actual performance with potential as desired performance . SWOT analysis is an initialism for strengths , weaknesses , opportunities and threats – and is a structural planning method that evaluates those four elements of a project .

2.5.1 Market Analysis

The overall purpos of DSSC's can be on the flexibility of low-cost solar energy. To reach that point, a number of issues must be solved. Life time and power conversion efficiency must be significantly improved, together with drastic cost reduction. Also increased R & D efforts toward large scale processing must be established. Low-cost large scale solar power will not come easily, but when it arrives , it can have unforeseen consequences on how energy is perceived today. The DSSC Technology is a booming academic field and a promising industry for those who are knowledgeable in this technology.

Micro Environment of DSSC's

The micro environment of DSSC's describes the part of this environmental framework that the industry influence directly (eg.suppliers, investors, distributors, academia, customers and competitors). As of 2010, the DSSC industry comprised mainly of Konarka Technologies Inc, Massachusetts, USA, Sustainable Technologies International – Dyesol Australia (Pvt) Ltd., Queenbeyan, Australia, Toshiba Research Europe Ltd, Cambridge, United Kingdom, Siemens Research & Development GmbH, Berlin, Germany, and Sharp Corporation, Osaka, Japan. These companies are supported in various ways by a number of central stakeholders in venture capital, academia and materials and purchasing.

Academia

Academia refers to the massive research effort from public and private universities and research institutes with a strong emphasis on Europe (Germany), North America (U.S.A) and Japan

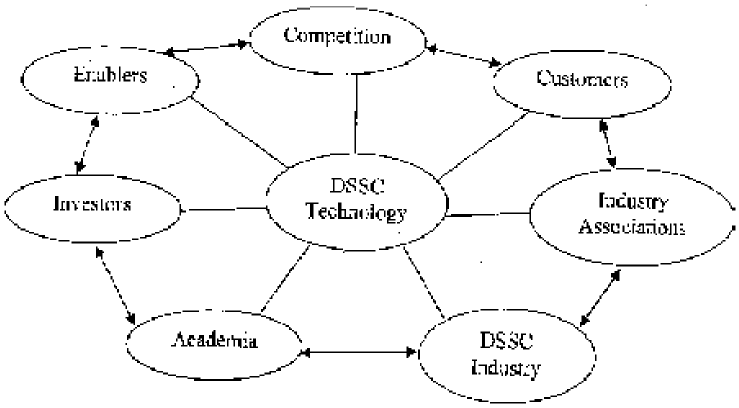


Figure 2.7 Overview of the micro environment for DSSC technology

Investors

Investors are the life blood of any new technology as it powers up for proof of market . When it comes to DSSCs , especially cheap, easy to make solar cells , investors are considerably eager to mgo the extra mile to conquer the promised Land . solar (PV) energy has shown growth rate of 25% – 35% annually for extended periods, and DSSCs seem to be competitive with Silicon wafer based industry .

Enablers

Enablers are Companies that, in one way or another, provide services to the industry inform of materials, processing equipment, processing of technology know – how, and supporting activities necessary to develop a technology.

Competition

Competition includes direct competition from other Companies and various types of solar cells –primarily thin film solar cells – like Cadmium telluride (Cd Te), Copper indium selenite (C I S), Organic solar cells (OPV's) and nanocrystalline based thin film and ridged substrate Silicon-solar-cell types.

Customers

The DSSC technology in not mature and large scale market penetration has yet not to happen.

DSSC Industry

Participants in the DSSC industry will, by default, be able to influence one another. Unit recently Konaka Technologies Inc has been setting the pace, nevertheless, once the industry develops t include a handful of on the market Companies, participants will have to face that they are all stakeholders in their own industry.

Macro Environment of DSSC's

This includes the economic, political, social, technological, environmental and legal factors that influence the industry and that the industry is not able to influence in any significant way. That is, the macro environment is the sphere in which the industry operates.

Economic factors

These are many economic factors, but here only a few are discussed. Among them are the central elements of functioning and variable interest rates related to billions, as venture capital or private equality, and US $ 4 billion, as public market new investments, in USA for example.

Political

Political factors that are directly related to solar energy include the application of subsidies, taxation, granting of research funds, national target for lowing carbon dioxide emissions, and national and regional ambitions to become dependent on renewable energy sources[106,107,108].

2.5.2 Gap Analysis of Solar PV's /DSSC's based on Nano-technology

This Thesis is part of an ongoing study on Nanotechnology developments in Sri Lanka pertaining to conversion of solar energy to electricity with Dye-Sensitized Solar Cells (DSSC's)/Organic Semiconductors.It provides a status overview in respect to key players, government of Sri Lanka programmes on above, along with a GAP Analysis on its implementation[106,107,108].

2.5.3 How Nanotechnology could convert Light to Electricity

Enabling energy storage, production and conversion within renewable energy frameworks had been cited as the primary area where nanotechnology applications might aid developing countries like Sri Lanka. Examples of nanotechnology based interventions include photovoltaic cells with TiO_2 nanopowders and organic light emitting devices based on Cds or PbS quantum dots, as well as carbon nanotubes in composite film coatings for solar cells. Nanotechnology can enable cost effective solar cells with higher efficiency. Efficient way to store electricity in batteries and super capacitors could also be made possible using nanomaterials. Overall nanotechnology interventions could enable the successful development of renewable energy solutions and reduce over dependence on fossil fuels.

2.5.4 International developments

A major new area of R & D focus in the nanodomain for countries at the global platform is in the area of DSSC solar photovoltaic. USA, Europe, Japan and China spearhead the research in SPV. In USA, the PV technology roadmaps were developed well ahead in 2007 whereas, the future roadmaps for Intermediate Band PV, Multiple – Exciting Generation PV, the road maps aim at developing solar cells based on inorganic semiconductor nanocrystals (NC's) such as spherical quantum dots (QD's), quantum rods (QR)-focusing on their potential to improve the single junction photovoltaic (PV) solar cell efficiency drastically from 33% to 44%.

The Nano Architecture roadmaps on the other hand targets to develop solar cells with nanocomponent like nanowires, nanotubes and nano crystals as absorbers or transporters. These technologies are mostly in the early demonstration stage compared to more matured technologies like Si, Cd Te, and GIG'S.

A new methodology has been adopted for targeted materials science and process engineering research by Universities in support of industry – led teams to facilitate commercialization of new PV systems by 2010 to 2015.

2.5.5 Nanotechnology R & D in the energy sector in Sri Lanka

Much like other countries, nanotechnology based interventions in solar energy system is one of the prominent areas of focus in Sri Lanka. The aim should be to improve the overall SPV process efficiency, reduce the cost of solar cells and search for alternative semiconductors in-lieu of the soaring shortage of silicon. The SPV research in Sri Lanka is primarily aimed at developing new materials, processes, devices structures modules using multicrystalline silicon, thin films, polymers, nanoparticles, nanorods, quantum dots etc, using indigenous and imported technologies to emphasize product development and commercialization. SPV research in energy storage devices and efficient lighting systems should also be undertaken.

2.5.6 Organic Photovoltaic Technology / Dye Sensitized Solar Cells

Background

Conventional solar cells convert light energy into electricity through the photovoltaic effect on semiconductor materials like crystalline silicon. Though effective, this methodology of harnessing solar energy has its drawbacks in the form of high manufacturing costs and prices, decreasing availability sufficient amounts of silicon, module assembly costs, rigidity of panels etc.

To counter these factors, new technologies have emerged that make use of technologies that cost effective raw materials and processes. These technologies, collectively termed 'Third generation technologies' primarily include Organic / Dye Sensitized technology, Nanotechnology and Spheral technology.

Research on developing organic based solar cells started 1991 by Prof., MichealGratzel of Switzerland. They are a potentially cost – effective option for utilizing solar energy. The technology itself is in the processof development, and shows promise because of its ease of use, diversity of applications and manufacturing process.

2.5.7 Organic Technology

Organic technology solar cells are essentially based on the photosynthesis process of plants. The absorption of sun light in organic cells is done by the natural dyes of plants which substitutes for the silicon in conventional cells. This light causes the dye molecules to get excided and release electrons that are converted to electrical energy.

The use of chemicals called dyes for the conversion process has led to organic cells also known as Dye –Sensitized Solar Cells (DSSC's).

The absorption of light occurs in dye molecules that are in a highly porous film of Titanium dioxide (TiO_2).. This causes the electrons to be injected into TiO_2 and is conducted to the transparent conductive oxide layer (TCO).

Main Features

Cost

Organic Solar Cells can reduce the overall cost of power generation using photovoltaic technology by lowering material and manufacturing / assembly costs.The exclusion of crystalline silicon material presents substantial savings in raw material and manufacturing/assembly costs.

Cost are limited through the use of Titanium dioxide, which is relatively inexpensive and technology that does not require assembly of cells into modules.

The costs however become higher due to lower efficiency and durability levels of organic solar cells. At present, research and development efforts and underway to bring down overall costs of manufacturing and set price levels at US$ 1/Watt.

Flexibility and versatility

Organic technology solar cells have been developed for use in a variety of indoor and outer applications. The substrates used for manufacture **canrange** from glass to plastics, and the method of application of the dye results in highly flexible solar panels that dispense with theproblems faced in use of more fragile conventional solar modules.

Organic-based solar modules have been developed by the U.S. Air Force Research Laboratories that can be sewn into tents and othermaterial to provide local energy solutions in remote camps. This technology has also been used in photovoltaic clothing that can provide power for small electronic equipment. Research is also underway to develop ‘self – assembling’ organic thin – films, which are able to self – organize from liquid into efficient cell coatings.

Efficiency

The organic solar cells developed in 1990’s demonstrated efficiencies of about 1%. Through research and development of technology, efficiency levels have increased to roughly 3 – 5% and up to 11% in laboratories.

Though many researchers aim for theoretical efficiencies of 33%, current levels remain around 5% for commercial cell production. Various experiments are presently underway that make use of alternate materials, like pantacene (at Georgia Institute of Technology, U.S.A.), that have the potential of increasing efficiencies while keeping costs level.

Use of nanotechnology in combination with organics is also being tested in order to improve the energy conversion levels of organic solar cells.

Life time & Recyclability

One of the main problems with organic technology is the short life-span of solar cells. Because of the nature of the dyes and otherchemical compounds used, the cells are prone to degrade relatively quickly at working temperatures and common weather conditions. Opting for higher efficiencies can further decrease the lifetime of solar cells.

However, recent research and development of technology had led to the possibility of manufacturing organic solar cells that have a projected lifetime of about 10 years. Also the concept of **recyclability** of DSSC’s by refilling of evaporated redox electrolyte between the two FTO glass electrodes through a small hole drilled through one electrode , and resealing it at regular intervals of time could extend their useful lifetimes .

Integration in manufacturing processes

Due to the unique nature of the components used in manufacturing organic cells, the technology cannot be suitably integrated with other existing cell production lines for silicon based solar cells.

Due to the unique nature of the components using in manufacturing organic cells, the technology cannot.

Reliable mass production also requires that the organic solvents used in the cells have a certain degree of durability and are able to withstand mechanical stress at working temperatures.

Market share

A list of main research organizations and established companies in the world carrying out R & D on Dye – Sensitized Solar Cells is at Appendix J [125] .

2.6 Main Research Organizations and Established Companies in the World carrying out R&D on DSSCs

A list of main research organizations and established Companies in the world carrying out R&D on DSSCs is at Appendix J. [125] .

2.7 Reasons why DSSC's have not been developed for commercial use in Sri Lanka.

- Identification of natural dye for low - cost , relatively high conversion efficiency
- (approximately 3% - 5%) amongst plants grown in Sri lanka . Efficiency of around 11% could be obtained with rutanium complexes , but they are very expensive .
- Use of liquid electrolyte which has temperature stability problems . At low temperatures the electrolyte can freeze ending power production and potentially leading to physical damage .Higher temperatures can cause the liquid to expand , making sealing the panels a serious problem .
- Proper and effective sealing of DSSC's which would ensure a useful operating life in excess of 10 years or more.
- Most of the research done in the Universities and research Institutions in Sri Lanka by Chemists and Physicist. This has not progressed beyond the design stage into development and practical usage stage due to unavailability of motivated and competent Chemists, Physicists and Electrical/Electronic/Systems Engineers to continue with this task. Team work is essential and multidisciplinary team element is emphasized.
- Leading Research institutions like the Institute of Fundamental Studies (IFS), Hantana, Kandy, have been carrying out only fundamental research on DSSC's since 1994, but not applied research.
- Facilities and equipment required to carryout development and practical construction of DSSC's for use in the field are not available at the IFS, as it has not been the intentionof this Institute to do so.
- Research on DSSC's have not been done in Sri Lanka utilizing Quantum Dot Technology which could give a theoretical conversion efficiency of up to 66% due to non-availability of Electronic Measuring and Analytical Equipment like Scanning Electron Microscope (SEM), FT-IR Spectrophotometer, Atomic Force Microscope, Raman Spectrophotometer etc. Non availability required funds, equipment and facilities to carry out latest State-of-the Art research on DSSC's in Sri Lanka.

CHAPTER 3

MATERIALS & METHODS

3.1 Methodology of Research

The research activities carried out on this project in the Laboratories of the Chemical & Process Engineering Department, University of Moratuwa, Moratuwa, Sri Lanka and in the Solid State Chemistry and Condensed Matter Physics Laboratories of the Institute of Fundamental Studies (IFS), Hantana, Sri Lanka are depicted hereunder.

Initially, all natural dyes of plants grown in Sri Lanka considered suitable for use in Dye-Sensitized Solar Cells (DSSC's) were identified, and analyzed electrically and electronically utilizing SANWA YX – 390 TR Electrical Multimeter, SHIMADZU UV-vis 1800 Spectrophotometer at the University of Moratuwa, and VIRAJ Current – Voltage Curve Tracing Computerized setup coupled to a KEITHLEY 2000 Electronic Multimeter with a Potentiostat via computer controlled software at the IFS. A 500 Watt Xenon Lamp with an AM 1.5 Filter calibrated with an Eko Pyronometer and Silicon Photodiode was used to obtain simulated sunlight at 100mW.cm^{-2} intensity in the laboratory, and a UV 245 SHIMADZU UV-vis Spectrophotometer for Absorbance Spectra Vs. Wavelength measurements at the IFS.

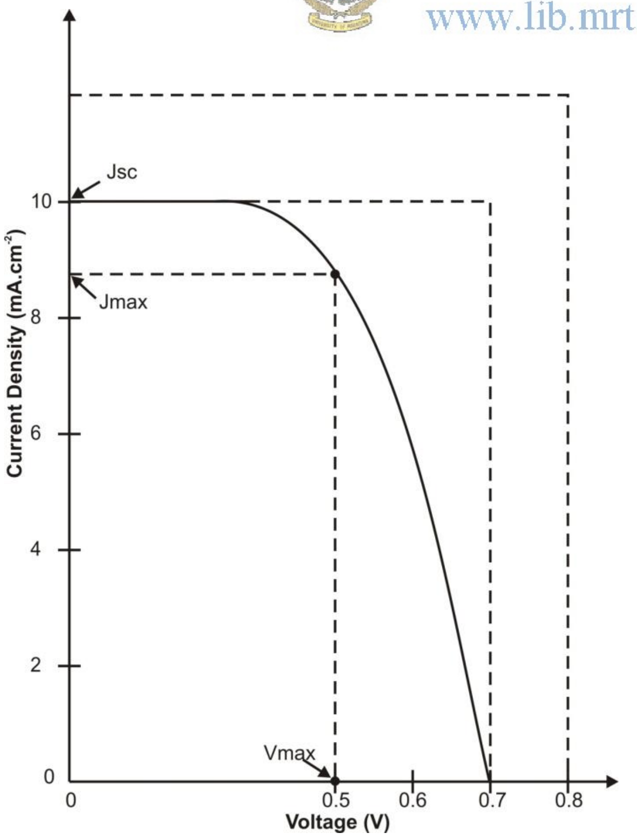


Figure 3.1 Current – Voltage characteristics of a typical DSSC.

A cross section of a list of plants and their use in DSSC's is listed at Table 3.1below. The selection of this list is based on option that they have never been tested before as per the review.

Table 3.1 Natural Dyes From Plants Grown In Sri Lanka

Sr. No.	Name	Botanical name	Parts used
1.	Thekka (Teak)	*Tectona grandis Linn*	Leaves, Bark, Root
2.	Dan pothu	*Syzygium cumini*	Stem, Bark
3.	Kohomba	*Azadirachtin indica*	Bark
4	Rambutan	*Nephelium lappaceum*	Fruit Skin
5	Bulath	*Piper Betle*	Leaves
6	Kos (Jack)	*Artocarpus hetorophyllus*	Saw dust
7	Venivel	*Coscinium fenestratum*	Stem
8	Kurundu	*Cinnamomum verum*	Bark
9	Kothala Himbutu	*Salicia reticulate*	Bark
10	Delum	*Punica granatum*	Fruit skin
11	Rath Handun	*Pterocarpus Santalinus*	Stem
12	Ranawara	*Gassia auriculata*	Flowers
13	Aralu	*Terminalia Chebula*	Fruit
14	Bulu	*Terminalia Belerica*	Fruit
15	Munamal Pothu	*Mimusop elengi*	Stem
16	Welmadata	*Rubia Cardifolia*	Root and stem
17	Mangoostein	*Garcinia mangostana*	Fruit rind
18	Daspethiya	*Tegetus erect*	Petals

19	Loku Luunu	*Allium cepa*	Skin
20	Wada	*Hibiscus rosa-sinensis*	Used leaves
21	The (Tea)	*Camellia Sinensis*	Used leaves
22	Katarou	*Clitoria ternated*	Flowers
23	Kuppamenia	*Acalypa indica*	Leaves
24	Kopi	*Coffea arabica*	Leaves, seeds
25	Kottamba	*Terminalia catappa*	Ripe leaves
26	Devadara	*Erithroxylum manogynum*	Stem
27	Beet root	*Beta vulgaris*	Rhysome
28	Kaippu	*Acacia catechu*	Wood
29	Pethangi	*Caesalpinia sappan*	Wood
30	Marathondi	*Lawsonia intermis*	Wood, leaves
31	Seyum wel	*Oldeulandia umbellate*	Roots and tubers
32	Rasandun	*Berberis aristate*	Roots and tubers
33	Ahu Dumbu	*Morinda citrifolia*	Roots and tubers
34	Kudu miris	*Toddalia asiatica*	Roots and tubers
35	Kaha	*Curcuma domestica*	Roots and tubers
36	Kela gas	*Butea monosperma*	Flowers
37	Sepalika	*Nyctanthus arbo-tristis*	Flowers
38	Maliththa	*Woodfordia fruitticosa*	Flowers
39	Anaththa	*Bixa Ovellana*	Seeds
40	Nil awariya	*Indigofera tinctora*	Leaves and stem
41	Hamparilla	*Mallotus phillipiueses*	Stem
42	Welikaha	*Memecyloa capitellatua*	Rhysome
43	Sen kottan	*Semecarpus*	Seed

		anacardium	
44	Kumbuk	*Terminalia arjuna*	Bark
45	Hik	*Lannea coromandelica*	Bark
46	Ipil Ipil	*Leucaena leucocephala*	Bark
47	Gas Penela	*Sapindus trifoliatus*	Seed
48	Wal inguru	*Zingiber cylindricum Moon*	Rhysome
49	Puwak	*Areca catechu*	Seed
50	Kothala Himbutu	*Salicia reticulata*	Wood and root
51	Bowitia	*Osbekia aspera*	Bark
52	Mal ehela	*Cassia fistula*	Bark
53	Mahogani	*Swietenia mahagoni*	Bark, Saw dust
54	Bulu	*Terminalia berelia*	Bark
55	Madan	*Syxgium cumini*	Bark
56	Rath mal	*Ixora coccinea*	Flowers
57	Kaju	*Anacardium occidentale*	Bark and fruit
58	Sera	*Cymbopogon cutratus*	Rhysome
59	Inguru	*Zingiber cylindricum Moon*	Rhysome
60	Rata kaha	*Bixa orellana*	Seed
61	Alisarin	*Hydrorcy anatharaquinones*	Stem
62	Masakka	*Quercus Infectoria*	Rhysome
63	Pipigngna	*Cucumis sativusl*	Stem
64	Gammalu	*Pterocarpus marsupium Roxb.*	Stem
65	Rata-embilla	*Morus Tinctoria*	Fruit
66	Annasi	*Ananas Comosus*	Leaves

67	Kesel	*Musa Sapientum*	Muwa
68	Goraka	*Garcinia Cambogia*	Fruit
69	Nelum	*Nelumbo Nucifera gaerin*	Flowers
70	Carrot	*Daucus carrota*	Fruit
71	Daisiya	*Chrysanthemum Leucanthemum*	Flowers
72	Grass	*Zingiber cylindricum Moon*	Leaves
73	Rosa	*Rosa Indica*	Flower
74	Suriyakantha	*Helianthus Annuus*	Flowers
75	Tomato	*Solanum Lycopersium*	Fruit
76	Eucalyptus	*Eucalyptus globules*	Bark
77	Lemon grass	*Zingiber cylindicum Moon*	Leaves
78	Nivithi	*Basella alba*	Seed
79	Koodalu	*Impatiens flaccida*	Flower
80	Cannas	*Canna edulis*	Flower
81	Boganvila	*Bougainvilla spectabilis*	Flower
82	Beligeta	*Aegle marmelos*	Fruit
83	Kaduru	*Cerbera manghas*	Fruit
84	Katakaluwa	*Myrica nagai*	Fruit
85	Thembili	*Eugenia bracteata*	Husk
86	Mulberry	*Morus alba*	Fruit
87	Mango	*Mangifera indica*	Fruit, leaves, bark
88	Blackberries	*Rubus Fruitcoses*	Fruit
89	Raspberries	*Rubus Edaem*	Fruit
90	Blueberries	*Vaccinum angustifolium*	Fruit
91	Star Fruit	*Averrhoa*	Fruit

		Carambola	
92	Bankoro	*Morinda Citrifolia*	Bark of roots
93	Annato	*Bixa ovellana*	Dried seed
94	Bayok	*Petaro Spermum*	Bark
95	Jack Fruit	*Artocarpus heterophyllus*	Sawdust
96	Bread Fruit	*Artocarpus affilis*	Inflorescence
97	Shoe Flower	*Hibiscus surattensis*	Flower petals
98	Pokuru Wada	*Hibiscus rocacinesis*	Flower petals
99	Kaneru	*Nerium oleander*	Flower petals
100	Rathu Kathuru murunga	*Sesbania grandiflora*	Flower petals
101	Maha ratmal	*Rhododendron arboretum*	Flower petals
102	Red Sandalwood	*Pterocarpus santalinus*	Wood
103	Big Onion	*Allium Cepa*	
104	Brazlin	*Nephelium Lappaceum*	Wood
105	Tumeric	*Curcuma domestica valet*	Rhizome
106	Walmadata	*Rubia coxdiflora*	Root, stem
107	Mery Gold	*Targets erectra*	Flower petals
108	Rathadun	Petericarpus Santalum	Stem
109	Kekum pothu	Carerium Zelanicum	Bark

Plant samples of Fire fern , Blue and Gray Tree Lichen were obtained from the National Botanical Gardens , Peradeniya . All others were collected from other local sources .

3.2 Characterization of Photoelectrochemical Parameters of Natural Dyes

The UV-vis Absorbance Spectra and I-V characteristics of about 9 natural dyes of plants grown in Sri Lanka were initially tested and analyzed at the IFS using equipment mentioned hereunder.

- Locally developed VIRAJ I-V Curve Tracing Computerized setup coupled to a KETHLEY 2000 Electronic via Computer controlled software .

- 500 Watt Xenon Lamp with AM 1.5 Filter calibrated with an Eko Pyronometer and Silicon Photodiode to provide simulated sunlight at 100mW.cm^{-2} .

- UV 2450 SHIMADZU UV-vis Spectrophotometer for UV-vis Absorbance Spectra Vs. Wavelength measurements of dye extracts.

The extracts of dyes from various fruits, vegetables and plant segments were obtained from clean, fresh plant materials. These were cleaned in fresh water, crushed and added to Ethanol (Merck). When necessary mixtures were centrifuged and all solutions were protected from direct light exposure.

All chemicals and reagents used throughout research work were of analytical and high purity grade suitable for analytical and research applications .

3.3 Preparation of nanocrystalline TiO_2 films

The TiO_2 paste was prepared by blending 200 mg powder of TiO_2 (P-25, Degussa) and one drop of Triton X 100 and 12 drops of Acetic acid in an agate mortar, then themixture was ground for 30 min, finally 3 mL of Ethanol was slowly added whilst grinding continuously for further 30 min. Above pastes were then applied on Fluorine –doped Tin oxide coated transparent conducting glass substrate by the Doctor Blade method to obtain approximately 10 micrometer thick TiO_2 film. Films were then heat – treated at 550^{o}C for 30 min. and cooled down to room temperature. Then they were immersed separately in alcoholic dye solutions for 12 hours.

The Flow chart for Preparation of DSSC's is at Appendix C.

3.4 Fabrication and characterization of solar cells

Photo electrochemical solar cells were then fabricated by sandwiching a Platinum spluttered conducting Tin oxide (CTO) glass plate with the dyed TiO_2 film. A redox electrolyte containing I_3^-/I^- redox couple (prepared with KI/I in the molar ratio of 10:1 dissolved in 10 mL of

Ethanol) was then introduced to the solar cells between the two glass slides with a micropipette by capillary action. The Current –Voltage characteristics (Open circuit voltage, short circuit current, Fill factor , and Efficiency) of the solar cells at 100 mW. Cm^{-2} (AM 1.5) simulated solar irradiance from a calibrated 500 Watt Halogen lamp with AM 1.5 Filters were measured using a 'VIRAJ' home-made Current – Voltage measuring setup with Keithley 2000 Electronic Multimeter with a Potentiostat via a Computer-controlled software (available at the Institute of Fundamental Studies, Hantana, Sri Lanka. The intensity of the light was calibrated using EKO Pyrometer and silicon photodiode .

The Absorbance or Transmittance spectroscopy measurements is one of the simplest, versatile and powerful techniques available for chemical analysis of various solutions. Transmittance is the ratio of transmitted light through a sample of incident light.Transmittance= $\frac{I}{I_0}$,where I is the transmitted light intensity and I_0 is the incident light intensity. This approach is especially important when dealing with highly scattering samples, as for example with solar cells using scattering layers or reflecting contacts.

The UV-vis Absorbance spectra vs. Wavelength measurements of the dye solutions were obtained using the SHIMADZU UV2450 UV –vis Spectrophotometer available at the IFS, Hantana, Sri Lanka.

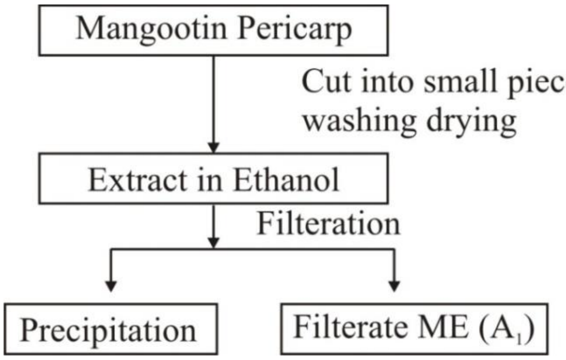
Also the effects of pH values on the Absorbance Spectra of Mangoostein fruit rind extract and turmeric root extract were also studied using the SHIMADZU UV 1800 Spectrophotometer at the Department of Chemical and Process Engineering, the University of Moratuwa, Moratuwa, Sri Lanka. This is depicted at Chapter 4..2.1. Fig. 9 .

Also the current Voltage characteristics of DSSC's fabricated with Mangoostein and Turmeric dyes for pH values ranges from 1 to 12 were studied .

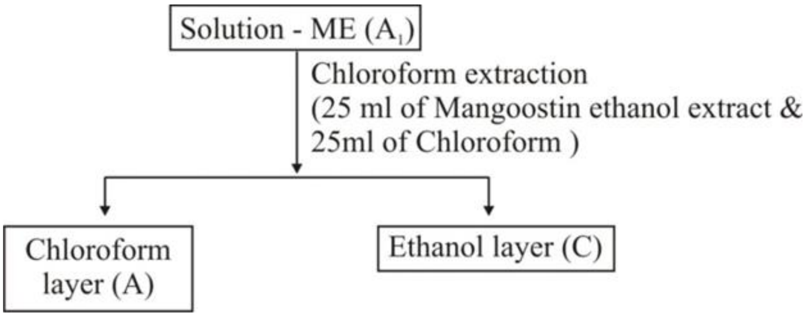
3.4.1 Purification and characterization of extracts from Mangoostein fruit pericarp to enhance conversion efficiency

Attempts were made to enhance the conversion efficiency of Mangoostein fruit rind (pericarp) extract, and to develop a 'Super-dye' for use in DSSC's. Stepwise purification of this extract was carried out at the University of Moratuwa, Industrial Chemistry Laboratory. Fig.3.2 presents this whole purification process. The purification procedure is as listed in the following Flow Charts I, II, III, IV, V, VI and VII.

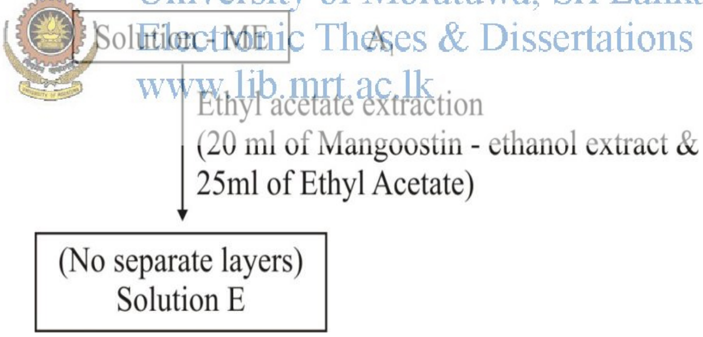
1. **Flow Chart I – Extract of Mangoostein using Ethanol**



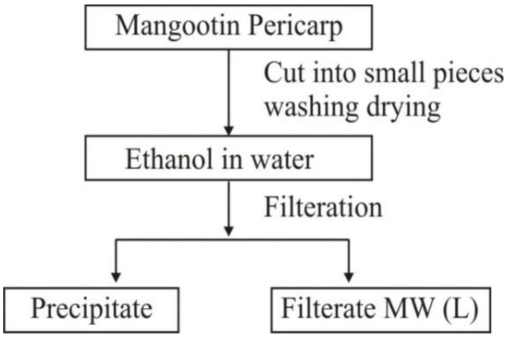
2. Flow Chart II – Purification with Chloroform



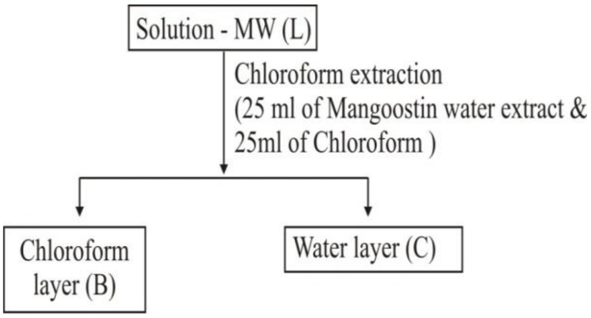
3. Flow Chart III – Purification with Ethyl Acetate



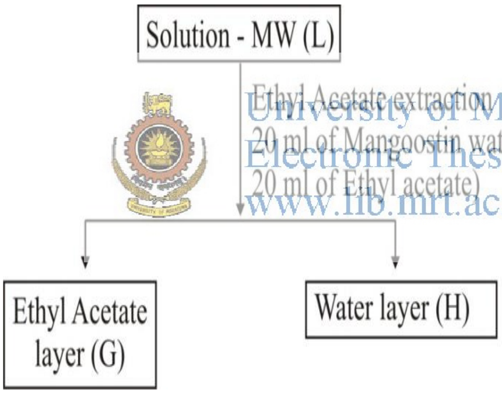
4. Flow Chart IV – Extract of Mangoostein in water



5. Flow Chart V – Purification of Mangoostein with Chloroform



6. Flow Chart VI – Purification of Mangoostein with Ethyl acetate



7. Flow Chart VII – Purification of Mangoostein using Chloroform (repeat)

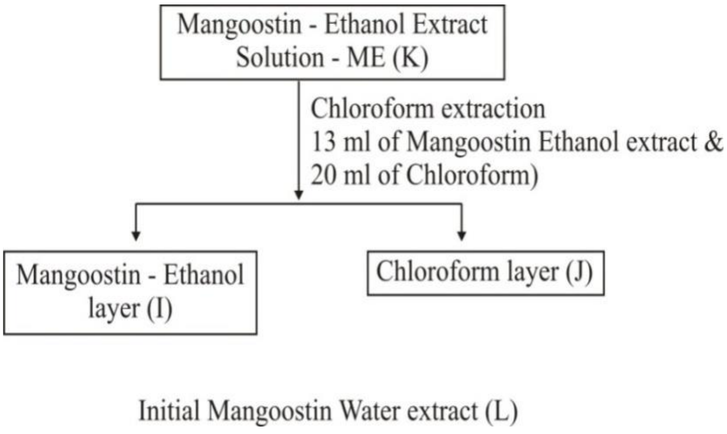


Figure 3.2 Full Flow Chart for the purification of extracts obtained from Mangoostein fruit rind (pericarp)

3.5 Preparation methods of FTO glasses of glasses DSSCs

Initially Soda lime glass slide of dimensions 6 cm x 3 cm were washed in Teepol detergent solution in distilled water, dilute Sulphuric acid and rinsed with Ethanol and left to dry at room temperature.

Thereafter 20 ml of commercial grade Alkyl Tin trichloride solution was saturated with 2.5 gm. Sodium floride powder in 30 ml Ethanol, heated to 70°C whilst stiring continuously. Sodium chloride crystals 1.6 gm was dissolved in 30 ml Acetic acid whilst string continuously at 70°C. It was subsequently found that it is best to dissolve the Sodium floride in 5 ml of distilled water, and the Sodium chloride in 5 ml distilled water separately at 70°C, and then to add these two solutions to the Alkyl Tin trichloride solution. This would ensure complete dissolution of NaF and NaCl before mixing with the Alkyl Tin trichloride solution. Then this solution was subjected spray pyrolysis (using a plastic spray gun) onto cleaned glass sheets heated in an electric oven at 580°C for 10 min. Thereafter the oven was switched off and the glass sheets allowed to cool down to room temperature the following day.

The best sheet resistance measured by a Multimeter registered 8-10 Ohms. cm^{-2}. These treated transparent glass slides, eventhough they do not possess a very uniform surface resistance due to the simple normal spray pyrolyis process of their preparation in the laboratory, have been found to be generally suitable for the assembly of practical DSSC's to demonstrate their concept of operation for use in the field. Also please refer to Chapter 4.8 and Table 4.10 on Preparation of FTO Conducting Glasses in this regard.

3.6 Enhancement of Conversion Efficiency of DSSC's by altering the pH of Electrolyte

The following equipment available at the Sri Lanka Institute of Nanotechnplogy at Biyagama, Sri Lanka was used for the above – mentioned task.

- SHIMADZU – UV 3600 – Vis – NIR Spectrophotometer.
- INROB 70 pH Meter.
- VIRAJ Current- Voltage Curve Tracing Computerized Setup coupled to a KEITHLEY 2000 Electronic Multimeter with a Potentiostat via a computer controlled software.

3.7 Enhancement of PV parameters of DSSC's including Conversion Efficiency by Co-Sensitization

The following equipment available at the Institute of Fundamental Studies, Hantana, Sri Lanka were used for above –mentioned activities :

- VIRAJ Current – Voltage Curve Tracing Computerized Setup coupled to a KEITHLEY 20000 Electronic Multimeter with a Potentiostat via computer controlled software.
- 500 Watt Xenon Lamp with AM 1.5 Filter calibrated with EKO Pyronometer and silicon Photodiode to obtain simulated sunlight at 100 mW .cm^{-2} intensity in the laboratory .
- UV 245 SHIMADZUUV –vis Specrophotometer .

The analyzed results obtained from DSSC's is depicted at Chapter 4.2.4 on " Effects of Co – Sensitization on Absorbance Spectra and I – V characteristics of DSSC's at page 134 and page 136 to 138.

3.8 Electrochemical Impedance Spectroscopy (EIS) of DSSC'S

It is an experimental method of characterizing electrochemical systems. This technique measures the impedance of a system over a range of frequencies, and therefore the frequency response of the system, including the energy storage and dissipation properties is revealed. Often data obtained by EIS is expressed graphically in a Bode plot or a Nyquist plot.

EIS also measures the dielectric properties of a medium as a fraction of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity.

Impedance is the opposition to the flow of alternating current (AC) in a complex system. A passive complex system comprises both energy dissipater (resistor) and energy storage (capacitor) elements. If the system is purely resistive, then the opposition to AC or direct current (DC) is simply resistance.

Almost in any physico- chemical system such as electrochemical cells possessing energy storage and dissipation properties and EIS examines them. Often EIS reveals information about the reaction mechanism of an electrochemical process: different reactions steps will dominate at certain frequencies, and the frequency response shown by EIS can help identify the rate limiting step.

For a redox reaction R O + e relationship between the current density and the electrode over potential is given by the Butler-Volmer equation;

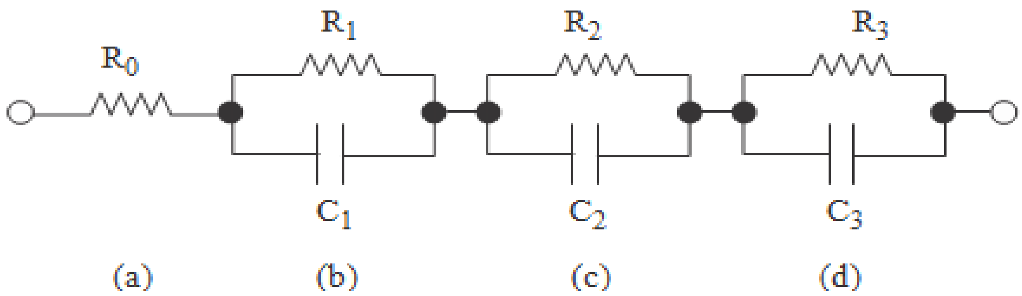
$J_t = j_0 [\exp(\alpha_0 f\eta -- \exp(-\alpha_r f\eta)]$

where,

$\eta = E -- E_{eq}$, $f = F/(RT)$

$\alpha_0 + \alpha_r = 1$.j_0 is the exchange current density and α_0 and α_r are the Symmetry Factors.

Nyquist Plot of a DSSC and it's equivalent circuit



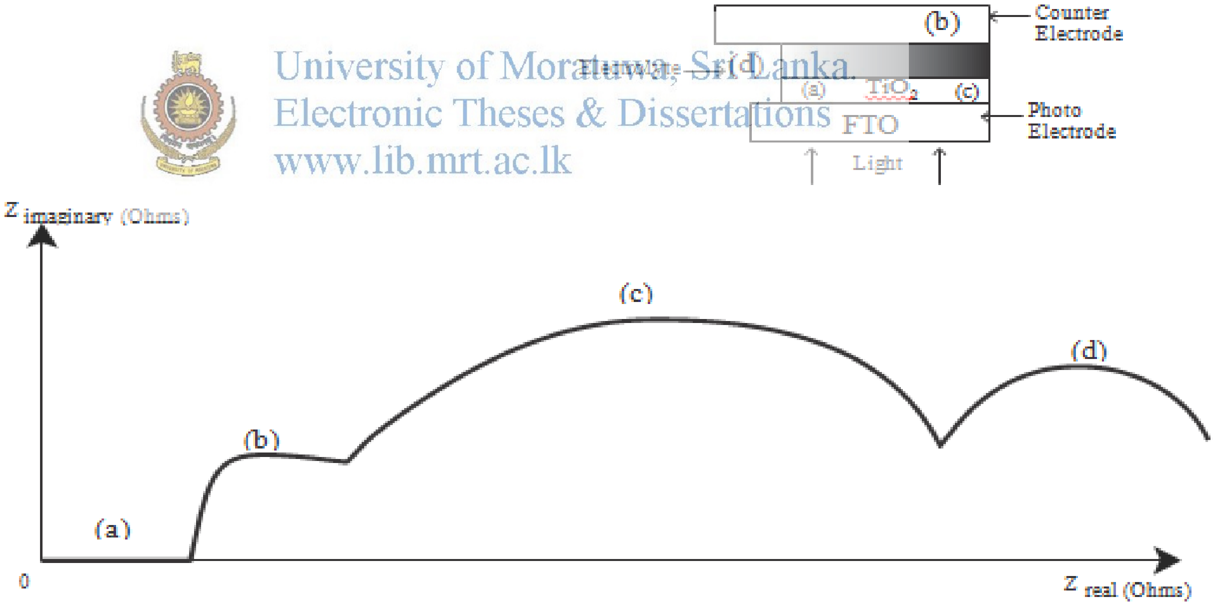


Figure 3.3 Nyquist plot of a DSSC

Each curve in the Nyquist plot expresses :

- Contact resistance between FTO and TiO_2 semiconductor film.
- Redox reaction at the Exfoliated Graphene oxide counter electrode.
- Electron transfer in TiO_2 film and electrolyte interface (including electron transfer in TiO_2 electrode and electron injection from the dye).
- Charge diffusion within the electrolyte.

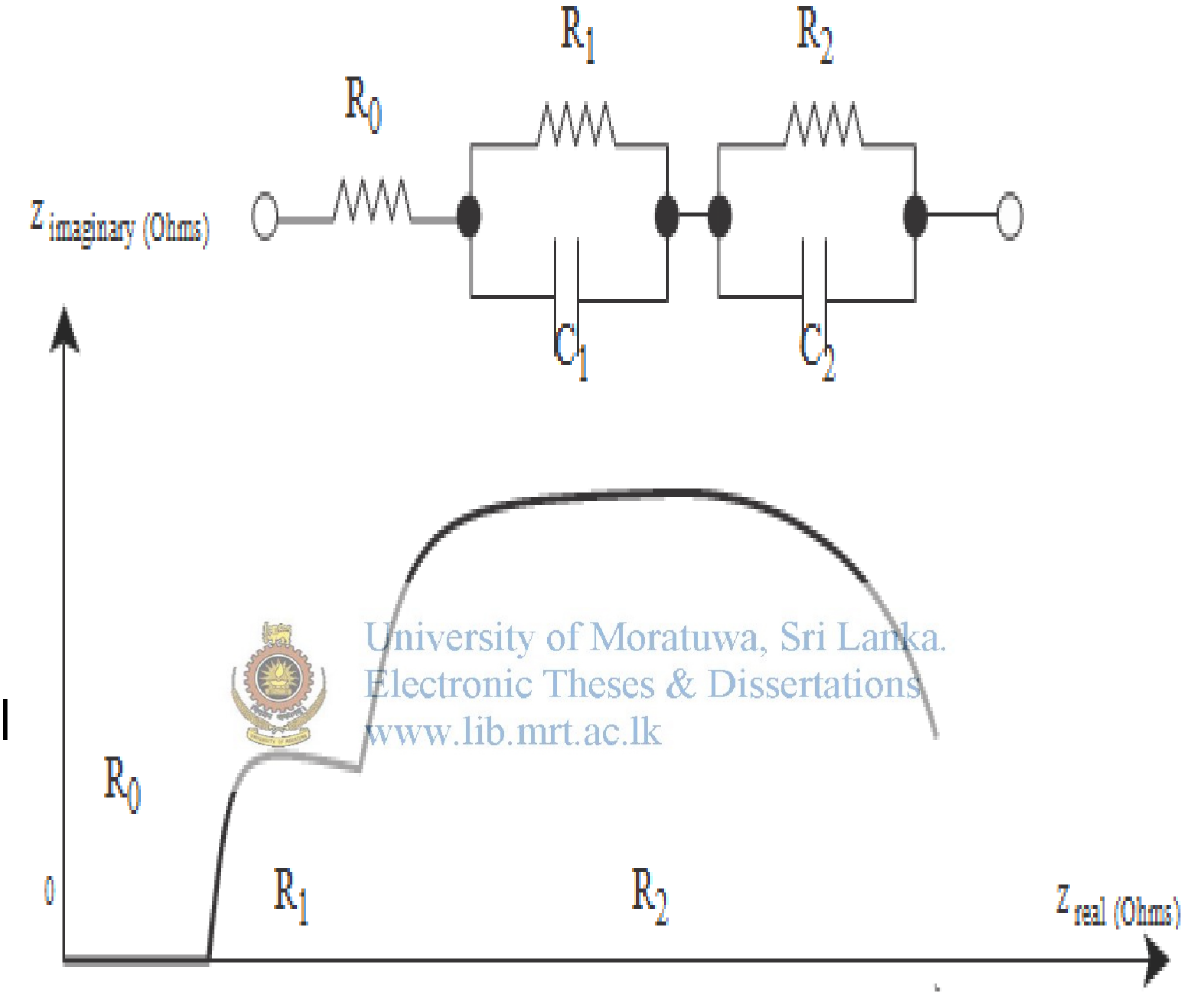


Figure 3.4 Nyquist plot of a DSSC

With this type of curves, the comparison of the contact resistance and resistances of the active layer of the different cells could be done.

Estimation life time of a electron in a DSSC

Time constant and RC in a circuit is :

$$\mathbf{T = RC = 1/\ 2\pi fC}$$

Therefore lifetime of germinated electron in TiO_2 semiconductor **$T = 1/\ 2\pi f C$.**

According to the above expression, when f C is large, lifetime is short and vice versa. Lifetime of electron in different DSSC’s can be compared using f vs θ curves.

3.8.1 CyclicVoltammetry, Bode Plots, Nyquist Plots & Mott Shottkey Plots

Cyclic Voltammetry or CV is a type of potentio- dynamic chemical measurement. It is a technique used to study electro-chemical processes of a species that can undergo oxidation and reduction reactions by the transfer of electrons. In such reactions, potential or voltage is applied as a driving force, while current is the electron flow resulting from the reaction. This process is measured using a potentionstat and an electrochemical cell (DSSC) containing three electrides: working, reference and counter. The potentionsatat is an electrical instrument that monitors and controls the difference in potential between the working and reference electrodes,as well as measures the current flow between the working and counter electrodes. Overall the electrochemical reaction takes place. The potential at this working electrode is varied over time with to a reference electrode of constant potential. In addition, the working electrode measures current response relating to a counter electrode that introduces current into the sysem. These electrodes are immersed in a solution containing a supporting electrode composed of non- reactive ionic species that provides excess electrons. When potential is applied to the electrodes, a fixed range is scanned in a forward and reverse manner at a constant rate. In CV a cyclic voltammogram is obtained by plotting the measured current against potential at a given range.

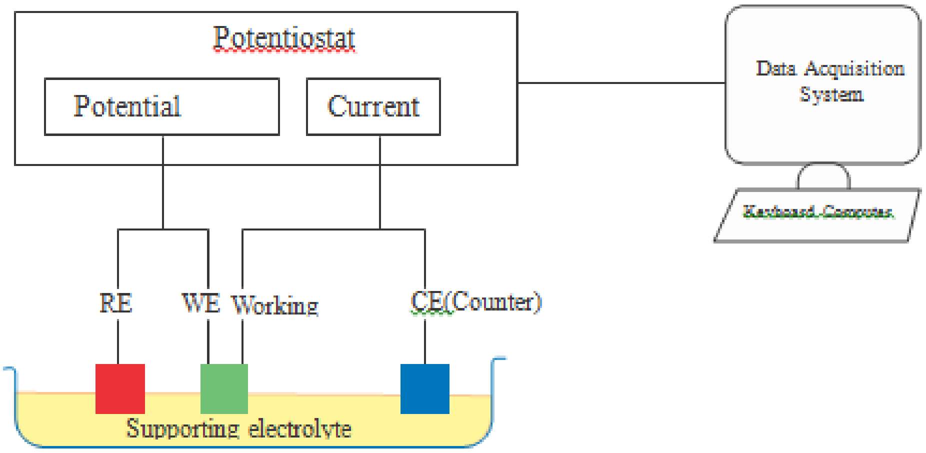


Figure 3.5 Representation of (a) Potential vs.Time plot and

(b) Current vs.Potential plot of Cyclic Voltammetry set up.

CV is identified as an effective tool to evaluate the HOMO-LUMO energy levels of semiconductor materials. Oxidation potential E_{ox} and reduction potential E_{red} can be correlated with HOMO and LUMO energy levels, respectively by the following empirical formula. Also the use of CV provides information on electron transfer properties such as redox potential of a species ,and it is calculated by an average of the anodic (EPa) and cathodic (Epa) Peak potentials. The bandgap (E_g) of a species can also be determined from these equations:

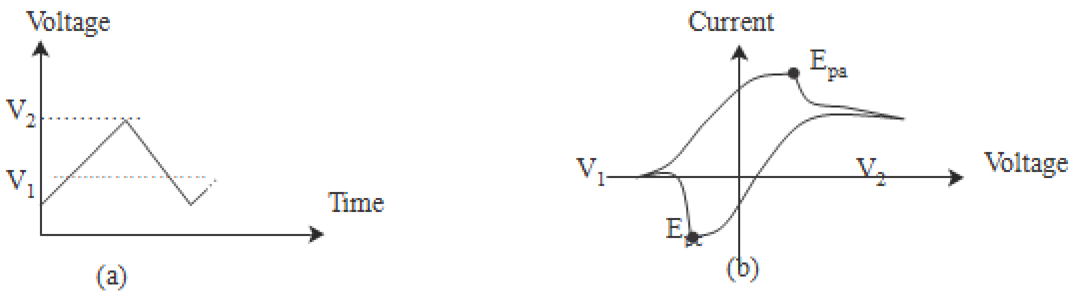


Fig. 3.6 Representation of (a) Potential vs.Time plot and (b) Current vs. Potential plot.

The use of CV provides information on electron transfer properties such as redox potential and band gap. In this regard, the redox potential of a species is calculated by an average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials.

Method of Calculation of HOMO, LUMO and Band GapEnergy Levels in a DSSC

$E_{(HOMO)} = e.\, E_{ox}$ (vs vacuum)

$E_{(LUMO)} = E_{(HOMO)} + h/\lambda$

$E_{(HOMO)} = -e\,(E_{OX} + 4.40).e\,V$--------------------(1)

$E_{(LUMO)} = -e\,(E_{red} + 4.40).\,e\,V$-------------------(2)

$E_g = 1243/\lambda_{onset}$ ---(3)

where,

f= Frequency (Hz)

E= Energy in eV

C= Speed of Light ($3x10^{8}\ ms^{-1}$)

h = Planks Constant ($6.625x10^{-36}\ Js^{-1}$)

e = Electron Charge($1.602x10^{-19}$Coulombs)

λ_{onset} = Onset wavelength of dye

$E_{LUMO} = E_{HOMO} + E_g$, $E = hv$, $c = f\lambda$, $E = hc/\lambda_{onset}\ .\ e$

3.8.2 Enhancement of PV parameters of DSSC's including Conversion Efficiency by examining the Impedance Characteristics of DSSC's

The following equipment available at the Solid State Chemistry Laboratory and Condensed Matter Physics Laboratory at the Institute of Fundamental Studies , Hantana, Sri Lanka , and at the Physics Spectrophometric Laboratory of the University of Kelaniya, Kelaniya, Sri Lanka were used for above – mentioned tasks .

- METROHM AUTOLAB Model AUT 85343 FRA Impedance Potentiostat Analyser (at the IFS).
- POTENTIOSTAT / GALVANOSTAT /ZRA GAMRY instruments Impedance Analyser Series G 300 incorporating Hewlett Packard Personal Computer HP PRO (at University of Kelaniya).

When using both types of equipment listed above , the photoanode of the DSSC under test was connected to the (+) ve input terminal , and the counter electrode to the (-) ve input terminal of the relevant equipment .

3.8.3 Investigating the Catalytic Activity of Exfoliated Graphene oxide coating on Counter Electrode using CV

To distinguish between specific catalytic activity and surface area effects, a cyclic voltagram was obtained at a rate of 50 m V for Ag /Ag (for ferrocene) for oxidation and reduction of I/I and I/I redox couples using normal FTO counter electrode or Exfoliated Graphene oxide coated counter electrode of a DSSC. Two pairs of oxidative and reductive peaks were observed for both materials. Although the exact charge transfer mechanisms are not fully understood. it is belived that A_{ox} and A_{red} are due to the oxidation and reduction of I/I . since the counter electrode of a DSSC is responsible for catalyzing the reduction of I/I. The characterisitics of the peak B_{ox} and B_{red} are the focus of this analysis. This with CV was to rely mostly on Epp between B_{red} and B_{ox} to gague catalytic activity of the modified electrode.

The CV obtained at a scan rate of 50 m Vs^{-1} for FTO glass electrode coated with Exfoliated Graphene oxide with TiO_2 photoelectrode sensitized with Mangoostein dye, with the respective redox electrode oxidation and reduction peak voltage values is shown at Fig 4.46.

3.9 Construction of an Electrically operated Natural Dye Extraction Unit

his unit was designed and developed in the Industrial Chemistry Laboratory of the University of Moratuwa . It consist of a 2 litre cylindrical stainless steel dye extraction can where fresh clean plant material is placed . Steam generated from distilled water contained in another stainless steel 2.5 litre cylindrical enclosed can fitted with a1.5 KW 230 V AC / 50 Hz operated Electric Immersion Heater is passed through perforated Copper tubing to burst the cells of the plant material and to release its natural dyes . the extracted dye solution along withy the plant material residue in the water could be taken out from the bottom tap of the vextractionunit and put into the top of the extraction unit again , and continue to pass steam through the coil several times to increase the concentration of the extract .

Please see the photograph at Appendix O.

3.10 Needed Achievements

Achievements

1. **Perfecting extraction (between multiple methods), concentration and perhaps shelf life**

The extracts of photosynthetic plant segments of fruits, flowers, leaves, roots, stems and bark were used on photo sensitizers for Dye-sensitized Solar Cells (DSSC's). Mangoostein fruit rind extract in Ethanol / Chloroform performed the best photosensitized effect, which was due to the better interaction between the carbonyl and hydroxyl groups of Rutin molecules in the extract and the surface of the TiO_2 film of the counter electrode. Also a prominent blue shift phenomenon was observed in the Absorption Spectrum of DSSC's sensitized with this natural dye.

a . 1st Method of Extraction of Plant Pigments

Petals of flowers and bark of trees chosen were cut into small pieces and extracted into Ethanol (Fluka, 96% V/V), by keeping overnight at room temperature. Then residual parts were removed by filtration and the filtrate was washed with Hexane several times to remove any oil or chlorophyll present. The Ethanol fraction was separated and divided into two solutions and one fraction was used as it was (without any further treatments, and the other fraction was treated with a few drops of conc. HCl acid so that the solution colour becomes dark (pH<1). These solutions were directly used as the dye solutions for the preparation of photovoltaic devices.

b. 2nd Method of Extraction of Plant Pigments

All dyes except for Rose, Lily, Coffee and leaves of Chinese Holly for which water was used as the extracting solvent. Dyes from Begonia flower, Rhododendron flower, Orange fruit rind, Mangoostein fruit rind, Ekkiriya wood, Fire fern leaf, Karawala kabilla fruit, Turmeric root, Black and Red Grapes, Red plum, Spinach leaf, Rambutan fruit skin, Red Chilies, Tomato, Blue and Gray Lichen etc were extracted with Ethanol.

The plant segments were washed with water and vacuum dried at 60°C. After crushing into a fine powder using a mortar, there materials were immersed in absolute Ethanol at room temperature in the dark for one week. Then the solids were filtered out and the filtrates were concentrated at 40°C for use as sensitizers. The dye obtained from Rose, Lily, Coffee and leaves of Chinese Holly plant were extracted by immersing these materials in boiling water for 2-3 hours and the solids were filtered out. The resulting filtrates were used as sensitizers.

c. 3rd Method of Extraction of Plant Pigments

Extracts of fresh Opuntia fruits, Red Turnip, Beetroot and Bougainvillea flowers were obtained by crushing and squeezing the fresh materials, and the prepared juices were filtered to remove solid fragments and stabilized at pH = 1.0 by addition of aqueous HCl or alternatively by adding Ascorbic acid until a final pH of 2.0 was reached. The Red Turnip root, Beetroot and Bougainvilla flower extracts were obtained by immersing then overnight in 0.1 M HCl solution respectively, and the resulting extracts were centrifuged to remove any solid residues, and used as such. If properly stored, protected from direct sunlight and refrigerated at about 4°C, the acidic natural dye solutions (pH≈5.0) were usually stable with a deactivation half-life time of more than 12 months (shelf life).

d. 4th Method of Extraction of Plant Pigment

Ekkiriya wood, Egg Plant fruit skin, Karawala Kabilla fruit etc which contain phenolic compounds and tanins which play a role in protection from predators / herbivores were cut into small pieces, washed in water, covered in Ethanol and heated to 50°C for 10 minutes whilst continuous stirring, and kept in the dark overnight at room temperature. The filtered extracts after centrifuging could be used as dark reddish to deep purple-brown coloured good sensitizers for DSSC's.

e. 5th method of Extraction of Plant Pigments

Purple Begonia flower petals and Indigo Indigofera leaves from fresh plants could be separately fermented for 24 hours in water. Thereafter Chloroform and Ethanol (1:1 by volume) mixture added at room temperature. The blue and red pigments dissolve in

Chloroform, whereas only red pigment dissolves in Ethanol. The addition of twice in volume of $Ca(OH)_2$ solution ($pH \approx 11$), and blowing of air for 15 minutes causes the precipitation of Indigo dye. The precipitated Indigo then washed twice with $Ca(OH)_2$ solution and centrifuged for 10 minutes.

f. 6th Method of Extraction of Plant Pigments

The natural colorant containing Anthrocyanins in Fire Fern leaf, Karawala Kabilla fruit, Green grapes, Rambutan fruit etc were extracted from clean fresh fruits by crushing 100g of each separately and immersing in 80 mL Ethanol solutions respectively, and kept in dark at room temperature overnight. The residues are removed by filtration and the pH of the dyes adjusted to $\underline{\Omega}<1$ by adding HCl acid or Tartaric acid.

g. 7th Method of Extraction of Plant Pigments

Reddish brown Betalain natural dye present in Beetroot tuber could be extracted with 1g of crushed vegetal matter and 10 ml of Ethanol solvent. The pH of the mixture was adjusted in the range 1.0-4.0 by adding HCl. The mixture kept in the dark for 24 hours and then filtered. The stability of the extracted dye could be improved by adding a trace amount of Citric acid or Ascorbic acid to get within a pH range of 2.0 - 4.0, and should be protected from direct sunlight exposure.

h. 8th Method of Extraction of Plant Pigments

Fresh Rosella or Blue Pea flowers of 1gm was extracted in 100 mL of two different solvents at different temperatures for 30 min. Solid residues were filtered out to obtain dye solutions. A mixed dye was prepared by mixing Rosella solution to Blue pea solution at a ratio of 1:1 by volume. The effect of extracting temperatures was studied at $25^{o}C$, $50^{o}C$, $70^{o}C$ and $100^{o}C$ using Ethanol and water separately as extracting solvents. The effect of extracting solvent was studied by a comparison of dyes extracted in Water and Ethanol. The effect of pH of the dye solutions was studied by adjusting pH from the original pH of 3.2 by using 0.1 M HCl acid solution to form different pH's (0.5, 1.0, 2.0, 3.0).

The Rosella extract was found to have higher photosensitizing performance as compared to Blue pea extract. This is due to better charge transfer between the Rosella dye molecules and the TiO_2 surface which is related to a dye structure. It was also found that the Conversion Efficiency and the stability of these DSSC's could be enhanced by adjusting the extracting temperatures and pH, of the dye extracts. The optimum Anthrocyanin extracting temperature and pH of Rosella and Blue pea extracts, were found at $50^{o}C$, $70^{o}C$ and pH = 2 and 1 respectively.

1. Extending operational Lifespan of DSSC's

DSSC's hold a promising future, but are not currently very suitable for commercial use due to a relatively short lifespan of about 2 years. Three main factors, that affect the lifespan of DSSC's are bacterial growth on the dye pigment, evaporation of the liquid electrolyte and rapid decrease in efficiency due to photo bleaching . Bacterial growth on the dye pigment could be inhibited by adding Benzoic acid as a preservative. The evaporation of the iodine electrolyte could be minimized or prevented by using several effective sealing agents like Silicone resin glue, melted Surlyn foil, Sodium silicate (water gloss), Epoxy glue etc, to prevent the evaporation of the electrolyte. The efficiency of DSSC's could be enhanced by minimizing the internal cell losses encountered in generating the open circuit voltage by recombination and by using very low surface resistance (< 8 Ohm.cm^{-2}) counter electrode and photo anodes. Also the efficiency could be further improved by using Exfoliated Graphene electrodes on glass sheets having a resistance surface of as low as about 6 Ohms. cm^{-2}.

2. Acceptable aesthetics in the cell

When DSSC type photovoltaic modules are integrated into buildings, other design considerations such as aesthetics compete with maximizing energy production, building integrated photovoltaics (BIPV) systems often produce a greater proportion of energy at low irradiance levels than conventional PV systems due to architectural considerations in the design of BIPV arrays. Important points are not only the efficiency of the solar cell panel itself, but also the effective applications under different conditions of buildings to reduce heating and cooling load.

The PV conversion efficiency of a DSSC has no dramatic changes according to the incident angle from 60° to 90°, the efficiency does not change much. Furthermore, DSSC cells have a very good temperature coefficient which is about 0.1% at 30°C to 50°C. The performance of a DSSC depends on irradiance and temperature of input means the DSSC's response to environmental factors based on BIPV application situations.

3. Cell ceiling concept

The maximum power conversion efficiency obtained with a test DSSC sensitized with Mangoostein fruit rind extract with Exfoliated Grapheme nanoplated (+) ve counter electrode having a minimum surface resistance of 6 Ohms.cm^{-2} was **1.317 %** (PhD Thesis pages 125 to 130 paragraph 4.10). In the case of a test DSSC prepared with standard imported FTO coated conducting glass counter electrode, the maximum power conversion efficiency obtained with purified Mangoostein fruit rind extract - C at Chapter 4 , Table of Results of this Thesis was **1.053%**.

4. The recyclable cell concept

Recyclability is important to reduce the cradle to grave environmental burden. The initial burden of solar cell production can partly be distributed over the original and the recycled products, and this tends to lower the environmental burden of the original product. Monocrystalline Silicon solar cells can be recycled into high quality secondary products at a relatively low cost. Silicon from discarded microcrystalline Silicon solar cells can be used as a resource for the production of new solar cells, and this has a substantial environmental benefit.

Recycling of nanoparticulate solar cells (DSSC's) has not drawn a major research effort so far. However experience with post-consumption recycling of waste from electrical equipment has shown that, when substantial amounts are present, the metals in nanoparticulate cells can in all probability be recycled into products with high quality applications. But beyond metals, recyclability seems low. In part, the design of nanoparticualte solar cells uses the interpretation of substances (FTO glass, Pt, TiO_2, dye extracts etc) and this is not conducive to recycling.

In case of Organic solar cells, recycling of corporate polymeric materials which are a major constituent may be important with relatively long service life has turned out to be a problem. Only low quality applications would still be possible. Thus it would seem likely to occur during a long service life, only low quality applications would still be possible. Thus it would seem likely that, given present cell design unlike in the case of me Si cells, only a very limited part of the nanoparticulate solar cells can be recycled into high quality applications (at acceptable cost). This negatively affects their environmental performance, if compared with mc Si cells.

However with some system planning it should be possibleto mke use of DSSCs as recyclable cells. This will be quite important with Building Integrated Photovoltaics (BIPV) Systems . Then trere is certain compensation of lower efficiency with high utility in low power applications .

5. Multiple trials with differently nanostructured TiO_2

Titania (TiO_2) may be nanostructure by a variety of techniques and from a range of sources. For example, colloidal TiO_2 may be formed from reactive precursors such as Titanium alkoxcides or chlorides, which readily hydrolyze with water to form Titanic by respective elimination of alcohol or HCl and gas. Due to an increased surface area , porocity and number of defects, the chemical reactivity and physical characteristics of nanostructure TiO_2 often vary significantly in comparison with bulk TiO_2. For instance, while the refractive index of bulk Antase is 2.5, the estimated indices for a film of amorphous colloidal TiO_2 and for inverse opaline TiO_2 are 1.5 and 2.3 respectively. It has been shown that in comparison to the bulk material, nanoparticulate TiO_2 displays a higher photo catalytic activity and is more sensitive to environmental factors. The ideal would be to produce TiO_2 with a high degree of order within the nanostructure material. This is as for TiO_2 the largest theoretical electron diffusion coefficient is for materials with the greatest degree of ordering between nanocrystals.

Due to its electrochemical properties, nanostructure TiO_2 holds potential application in DSSC's. DSSC's have low efficiencies of about 11% maximum using synthetic dyes and about 1% using natural dyes. However, researchers are using TiO_2 nanotubes, instead of nanoparticles, to improve these efficiencies, due to the TiO_2 nanotubes efficiency improvement of the electron transport from the PV cell to the negative electrode.

The majority of catalytic and photocatalytic applications of nano TiO_2 for use in DSSC's are under research and development or are only emerging uses. Information on the manufacture of nano TiO_2 to produce catalysts or photocatalysts has not been identified although DuPont Corporation in U.S.A notes that most photocatalytic applications of TiO_2 use untreated Antaphase phases.

Nano TiO_2 could also be used as a UV stabilizer or blocker (and to permit the passage of other parts of the visible light spectrum including IR) in DSSC's to reduce the heat absorption causing damage due to high temperatures to these cells when exposed to direct sunlight. These UV stabilizers use less than three weight percent of polymers such as Polyethylene Polycarbonate etc.

6. Beating the Chinese record and having a Super Dye (with Natural Dyes)

According to the research article titled "Dye sensitized solar cells using 20 natural dyes as sensitizers" published online on 23 Feb 2011 by Huizhi Zhou et al of the State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, China in the Elsevier Journal of Photochemistry and Photobiology A. Chemistry, the highest maximum power conversion efficiency of **1.17%**(after purification with Chloroform) for DSSC's sensitized with Mangoostein fruit rind Natural Dye extract in Ethanol has been achieved, out of dyes from all trees and plants grown in Asia. This record was beaten by the Author at the University of Moratuwa / Institute of Fundamental Studies , Hantana, Sri Lanka with a maximum power conversion efficiency of **1.317 %** using Mangoostem fruit rind extract in Ethanol in a DSSC having a (+) ve counter electrode of Exfoliated Graphene nanoplate with a surface resistance of 6 $Ohm.cm^{-2}$.It is believed that Mangoostein fruit rind extract Natural Dye in Ethanol/ Chloroform after detailed purification with Chloroform for use in a DSSC's is a **Super Dye** . It's power conversion efficiency could be possibly enhanced up to 5% - 6 % with further research, as personally advised recently by Professor Keerthi Tennakone , the former Principal Researcher and Director of the Institute of

Fundamental Studies (IFS) , Hantana, Sri Lanka , who is presently researching on DSSC's at the University of Cincinati ,U.S.A .

7. Boat- deployment of DSSC's and demonstration

Please refer to Chapter 4.4.10 of this Thesis.

8. Simple charging device

Please refer to Chapter 4.4.11 of this Thesis.

9. Window - Building integrated DSSC

Please refer to Chapter 4.4.13 of this Thesis .

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1 Characterization of Natural Dyes

Figure 4 indicates the Current - Voltage characteristics of test DSSC's of 9 natural dyes of plants grown in Sri Lanka initially tested at the IFS. The Absorbance vs. Wavelength spectra of these 9 natural dyes, and their Current –Voltage curves are shown at Figure 4.2 and Figure 4.3 respectively. Thereafter test DSSC's of 50 natural dyes of plants grown in Sri Lanka were analysed at the IFS and their summary of their photoelectrochemical parameters is shown at Table 4.2. The Current-Voltage curves of these test DSSC's sensitized with these 50 natural dyes is depicted at Figure 4.4.

Table 4.1 Current – Voltage characteristics of 9 natural dyes tested and analysed at the IFS.

Initial Summary of Results

Ser. No.	**Dye**	**Voc (mv)**	**Isc(mA)**	**Id (mA/cm^2)**	**Fill Factor (%)**	**Efficiency (%)**	**Solvent**
01	Mangoostein (a)	556	0.108	0.432	64	0.153	Ethanol
02	Rabutan (b)	504	0.078	0.312	46	0.072	Ethanol
03	Mango (c)	567	0.052	0.210	43	0.050	Ethanol
04	Tomato (d)	577	0.048	0.194	44	0.052	Ethanol
05	Carrot (e)	641	0.038	0.154	35	0.035	Ethanol
06	King coconut (f)	256	0.037	0.150	30	0.011	Ethanol
07	Pumpkin (g)	622	0.018	0.076	36	0.017	Ethanol
08	Red Banana (h)	473	0.008	0.034	52	0.008	Ethanol
09	Beetroot (i)	256	0.004	0.018	37	0.002	Ethanol

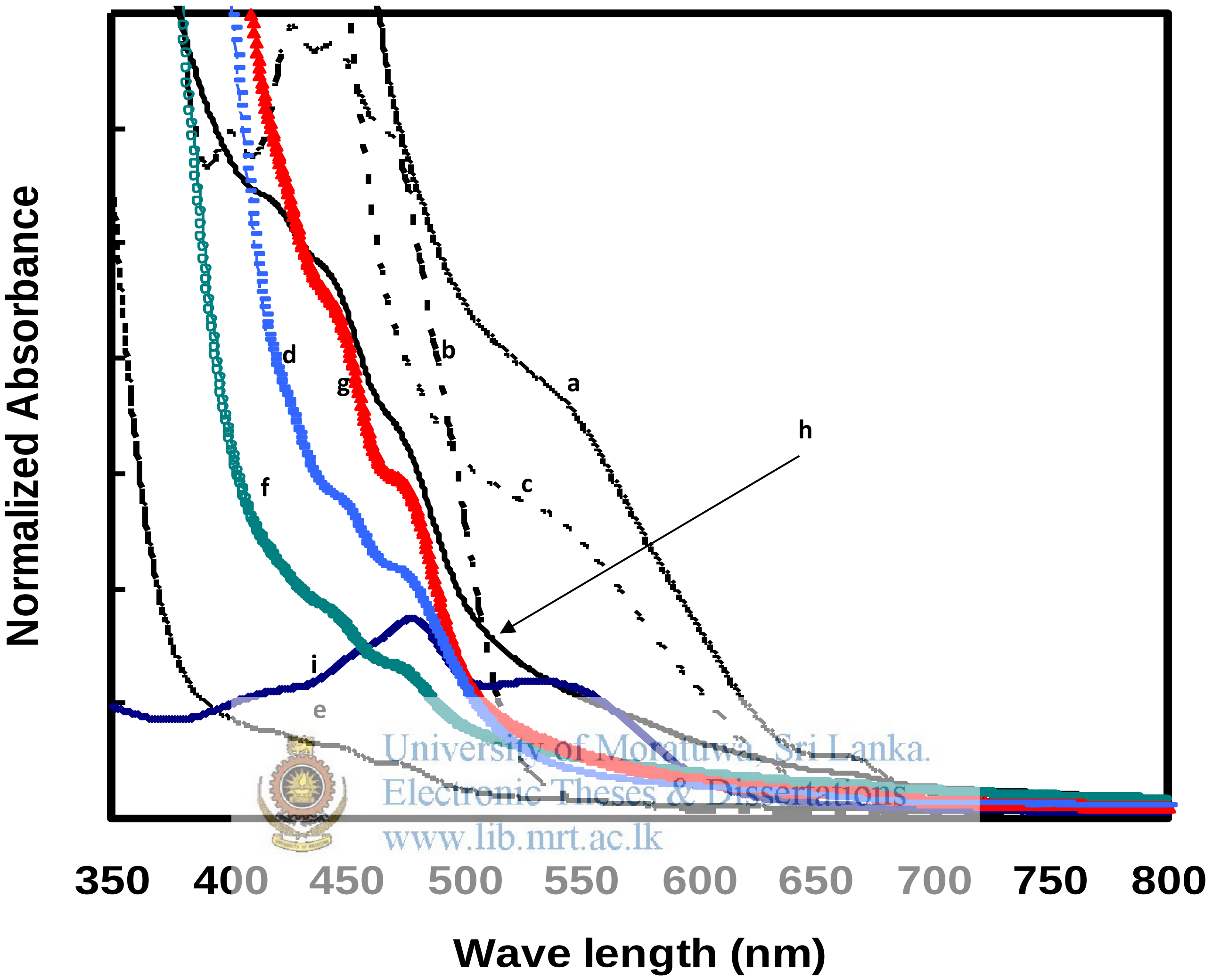


Figure 4.1 UV-vis Absorption Spectra of dye solutions extracted from (a) Mangoostein (b) Rabutan (c) Mango (d) Tomato (e) King Cocount (g) Pumpking (h) Red Bannana (i) Beetroot.

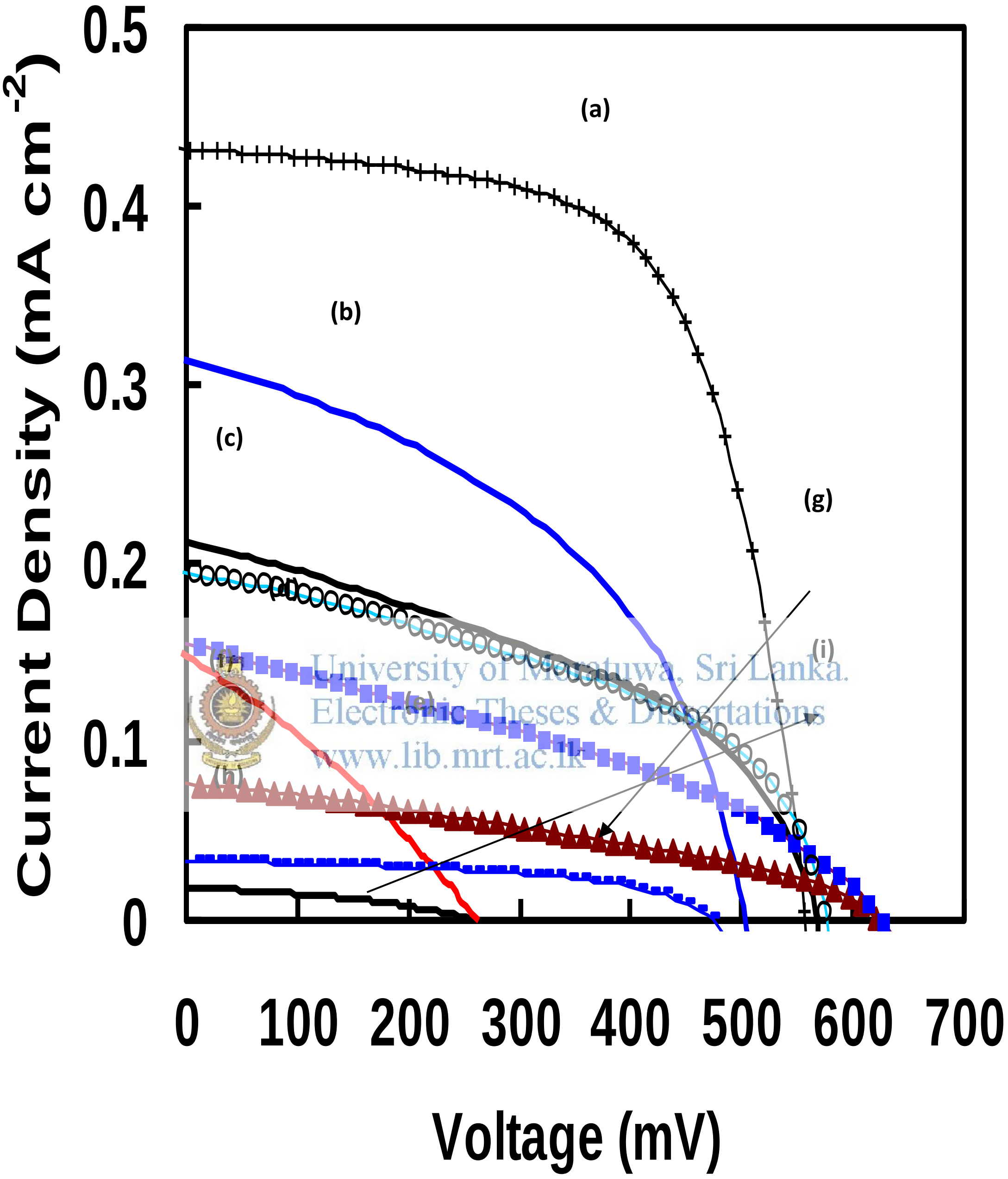


Figure 4.2 Current – Voltage characteristics of DSSCs sensitized with (a) Mangoostein (b) Rambutan (c) Mango (d) Tomato (e) Carrot (f) King Coconut (g) Pumpkin (h) Red Bannana (i) Beetroot

Table 4.2 Summary of Photo Electro Chemical Parameters of DSSC's using natural dyes (with Decreasing Efficiency Values)

Ser. No.	Dye	VOC (mv)	ISC (mA)	ID (mA/cm^2)	Fill Factor (%)	Efficiency (%)	Solvent
01	Turmeric	599.1	0.135	0.540	69.03	0.223	Ethanol
02	Mangoostien	565.2	0.111	0.444	65.66	0.165	Ethanol
03	Mangoostien-skin	635	0.087	0.348	69.41	0.153	Ethanol
04	Mangoostien	563.6	0.206	0.412	63.63	0.148	Ethanol
05	Mangoostien-skin	567.5	0.094	0.376	57.38	0.142	Ethanol
06	Mangoostien-skin	593.4	0.081	0.324	68.6	0.131	Ethanol
07	Mangoostien-pulp	631	0.065	0.260	67.73	0.111	Ethanol
08	Venivel	529.9	0.079	0.316	57.59	0.097	Ethanol
09	Orange	627.5	0.05	0.200	73.1	0.091	Ethanol
10	Mangoostien + Orange + Grapes	600.8	0.042	0.168	71.91	0.073	Ethanol
11	Rambutan	504.1	0.156	0.312	45.53	0.072	Ethanol
12	Mangoostien + Orange + Grapes	594.7	0.045	0.180	59.35	0.063	acetonitrile with tert
13	Orange	624.9	0.039	0.156	64.6	0.063	acetonitrile with tert
14	Grapes	498	0.049	0.196	60.28	0.058	acetonitrile with tert
15	Rambutan	493.9	0.047	0.188	61.67	0.057	Ethanol
16	Orange	558.3	0.034	0.228	73.86	0.057	Ethanol
17	Rathadun	427.2	0.069	0.276	74.39	0.056	Ethanol
18	Venivalgata	538.4	0.039	0.156	67.37	0.056	Ethanol
19	Orange	619.4	0.039	0.156	55.25	0.053	acetonitrile with tert
20	Mango	584.4	0.093	0.186	46.92	0.051	Ethanol
21	Mangoostien-skin	665.5	0.034	0.136	57.03	0.051	acetonitrile with tert
22	Grapes	557.8	0.035	0.140	62.86	0.049	Ethanol
23	Spinach	546.5	0.032	0.128	66.43	0.047	Ethanol
24	Bulu	493.7	0.041	0.164	74.44	0.038	Ethanol
25	Mangoostien + Orange + Grapes	608.9	0.026	0.104	56.82	0.036	acetonitrile with tert
26	Carrot	641.2	0.077	0.154	35.4	0.035	Ethanol

27	Grapes	538.2	0.024	0.096	61.32	0.032	acetonitrile with tert
28	Grapes	566.8	0.015	0.060	72.22	0.025	Ethanol
29	Rathadun	415	0.026	0.104	48.58	0.021	Ethanol
30	Beli Flower	490.2	0.019	0.076	49.72	0.018	Ethanol
31	Nelum Seed	497.1	0.022	0.088	39.04	0.017	Ethanol
32	Pumpkin	622.2	0.038	0.076	36.28	0.017	Ethanol
33	Kothala Himbutu	450.1	0.022	0.088	38.87	0.016	Ethanol
34	Tomato	507.5	0.016	0.032	79.69	0.013	Ethanol
35	Aralu	468.9	0.026	0.104	26.83	0.013	Ethanol
36	Purple Makaral	380.7	0.025	0.100	34.13	0.013	Ethanol
37	Walmadata	520.7	0.084	0.336	68.54	0.012	Ethanol
38	Ginger	489.5	0.013	0.052	40.72	0.011	Ethanol
39	King Coconut Nut Husk	256.7	0.073	0.146	30.48	0.011	Ethanol
40	Banana	599.2	0.021	0.084	78.77	0.004	Ethanol
41	Red Banana	476	0.016	0.016	48.62	0.004	Ethanol
42	Beetroot	252.7	0.009	0.018	37.54	0.002	Ethanol
43	F.Berry	383.3	0.006	0.024	26.3	0.002	Ethanol
44	B.Onion	331.8	0.002	0.008	32.87	0.001	Ethanol
45	Beli	194.3	0.003	0.012	23.01	0.001	Ethanol
46	Purple Maakaral	165.1	0.003	0.012	35.56	0.001	Ethanol
47	Adesia Fruit	182.1	0.002	0.008	29.2	0.001	Ethanol
48	Rata Lovi	164.4	0.001	0.004	36.1	0.001	Ethanol
49	Wadukuda Fruit	178.2	0.003	0.012	34.9	0.001	Ethanol
50	Goraka	323.3	0.002	0.008	27.91	0.001	Ethanol

Table 4.3 **Current Voltage Characteristics of DSSC'S Using Natural Dyes measured with KEITHLY 2000 Electronic Multimeter (In decreasing voltage values)**

Ser.No.	Dye	Voc (mV)	Isc (mA)
51	Rathadun Wood	985	0.012
52	Ginisapu Wood	871	0.0025
53	Red Chillie Fruit	637	0.0026
54	Crab Claws flower	621	0.008
55	Purple Cabbage bud	618	0.0286
56	Jack Wood	607	0.097
57	Rata Kaha	598	0.0239
58	Purple leaf	588	0.044
59	Purple makaral	580	0.009
60	Mangoostein Fruit rind (With Pt electrode)	570	2.7
61	Wada mal	557	0.116
62	Burula fruit	542	0.086
63	Mulberry Fruit	541	0.077
64	Kekumpothu wood	533	0.027
65	Purple yarn	525	0.0186
66	Thuran Wood	523	0.0207
67	Mahagony wood	517	0.0198
68	Gandis wood	509	0.0238
69	Burulu nut	490	0.0155
70	Red Plumaria flower	489	0.0248
71	Wadukuada fruit	488	0.0176
72	Buul lovi fruit	486	0.022
73	Purple begonia flower	451	0.033
74	Mangoostein fruit wood (with graphite electrode)	450	0.062
75	Naa leaf	408	0.022
76	Blue himbutu yarn	404	0.005
77	Red Balan wood	398	0.158
78	Pani gedi	390	0.0133
79	Beli fruit	388	0.012

80	Lavulu fruit	380	0.0622
81	Aphelamdra Spectrocia flower	380	0.033
82	Rata Lovi fruit	368	0.0038
83	Purple Kapuru fruit	367	0.004
84	Cannas flower	348	0.002
85	Kukul karamal flower	347	0.003
86	Goraka flower	346	0.0037
87	Wood apple fruit	346	0.0024
88	Wattakka fruit	340	0.062
89	Croton leaf	335	0.002
90	Begonia flower	328	0.002
91	Balu wood	327	0.0042
92	Purple brinjal	307	0.0056
93	Purple dawn flower	288	0.002
94	Ginger rhizome	282	0.0027
95	Karawila seed	280	0.001
96	Ratmal flower	277	0.005
97	Atasia flower	167	0.0221
98	Java almond	147	0.00095
99	Dan fruit	119	0.00127
100	Spinach seed	117	0.0012

Table 4.4 Table of Results (In Decreasing Efficiency Values

Ser No	Dye	Open Circuit Voltage *Voc* *(mV)*	Short Circuit Current *Isc* *(mA)*	Current Density I_D *(mA/cm^2)*	Fill Factor*(ff)*	Efficiency(η)	Solvent
1	Mangoostein	685.3	0.640	2.56	60.02	1.053	Chloroform
2	Fire Fern + HCL	405.1	1.032	4.128	47.97	0.802	Ethanol
3	Fire Fern + HCL	404.2	0.999	3.996	47.58	0.768	Ethanol
4	Ruthanium	708.6	1.532	1.534	62.3	0.677	Ethanol
5	Ruthanium bipiridyl (reference)	708.6	1.532	6.128	62.3	0.677	Ethanol
6	Ekkiriya Wood	414.2	0.58	2.32	56.86	0.547	Ethanol
7	Egg Plant	410.4	0.524	2.096	56.42	0.485	Ethanol
8	Fire Fern (14 days)	365.7	0.584	2.336	51.77	0.442	Ethanol
9	Purple Fruit (Karawala Kobilla)	443.5	0.348	1.395	58.58	0.362	Ethanol
10	Banana Flower Inflorescence	414	0.477	0.763	45.2	0.357	Ethanol
11	Mangoostein 2	638.2	0.194	0.778	68.46	0.34	Ethanol
12	Fire Fern + Acetic acid	442.2	0.333	1.332	55.03	0.325	Ethanol
13	Beetroot	441.2	0.328	1.312	55.36	0.32	Ethanol
14	Fire Fern (1 hour)	335.6	0.459	1.836	50.13	0.309	Ethanol
15	Turmeric	601.9	0.16	0.64	68.31	0.264	Ethanol
16	Ruthanium	584.5	0.205	0.822	53.59	0.257	Ethanol
17	Ruthanium	584.5	0.205	0.822	53.59	0.257	Ethanol
18	Turmeric (1 hour)	542.6	0.26	1.04	45.61	0.257	Ethanol
19	Mangoostein + HCL (15 hrs)	490.2	0.246	0.983	50.84	0.245	Ethanol
20	Mangoostein + HCL	609.2	0.131	0.527	72.98	0.234	Ethanol
21	Turmeric	599.1	0.135	0.54	69.03	0.223	Ethanol
22	Mangoostein (14 days)	308.9	0.557	2.228	31.86	0.219	Ethanol
23	Mangoostein + HCL (14 days)	499.9	0.263	1.052	40.26	0.211	Ethanol

24	Mangoostein	606.7	0.148	0.591	57.62	0.207	Ethanol
25	Mangoostein 2	603.1	0.131	0.524	65.2	0.206	Ethanol
26	Mangoostein (3 hrs)	576.9	0.136	0.544	65.18	0.204	Ethanol
27	Mangoostein 1	633.9	0.114	0.456	68.58	0.198	Ethanol
28	Mangoostein	605	0.114	0.456	64.8	0.178	Ethanol
29	Fire Fern + HCL (14 days)	606	0.11	0.44	64.33	0.171	Ethanol
30	Mangoostin (15 hrs)	654.6	0.099	0.396	65.21	0.169	Ethanol
31	Mangoostein	565.2	0.111	0.444	65.66	0.165	Ethanol
32	Mangoostein Skin	635	0.087	0.348	69.41	0.153	Ethanol
33	Mangoostein	603.7	0.099	0.396	63.52	0.152	Ethanol
34	Fire Fern	418.8	0.162	0.648	54.92	0.149	Ethanol
35	Mangoostein	563.6	0.206	0.412	63.63	0.148	Ethanol
36	Mangoostein (1 hour)	600.7	0.088	0.352	70.08	0.147	Ethanol
37	Black Grape	416.5	0.161	0.644	54.87	0.147	Ethanol
38	Ruthanium bipiridyl (reference)	416.5	0.161	0.644	54.87	0.147	Ethanol
39	Mangoostin Skin	657.5	0.094	0.376	57.38	0.142	Ethanol
40	Mangoostin 1	596.5	0.082	0.33	69.35	0.136	Ethanol
41	Mangoostin Skin	593.4	0.081	0.324	68.6	0.131	Ethanol
42	Croton Leaf	416.3	0.137	0.548	56.62	0.13	Ethanol
43	Begonia Black Velvet Leaf (15hrs)	442.8	0.125	0.5	57.66	0.128	Ethanol
44	Turmeric (14 days)	627.1	0.079	0.316	63.23	0.126	Ethanol
45	Croton Leaf	584.9	0.071	0.284	71.9	0.12	Ethanol
46	Walmadata	520.7	0.084	0.336	68.54	0.12	Ethanol
47	Mangoostein HCL	561.8	0.075	0.3	70.51	0.119	Ethanol
48	Mangoostein + Acetic acid	562.9	0.075	0.03	70.07	0.119	Ethanol
49	Fire Fern + Acetic acid (14 days)	590.8	0.081	0.324	60.95	0.117	Ethanol
50	Purple Fruit	479.1	0.088	0.352	65.51	0.111	Ethanol
51	Mangoostein	631	0.065	0.26	67.73	0.111	Ethanol

	Pulp						
52	Red Hart	500.7	0.82	0.028	64.81	0.106	Ethanol
53	Mangoostein 2	595.2	0.061	0.244	69.3	0.1	Ethanol
54	Mangoostein	608	0.058	0.232	68.9	0.098	Ethanol
55	Begonia Black Velvet	608	0.058	0.232	68.9	0.098	Ethanol
56	Venivel	529.9	0.079	0.316	57.59	0.097	Ethanol
57	Orange	627.5	0.05	0.2	73.1	0.091	Ethanol
58	Red Plum	527.4	0.062	0.246	63.59	0.083	Ethanol
59	Red Plum	527.4	0.062	0.246	63.69	0.083	Ethanol
60	Turmeric + HCL	583.8	0.056	0.224	58.7	0.076	Ethanol
61	Spinach	586.7	0.055	0.22	58.41	0.075	Ethanol
62	Mangoostein + Orange + Grapes	600.8	0.042	0.168	71.91	0.073	Ethanol
63	Purple Fruit (Karawala kabilla)	599.1	0.044	0.176	69.48	0.073	Ethanol
64	Red Onion Bulb	433	0.062	0.249	66.63	0.072	Ethanol
65	Rambutan	504.1	0.156	0.132	45.53	0.072	Ethanol
66	Anthurium Flower	527.8	0.048	0.192	70.43	0.071	Ethanol
67	Fire Fern 2	437.9	0.066	0.264	57.97	0.067	Ethanol
68	Fire Fern	437.9	0.066	0.264	57.97	0.067	Ethanol
69	Turmeric + HCL (14 days)	527.4	0.046	0.184	69.28	0.067	Ethanol
70	Beetroot	487.9	0.049	0.196	67.62	0.065	Ethanol
71	Beetroot	487.9	0.049	0.196	67.62	0.065	Ethanol
72	Mangoostein + Orange + Grapes	594.7	0.045	0.18	59.35	0.063	Acetonitrile
73	Orange	624.9	0.039	0.156	64.6	0.063	Acetonitrile
74	Anthurium	528.7	0.041	0.166	66.55	0.058	Ethanol
75	Grapes	498	0.049	0.196	60.28	0.058	Acetonitrile
76	Red Hart	599.7	0.032	0.129	73.53	0.057	Ethanol
77	Rambutan	493.9	0.047	0.188	61.67	0.057	Ethanol
78	Orange	558.3	0.034	0.228	73.86	0.057	Ethanol
79	Rathadun	427.2	0.069	0.276	47.39	0.056	Ethanol
80	Venivelgata	538.4	0.039	0.156	67.37	0.056	Ethanol
81	Orange	519.4	0.039	0.156	55.25	0.053	Acetonitrile
82	Mango	584.4	0.093	0.186	46.92	0.051	Ethanol

83	Mangoostein Skin	665.5	0.034	0.136	57.03	0.051	Ethanol
84	Grapes	557.8	0.035	0.14	62.86	0.049	Ethanol
85	Fire Fern (15 hrs)	457.7	0.05	0.202	52	0.048	Ethanol
86	Red Hart (14 days)	587.6	0.032	0.128	63.76	0.048	Ethanol
87	Spinach	564.5	0.032	0.128	66.43	0.047	Ethanol
88	Black Grape	562.9	0.026	0.025	71.88	0.042	Ethanol
89	Fire Fern (25 hrs)	445.2	0.043	0.173	54.42	0.042	Ethanol
90	Black Grape	553.2	0.026	0.105	73.04	0.042	Ethanol
91	Red Onion	586.4	0.025	0.1	71.23	0.042	Ethanol
92	Red Hart	586	0.025	0.1	71.48	0.042	Ethanol
93	Turmeric + HCL	408.9	0.042	0.169	57.68	0.04	Ethanol
94	Banana	599.2	0.021	0.084	78.77	0.04	Ethanol
95	Bulu	493.7	0.041	0.164	47.44	0.038	Ethanol
96	Croton Leaf	469.8	0.035	0.14	55.64	0.037	Ethanol
97	Croton Leaf	469.8	0.035	0.14	55.64	0.037	Ethanol
98	Mangoostein + Orange + Grapes	608.9	0.026	0.104	56.82	0.036	Acetonitrile
99	Anthurium (14 days)	263.8	0.1	0.4	34.49	0.036	Ethanol
100	Hibiscus Sabdrilla	546	0.027	0.108	59	0.035	Ethanol
101	Carrot	641.2	0.077	0.154	35.4	0.035	Ethanol
102	Grapes	538.2	0.024	0.096	61.32	0.032	Acetonitrile
103	Blue Lichen (15 hrs)	535.1	0.029	0.117	48.52	0.03	Ethanol
104	Red Hart Leaf (15 hrs)	630.4	0.016	0.065	67.24	0.028	Ethanol
105	Turmeric	546.6	0.022	0.087	58.55	0.028	Ethanol
106	Turmeric	546.6	0.022	0.087	58.55	0.028	Ethanol
107	Grapes	566.8	0.015	0.06	72.22	0.025	Ethanol
108	Rathadun	415	0.026	0.104	48.58	0.021	Ethanol
109	Mangoostein 1	508	0.017	0.068	55.03	0.019	Ethanol
110	Beli Flower	490.2	0.019	0.076	49.72	0.018	Ethanol
111	Turmeric	473.5	0.016	0.064	58.27	0.018	Ethanol
112	Nelum Seed	497.1	0.022	0.088	39.04	0.017	Ethanol
113	Wattaka	622.2	0.038	0.076	36.28	0.017	Ethanol
114	Mangoostein + Acetic Acid (14	526.8	0.014	0.056	55.3	0.017	Ethanol

	days)						
115	Kothala Himbutu	450.1	0.022	0.088	38.87	0.016	Ethanol
116	Turmeric (15 hrs)	596.2	0.012	0.04	53.88	0.015	Ethanol
117	Tomato	507.5	0.016	0.032	79.69	0.013	Ethanol
118	Aralu	468.9	0.026	0.104	26.83	0.013	Ethanol
119	Purple Makaral	380.7	0.025	0.1	34.13	0.013	Ethanol
120	Spinach	426.5	0.017	0.067	42.59	0.012	Ethanol
121	Spinach	426.5	0.017	0.067	42.59	0.012	Ethanol
122	Spinach	323.7	0.017	0.068	48.39	0.011	Ethanol
123	Ginger	489.5	0.013	0.052	40.72	0.011	Ethanol
124	King Coconut Nut Husk	256.7	0.073	0.146	30.48	0.011	Ethanol
125	Egg Plant	409.9	0.012	0.047	51.26	0.01	Ethanol
126	Egg Plant	460.7	0.015	0.06	36.59	0.01	Ethanol
127	Egg Plant	460.7	0.015	0.06	36.59	0.01	Ethanol
128	Egg Plant	409.9	0.012	0.047	51.26	0.01	Ethanol
129	Grey Lichen (15 hrs)	531.3	0.008	0.03	57.48	0.009	Ethanol
130	Turmeric (3 hrs)	41.9	0.208	0.832	24.84	0.009	Ethanol
131	Ekkiriya Wood	211.7	0.011	0.044	39.91	0.004	Ethanol
132	Begonia Black Velvet Leaf	298.9	0.005	0.0188	66.24	0.004	Ethanol
133	Red Banana	476	0.016	0.016	48.62	0.004	Ethanol
134	Banana Flower Inflorescence	339.5	0.005	0.021	47.19	0.003	Ethanol
135	Spinach	329.8	0.005	0.02	41.84	0.003	Ethanol
136	Banana Flower Inflorescence	385.5	0.005	0.021	43.01	0.003	Ethanol
137	Beetroot	252.7	0.009	0.018	37.54	0.002	Ethanol
138	F. Berry	383.3	0.006	0.024	26.3	0.002	Ethanol
139	Turmeric	311.3	0.003	0.012	53.49	0.002	Ethanol
140	Yellow Chille	210.2	0.009	0.037	13.75	0.001	Ethanol
141	B. Onion	331.8	0.002	0.008	32.87	0.001	Ethanol
142	Beli	194.3	0.003	0.012	23.01	0.001	Ethanol
143	Purple Makaral	165.1	0.003	0.012	35.56	0.001	Ethanol
144	Goraka	323.3	0.007	0.028	27.91	0.001	Ethanol

Table 4.5 Table of Results of Best Natural Dyes Suitable for DSSC's (In decreasing Efficiency values)

Serial No.	**Dye**	Open Circuit Voltage V_{OC} (Mv)	Short Circuit Current I_{sc}(mA)	Current Density I_D (m A/ cm^2)	Fill factor (ff)	Efficiency (η)	Solvent
1	Mangoostein	685.3	0.640	2.56	60.02	1.053	Chloroform
2	Fire Fern + HCL	405.1	1.032	4.128	47.97	0.802	Ethanol
3	Ekkiriya Wood	414.2	0.58	2.32	56.86	0.547	Ethanol
4	Egg Plant	410.4	0.524	2.096	56.42	0.485	Ethanol
5	Fire Fern	365.7	0.584	2.336	51.77	0.442	Ethanol
6	Purple Fruit (Karawala kabilla)	443.5	0.348	1.395	58.58	0.362	Ethanol
7	Banana Flower Inflorescence	414	0.477	0.763	45.2	0.357	Ethanol
8	Mangoostein	638.2	0.194	0.778	68.46	0.34	Ethanol
9	Fire Fern + Acetic Acid	442.2	0.333	1.332	55.03	0.325	Ethanol
10	Beetroot	441.2	0.328	1.312	55.36	0.32	Ethanol
11	Fire Fern (1 hour)	335.6	0.459	1.836	50.13	0.309	Ethanol
12	Turmeric	601.9	0.16	0.64	68.31	0.264	Ethanol
13	Turmeric (1 hour)	542.6	0.26	1.04	45.61	0.257	Ethanol
14	Mangoostein + HCL	609.2	0.131	0.527	72.98	0.234	Ethanol
15	Mangoostein (14 days)	308.9	0.557	2.228	31.86	0.219	Ethanol
16	Mangoostein + HCL (14 days)	499.9	0.263	1.052	40.26	0.211	Ethanol
17	Mangoostein (3 hrs)	576.9	0.136	0.544	65.18	0.204	Ethanol
18	Fire Fern + HCL (14 days)	606	0.11	0.44	64.33	0.171	Ethanol
19	Mangoostein (1 hour)	600.7	0.088	0.352	70.08	0.147	Ethanol
20	Black Grape	416.5	0.161	0.644	54.87	0.147	Ethanol
21	Croton Leaf	416.3	0.137	0.548	56.62	0.13	Ethanol
22	Begonia Black Velvet Leaf (15hrs)	442.8	0.125	0.5	57.66	0.128	Ethanol
23	Walmadata	520.7	0.084	0.336	68.54	0.12	Ethanol
24	Purple Fruit	479.1	0.088	0.352	65.51	0.111	Ethanol
25	Red Hart	500.7	0.82	3.28	64.81	0.106	Ethanol
26	Begonia Black Velvet	608	0.058	0.232	68.9	0.098	Ethanol
27	Venivel	529.9	0.079	0.316	57.59	0.097	Ethanol
28	Orange	627.5	0.05	0.10	73.1	0.091	Ethanol
29	Red Plum	527.4	0.062	0.246	63.59	0.083	Ethanol

30	Spinach	586.7	0.055	0.22	58.41	0.075	Ethanol
31	Mangoostein + Orange + Grapes	600.8	0.042	0.168	71.91	0.073	Ethanol
32	Red Onion Bulb	433	0.062	0.249	66.63	0.072	Ethanol
33	Rambutan	504.1	0.156	0.132	45.53	0.072	Ethanol
34	Anthurium Flower	527.8	0.048	0.192	70.43	0.071	Ethanol
35	Red Grapes	498	0.049	0.196	60.28	0.058	Acetonitrile
36	Red Hart	599.7	0.032	0.129	73.53	0.057	Ethanol
37	Rambutan	493.9	0.047	0.188	61.67	0.057	Ethanol
38	Rathadun	427.2	0.069	0.276	47.39	0.056	Ethanol
39	Venivelgata	538.4	0.039	0.156	67.37	0.056	Ethanol
40	Mango	584.4	0.093	0.186	46.92	0.051	Ethanol
41	Green Grapes	557.8	0.035	0.14	62.86	0.049	Ethanol
42	Red Chillies	587.6	0.032	0.128	63.76	0.048	Ethanol
43	Spinach	564.5	0.032	0.128	66.43	0.047	Ethanol
44	Red Banana	599.2	0.021	0.084	78.77	0.04	Ethanol
45	Bulu	493.7	0.041	0.164	47.44	0.038	Ethanol
46	Hibiscus Sabdrilla	546	0.027	0.108	59	0.035	Ethanol
47	Carrot	641.2	0.077	0.154	35.4	0.035	Ethanol
48	Blue Lichen (15 hrs)	535.1	0.029	0.117	48.52	0.03	Ethanol
49	Beli Flower	490.2	0.019	0.076	49.72	0.018	Ethanol
50	Nelum Seed	497.1	0.022	0.088	39.04	0.017	Ethanol
51	Wattaka	622.2	0.038	0.076	36.28	0.017	Ethanol
52	Kothala Himbutu	450.1	0.022	0.088	38.87	0.016	Ethanol
53	Tomato	507.5	0.016	0.032	79.69	0.013	Ethanol
54	Aralu	468.9	0.026	0.104	26.83	0.013	Ethanol
55	Purple Makaral	380.7	0.025	0.1	34.13	0.013	Ethanol
56	Ginger	489.5	0.013	0.052	40.72	0.011	Ethanol
57	King Coconut Nut Husk	256.7	0.073	0.146	30.48	0.011	Ethanol
58	Grey Lichen	531.3	0.008	0.03	57.48	0.009	Ethanol
59	Yellow Banana	476	0.016	0.016	48.62	0.004	Ethanol
60	Yellow Chille	210.2	0.009	0.037	13.75	0.001	Ethanol
61	Beli	194.3	0.003	0.012	23.01	0.001	Ethanol
62	Goraka	323.3	0.007	0.028	27.91	0.001	Ethanol

Current – Voltage Characteristics of 12 best Natural Dyes out of 50 initially tested

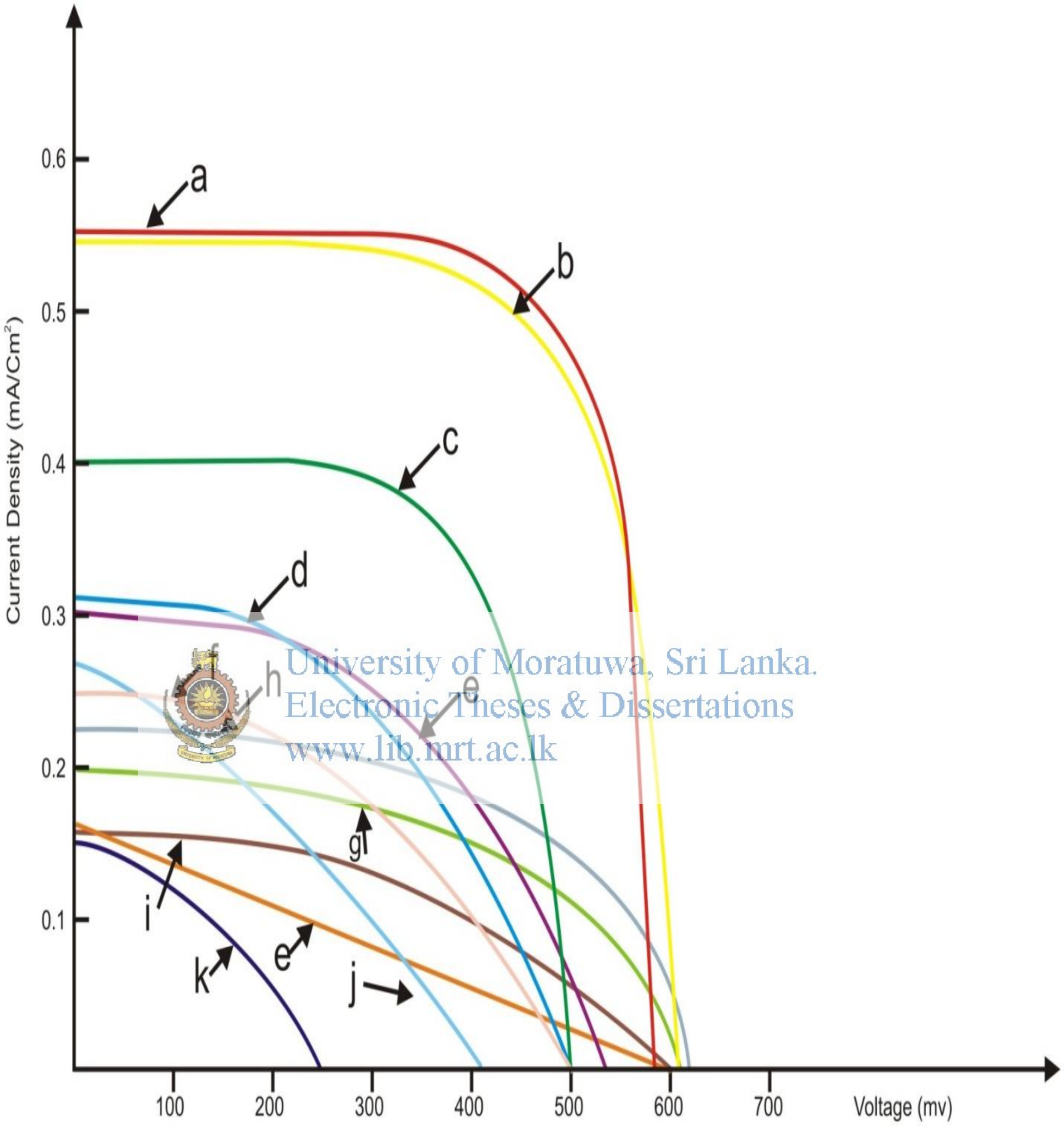


Figure 4.3 Current –Voltage characteristics of best 12 out of 50 Natural Dyes tested

(a) Mangoostein (b) Turmeric (c) Walmadata (d) Rambutan (e) Venivel (f) Grapes (g) Orange (h) Mango (i) Tomato (j) Rathadun (k) King Coconut husk

4.1.1 Photoelectochemical, Electrochemical, Structural and Electronic Impedance Spectroscopic Characterization of Natural Dyes

4.1.1.2 Photoelectrochemical Characterization of Natural Dyes

Thereafter testing and analysis of about further 144 natural dyes and their dye mixtures of plants grown in Sri Lanka were carried out. These results are tabulated at Table 4.4. (144 best natural dyes identified). The summarized Table of Results obtained in listed at Table4. 5. (best 62 natural dyes identified). The Absorbance Spectra of the best 15 natural dyes identified is at Figures 4.5, 4.6 and 4.7. The I-V characteristics of the best 15 natural dyes tested is at Figure 4. 8.

From these results it is observed that extracts of maroon-red Fire fern leaf (not endemic to Sri Lanka but recently imported from Central America to the Royal Botanical Gardens, Peradeniya, Sri Lanka) achieved a highest conversion efficiency of 0.802%. Amongst plants grown in Sri Lanka, extracts of Turmeric root (dark yellow), Beetroot tuber (purple), Mangoostein fruit rind (dark purple), Banana flower inflorescence (purple), Karawalla kabilla fruit (reddish brown), Egg plant fruit (purple), Ekkiriya wood (reddish brown) have achieved better solar energy conversion efficiency of 0.264%, 0.320%, 0.340%, 0.357%, 0.362%, 0.485% and 0.547% respectively amongst these dyes tested.

4.1.2.1 Absorbance Spectra of various Natural Dyes

The UV-vis Absorption Spectra of various natural dyes of plants grown in Sri Lanka were also obtained with UV 2450 SHIMADZU UV –visSpectrophotometer available at the IFS, Hantana, Sri Lanka.

Figures 4.5,4.6 and 4.7 depict the UV-vis Absorbance Spectra of a cross section of natural dyes of plants grown in Sri Lanka, in ethanolic dye solutions. It can be seen that, the dye solutions obtained from Turmeric and Mangoostein absorb more in the blue side of the electromagnetic spectrum than the other dyes. Absorbance peaks at 220 nm, 250 nm, 325 nm have been obtained for Mangoostein; 210nm, 280 nm, 330 nm, 430 nm for Turmeric; 206 nm for Ekkiriya wood, and 205 nm for Fire fern.

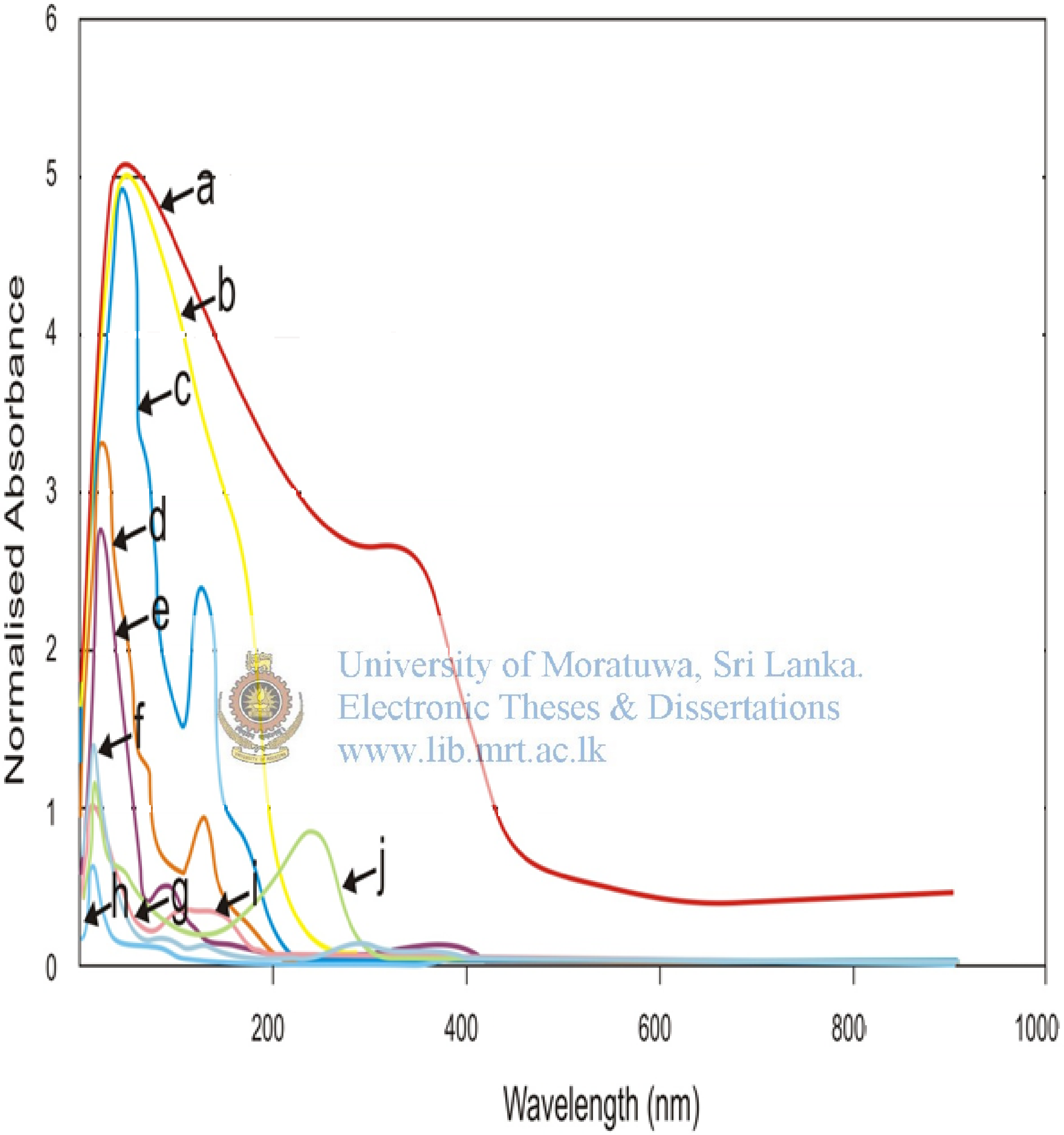


Figure 4.4 UV-vis Absorbance Spectra of Dye Solutions extracted from (a) Mangoostin (b) Dan purple fruit (Karawela Kabili) (c) Turmeric (d) Red Pium (e) Australian Orange fruit rind (f) Red Cabbage (g) Croton leaf (h) Red Globular Chillie fruit (i) Beetroot (j) Red Onion.

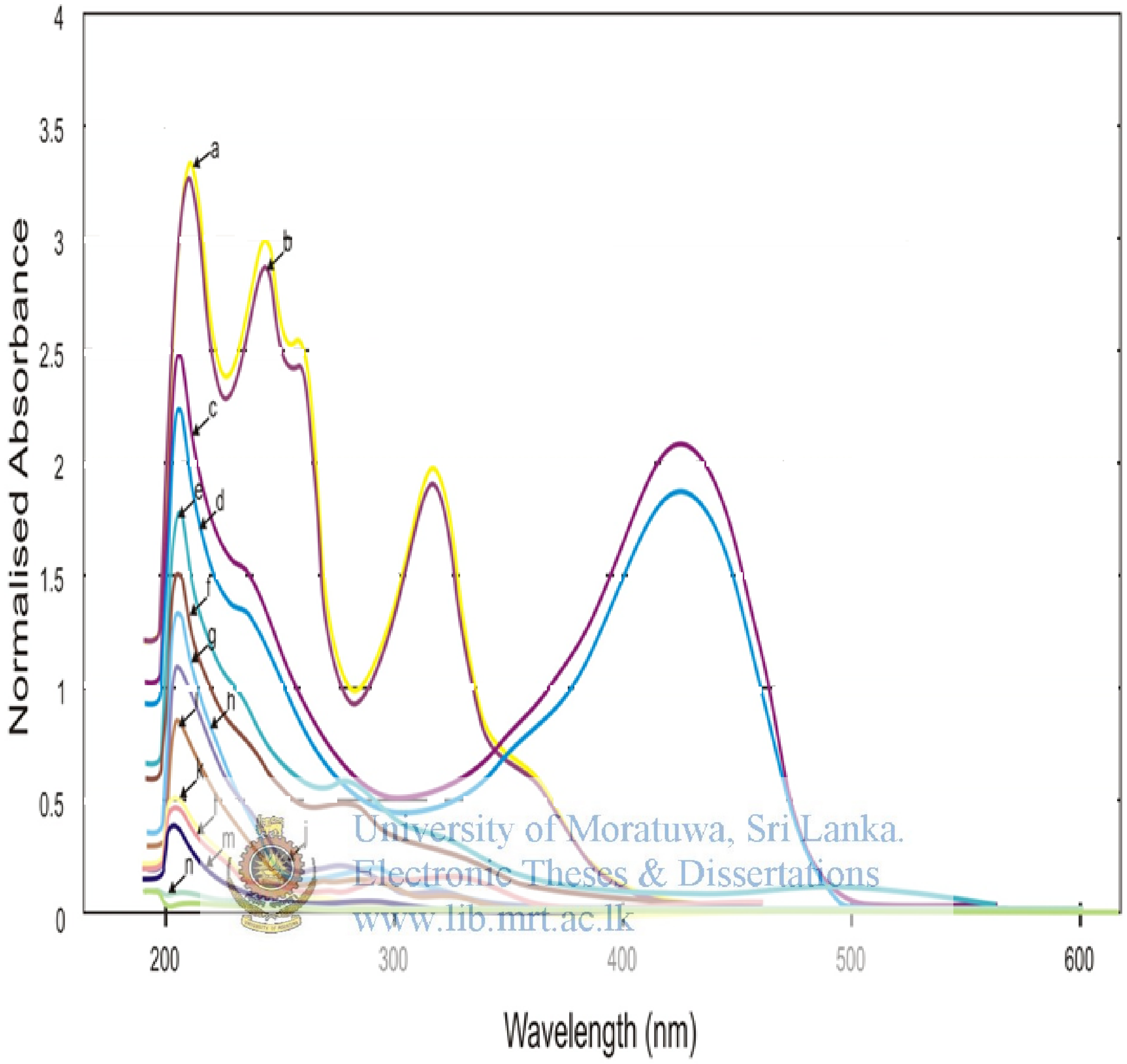


Figure 4.5 UV-vis AbsorbanceSpectra of Dye Solutions extracted from (a) Mangoostin +Hl (b) Mangoostin (c) Turmeric +HCl (d) Turmeric (e) Ekiriya +HCl (f) Ekiriya

(g) PurpleFruit+HCl(h) Purple Fruit (i) Red Plum +HCl (j) Red Plum (k) Black Grape (l) Beetroot (m) Eggplant (n) Spinach.

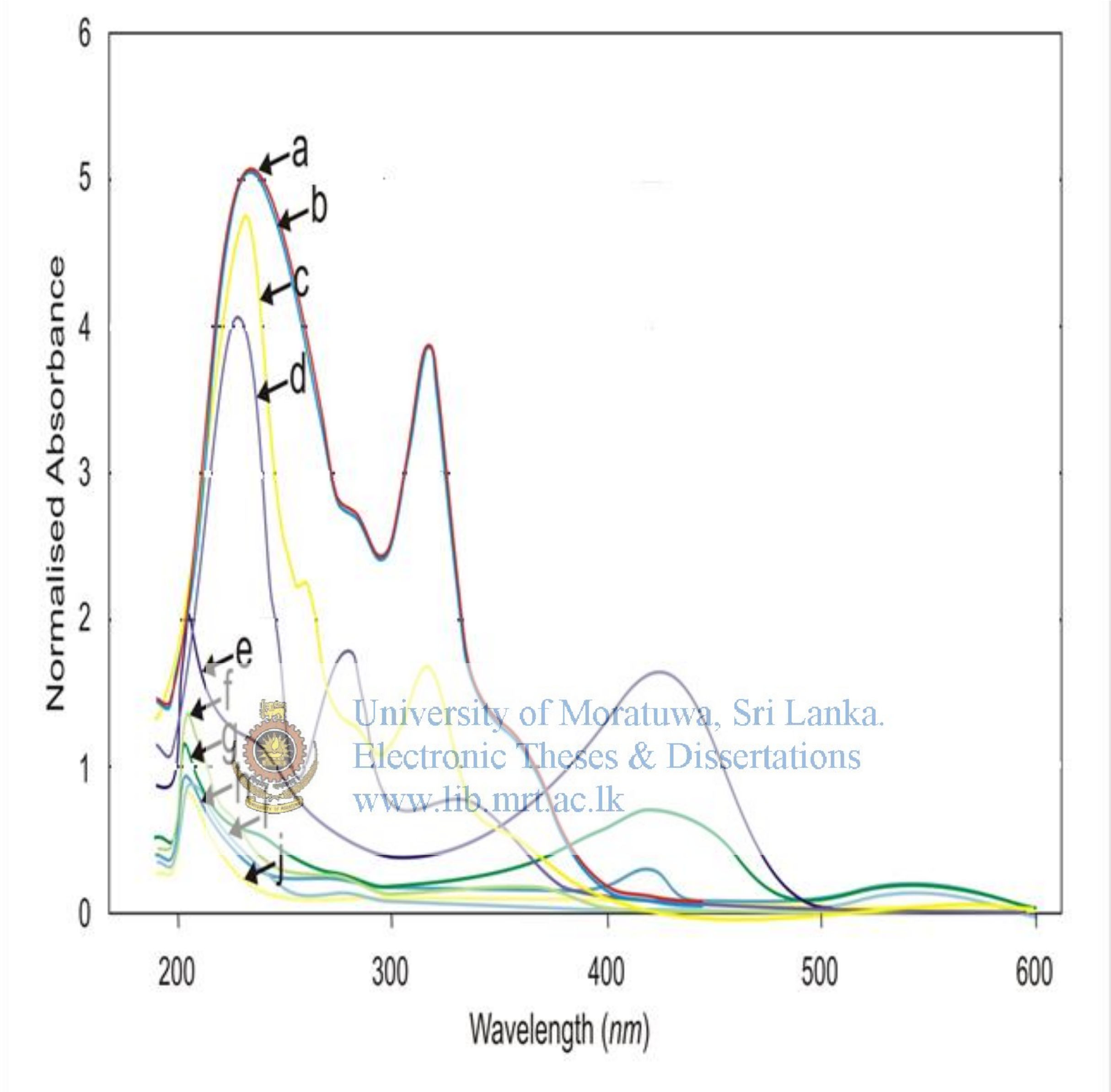


Figure 4.6 UV-vis Absorption of Spectra of dye solutions extracted from (a) Mangoostin +Acetic acid (b) Mangoostin +HCl (c) Mangoostin (d) Turmeric +HCl (e) Turmeric (f) Fire Fern+HCl (g) Fire Fern (h) Begonia (i) Red Hart (j) Anthurium

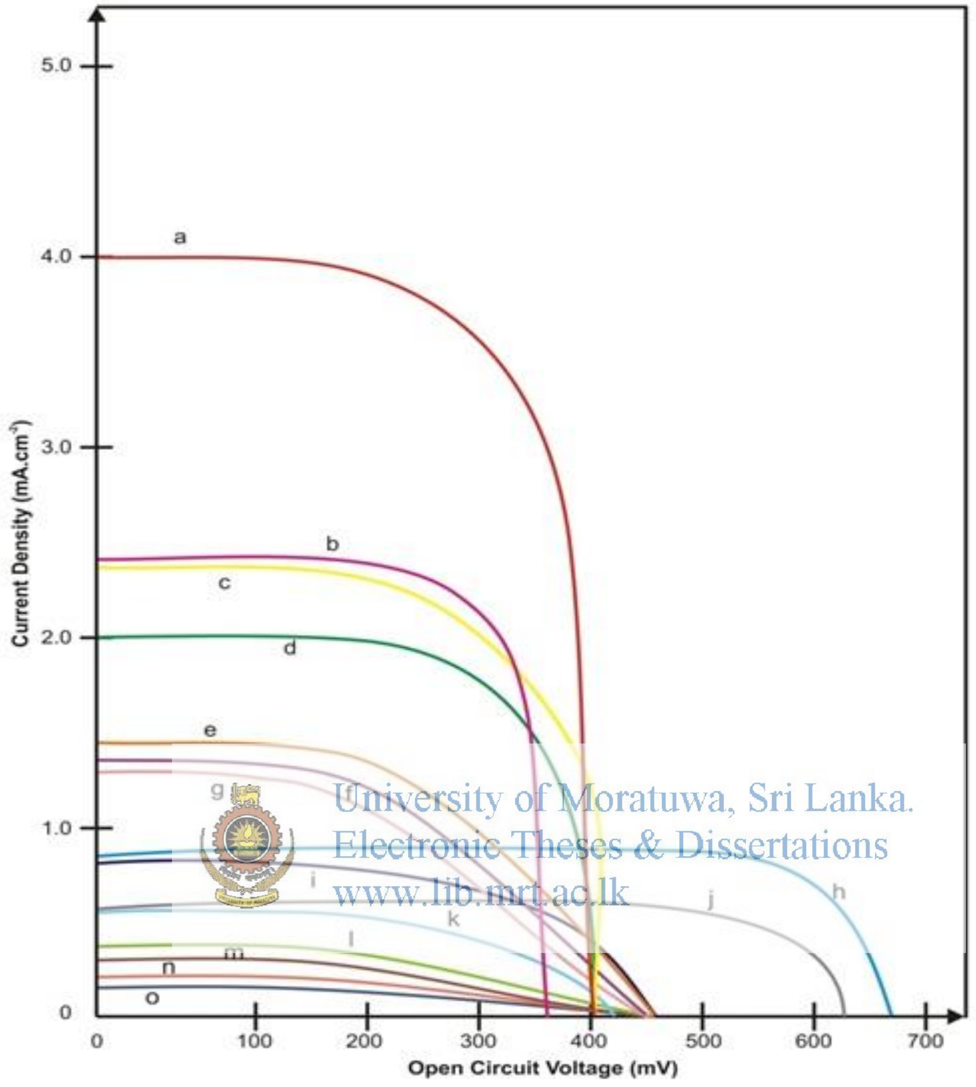


Figure 4.8 Current Voltage Characteristics of Dye Sensitized Solar Cells

(a) Fire Fern + HCL (b) Fire Fern (c) Ekkiriya wood (d) Egg Plant (e) Karawila Kabilla (f) Fire Fern + Acetic acid (g) Beet root (h) Mangoostein (i) Banana inflorescence (j) Turmeric (k) Black grapes (l) Croton (m) Begonia BV (n) Walmadata (o) Venival

Figure 4.7 This graph depicts the Current Density Vs. Open Circuit Voltage characteristics of some DSSC cells tested.

It is observed that Ethanol extracts of Fire Fern, Ekkiriya, Egg plant, Karawila Kabilla, Beetroot, Mangoostein, Banana, Turmeric gave fairly good Current Densities and Open Circuit Voltages amongst all natural dyes analyzed.

4.1.2.2 Effect of pH on Absorbance Spectra and I – V Characteristics of DSSC's

Introduction

Also the effects of pH on the Absorbance Spectra of Mangoostein and Turmeric extracts were studied using the SHIMADZU UV 3600 Spectrophotometer at the Sri Lanka Institute of Nanotechnology, Biyagama, Sri Lanka. INROB 70 pH meter available there was used for pH measurements. The following observations were made at Figure 4.9 and 4.10 and Tables 4.6 and 4.7.

Table 4.6 Characteristics of DSSC's fabricated using Mangoostein and Turmeric dyes whose pH values were controlled with Hydrochloric acid and Sodium hydroxide.

Mangoostein Dye

pH	Isc (mA)	Id (mA.cm^{-2})	Voc (mV)	ff %	η%
2	0.351	1.404	515.1	50.41	0.364
4	0.158	0.632	544.3	44.83	0.153
6	0.076	0.304	539.6	65.91	0.107
8	0.013	0.052	511.3	33.71	0.009
10	0.021	0.84	624.9	52.56	0.028
12	0.011	0.044	231.7	29.78	0.003

Table 4.7 Turmeric Dye

pH	Isc (mA)	Id (mA.cm^{-2})	Voc (mV)	ff %	η%
2	0.027	0.508	514.8	58.89	0.154
4	0.03	0.012	475.3	42.83	0.024
6	0.005	0.020	564.1	41.53	0.005
8	0.009	0.036	497.8	27.13	0.005
10	0.003	0.012	567.5	39.84	0.003
12	0	0	487.8	2.63	0

The effects of pH on the Absorbance spectra and Current – Voltage Characteristics of natural dyes (Mangoostein fruit rind and Turmeric rhizome root extracts) were also ascertained.

For this purpose in respect of Mangoostein and Turmeric dyes respectively, these were filled with five glass beakers each of 20 ml of distilled water (pH = 7) and solution having a pH of 2, 4, 6, 8 and 10 were prepared by adding few drops of 0.1 M HCL (acidic pH< 7), and few drops of 0.1 M NaOH (basic >7) as appropriate.

Then 2 drops of Mangoostein fruit rind extract in Ethanol were added to the five beakers having solution with pH of 2, 4, 6, 8 and 10.

Also 2 drops of Turmeric root extract in Ethanol were added to the five beakers having solutions with pH of 2, 4, 6, 8 and 10. (pH measurement were made with the INROB 70 pH meter at SLINTEC.)

Therefore Absorbance Vs. Wavelength Spectra for individual Mangoostein and Turmeric extracts were obtained for wavelength range of 250 nm to 800 nm with the UV 3600 UV-Vis-NIR SHIMADZU Spectrophotometer at the Sri Lanka Institute of Nanotechnology (SLINTEC) at Biyagama, Sri Lanka.

The Absorbance Vs. Wavelength spectra obtained for Mangoostein and Turmeric dyes are listed at Figure 4.9 and 4.10 respectively. It is observed that absorption peaks at 268 nm, 322nm and 372nm were obtained for Mangoostein extract corresponding to pH of 4, 6, 8, 10 and 419 nm, 419 nm, 419 nm, 425 nm for Turmeric extracts corresponding to pH of 2, 4, 6, 8, 10 respectively. These indicate that generally the Absorbance peaks decrease in amplitude as the pH of dye extract solutions increase from acidic to basic media. However the pH of 10 for both Mangoostein and Turmeric indicated high Absorbance peaks at 372 nm and 425 nm respectively, probably due to hydroxyl group get anionised. Both these two test were repeated for Mangoostein and Turmeric dyes of pH = 10 and again identical results were obtained to confirm this fact.

Therefore the effects of pH on DSSC's fabricated and sensitized with Mangoostein and Turmeric dye extracts respectively were obtained with IV Curve Tracing and Analyzing Equipment available at the Sri Lanka Institute of Fundamental Studies (IFS), Hantana, Sri Lanka and are depicted at Table 4.7 and 4.8. These indicate that good absorbance is obtained for dye solutions having pH of 2 to 4 (acidic) ; and for pH above 6 to 12 (basic or alkali) the absorbance significantly decreases .

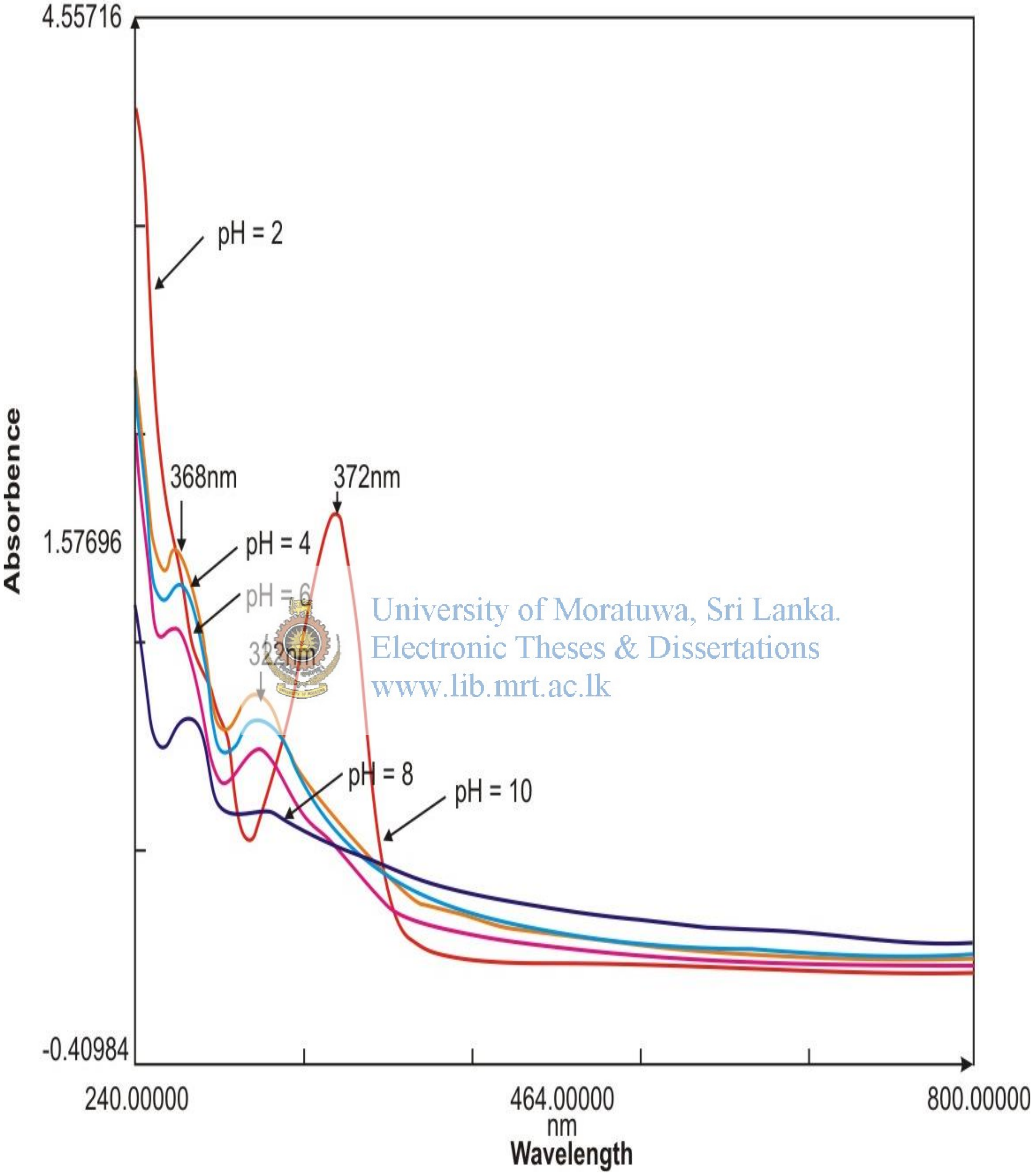


Figure 4.8 Effect of pH on absorbance spectra of Mangoostein dye

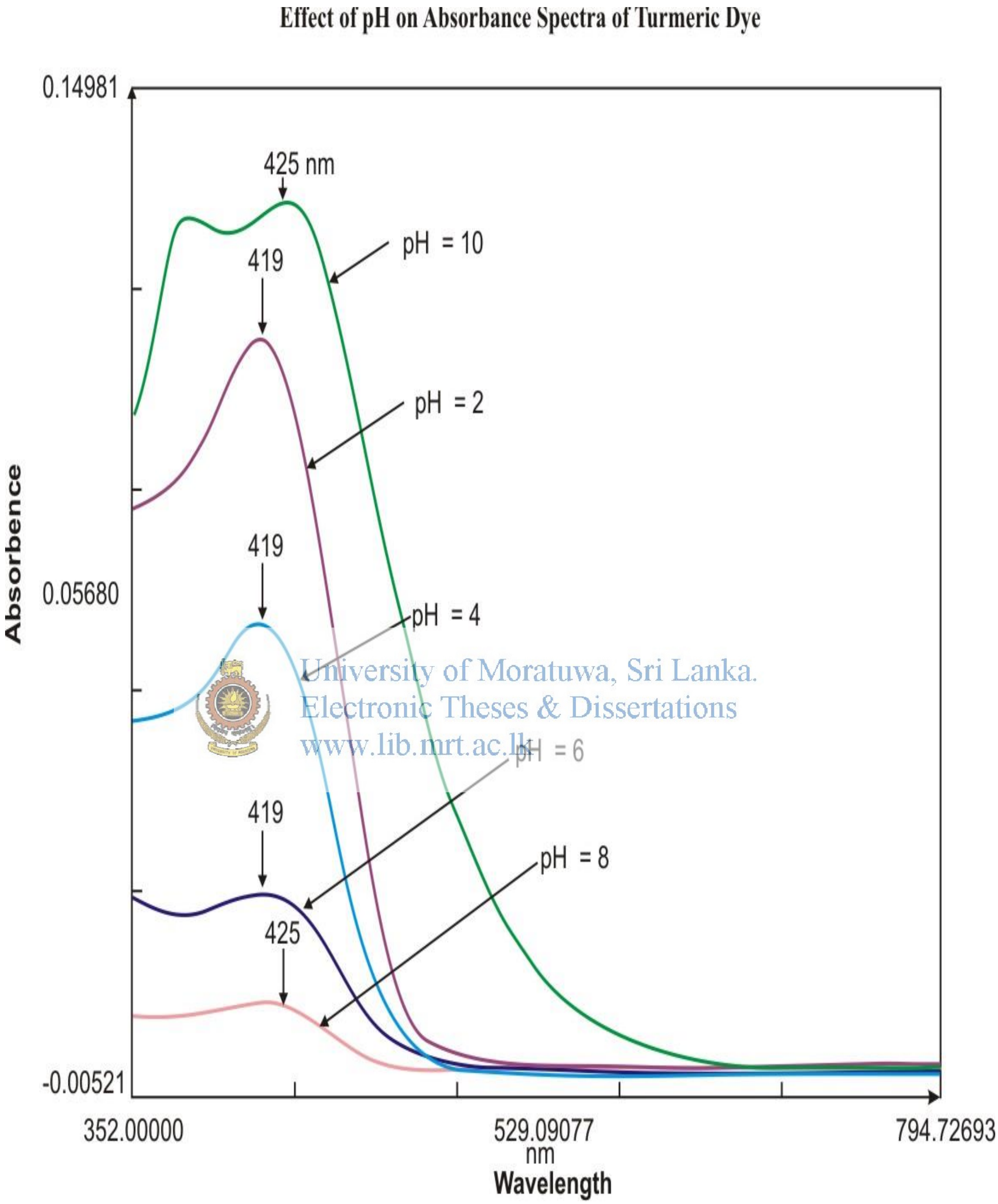
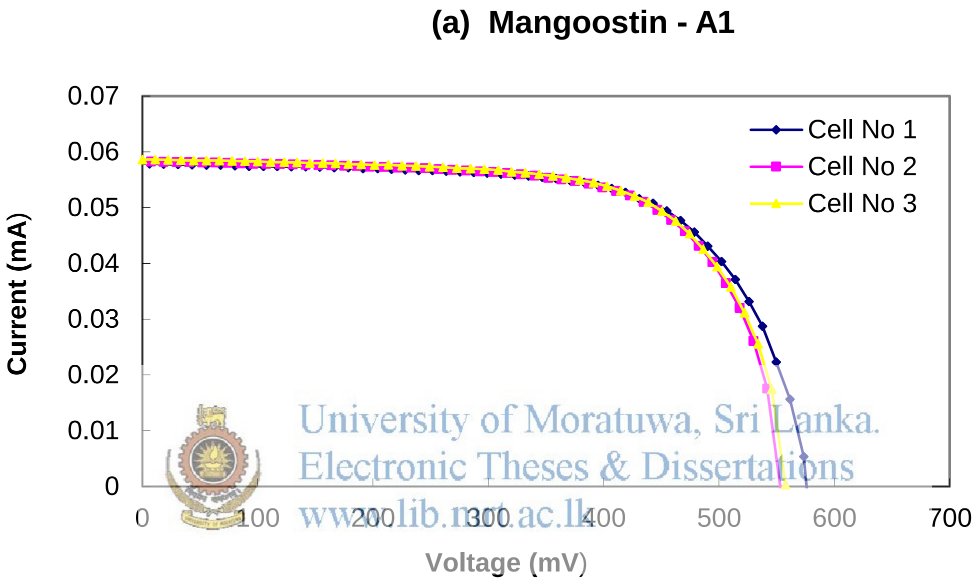


Figure 4.9 Effect of pH on UV-vis Absorbance Spectra of Turmeric Dye

4.1.2 Purification of Natural Dyes

The Current – Voltage Characteristics of the purified Mangoostein fruit rind extracts with various solvents is listed below at (a) to (m).

The Mangoostein C extract (purified with Chloroform) also exhibited a Short Circuit Current 0.64 mA, Open Circuit Voltage of 685.3 mV, Fill Factor of 60.02% and the highest conversion efficiency of 1.053% comparable with the best natural dyes identified by the other researchers.



(a) Mangoostin - A1

Figure 4.10 IV Characteristics of Mangoostein – A1

Cell Description	**Cell No1**	**Cell No 2**	**Cell No 3**
Open V (mV)	574.3	543.9	547.3
Short I (mA)	0.058	0.058	0.059
Fill Factor (%)	67.76	70.04	69.75
Efficiency (%)	0.09	0.089	0.089
Max Power Point V(mV)	442.6	434.6	438.7
Max Power Point I(mA)	0.051	0.051	0.051
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	49	48	49

(b) Mangoostin - A

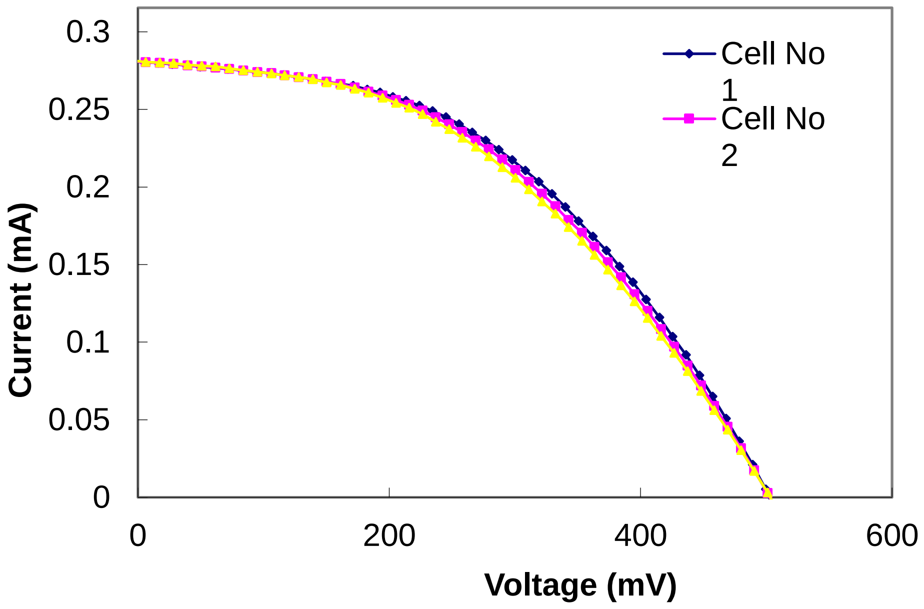


Figure 4.11 IV Characteristics of Mangoostein – A

Cell Description	**Cell No 1**	**Cell No 2**	**Cell No 3**
Open V (mV)	501.4	501.6	502.3
Short I (mA)	0.28	0.281	0.281
Fill Factor (%)	46.24	44.99	43.82
Efficiency (%)	0.26	0.253	0.247
Max Power Point V(mV)	308.3	300.4	300.4
Max Power Point I(mA)	0.211	0.211	0.206
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	48	48	48

(c) Mangoostin - B

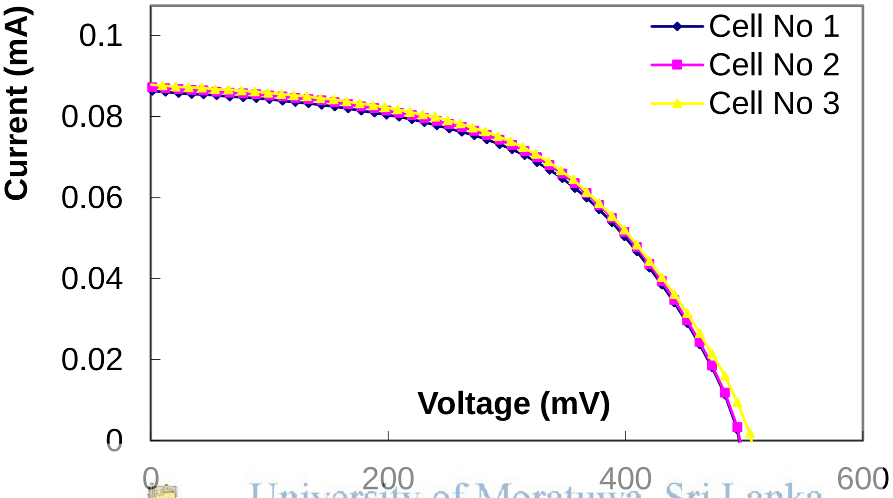


Figure 4.12 IV Characteristics of Mangoostein – B

Cell Description	**Cell No 1**	**Cell No 2**	**Cell No 3**
Open V (mV)	495.1	495.1	505.3
Short I (mA)	0.086	0.087	0.088
Fill Factor (%)	52.76	53.1	52.06
Efficiency (%)	0.09	0.091	0.092
Max Power Point V(mV)	346.7	336.1	334.8
Max Power Point I(mA)	0.065	0.068	0.069
Cell Area(cm^2)	0.25		0.25
Source Intencity	1000	1000	1000
No of Data	48	0.25	48

(d) Mangoostin - C

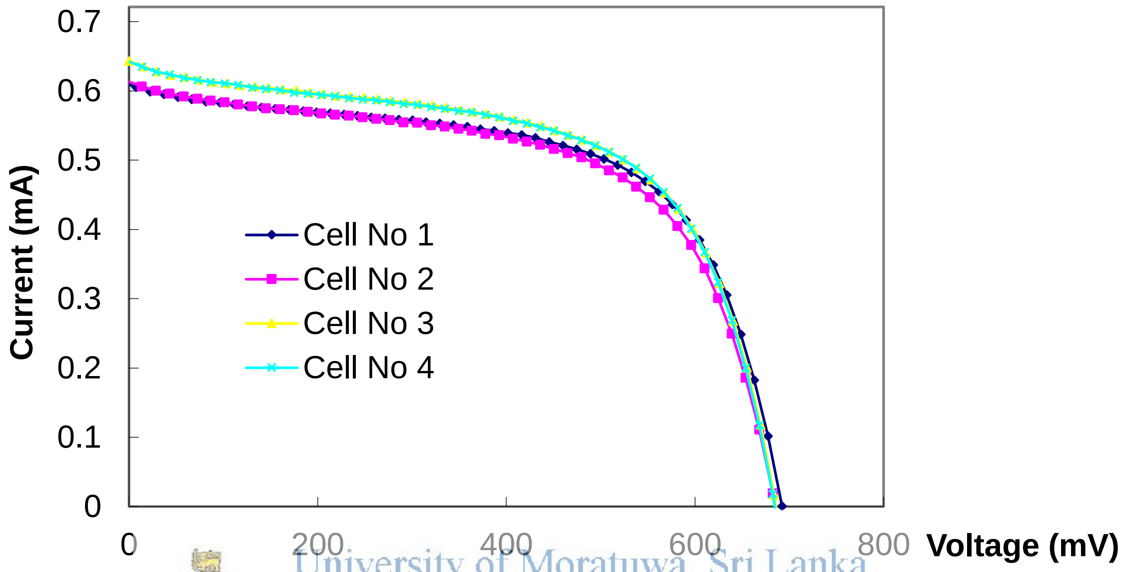


Figure 4.13 IV Characteristics of Mangoostein – C

Cell Description	**Cell No 1**	**Cell No 2**	**Cell No 3**	**Cell No 4**
Open V (mV)	693.9	684	685.3	684.2
Short I (mA)	0.607	0.611	0.64	0.641
Fill Factor (%)	61.03	59.47	60.02	59.95
Efficiency (%)	1.028	0.995	1.053	1.052
Max Power Point V(mV)	547.1	523.3	539.1	537.8
Max Power Point I(mA)	0.47	0.475	0.488	0.489
Cell Area(cm^2)	0.25	0.25	0.25	0.25
Source Intensity	1000	1000	1000	1000

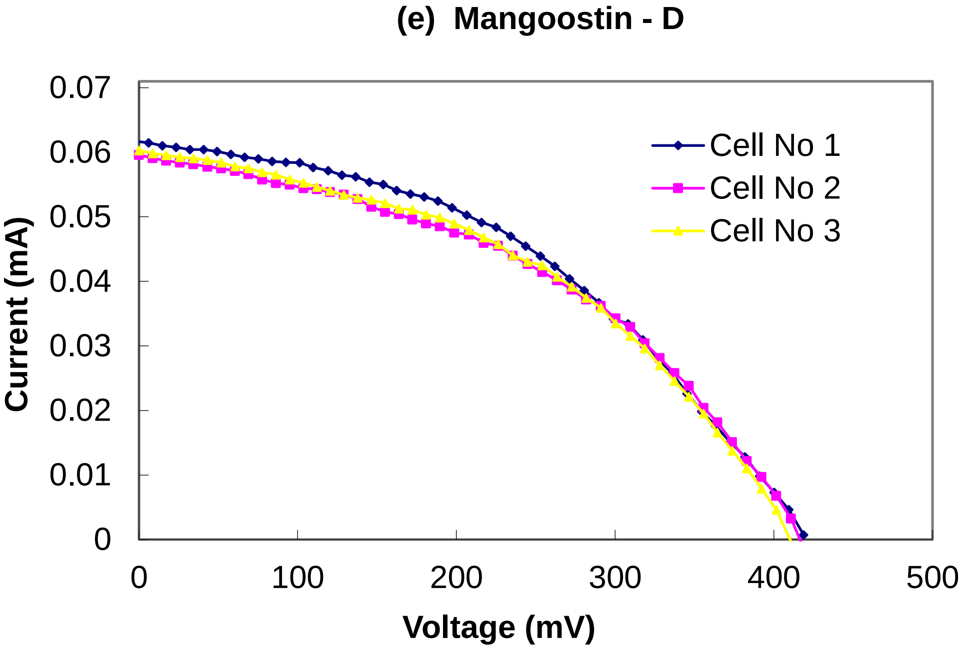

(e) Mangoostin - D

Figure 4.14 IV Characteristics of Mangoostein – D

Cell Description	Cell No 1	Cell No 2	Cell No 3
Open V (mV)	411.1	413.1	403.8
Short I (mA)	0.062	0.059	0.06
Fill Factor (%)	43.91	43.16	44.63
Efficiency (%)	0.044	0.042	0.043
Max Power Point V(mV)	252.9	263.5	254.2
Max Power Point I(mA)	0.044	0.04	0.042
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	47	48	47

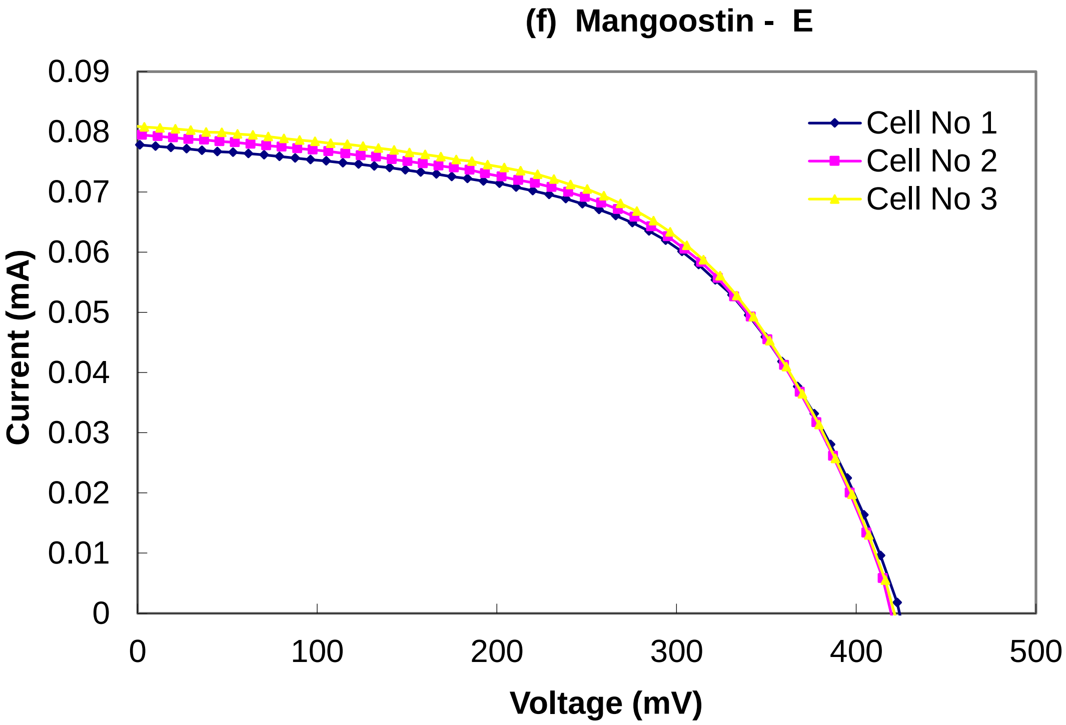


Figure 4.15 IV Characteristics of Mangoostein – E

Cell Description	Cell No 1	Cell No 2	Cell No 3
Open V (mV)	423.8	416.6	417.4
Short I (mA)	0.078	0.079	0.081
Fill Factor (%)	55.26	55.84	55.65
Efficiency (%)	0.073	0.074	0.075
Max Power Point V(mV)	303	295.2	296.5
Max Power Point I(mA)	0.06	0.063	0.063
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	49	48	48

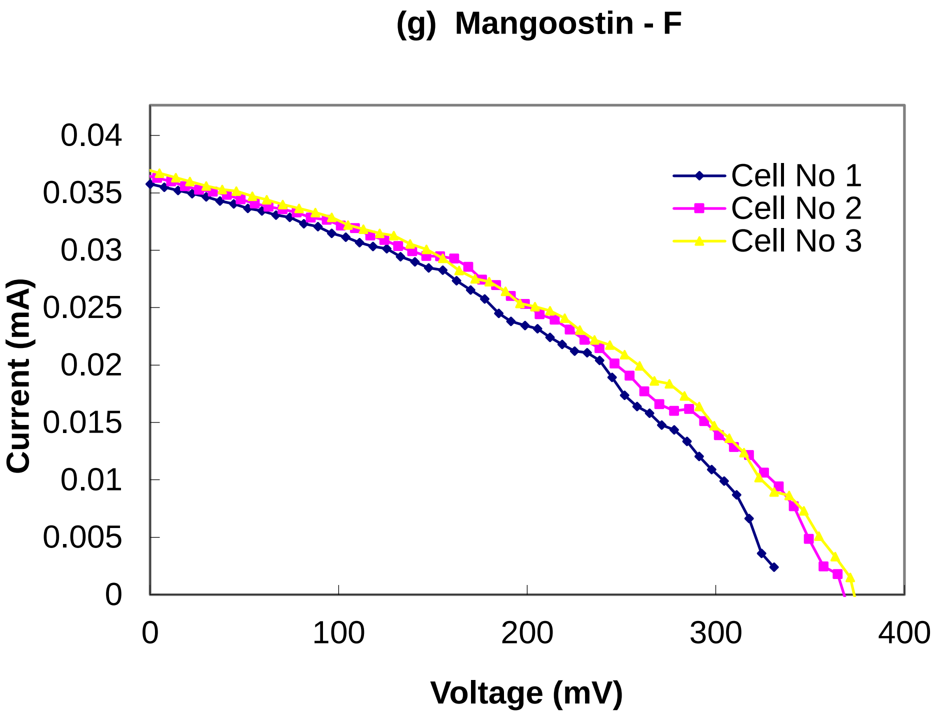

(g) Mangoostin - F

Figure 4.16 IV Characteristics of Mangoostein – F

Cell Description	Cell No 1	Cell No 2	Cell No 3
Open V (mV)	325.3	366.2	372.9
Short I (mA)	0.036	0.036	0.037
Fill Factor (%)	42.15	38.64	38.57
Efficiency (%)	0.02	0.021	0.021
Max Power Point V(mV)	231.8	214.5	243.7
Max Power Point I(mA)	0.021	0.024	0.022
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	48	49	47

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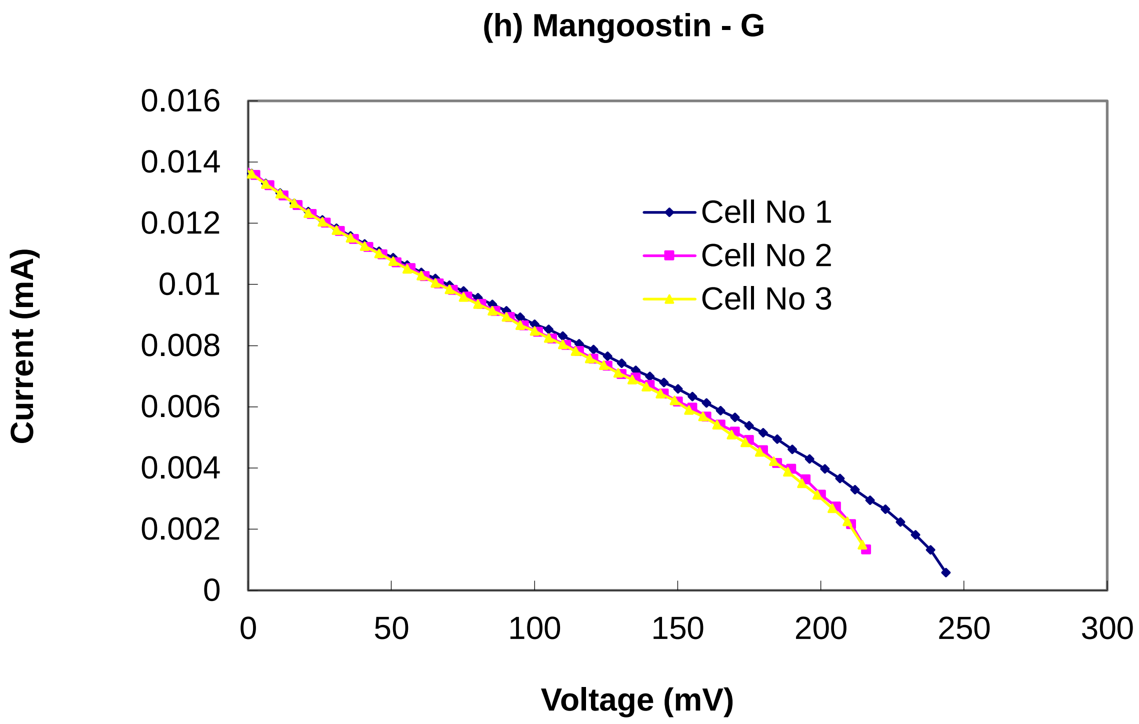


Figure 4.17 IV Characteristics of Mangoostein – G

Cell Description	Cell No 1	Cell No 2	Cell No 3
Open V (mV)	239.6	211.9	211.4
Short I (mA)	0.014	0.014	0.014
Fill Factor (%)	30.2	32.41	32.12
Efficiency (%)	0.004	0.004	0.004
Max Power Point V(mV)	150.2	140.3	144
Max Power Point I(mA)	0.007	0.007	0.006
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	49	44	44

(i) Mangoostin - H

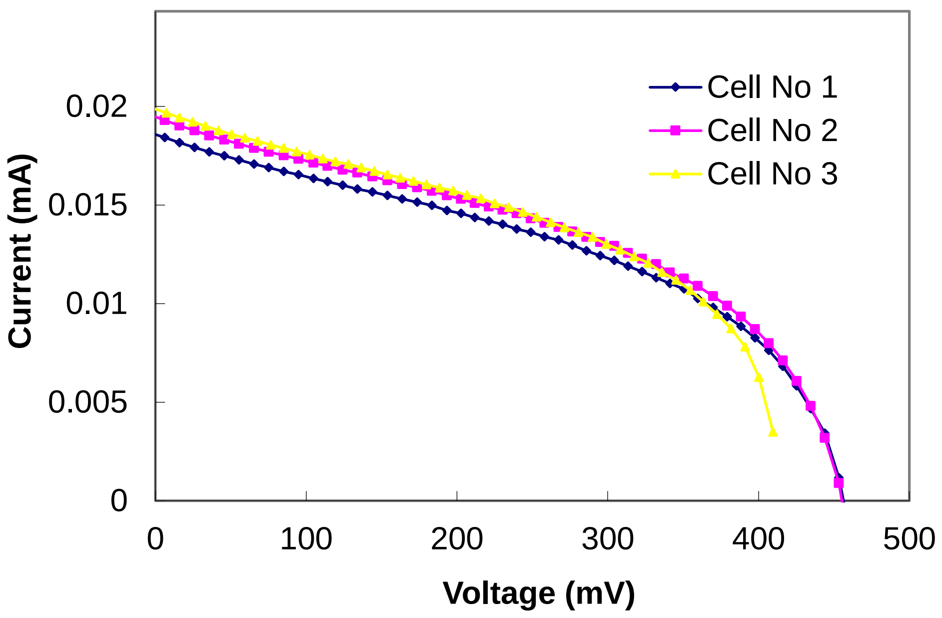


Figure 4.18 IV Characteristics of Mangoostein – H

Cell Description	**Cell No 1**	**Cell No 2**	**Cell No 3**
Open V (mV)	454.2	453.8	402
Short I (mA)	0.018	0.019	0.02
Fill Factor (%)	45.09	45.46	49.71
Efficiency (%)	0.015	0.016	0.016
Max Power Point V(mV)	350.6	332.1	326.9
Max Power Point I(mA)	0.011	0.012	0.012
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	49	49	46

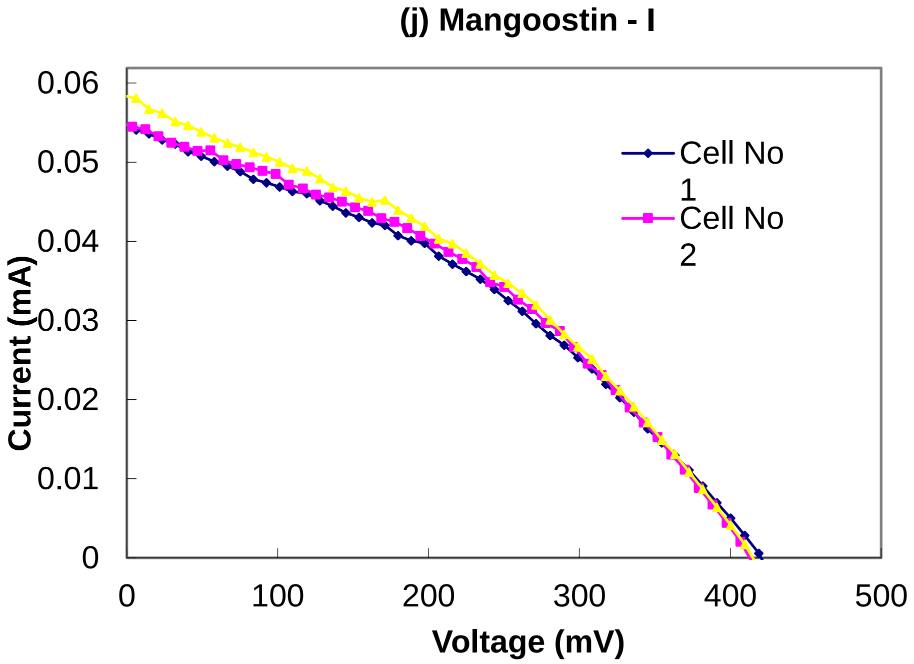


Figure 4.19 IV Characteristics of Mangoostein – I

Cell Description	Cell No 1	Cell No 2	Cell No 3
Open V (mV)	420.3	409.3	411.2
Short I (mA)	0.054	0.055	0.058
Fill Factor (%)	36.13	38.33	36.51
Efficiency (%)	0.033	0.034	0.035
Max Power Point V(mV)	243.7	250.2	252.9
Max Power Point I(mA)	0.034	0.034	0.035
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	48	47	47

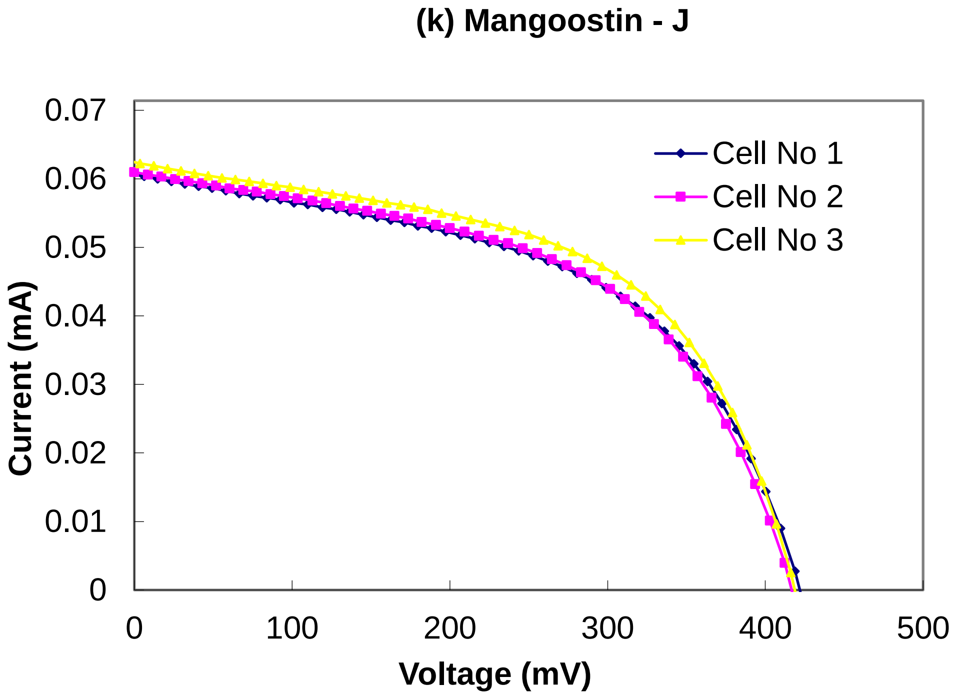


Figure 4.20 IV Characteristics of Mangoostein – J

Cell Description	**Cell No 1**	**Cell No 2**	**Cell No 3**
Open V (mV)	420.7	414.4	417.7
Short I (mA)	0.061	0.06	0.062
Fill Factor (%)	51.85	52.88	54.04
Efficiency (%)	0.053	0.053	0.056
Max Power Point V(mV)	308.3	301.7	305.7
Max Power Point I(mA)	0.043	0.044	0.046
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	48	48	48

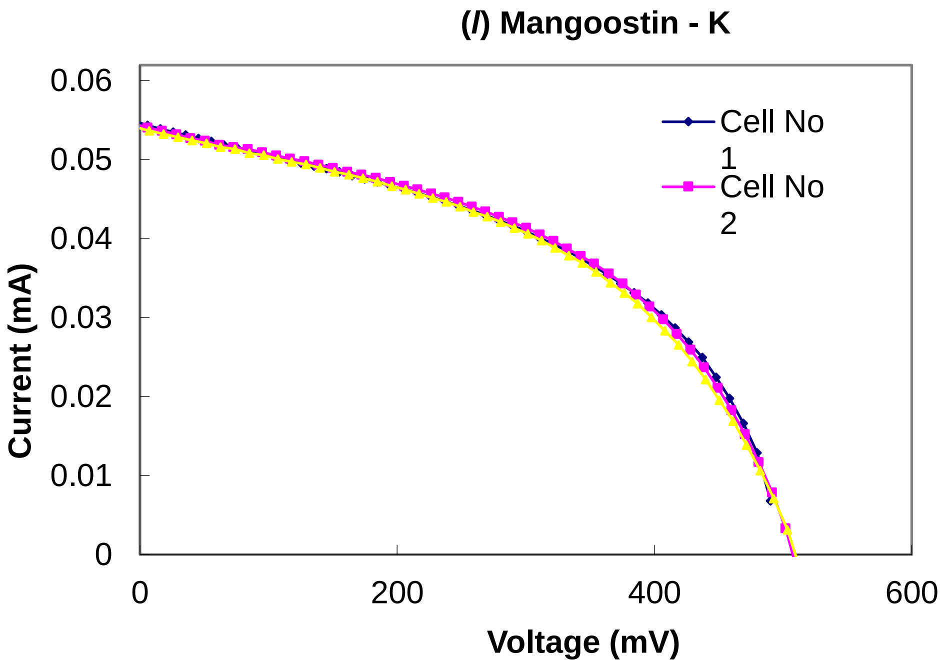


Figure 4.21 IV Characteristics of Mangoostein – K

Cell Description	**Cell No 1**	**Cell No 2**	**Cell No 3**
Open V (mV)	481.7	503.1	504.7
Short I (mA)	0.055	0.054	0.054
Fill Factor (%)	49.12	47.71	46.7
Efficiency (%)	0.052	0.052	0.051
Max Power Point V(mV)	363.3	353.2	344
Max Power Point I(mA)	0.035	0.037	0.037
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	48	48	48

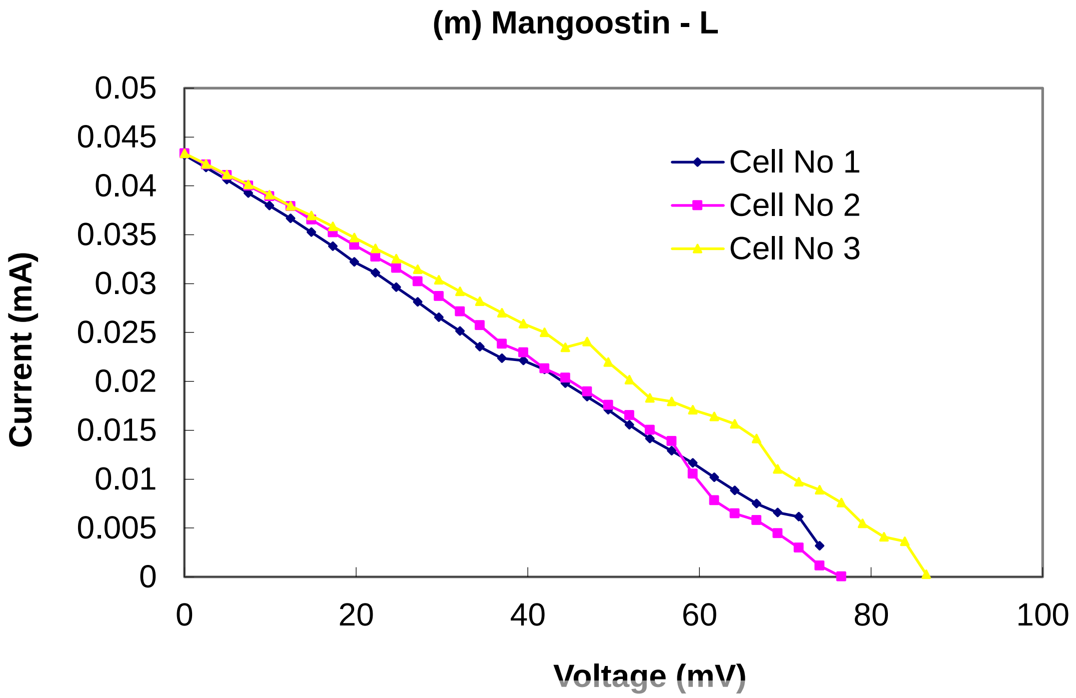


Figure 4.22 IV Characteristics of Mangoostein – L

Cell Description	**Cell No 1**	**Cell No 2**	**Cell No 3**
Open V (mV)	73	75.5	85.8
Short I (mA)	0.043	0.043	0.043
Fill Factor (%)	28.28	27.72	30.38
Efficiency (%)	0.004	0.004	0.005
Max Power Point V(mV)	42	39.5	46.9
Max Power Point I(mA)	0.021	0.023	0.024
Cell Area(cm^2)	0.25	0.25	0.25
Source Intensity	1000	1000	1000
No of Data	31	32	36

Table 4.8 Summary of Purified Mangoostein Dye Extracts

Ser. No	Dye	Open Circuit Voltage V_{OC}(mV)	Short Circuit Curent I_{SC}(mV)	Current Density ID (MA.cm^{-2})	Fill Factor *ff* (%)	Efficiency (η) (%)
1	Mangoostein A_1	574.3	0.058	0.232	67.76	0.09
2	Mangoostein A	501.4	0.28	1.12	46.24	0.26
3	Mangoostein B	495.1	0.08	0.348	53.1	0.09
4	Mangoostein C	685.3	0.64	2.56	60.02	1.053
5	Mangoostein D	411.1	0.62	0.248	43.91	0.044
6	Mangoostein E	47.4	0.081	0.324	55.65	0.075
7	Mangoostein F	372.9	0.037	0.148	38.57	0.021
8	Mangoostein G	239.6	0.014	0.056	30.2	0.004
9	Mangoostein H	453.8	0.019	0.076	45.46	0.016
10	Mangoostein I	411.2	0.058	0.232	36.51	0.035
11	Mangoostein J	417.7	0.062	0.248	54.04	0.056
12	Mangoostein K	503.1	0.054	0.216	47.71	0.052
13	Mangoostein L	85.8	0.043	0.172	30.38	0.005

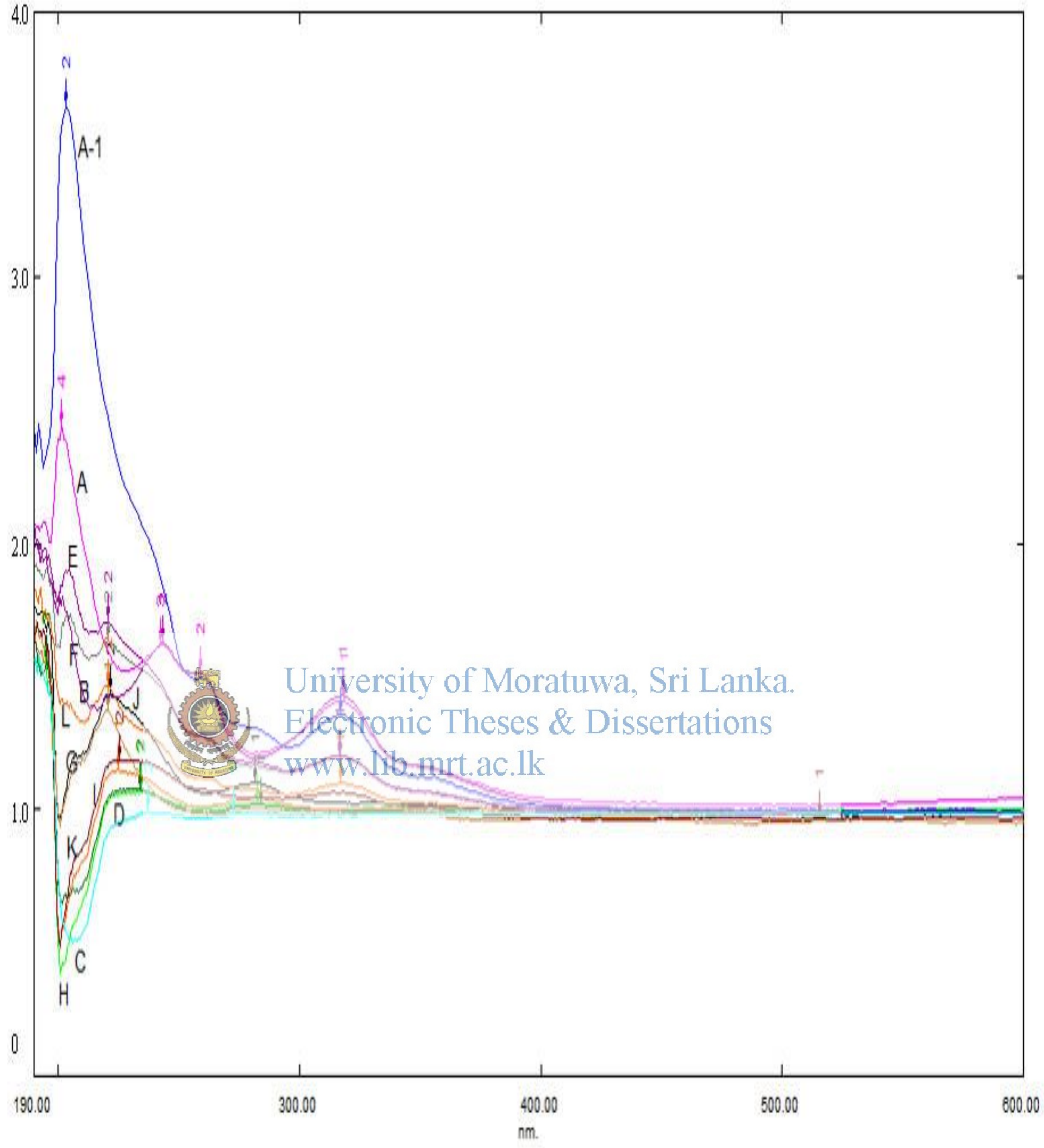


Figure 4.23 UV-visAbsorbance Spectra of Purified Mangoostin Extracts

Reference Figure 4.12, the purified dye extracts of Mangoostin fruit rind A1 (raw), A, B, C,D, E, F, G,H,I,J and K exhibited absorbance peaks mainly in the UV regions of the spectrum at (215 and 320 nm, 210 nm, 205 nm, 202 nm, 220 nm, 215 nm, 212 nm, 232 nm, 198 nm, 196 nm, 195 nm, 194 nm and 194 nm respectively. In addition purified extract A exhibited lesser peaks of decreasing magnitude at 230 nm, 260 nm, 320 nm and 525 nm. Extract C also exhibited the lesser magnitude peak at 240 nm.

Subsequently, detailed purification of the Mangoostein fruit rind extracts as enumerated at Chapter 3.4 Flow Charts I, II, III, IV, V, VI and VII were carried out at the University of Moratuwa and at the IFS , and a highest conversion efficiency of 1.053% obtained for Mangoostein C extract purified with Chloroform. (IV characteristics at para 'd'). Please also see the relevant Absorbance Spectra at Figure 4.12. It has been observed from these results that darker the colour of these dyes, greater would be their conversion efficiencies. Also the addition of trace amounts of concentrated Hydrochloric acid, Acetic acid etc to these natural dyes have been observed during recent tests to alter their pH to < 2 and possibly change their chemical structure, hence to make them appear darker in colour and to increase their conversion efficiencies.

Thereafter when extracts of fruits and vegetables grown in Sri Lanka were used on sensitizers for DSSC's . Mangoostein fruit rind extract in Ethanol consisting of Xanthones and Rutin when purified with Chloroform gave the highest conversion efficiency of 1.053%. This is due to the better charge transfer between this dye and the TiO_2 photoelectrode surface. DSSC's with extract of Fire fern leaf (not endemic to Sri Lanka) consisting of Anthrocyanins , Xanthophylls and Carotenoids , and Ekkiriya wood consisting of Tannins and polyphnolic compounds gave a reasonable efficiencies of 0.802% and 0.547% respectively. Also Anthrocyanins in berry type fruits like Karawalla kabilla, Egg Plant fruit peel etc. have shown relatively high photosensitized performance. This is due the number of = 0 and –OH groups relative to the total number of atoms per molecule is higher for most Anthrocyanins so that they can connect better to TiO_2 photoelectrode surface.

Finding appropriate additives or molecular engineering of dyes to improve the kinetic and energetic properties of dyes for improving Voc without causing dye degradation may result in a further improvement of cell performance, making practical applications of such systems more suitable for economically suitable solar energy devices for our society. The most probable range of target conversion efficiencies of these natural dyes suitable for use in DSSC's would be around 2%.

Even though the efficiency values obtained in this study are not significant with values obtained in the system with very expensive synthetic Ruthenium bipiridyle complexes, the straightforward preparation of photo anodes with semiconductor oxides sensitized with cheap, locally available environmentally friendly natural dyes still enables a much cheaper production of solar cells. Further it provides an interesting and cheap alternative to commonly used expensive and rare synthetic dyes. Therefore investigations are being carried out in searching for efficient natural dyes which can have potential use in these DSSC's.

4.1.2.3 Effect of Co-Sensitization on Absorbance spectra and IV Characteristics of DCSC’s

Introduction

Double layered co-sensitization of test DSSC’s were accomplished as described below using natural dye pigments of Mangoostein and Turmeric. Co-sensitization was done by first adsorbing the dye from Turmeric into the TiO_2 coated FTO glass by dipping it, and then by removing adsorbed dye of the top layer of TiO_2 using a desorption solution before the Mangoostein dye was allowed to adsorb.

Using two natural dyes in a single DSSC for double layered co-sensitization is a novel method employed in DSSC’s in order to improve the absorption of light over a broader wavelength region and hence to improve the current output of them and the overall conversion efficiency. When two different dyes are used as sensitizers by resorting to co-sensitization, it makes light absorption more efficient when a shorter wavelength absorbing dye is positioned in series with a longer wavelength absorbing dye. Thus co-sensitization would increase the conversion efficiency of DSSC’s. Literature review on this aspect of DSSC’s has revealed that it has been first accomplished vide reference [213].

Experimental Details

Initially TiO_2 photoelectrodes were constructed in the usual manner using TiO_2 paste coated on pre-cleaned commercial Flourine doped Tin oxide (FTO) glasses having a surface sheet resistance of 10-12 Ohms. cm^{-2} by the Doctor Blade method. These electrodes were pre-heated to approximately $50^{\circ}C$ using an electric hair drier, and sintered at $450^{\circ}C$ for 30 min.

The natural dye extracts were prepared from fresh, clean cut pieces of 10gm vegetal matter mixed with 100 ml Ethanol Repack Solvent, and heated to $50^{\circ}C$ for 10 min. The residual solids were filtered off, and the extracts were centrifuged to remove any remaining solid pieces. The extracted pigments were stored in dark coloured bottles, to protect them from direct sunlight and stored in a cool dark place until used in DSSC’s.

TiO_2 electrodes were then dipped in respective dye solutions for 24 hours to allow dye molecules sufficient time for adsorption.

The dye mixtures were prepared by mixing two dyes in 1:1 ratio by volume. The TiO_2 electrodes were then taken out and rinsed with Ethanol and air dried. Thereafter test DSSC's were assembled by introducing redox electrolyte of KI//I between the dyed TiO_2 electrode and Platinum counter electrode.

Co-sensitization of two dye layers were introduced to the TiO_2 anodes, consequently, using a co-sensitization procedure described below. First a dried TiO_2 layer was fully immersed in Turmeric extract for 24 hours, taken out and dried without heating. A desorption solution consisting of Ammonium hydroxide in Methanol was introduced to the upper region of the TiO_2 electrode for 30 seconds, and then it was immediately washed away with Ethanol for 20seconds before drying. This de-adsorption process was repeated 3 times. Each repeated de-adsorption effects the desorption depth. Then it was dipped into the second sensitizer of Mangoostein for another stage of adsorption for a period of 24 hours.

Results and Discussion

Table 4.9 Photovoltic parameters of Co- Sensitized DSSC, Mangoostien, Tumeric and their mixture

Sensitizer	Voc (m V)	Isc (m A)	Jsc (m A.cm^{-2})	ff %	η%
Mangoostien	620.2	0.188	0.752	67.26	0.344
Turmeric	533.13	0.173	0.692	61.26	0.234
Mixture	607.00	0.297	1.19	65.4	0.47
Co - Sensitization	585.01	0.37	1.50	45.95	0.64

Table 4.9 and Figure 4.25 shows the Current – Voltage characteristics of DSSC's sensitized with Mangoostien dye, Tumeric dye, their mixture, and the co-sensitized cell obtained from the VIRAJ home –made Current- Voltage Curve Tracing computerized setup coupled to KEITHLEY 2000 Electronic Multimeter with a Potentiostat via computer controlled software at the IFS. A 500 Watt Xenon Lamp with an AM1.5 Filter calibrated with and Eko Pyronometer and Silicon Photo diode was used to obtain simulated sunlight at 100mW. cm^{-2} intensity in the laboratory.

The best performance was exhibited by the co- sensitized cell which showed the conversion efficiency of 0.64% ,with an open circuit voltage (Voc) of 585.01 m V, short circuit current density (Jsc) of 0.37 m A. cm $^{-2}$ Fill factor of 48.95 % under normal irridance of 100W.cm $^{-2}$.

The absorption spectra of Mangoostein dye, Tumeric dye and their mixture (1:1 by volume) were mesarused using the UV245 SHIMADZU UV –vis Spectrophotometer at the IFS with Ethanol as the solvent reference. A trace of Hydrochloric acid (HCl) was added to the dye solutions in order to increase the performance of the absoption.Fig.4.26 depicts the UV –vis absorption spectra of dyes which were already adsorped on to TiO_2 (photo electrode). When a layer of Turmeric dye was adsorbed on to the top of Mangoostein dye layer of TiO_2 electrode the absorption of this co-senstized electrode increased rather significantly.

It was observed from Table 4.9 that the conversion efficiencies of Mangoostein (0.344%) and Tumeric (0.234%) dyes were enhance to 0.47% when equal volumes were mixed. This was futher enhance to 0.64% when the TiO_2 coated electrode of DSSC was sensitized with Mangoostein dye with a thin layer of Tumeric dye deposited on top of it to co-sensitized the DSSC. This technique demonstrates the effectiveness of selective positioning of dyes on DSSC photo electrode to utilize inherent properties such as absorption and adsorption of individual dyes without any alterations or modifications to their structure{215}.

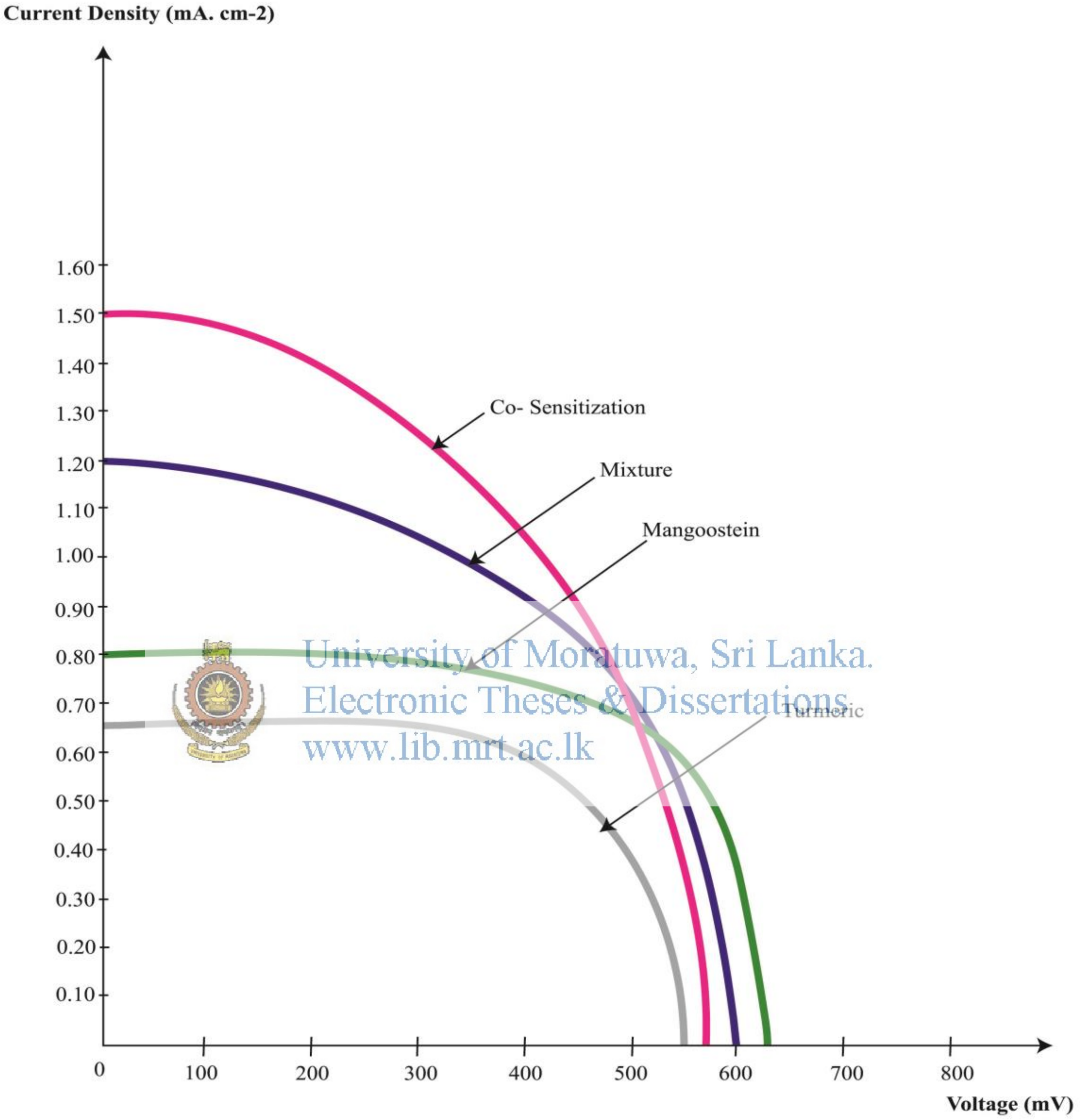


Figure 4.24 Comparison of Current - Voltage Characteristics of the Co- Sensitized DSSC and DSSC's sensitized with Mangoostein, Turmeric and their mixture.

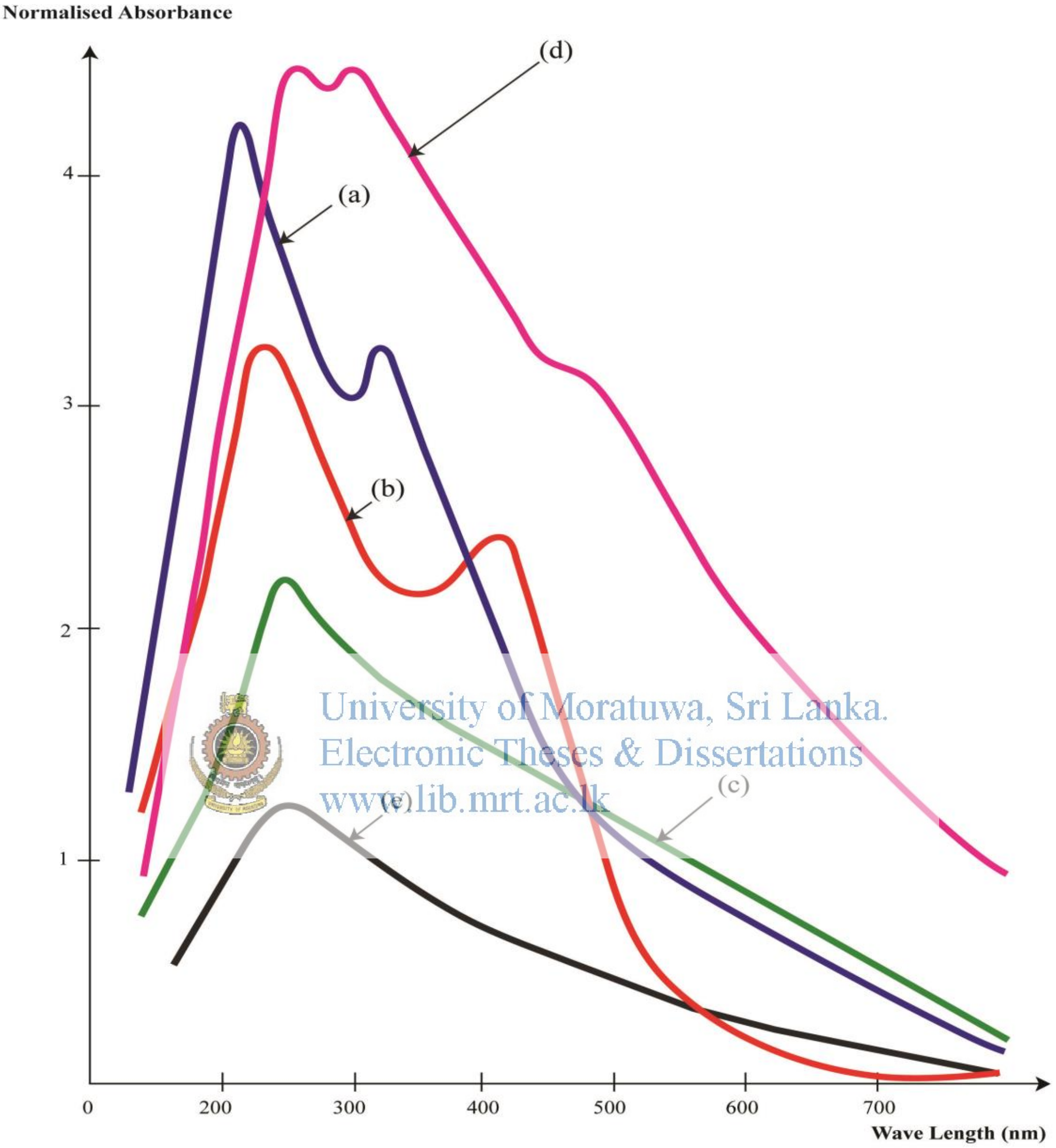


Figure 4.25 UV-vis Absorbance Spectra of DSSC's sensitized with (a) Mangoostein (b) Turmeric (c) their Mixture (d) Co- sensitization (e) TiO_2 .

4.1.2.4 Analysis of Characterization of Natural Dyes

Thus temperature light and pH are the man factors that destabilize the molecular Structure of Natural Dyes of Plants Comprising of Chlorophylls, Carotenoids, Flavonoids, Anthrocyanins and Betalains.

Plant pigmentation occurs due to the electronic structure of the pigments interacting with sunlight to alter the wavelengths that are either transmitted or reflected by the plant tissues. The specific colour will depend on the abilities of the observer, and humans without colour blindness can detect wavelengths between approximately 430 nm and 680 nm representing the visible spectrum of electromagnetic radiations from the Sun. The pigments can be described in two ways: the wavelength of maximum absorbance (λ_{max}) , and the colour perceived by humans. Please also refer to Table.4.9.

(a) Chlorophylls

Chlorophylls which are generally green in colour occur as chlorophyll a, b, c_1, c_2, d and f in chloroplasts of all photosynthetic plants and algae. Chlorophyll a and b occur universally in all plants, and the others in various algae and cynobacteria is an extremely important bimolecular which is critical in photosynthesis, which allows plants to absorb energy with H_2O and CO_2 to make glucose. Chlorophyll in thalakoid membranes of Chlorophyll absorbs light most strongly in the blue portion of the spectrum, followed by the red portion. However, it is a poor absorber of green and near green portions of the spectrum, hence the green colour of chlorophyll – containing tissues. The molecular formula for various types of Chlorophylls are as follows:

Chlorophyll a – $C_{55} H_{72} O_5 N_4 Mg$

Chlorophyll b – $C_{55} H_{70} O_6 N_4 Mg$

Chlorophyll c_1 – $C_{35} H_{30} O_5 N_4 Mg$

Chlorophyll c_2 – $C_{35} H_{28} O_5 N_4 Mg$

Chlorophyll d – $C_{54} H_{70} O_6 N_4 Mg$

Chlorophyll f – $C_{55} H_{72} O_6 N_4 Mg$

Chlorophyll is a chlorine pigment which is structurally similar to and produced by porpherin pigments. At the centre of the chlorine ring is a Magnesium ion. Chlorophylla has a absorption peak of 665 nm or 465 nm, whilst Chlorophyll b of 640 nm and 450 nm.

When leaves degreen in the process of plant senescence, Chlorophyll is converted to a group of colourless tetrapyrroles known as non-fluorescent Chlorophyll catabolites. These compounds have been identified in several ripening fruits also. These compounds have been identified in several ripening fruits also [9], [10] .

It was observed that DSSC's sensitized with natural dyes composed of chlorophyll derivatives in this work such as spinach leaves did not offer good conversion efficiency (16th highest of 0.075%). This is because there are no available bonds between the chlorophyll dye and TiO_2 molecules through which electrons can transport from the excited dye molecules to the TiO_2 film. This result indicates that the interaction between the sensitizer and the TiO_2 film is significant in enhancing the energy conversion efficiency of DSSC's . However these DSSC's yielded a good Open Circuit Voltage of 586.7mV, Short Circuit Current of 0.055 mA. Current Density of 0.22 mA cm^{-2} and a Fill Factor of 58.41%.

(b) Carotenoids

Carotenoids are organic pigments that are found in the chloroplasts and chromoplasts of plants, algae, some bacteria and some fungi. There are over 600 known Carotenoids and they are split into two classes – xanthophylls (which contain oxygen) and carotenes hydrocarbons without oxygen). Cartenoids in general absorb blue and indigo light. They serve two key roles in plants and algae: they absorb light energy for use in photosynthesis, and they protect chlorophyll from photodamage. Carotenoids comprise of α-carotene, β – carotene and lycopene are known as carotenes . Carotenes typically contain only carbon and hydrogen (hydrocarbons) and are in the subclass of unsaturated hydrocarbons. Carotene found in carrots, mangoes, apricots, yams and fall leaves are responsible for their yellows, reds and bright orange colour.

Their colour ranging from pale yellow through bright orange to deep red is directly, linked to their structure. Xanthophylls are often yellow, hence their class name. The double carbon – carbon bonds interact with each other in a process called conjugation which allows electrons in the molecule to move freely across these areas of the molecule. As the number of conjugated double bonds increase, electrons associated with conjugated systems have more room to move, and require less energy to change states.

This causes the range of energies of light absorbed by the molecule to decrease. As more frequencies of light are absorbed from the short end of the visible spectrum, the compounds acquire an increasingly red appearance.

The most common carotenoids include lycopene, canxanthin, astraxanthin and beta carotene . In plants the xanthophyll lutin is the most abundant carotenoid found in mature leaves are often not obvious because of the masking presence of chlorophyll. When chlorophyll is not present as in young foliage and in dying deciduos foliage such as Autumn leaves in temperate climates, the yellows, reds, and oranges of the carotenoids are predominant. For the same reason, carotenoid colours due to lycopene often predominate in ripe fruit like oranges, bannas, guava, tomatoes, red grape fruit, papaya, watermelon etc. after being unmarked by the disappearance of chlorophyll .

However, the reds, the purples, and their blended combinations that decorate autumn foliage usually comes from another group of pigments in the cells called anthrocyanins. Unlike the cerotenoids, these pigment not present in the leave throughout the growing season, but are actively produced towards of the summer [176] , [209] , [210] .

The Barna Flower inflorescence is a purple coloured scathe with high concentrations of Carotene, Pantothenenate, Biotin, Pantothermic acid, Niacin, Pyridoxine, Glyoalkaloids and reddish brown Tannins. It is not known which chemical is mainly responsible for its fairly good sensitization of DSSC's using this dye extract, but it is considered that Tannins may be reason. It yielded a conversion efficiency of 0.357% (6th highest) with an Open Circuit Voltage of 414 mV, Short Circuit Current of 0.477 mA, Current Density of 0.763 mA. cm^{-2}, and a Fill Factor of 45.2% .

The root of Venivel plant yielded a yellowish dye comprising Carotenoids, Berberine, Protoberine and Jatrorrhizine. It yielded a conversion efficiency of 0.097% (13th highest), good Open Circuit Voltage of 529.9mV, Short Circuit Current of 0.079 mA, Current Density of 0.316 $mA.cm^{-2}$ and Fill Factor of 57.59%.

The skin of orange fruit extracted with Ethanol gave a yellow coloured dye comprising of caretenoids and flavanoids and flavones. The conversion efficiency was 0.091% (14th highest) with a good Open Circuit Voltage of 627.5 mV,Short Circuit Current of 0.05 mA, Current Density of 0.1 0 mA. cm^{-2}, and a good Fill Factor of 73.1%.

(c) Flavanoids

Flavanoids are the yellow plant pigments seen in lemons , oranges and grapefruit . For flower colouration, they produce yellow or red/blue pigmentation in petals designed to attract pollinator insects. In higher plants, flavanoids are involved in UV filtration symbiotic nitrogen fixation and floral pigmentation. There are over 5000 naturally occurring flavanoids and have been subdivided into Flavorones, flavanols, Flavanones and Flavanonols comprise Luteolin, Apigenin, Tangeritin; Flavanols comprise Overcetin, Kaempterol, Myricetin, Fisetin, Galangnis, Pachypodol, Pyronflavonols and Furanflavonoids; Flavanones comprise Hesperetin, Narinigenin, Eriodictyol and Havoeriodityl Flavanonols comprise Taxifolin, Dihydroquercetin and Dihydrokaemperol.

The ripe fruit rind of Mangooestein(Garcinia mangostana) which is reddish brown in colour is rich in flavonoid antioxidants of 48 different Xanthones. These consist of Alpha Mangoostein, Beta-Mangoostein, Gamma Mangoostein, Mangoosteione, Smeathxanthone A, Rutin ,3-Mangoostein ,8-Desooxygatnin, Getamin and 9 – Hydroxycolaboxanthone, and is considered nature’s most abundant source of xanthones. As well as the most potent source of Xanthones in any single fruit, the whole fruit of Mangoostein is also an excellent source of other flavanoids. These include Rutin, Pyroenthrocyanins and EGFC Catechins [178] , [179] .

Rutin which has the identical Absorption vs. Wavelength Spectra of Mangoostein fruit rind extract is considered to be essential ingredient of Mangoostein which has the highest conversion efficiency of 1.053% after purification with Chloroform (0.34% initially)of all Natural Dyes of Plants growing in Sri Lanka tested and analysed. Also it has a good open circuit voltage of 685.3 mV, short circuit current of 0.640 mA, Current Density of 2.56 mA and a Fill Factor of 60.02%. Please refer to Table 4.6 – Table of Results, Serial No.1.

The wood extract of Ekkiriya wood (Querns rubra) is dark red to deep brown interlocked grain with a coarse even texture, and is similar to European Oak tree. The wood consists of cellulose, hemicelluloses, lignin, tannins and traces of lipids (oils, fats, and waxes) and they bind the wood because of their chemical structure. The essential chemical compound in Ekkiniya wood is its dark reddish brown Tannin which is astringent, bitter plant phenolic compound that binds to and precipitates amino acid and alkaloids. Thus sufficient hydroxyls and other suitable groups such as carboxyls form strong complexes and proteins and other macromolecules. The tannins compounds ploy as pesticides and in plant growth regulation. These comprise hydrolysable tannins (Gallic acid) and non-hydrolysable or condensed tannins which are flavones. The extracts of Ekkinya wood when used as a sensitizer in DSSC’s yielded a good conversion efficiency of 0.547% 3rd highest open circuit voltage of 414.2%, good short circuit current of 0.58 mA, current Density of 2.32 mA and a fill factor of 56.86%. Please see Table 4.6 – Table of Results, Serial Nos. 3.

Egg Plant (Solanum melongenal fruit skin is rich in about 14 phenolic compounds which as components of ligroin, tannins, masunin, (as anthrocyonin) and occurs as enter in glucosides. The block to purple pigments of Egg Plant fruit skin is attributed to the anthrocyanin content and the presence of several unique phenolic and condensed tannins. They also central Ghycoalkaloids which are defensive allelochemicals against a number of pathogens and predators including fungi, viruses, bacteria, insects and worms. The black-purple coloured Anthrocyanus and Glyvoalkaloid pyrrents in Egg Plant fruit skin contribute to their good sensitization when used in DSSC's. This yielded a good conversion efficiency of 0.485% (4^{TH} highest,) Open circuit voltage of 410.4 mV, short circuit Current of 0.524 mA, good current Density of 2.09 mA and Fill Factor of 56.42%. Please see Table 4.6 – Table of Results, Serial No.4.

The skin of the fruit of Black Grape is rich in flavanoids, plenolic compounds like natural phenol, polypherols, phenolic acids, stiberoids, dihydro flavanols and anthrocyanins. Its deep purple dye yielded a mesondale concession efficiency of 0.147% (9th highest) with an Open Circuit Voltage of 416.5 mV, Short Circuit Current of 0.161 mA, Current Density of 0.644 mA. Cm-2 and a Fill Factor of 54.87%. It is considered that the combination of all chemical compounds present in its deep purple dye extract in Ethanol is responsible for its reasonable sensitization when used in DSSC's.

The dye extract of Walmadata tree trunk wood comprising cellulose, hemicellulose, tannins and linguine yielded a yellowish dye when extracted with Ethanol. I yielded a conversion efficiency of 0.12% (12th highest) with a good Open Circuit Voltage of 520.7 mV, Short Circuit Current of 0.084 mA, Current Density of 0.336 mA. cm^{-2} with a Fill Factor of 57.66%.

(d) Anthrocyanins

Anthrocyanins uses in DSSC's play role in the colour of ripping fruit and are water soluble red, purple or blue depending on their pH. Anthrocyan's are found in most berries egg plant peels grapes, red cabbage, black rice and lives. They belong to a parent class of polyphenoly called flavanoids. Anthrocyanins occur in all tissue of higher plants, including leaves, stems, flowers, fruits and stems. Anthrotanthins are clear, white to yellow counterparts of Anthrocyanins occurring in plants. Anthrocyanins are derived from Anthrocyanidins by adding pendent sugars.

In flowers bright-reds and purples are adeptive for attracting pollinators. In fruits the colourful skins also attract the attentionof animals, which may eat the fruits and disperse the seeds. Also in photosynthetic tissues such as leaves, arthronyanins act as a "sunscreen" to protect the cells from high-light damage by absorbing blue-green and ultraviolet light, thereby protecting the tissues from highlight damage by absorbing blue-green and ultraviolet light, thereby protecting the tissues from high light stress.

Also in addition to their role as light –attenuators , anthrocyanins also act as powerful antioxidants.

Anthrocyanins can be used as pH indicators because their colour changes with pH: they are pink in acidic solutions with pH <7, purple in neutral solutions (pH ≈ >), greenish-yellow in alkaline solutions (pH>7) , and colourless in very alkaline solutions, where the pigment is completely reduced.

Anthronyanins and betalains have never been found in the same plant.

Plants rich in anthrocyanins are fruit berries of strawberry, blackberry, black current, raspberry, cranberry, bilberry, black rice, turmeric, eggplant peel, mango, grapes, pears, pineapple, red cabbage, peaches , watermelon and olives etc [216].

The Fire Fern plant, has prominent maroons red- leaves. These leaves contain maroon-red Anthrocyanins and yellow Xanthophylls which mask the green coloured Chlorophyll essential for photosynthesis. It also contains Carotenoids comprising Carotene (yellow) and Lycopene (orange red). These Anthrocyanins appear red, blue, purple or magenta depending on pH. Also Xanthophylls comprising flavanoids such as Flavone (deep yellow) and Lycopene (orange red) and Flaval (yellow) are also present in these leaves. It is considered that the presence of high concentration of maroon-red Anthrocyanins with lesser amount of yellow Xanthophylls, Carotene (yellow) and Lycopene (orange red) are the factors which attribute to the high sensitization of test DSSC's produced from Fire fern leaf extracts (with a trace of conc HCl) in Ethanol. These DSSC's possess a good conversion efficiency of 0.802% (2nd highest), good Open Circuit Voltage of 405.1 mV, Short Circuit Current of 1.032 mA, Current Density of 4.128 mA cm-2 and a Fill Factor of 47.97's. Please see Table 4.6 – Table of Results Serial No.2.

(e) Betalains

Betalains are a class of red and yellow indole derived pigments found in plants of caryophylales where they replace the anthrocyanin pigments. They are found in fruits, leaves stem and root of plants. The red to purple colour of beetroot tuber comes from Betalain pigments. Betalains include red to violet Betacyanins comprising betanin, isobetanin, probetarin and neobetarin. They also include Betaxanthins which appear yellow to orange comprising Vulgaxanthin, miroxanthin, portulaxantin and indicaxanthin. Beetroot contains 2 Betacyanins, Betanin and a derivative.

The reddish pigments found in most plant are not due to betalains but anthrocyanins. Although both are water-soluble pigments they are not chemically alike (only Betalains contain nitrogen) and so far have never both been found within the same plant. Betalains contain nitrogen but anthrocyamins do not.

Betacyanins absorb in the 535-550 nm range and betaxanthins in the 475 – 480 nm range. Like caroteroids and flavanoids, betalains also seem to play an important role in attracting animals to flowers and fruits, and produce a similar range of colours. Betalain may occur in any part of the plant , including the petals of flowers fruits leaves stems and roots[176].

Beetroot tuber contains Betacyanins which is a water soluble reddish-purple pigmen containing Betanins which is a glycoside. Other Betalains present are isobetanin, probetanin and neobetains The natural dyes present in the beetroot tuber when used as a sensitizer in DSSC's yielded a conversion efficiency of 0.32% (7th highest) with an Open Circuit Voltage of 441.2 mV, Short Circuit Current of 0.328%,Current Density of 1.32%, Factor of 55.36%. It is considered that reddish-purple Betalains and Betanins present in Beetroot contribute to its fairly good conversion efficiency.

Please refer to paragraph 4.2.2. on Results obtained on measurements of Absorbance Spectra measurements of various natural dyes. To summarise absorbance peaks at 210 nm, 240 nm, 320 nm have been obtained for Mangoostein fruit rind extract dye (Figure 4.6); 210 nm, 42.5 nm for Turmeric root dye; 206 nm for Ekkiriya wood dye ;205 nm for Fire fern dye (Figure 4.7) . Also 210 nm for Ekkiriya wood, 208 nm for Karawela Kakbilla (Purple fruit), 206 nm for Red Plum, 206 nm for Black Grape ,206 nm for Begonia, 207 nm for Beetroot, 207 nm for Red Hart, 204 nm for Eggplant, 200 nm for Spinach.

It is observed that dye solutions obtained from Mangoostein and Turmeric absorb more in the blue side (left) of the electro-magnetic spectrum than the other dyes. Also the absorbance peaks of Mangoostein at 320 nm and that of 425 nm for Turmeric indicate that they absorb near the centre of the spectrum and towards the red end of the spectrum for these dyes suggest that if these peks could be moved towards the red end of the spectrum could provide enhanced conversion efficiencies. Thus mixtures of these two dyes in equal volumes should provide a synergistic effect. It was also observed when the pH values of these dyes when closer to 1 (acidic) gave enhanced conversion efficiencies. However these acidic solutions could adversely affect corrosiveness of the two electrodes on FTO glasses of DSSC's in the long run.

Also as observed at paragraph 4.2.4 on the effect of Co-sensitization of selected natural dyes deposited on top of each other in DSSC's could be used to further enhance their conversion efficies than when used as single layered dyes.

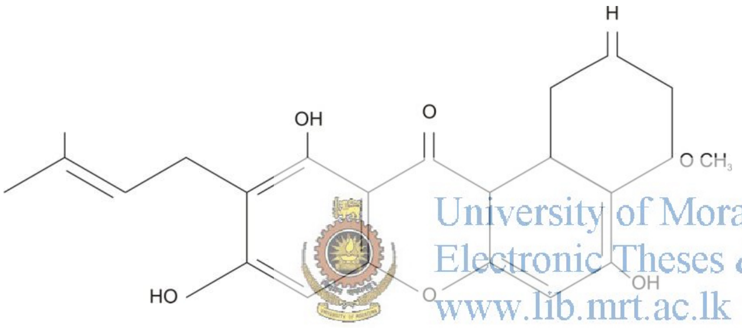
Therefore it is proposed that further research be done on dark coloured natural dyes to identify a 'super dye' which is also of low cost, environmentally friendly and having a useful lifetime in excess of 10 years or more

4.1.3 STRUCTURAL CHARACTERISTICS OF BEST NATURAL DYES OF PLANTS IDENTIFIED FOR SENSITIZERS

(a) Mangoostein fruit rind (Garcinia mangostana)

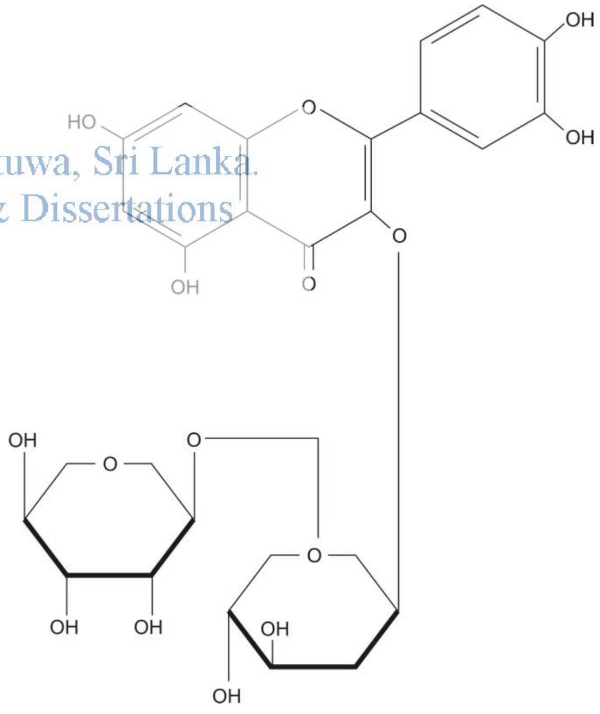
Mangoostein fruit is endemic to South East Asia (including Sri Lanka), and produces a fruit with a white sweet pulp covered by a reddish brown colour pericarp (rind). The rind is rich in flavonoid antioxidants of 48 different Xanthones. These consist of Alpha-Mangoostein (brown red), Beta-Mangoostein, Gamma Mangoostein, Mangoosteinone, Smeathxanthone A, Rutin ; 3 – Isomangoostein, 8 – Desooxygatanin, Getanin and 9 – Hydroxycolaboxanthone and is considered nature's most abundant source of Xanthones.

As well as the most potent source of Xanthones in any single fruit, the whole fruit of Mangoostin is also an excellent source of other flavanoids. These include Rutin (reddish brown), Pyroanthrocyanins and EGEC Catachins.



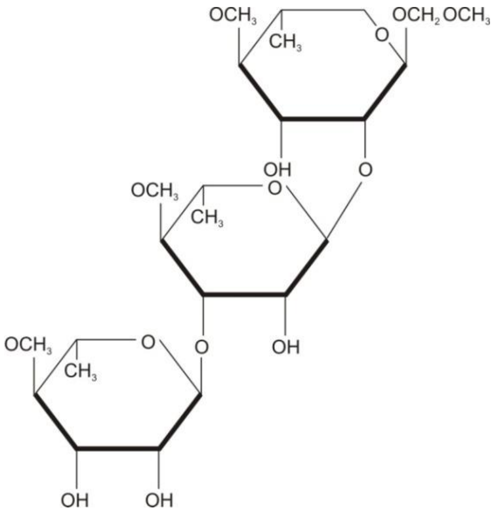
Mangoostein

Molecular formula $C_{24} H_{26} O_6$



Rutin

Molecular formula $C_{27} H_{36} O_{16}$



Mangoosteen trihamnasid

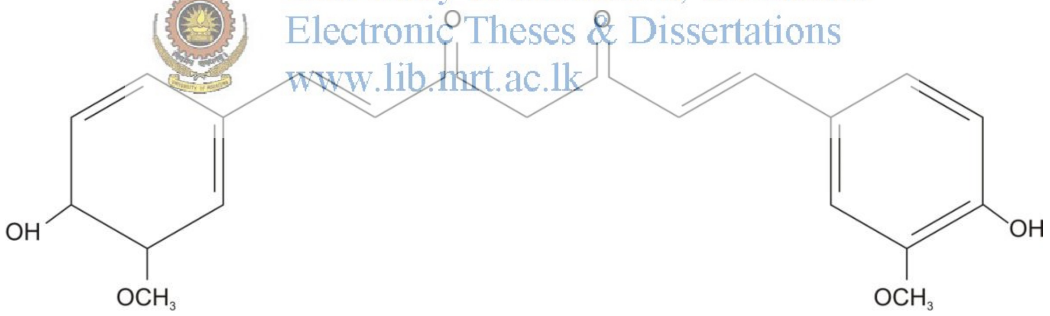
Figure 4.26 Chemical structure of Mangoosteine fruit rind dye

It is believed that the presence of 48 Xanthones,Rutin and other Flavanoids in the ripe Mangoostein fruit rind exact in Ethanol is mainly responsible for its relatively high sensitization in DSSC's due to the combined synergistic effect of these individual dyes.

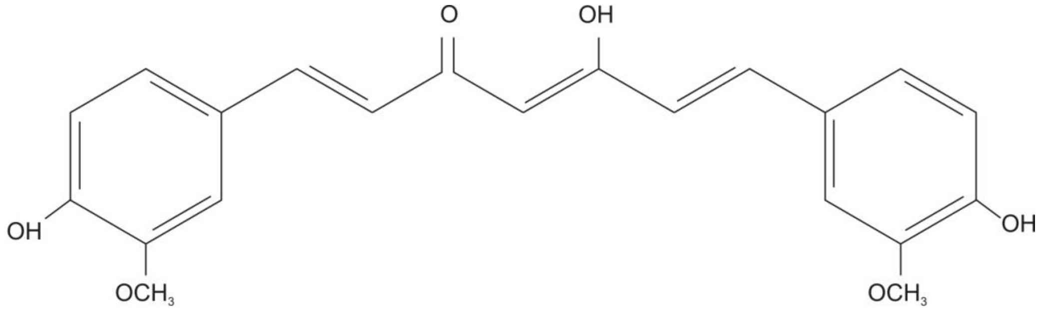
(Please note that the substitution of ripe Mangoostein fruit rind unpurified dye extract to sensitize DSSC’s by synthetic Rutin was tested and analysed vide “List of Publications”,item VII at page xx of this Thesis.It was observed that both these dyes have almost identical chemical, electrical and electronic characteristics . However, as synthetic Rutin dye is scarce and very expensive (US$ 30 per 50 mg)compared to natural Mangoostein dye which is cheap,freely available ,envioronmentally friendly and durable, it would be very cost effective to develop practical DSSC’s with Mangoostein dye after conducting further research to enhance it’s conversion efficiency).

(b) Turmeric *(Curcumin longa)*

Turmeric rhizome root contains upto 5% curcumin, a polyphenol. Curcumin is the active ingredient of Turmeric. It exists at least in two tautomeric forms, Keto and Enol. The Keto form is preferred in solid phase and the Enol form in solution. Curcumin is a pH indicator and in acidic solutions (pH <7.4) it turns yellow whereas in basic (pH >8.6) solutions it turns bright red. The extract of Turmeric root yields a deep orange yellow dye.



Curcumin – Keto form



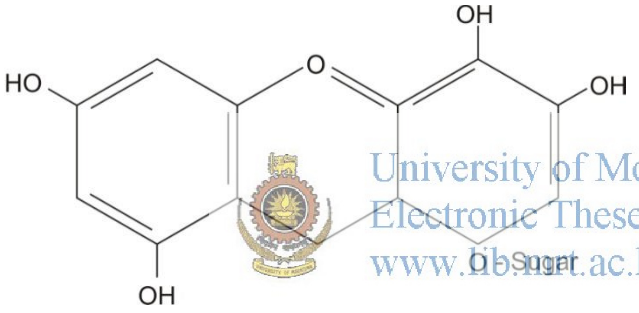
Curcumin – Figure 4.27 Enol form Chemical structure of Turmeric root dye

The presence of deep orange yellow Curcumin in the Turmeric rhizome root extract in Ethanol is the essential ingredient which accounts for its relatively high sensitization in test DSSC's.

(c) Fire Fern (Oxalis hedyscoroides)

The Fire fern a rare exotic garden plant grows to a height of about 1 foot and in a native of Colombia, Venezuela and Ecuador in Central America. It thrives in bright sunny areas with hot and humid temperatures. It has prominent maroon-red leaves with a deterrent sour taste to animals and humans due to its Oxalic acid. The leaves also contain chlorophyll (green) essential for photosynthesis, even through the colour of its leaves is masked by the excessive maroon-red Anthrocyanins and yellow Xanthophylls. It also consists of Carotenoids comprising Carotene (yellow) and Lycopene (Orange red).

Anthrocyanins are water soluble vacuole pigments and they appear red, blue, purple or magenta depending on pH.



Red at pH<3
Violet at pH = 7 – 8
Blue at pH > 7 - 8

Cynodin Anthrocyanin

Figure 4.28 Chemical structure of Fire fern leaf dye

Xanthophylls of this plant consists of flavanoids comprising flavone (deep yellow) and Flaval (yellow).

It is evident that the presence of high concentration of maroon-red Anthrocyanins with lesser amount of yellow Xanthophylls, Carotene (yellow) and Lycopene (orange red) are the factors which attribute to the high sensitization of test DSSC's produced from Fire fern leaf extracts in Ethanol.

(d) Ekkiriya Wood (Quercus rubra)

The wood of this tree consists of dark red to deep brown interlocked grain with a coarse/ even texture and is used for boat building, bridge construction, railway sleepers etc. It is similar to European Oak tree. The wood consists of cellulose, hemicellulose, lignin, tannins and traces of lipids (oils, fats and waxes) and they bind the wood because of their chemical structure.

The essential chemical component in Ekkiriya wood is its dark reddish-brown Tannin which is as astringent, bitter plant polyphenolic compound that binds to and precipitates amino acids and alkaloids. Thus sufficient hydroxyls and other suitable groups such as carboxyls to form strong complexes with proteins and other macromolecules. These tannin compounds play as pesticides, and in plant growth regulation. There are two classes of Tannins in plants – Hydrolysable tannins (Gallic acid) and Non Hydrolysable or condensed tannins (Flavone) as shown below.

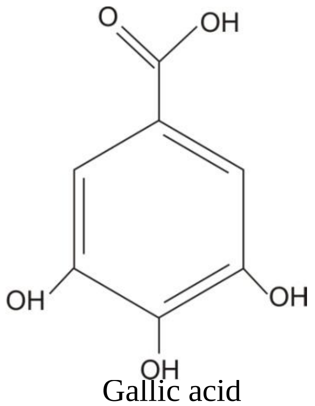
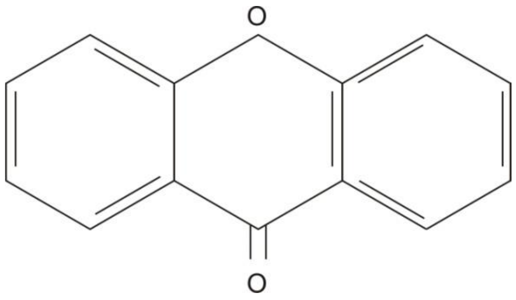
Base Unit :	 Gallic acid	 Flavone
Class/Polymer :	Hydrolysable Tannins	Non Hydrolysable or Condensed Tannins

Figure 4.29 Two classes of Tannins

The presence of dark reddish brown Tannins in Ekkriya wood extract in Ethanol is mainly responsible for relatively good sensitization for use in DSSC's.

(e) Eggplant Fruit Skin (Solanum melongenal)

Eggplant or brinjal is a native plant of India, China, Africa, Central America and Sri Lanka for a long time. Eggplant fruit has been a common vegetable in our diet since ancient times and when fresh contains about 7% of dry matter, 1% protein and 4% carbohydrates and the rest being water. It also contains Vitamins B1, B2, B6 and C and minerals Sodium, Copper, Potassium, Sulphur and Chlorine. It is also rich in about 14 phenolic compounds which are components of lignins, tannins, masunin (an anthrocyanin), and also occurs as esters in glucosides.

The black to purple pigmentation of eggplant fruit peel is attributed to the anthrocyanin content and the presence of several unique phenolic and condensed tannins as shown in Figure 15. They also contain Glycoalkaloids which are defensive allelochemicals against a number of pathogens and predators including fungi, viruses, bacteria, insects and worms. These Glycoalkoids consists of three portions: a non polar steroid unit and a basic portion with either an indolizidine or oxa-aglycone part: a polar water soluble moiety with three or four monosaccharides attached to the 3 –OH group of the fruit ring of the aglycone. The common glycoalkaloid aglycones in eggplant fruit peel is presented here.

The black-purple coloured Anthrocyanins and Glycoalkaloids pigments in Eggplant fruit peel contribute to their good sensitization when used in DSSC's.

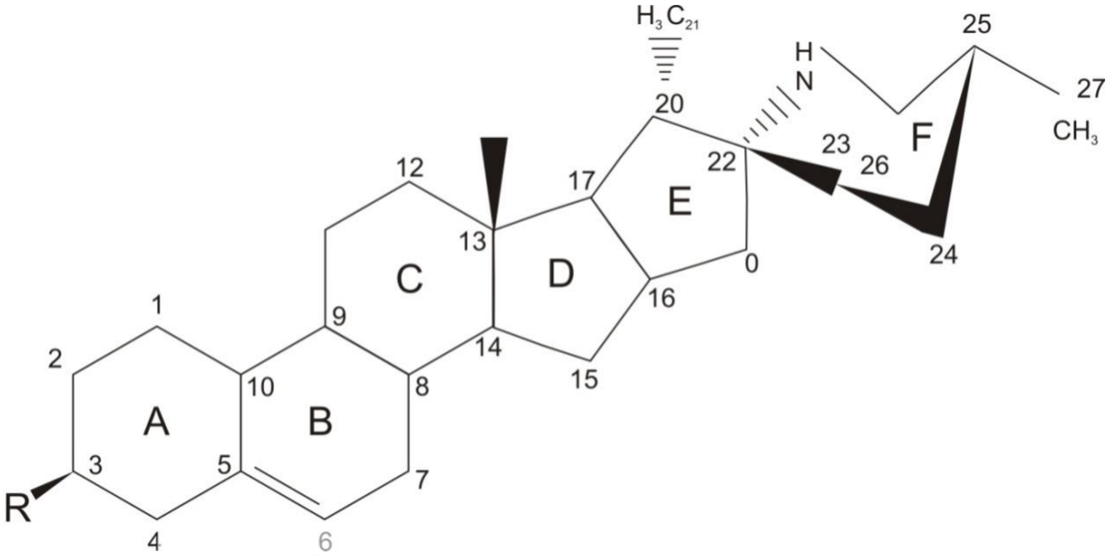


Figure 4.30 Common Glycoalkoid aglycones in Eggplant fruit peel.

(f) Karawala kabilla fruit (B. Caylonicus)

It is a small round reddish – purple coloured sweet-sour berry type fruit endemic to South East Asia. It is high in fibre, Vitamin C, sugars and anthrocynins, Formic acid, Tannic polyhenol compounds. Tannic acid is considered to be the essential ingredient providing a natural dye for this plant fruit. Tannic compounds play a role in protection from predators and they comprise Gallic acid esters and proanthrocyanadins.

The reddish-purple coloured Tannin polyphenol compounds along with Anthrocyanins providing a natural dye is responsible for fairly good sensitization.

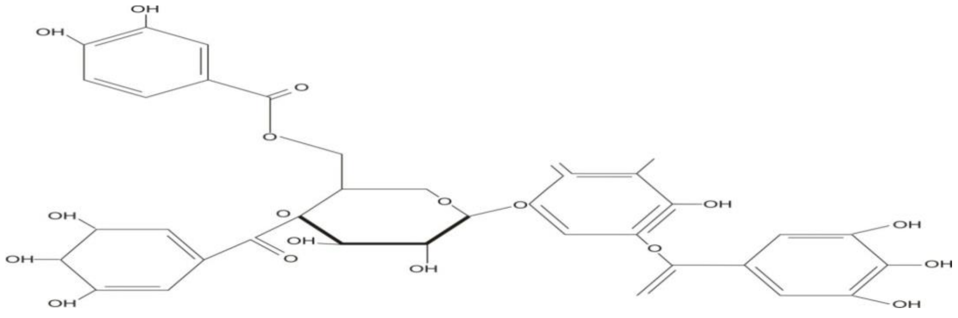


Figure 4.31 Tannic acid a type of Tannin present in Karawala kabilla fruit

(g) Banana Flower Inflorescence (Mussa acuminata)

Banana is a herbaceous plant of genus Mussa and is one of the oldest cultivated plants in South East Asia, Africa and Papua New Guinea. Its fruit which is yellow, purple or red is soft and sweet and rich in starch and grows in clusters hanging from the top of the plant. The inflorescence of banana flowers bear purple coloured scathes enclosing and protecting its flowers prior to their pollination. It is rich in Carotene, Pantothermic acid, Niacin, Pyridoxine, Choline, Folic and Thiamine, Riboflavine, Pantothenate, Biotin, Folate and minerals Potassium, Iron, Magnesium, Calcium, Phosphorous, Iron and Zinc. It is also rich in Glycoalakaloids and reddish brown Tannins for protection of individual flowers from predators.

(h) Beetroot tuber (Beta vulgarins)

Beetroot is a common edible root vegetable grown in North America, Europe, Asia and Africa. It contains a Betalain which is a water solvable reddish – purple pigment containing Betamin which is a glucocide and it hydrolyses into sugar glucose and betanidin. Its colour is sensitive to pH. Other betalains known to occur in beets are isobetanin, probetanin and neobetanin. Betalanins are aromatic indole derivatives synthesized from tyrosine. Each betalain is a glucoside and consists of a sugar and a coloured portion. Their synthesis is promoted by light.

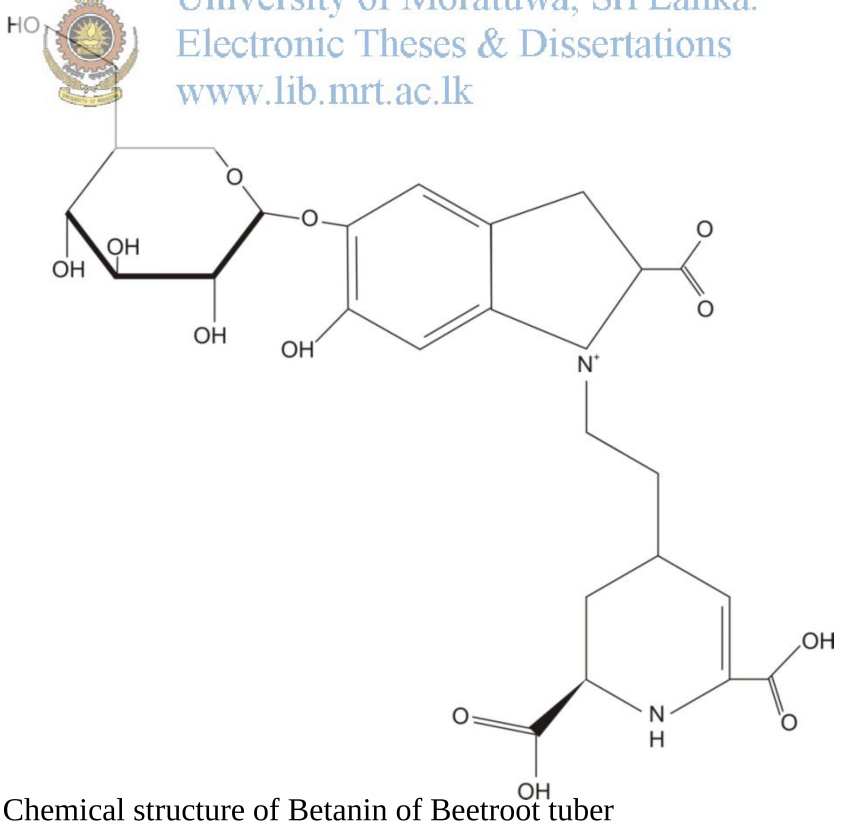


Figure 4.32 Chemical structure of Betanin of Beetroot tuber

Reddish purple Betalain natural dye present in Beetroot tuber accounts for good sensitization in test DSSC's.

(i) Black Grape Skin (Vitis vinifera)

Black grape skins conisit of phenolic compounds – natural phenol and polyphenols, phenolic acids, stibenoids, flavanoids, dihydraflavanols, anthrocyanins, flavanal monomers (catachins) and flavanol polymers (proanthrocyanadins). This large group of natural phenols can be broadly separated into two categories – flavanoids and non-flavanoids. Flavanoids include anthrocyanins and Tannins which contribute to the reddish colour and its taste especially when fermented to produce wines. The non flavanoids include silbenoids such as reseveratrol and phenolic acids such as benzonic, cafferic and cinnamic acids. The natural dye extracted from black grapes with their skin is essentially due to its Flavane Non-Hydrolysable or condensed Tannins. Please see Figure 4 also.

(j) Croton leaf (Croton gratissimus)

Croton is a garden plant endemic to South East Asia. Its reddish-brown-yellow leaves yield Cembranolides, Cupeol, Edesmene 1B, 6 α – dial, α glutinol, 24- ethylcholastra - 4 etc. Crotonaldehyde is a multifunctional molecule and a chemical compound with formula CH_3 CH = CHCHO. It is an unsaturated aldehyde molecule soluble in water and miscible in organic solvents, and is an irritant to humans and animals.

Figure 4.33 Crotonaldehyde from Croton leaf

(k) Begonia Black Velvet leaf (Begoniaceae)

It is garden plant endemic to South East Asia with deep purple-brown coloured leaves. The defense chemicals produced by this plant are phytoanticipin toxins phenolic and iridoid glycosides, glucosinolates and saponins which are stored in vacuoles of plant cells. The deep purple-brown coloured dye consisting of phytoanticipin phenolic glucosides and saponins contribute to the fairly good sensitization characteristics in test DSSC's.

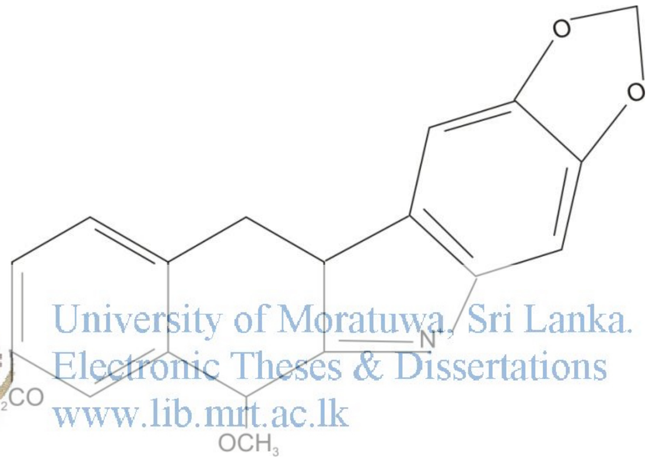
(l) Red Hart leaf (Ceanothusspinosus)

This tree is endemic of Japan, North America and Africa. Its reddish – coloured leaves produces phenolic toxins to protect it from its predators, and this contributes to the reasonable sensitization of DSSC test cells.

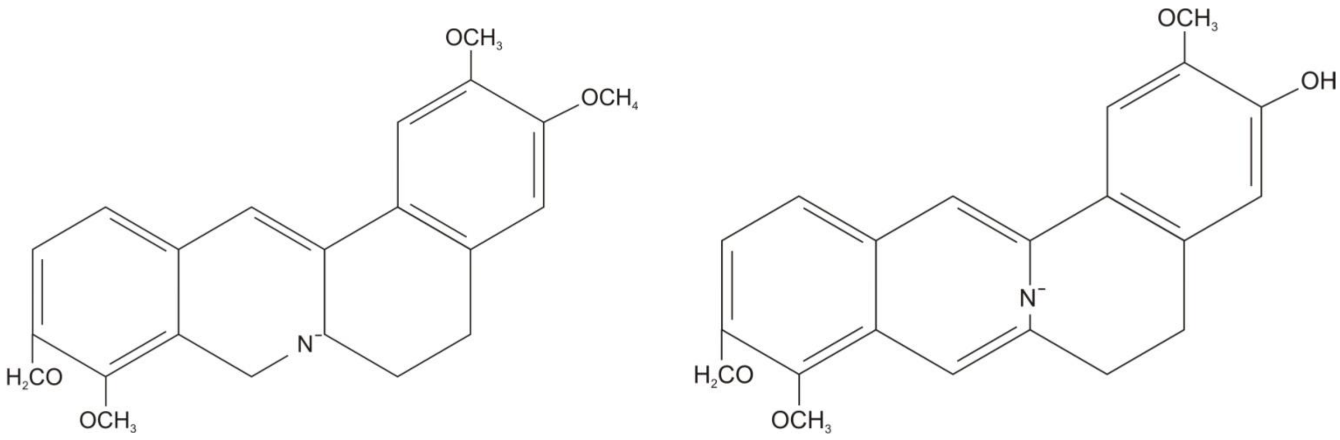
(m) Venivel root /stem (Coscinium fenestratun)

It is a very important aurvedic medical plant widely grown in India and Sri Lanka due to huge demand in medical plant sector. It yields a yellow dye and bitter tonic from dried stems and roots. The yellow dye obtained from the wood is used in fabric dyeing. The major alkaloids present in venivel are yellow crystalline berberine, protoberine and jatrorrhizine.

Other alkaloids are magnoflorine, beberrine, thaliferdine, palmative and oxyberine. It also contains cerylalcohol, saponins, hentriacontane, sistosterol, palmatic acid, oleic acid and sistosterol glucoside. The essential chemical constituents present in this plant which contributes to the sensitization of DSSC test cells are as follows :



Berberine



Palmitine

Jatrorrhizine

Figure 4.34 Chemical structure of major compounds present in Venivel.

4. 2 Why is the performance of natural dye based DSSC's low?

As observed from Tables 4.2 and 4.3 the conversion efficiencies of DSSC's tested using natural dyes of plants has been less than 1% ranging from 0.001% to 0.223%. Table 4.5 and 4.6 indicate a highest conversion efficiency of 1.053% for Mangoostein fruit rind extract after detailed purification procedure. The reason for such low efficiency is the interaction between these natural dye pigments with TiO_2 would have been low. The structure of the pigment also affects the performance, i.e, if the structure has a longer R group, this results in the steric hindrance for the pigment to form bond with the oxide surface of the TiO_2 and hence prevent the molecule from arranging on the TiO_2 film effectively.

Hence there is a lack of electron transfer from the dye molecule to the conduction band of TiO_2. The intensity and range of light absorption of the extract also affects the performance. The distance between the dye skeleton and the point connected to the TiO_2 surface facilitates electron transfer from the dye which accounts for the performance of the cell.

The interaction between TiO_2 and the dye plays an important role towards the efficiency of DSSC's. In general, natural dyes suffer from low Voc. This can be due to possible inefficient electron/dye cation recombination pathway and the acidic dye absorption environment. In fact H^+ is the potential determining ions for TiO_2 and that proton absorption causes a possible shift of the Femi level of the TiO_2, thus limiting the maximum photovoltage that could be delivered by the cells.

The charge transfer in the TiO_2/ dye/ electrolyte interface resistance leads to a decrease in Jsc. Thus, introducing a functional group, such as carboxyl group and optimizing the structure of the natural dye are necessary to improve the efficiency of natural dye based DSSC's.

Some complication such as dye aggregation on nanocrystalline films produces absroptivity that results in no electron injection. Dye aggregation is a serious issue that occurs when compounds fill the free space between the dye molecules, particularly blocking the physical contact between the Iodine solution and TiO_2 semiconductor film surface, reducing reaction and inhibiting dye aggregation.

4.3 Research priorities for DSSC performance improvement

The main research concerns for dye sensitized solar cells are the reduction of material degradation that leads to poor device longevity, affordable encapsulation methods to protect against environmental degradation, alternatives to dyes as sensitizers, and the development of solid electrolytes to avoid leakage problems.

4.3.1 Research Priorities

During the study and related research done on the use of natural dyes for the sensitization of DSSCs, the following aspects have been ascertained to be necessary to accomplish their designs and development for the practical commercial uses.

The main research concerns for DSSC's are :-

- Reduction of natural degradation that leads to poor device longevity.
- Affordable encapsulation methods to protect against environmental degradation.
- Alternations to dyes as sensitize.
- Development of Solid electrolytes to avoid leakage problems.

4.3.2 Reduction of Material degradation that leads to poor device longevity

For successful use of DSSC's for outdoor applications, several factors are of importance e.g., technical performance and manufacturability, cost, design, market demand, and last but not least long term stability. The overall stability of thin cells is controlled by two factors – namely, physical and chemical stability. Physical stability is related to the possible evaporation of the liquid electrolyte at elevated temperatures. This is a technological problem, for which solution can be found by using suitable sealing materials and techniques. The intrinsic chemical stability is related irreversible (photo) electro chemical and thermal degradation of the dye or electrolyte, which might occur during operation of the cell.

Accelerated ageing tests done by other researches on large number of DSSC's have shown that, to first order, a separation between the effects of the stresses of viable light soaking, UV illumination and thermal treatment on the long-term stability is possible. The corresponding machinery are electrochemical, photochemical and purely chemical in nature. Intense light soaking with 2.5 Sun equivalent intensity is not a dominant stress factor. Cell stability up to 8300 hours has been demonstrated by other researches under these conditions electrochemically, this result corresponds to a number of red ox cycles equivalent to operation at least 10 years outdoor operation.

Also understand that a dramatic improvement in stability under strong UV illumination has been reached by other researches using Mg I_2 as an additive to electrolyte, and 3300 hours of operation corresponding to 3 year outdoor operation with no additional UV filter has been observed. In combination with a simple UV filtering top layer, DSSC's can be UV stabilized for significant (10 years) long term outdoor operation.

The long term extrapolation of the thermal stability achieved so far is still of critical importance. further experiments in the range 80^0C – 100^0C still need to be made to learn more about thermal activation temperatures of DSSC's depend on the location and module mounting (roof, standalone, facade) have to be determined.

4.3.3 Affordable encapsulation methods to protect against environmental degradation

Sealing the DSSC's has been a difficult aspect because of the corrosive and volatile liquid iodide electrolyte used in the cells. Being directly related to the long term stability of the cells, it seems to be one of the main technological challenges of the DSSC technology. A suitable sealing material should be :-

- Leak proof to the electrolyte components and impregnable to both ambient oxygen and water vapour.
- Be chemically insert towards the electrolyte and other cell components.
- Adhere will to the glass substrate and TCO coating.

Several sealing materials have been used by other researches such as epoxy glue, water glass (Sodium silicate), an ionomer resin Surlyn (grade 1702) from Du Pont, Aluminum laminated with polymer foil, a vacuum sealant Torr Seal, or a combination of these. Especially for research purposes sealing technology based on O-ringes and glass soldering have been developed.

One improvement question when selecting the sealant is the tolerance of the sealing material towards iodide and tri iodide in the electrolyte. Interestingly despite the fact that the often used sealant, the Surlyn inomer resin from Du Pont has been classified by the manufacturer as not resistant (in KI solution) for the stable long term operation demonstrated for DSSC's utilizing Surlyn sealing with iodide electrolyte. The Author has observed that commercial grade Silicone glue adhesive has been successfully used as a sealant for DSSC's constructed by him over a period of about 1 ½ years, without any degrading effects.

4.3.4 Alternatives to dyes as sensitizers

Ruthenium bipiridyle complexes which are expensive and rare Synthetic dyes have a high conversion efficiency of about 11%. However, natural dye extracts from Mangoostein fruit rind and Turmeric rhizome root containing Rutin and Curcumin respectively have found by the author to be good sensitizesr for DSSC's. Also tropical Fire Fern leaves and Begonia Black Velvet leaves rich in Anthrocyanins and Ekkiriya wood, Egg plant fruit peels and Venivel could also be used as sensitizers (and a mixture of these extracts). As an alternative, semiconductor Quantum Dots (Q dots) that absorb light in the visible region such as CdS, CdSe and PbS could also be used as sensitizers for DSSC's. In general Q dots (which are very costly) have significant advantages are dyes. In order to absorb a broad spectrum in the visible region vertically aligned TiO_2 nanotubes could be co-sensitized with different size of CdSe Quantum dots. The power conversion efficiency of co-sensitized Q dots practical solar cells have shown conversion efficiencies of about 2% to 3%. The co-sensitization of Q dots have shown higher performance than the single size sensitizers particularly in the 500-600 nm wavelength domains.

However, it has been observed that due to their simple preparation technologies, wide availability and very low cost, natural dyes of plants are promising alternative sensitizers for use in environmentally friendly solar energy devices.

4.3.5 Development of Solid electrolytes to avoid leakage problems

A recent alternative embodiment of the DSSC concept in the sensitized heterojunction usually with an inorganic wide band gap nanocrystalline semiconductor of n-type polarity as electron acceptor. The charge neutrality on the dye is restored by a hole delivered by the complementary inorganic or organic semiconductor of the P- type polarity. The photoelectrochemical variant has an AM 1.5 solar conversion efficiency of over 10% (with synthetic dyes), while that of the solid state device is significantly lower (about 4%) by using a DSSC's containing CuI as a hole conductor instead of a liquid redox electrolyte like KI / I.

4.3.6 Important assessments

The DSSC's using natural dyes of plants would be credible solar energy to electricity conversion devices, if their conversion efficiencies could be significantly increased from about 1% at present to about 3%. The crucial parameters that determine the efficiency and stability of a DSSC are :

a.The performance of a DSSC largely depends on the dye used to sensitize the TiO_2nanocrystallites .

b.The advantage of the DSSC's with respect to competing technologies is that its performance is remarkably insensitive to temperature changes, as raising the temperature from 20^0C to 60^0C has practically no effect on the power conversion efficiency.

c. The matching of the absorption spectra of the dye to the solar spectrum andthe photo redox properties of the dye .

d.The anchorage of the dye to the surface of the nanocrystallites .

e.Very low surface resistance (high conductivity) of the counter electrode .

f. The thickness of the nanostructured TiO_2 layer which must be less than 20 nm to ensure that the diffusion length of the photoelectrons is greater than that of the nanocrystalline TiO_2layer .

g. Also the use of sensitized wide band gap semiconductor like TiO_2 results in high chemical stability of the cell due to it’s resistance to photocorrosion .

h. One approach to enhance light harvesting efficiency (LHE) and hence the light to current conversion efficiency is to increase the surface area (roughness factor) of the TiO_2 nanoporous sensitized photoelectrode .The LHE increases with the concentration of the dye extract .

i. The redox electrolyte containing I^-/ I_3^- redox ions is used in a DSSC to regenerate the oxidized dye molecules , and hence completing the electric circuit by mediating electrons between the nanostructured electrode and the counter electrode. Thus the cell performance is also greatly affected by the viscosity of the solvent electrolyte.

The Best Research – Cell Efficiencies of DSSC’s sensitized with Synthetic Dyes tested at the IFS since inception is at Appendix F.   The Best Research – Cell Efficiencies of DSSC’s sensitized with Natural Dyes of Plants and Trees growing in Sri Lanka identified at the University of Moratuwa is at Appendix G.

The Best Research – Cell Efficiencies of all types of Thin Film Solar Cells evaluated at the National Renewable Energy Laboratory (NREL) , Colorado, U.S.A is at Appendix H.

4. 4 New Developments

4.4.1 Preparation of Fluorine – doped Tin Oxide (FTO) Transparent Conducting Glasses for developing DSSC's of Catamaran Boat

4.4.2 Introduction

Transparent conducting glasses (TCO's) are becoming increasingly important as artificial components for a variety of thin film technologies such as solar cells, smart windows, flat panel displays, oven windows, electromagnetic shielding, electrochromic mirrors and windows, defrosting aircraft cockpit canopies, defrosting windows, invisible security circuits, touch panel controls, low emissivity windows and DSSC operated vertical glass window panes of high-rise buildings (BIPV’s) etc. This is mainly due to the co existence of both high transparency in the visible region and high conductivity with values comparable to those of metals. In particular thin film solar cells having shown high market growth (about 30% per year) in recent years and will continue playing an important role in minimizing the cost of photovoltaic power generation.

In order to be implemented in DSSC's, TCO's should be highly transparent in the visible region (transmittance >75%), and highly conductive ($R_{sh} \leq 10$ Ohm.cm^{-2}). Moreover, in order to be implemented in a large scale production, the material of the TCO should be abundant, low cost and if possible environmentally friendly. Among the different TCO's available, Fluorine – doped Tin Oxide (SnO_2 : F or FTO) can fulfill most of these requirements. In fact, Tin oxide in a transparent conductive oxide even in its undoped state. The conductivity in due to an intrinsic non-stoichiometry created by the presence of oxygen vacancies (Vo) and interstitial Tin (Sn_i) inside the structure which, which are easily tolerated due to the multivalance of Tin. Spontaneous acceptor like intrinsic defects, like interstitrial Oxygen or Tin vacancies are absent, therefore the electrons released by the Vo or Sn_i are not compensated. Transparency, instead is a consequence of the large gap between the top of the valancy band and the first unoccupied state, so that direct optical transitions in the visible range are not allowed. In this way, it is possible to have a simultaneous high carrier concentration with minor effects on Transparency. However, in order to further improve the conductivity, Tin oxide is generally doped with either Antimony (Sb) or Fluorine (F) as subsitutes for Tin and Oxygen respectively. Due to differences in the valence state and in hybrid orbital configuration in both cases a free electron is released if one of these few doping atones in present. However, F is normally preferred to Sb because at high doping concentration, a reduction in mobility and lower transparency can be observed on Sb doped film. For these reasons FTO is a widely used TCO in thin film Cd Te and amorphous Silicon based cells and DSSC's.

On a laboratory scale, SnO_{2}- based film could be grown with wide range of deposition technologies such as sputtering, sol-gel and various chemical vapour deposition (CVD) technology for the TCO growth in the photovoltaic sector only sputtering and CVD variants (in particular plasma enhanced CDV) are in widespread use due to their cost efficiency and scalability. It is well known that widespread use of solar cells will only be possible if abundant, non-toxic materials are used and if a fast, inexpensive and scalable technique in available for the deposition. Spray pyrolysis could fulfill these requirements providing film with optical and electrical properties comparable with those grown by the more expensive vacuum deposition techniques currently used.

4.4.3 Construction of Fluorine – doped Tin oxide coated transparent conducting glasses for DSSC's

As the commercial grade Fluorine-doped Tin oxide coated transparent conducting glasses are expensive (A4 size conducting glass sheet costs about US $ 200 in the very limited international markets), research was carried out in the Industrial Chemistry Laboratory of the Chemical & Process Engineering of the University of Moratuwa, Moratuwa, Sri Lanka to indigenously develop them.

Initially soda lime glass slides of dimensions 6 cm x 3 cm were washed in Teepol detergent solution in distilled water, dilute Sulphuric acid and rinsed with Ethanol and left to dry at room temperature. Thereafter 20 mL of commercial grade Alkyl Tin trichloride solution was saturated with 2.5 gm of Sodium fluoride powder in 30 mL Ethanol, heated to 70^{0}C whilst stirring continuously. Sodium chloride crystals 1.6 gm was dissolved in 30mL Acetic acid whilst stirring continuously at 70^{0}C. These solutions were filtered, mixed and heated to 70^{0}C for 5min. Then this solution was subjected to spray pyrolysis (using plastic spray gun) onto a cleaned glass sheet heated in an electric oven at 580^{0}C for 10 min. Thereafter the oven was switched off and the glass sheet allowed to cool down overnight to room temperature the following day. It was observed that the surface conductivity could be improved by spraying several layers on top of the glass surface being treated by spray pyrolysis.

36 Nos DSSC’s (4" x 3" x 0.3") for the Catamaran Boat are being constructed in accordance with above procedure for the (--) ve and (+) ve electrodes with FTO conducting glasses described above . The treated surfaces of the (+) ve counter electrodes are covered with fine Graphite powder uniformly rubbed in . The TiO2 semiconductor coated (--) ve photoelectrodes will be sensitized with Mangoostein fruit rind dye extract which could be activated by redox electrolyte (KI/I).

In order to further reduce the conductivity of FTO glasses for (+) ve and (-)ve electrodes, arrangements will be made to displace the oxygen in air present in the anealing oven possibly with the introduction of continuous flow of nitrogen gas during the spray pyrolysis of Alkyl Tin trichloride solution doped with Sodium fluoride .

Also attempts are being made to reduce the conductivity of the (--) ve FTO glass electrodes by blending the Rutin of Mangoostein fruit rind extract dye coated TiO_2 surface by introducing x GnP solution (exfoliated Graphite nanoplatelet solution) available at the Sri Lanka Institute of Nanotechnology (SCINTEC). This shall further enhance the Voc and Isc of DSSCs.

Table 4.10 PREPARATION OF FTO CONDUCTING GLASS (3" X 2")

Trial No.	ALKYL TIN TRICHLORIDE	TIN TETRA CHLORIDE ($SnCl_4$)	Na F	ETHANOL	NaCl	ACETIC ACID	TIN OXIDE ($Sn O_2$)	HCl	SYNTERING TEMP ^{0}C (10 min)	RESISTIVITY Ohms Cm^{-2}
01 (PIRAMAL GLASS PLC HORANA)	20 mL 20 mL	- -	2 gm 2 gm	100 mL 100 mL	- -	- -	- -	- -	550 ^{0}C 550 ^{0}C	100 K 1.2 K 2.0 K 50 $\Omega.Cm^{-2}$ 50 $\Omega.Cm^{-2}$
02 (PIRAMAL GLASS PLC HORANA)	20 mL 20 mL	- -	2 gm 2 gm	100 mL 100 mL	- 1 gm	- -	- -	- -	550 ^{0}C 550 ^{0}C	600 - 1000 $\Omega.Cm^{-2}$ 180-800 $\Omega.Cm^{-2}$
03 (UOM from here onwards)	20 mL 20 mL 20 mL	- - -	2 gm 2 gm 2 gm	100 mL 100 mL 100 mL	- 0.5 gm 0.5 gm	- 20 mL 20 mL	- - -	- - -	580 ^{0}C 580 ^{0}C 580 ^{0}C	20-50 $\Omega.Cm^{-2}$ 30-50 $\Omega.Cm^{-2}$ 15-22 $\Omega.Cm^{-2}$
04	20 mL	-	-	-	0.5 gm	20 mL	-	-	580 ^{0}C	10 K$\Omega.Cm^{-2}$
05	20 mL	-	2 gm	100 mL	0.5 gm	20 mL	-	-	580 ^{0}C	30-50 $\Omega.Cm^{-2}$

06	20 mL	-	2 gm	100 mL	0.5 gm	20 mL	-	-	600 ^{0}C (catches fire)	25-50 Ω.Cm^{-2}
07	20 mL	-	2 gm	100 mL	0.5 gm	20 mL	-	-	580 ^{0}C	25-55 Ω.Cm^{-2}
08	-	-	-	-	-	1 mL	1 mg	30 mL (1 mole)	580 ^{0}C	3K-20K Ω.Cm^{-2}
09	-	-	2.5 gm	-	2.165 gm	10 mL	0.5 gm	30 mL (11.32 mole	580 ^{0}C	5K-30K Ω.Cm^{-2}
10	-	-	0.25 gm	30 mL	-	-	5 gm	-	580 ^{0}C (20 min)	6K-20K Ω.Cm^{-2}
11	-	2.5 gm	0.25 gm	50 mL	1 gm	20 mL	-	-	580 ^{0}C	4K,12K,60K, 100KΩ.Cm^{-2}
12	-	2.5 gm	0.25 gm	25 mL	1 gm	-	-	-	580 ^{0}C	8K,18K,20K,40 KΩ.Cm^{-2}
13	-	2.5 gm	0.25 gm	-	0.25 gm	65 mL	-	-	580 ^{0}C	20K,50K, 100KΩ.Cm^{-2}
14	-	1.0 gm	1.0 gm	-	0.5 gm	65 mL	-	-	280 ^{0}C 580 ^{0}C	1M, 500KΩ.Cm^{-2} >100K, >100 KΩ.Cm^{-2}
15	-	1 gm	1 gm	10 mL	1 gm	-	-	-	480 ^{0}C	>100

										KΩ.Cm^{-2}
16	-	2 gm	2 gm	20 mL	-	-	-	-	580 ^{0}C	3K,5K, 20KΩ.Cm^{-2}
17	-	2 gm	2 gm	10 mL	1 gm	5 mL	-	-	580 ^{0}C	1K,2K,3K 10KΩ.Cm^{-2}
18	-	2 gm	2 gm	10 mL	1 gm	5 mL	-	-	480 ^{0}C	100K,200K, 400K 500KΩ.Cm^{-2}
19	1 mL	-	1 gm	25 mL	-	-	-	-	580 ^{0}C	100 – 150 Ω.Cm^{-2}
20	1 mL	-	1 gm	20 mL	1 gm	10 mL	-	-	580 ^{0}C	85 -130Ω.Cm^{-2}
21	1 mL	-	1gm	20mL	2gm	10mL	-	-	580 ^{0}C	25 - 40Ω.Cm^{-2}
22	1 mL	-	1gm	20mL	2gm	10mL	-	-	580 ^{0}C	15 - 32Ω.Cm^{-2}
23	1 mL	-	1gm	20mL	2gm	10mL	-	-	580 ^{0}C	12 – 25 Ω.Cm^{-2}
24	20 mL	-	2 gm	30 mL	1 gm	30 mL	-	-	580 ^{0}C	15-25 Ω.Cm^{-2}
25	20 mL	-	2 gm	30 mL	1 gm	30 mL	-	-	580 ^{0}C	15-22 Ω.Cm^{-2}
26	20 mL	-	2.5 gm	30 mL	1 gm	30 mL	-	-	580 ^{0}C	14-18 Ω.Cm^{-2}
27	20 mL	-	2.6 gm	30 mL	1.5 gm	30 mL	-	-	580 ^{0}C	14-18 Ω.Cm^{-2}
28	20 mL	-	2.5 gm	30 mL	1.6 gm	30 mL	-	-	580 ^{0}C	12-15 Ω.Cm^{-2}
29	20 mL	-	2.5 gm	30 mL	1.6 gm	30 mL	-	-	580 ^{0}C	8-10 Ω.Cm^{-2}
30	20 mL	-	2.5 gm	30 mL	1.6 gm	30 mL	-	-	580 ^{0}C	8-10 Ω.Cm^{-2}
31	20 mL	-	2.5 gm	30 mL	1.6 gm	30 mL	-	-	580 ^{0}C	8-10 Ω.Cm^{-2}

The transmittance Vs. Wavelength characteristics of the FTO glasses indigenously constructed at the Industrial Chemistry Laboratory of the University of Moratuwa was obtained at the Sri Lanka Institute of Nanotechnology (SLINTEC) and is attached at Figures 4.11 and 4.12 . Figure 4.13 indicates the effect on Transmittance on imported FTO glasses for DSSC's for IR heat absorption in BIPV's as well as voltage and current generation due to sunlight.

It is understood that there are about 12 leading industrial Companies in the world such as SPD Laboratory Inc, Ashai Technologies, Nippon Sheet Glass, Pecell Technologies all in Japan; Kaivo Zhulai Kivo, Gendong, China, Heln, Zentmn, Germany, Pilkington Glass , England, Beneq Oy Finland; Solaronix ,Sonotech Corporation, Milton, New York, U.S.A, Abrisa Technologies , Santa Paula, U.S.A., who manufacture laboratory analytical grade FTO glasses for research purposes having a surface conductivity of about 10-15 Ohm.cm^{-2}, with a best Transmittance of about 75 - 80%/. These FTO glasses cost about US$ 100 per A4 size sheet.

The FTO glasses prepared at the Universality of Moratuwa had a best surface conductivity of 8 – 10 Ohm.cm^{-2} when five sprayings (coatings) of Alkyl Tin tricholoride solution doped with Sodium fluoride and sodium chloride, and had a best transmittance of about 35%. However , when two sprayings (coatings) of this solution was used, it had a surface conductivity of 12 - 15 Ohm.cm^{-2}, and a best Transmittance of about 75%. Figure 4.11 and 4.12 relevant. These FTO glasses cost only about US$ 15 per A4 size sheet, which would be a significant breakthrough for the mass production of low cost commercial grade FTO glasses for the construction of natural dye sensitized DSSC's on glass substrates for low power field applications.

The Band Gaps of all types of Solar Cells is listed at Appendix I, and their Commercialization and Market Potential is at Appendix J.

The Efficiency vs. Cost Evaluation of I , II, and III Generations of Solar Cells is listed at Appendix K.

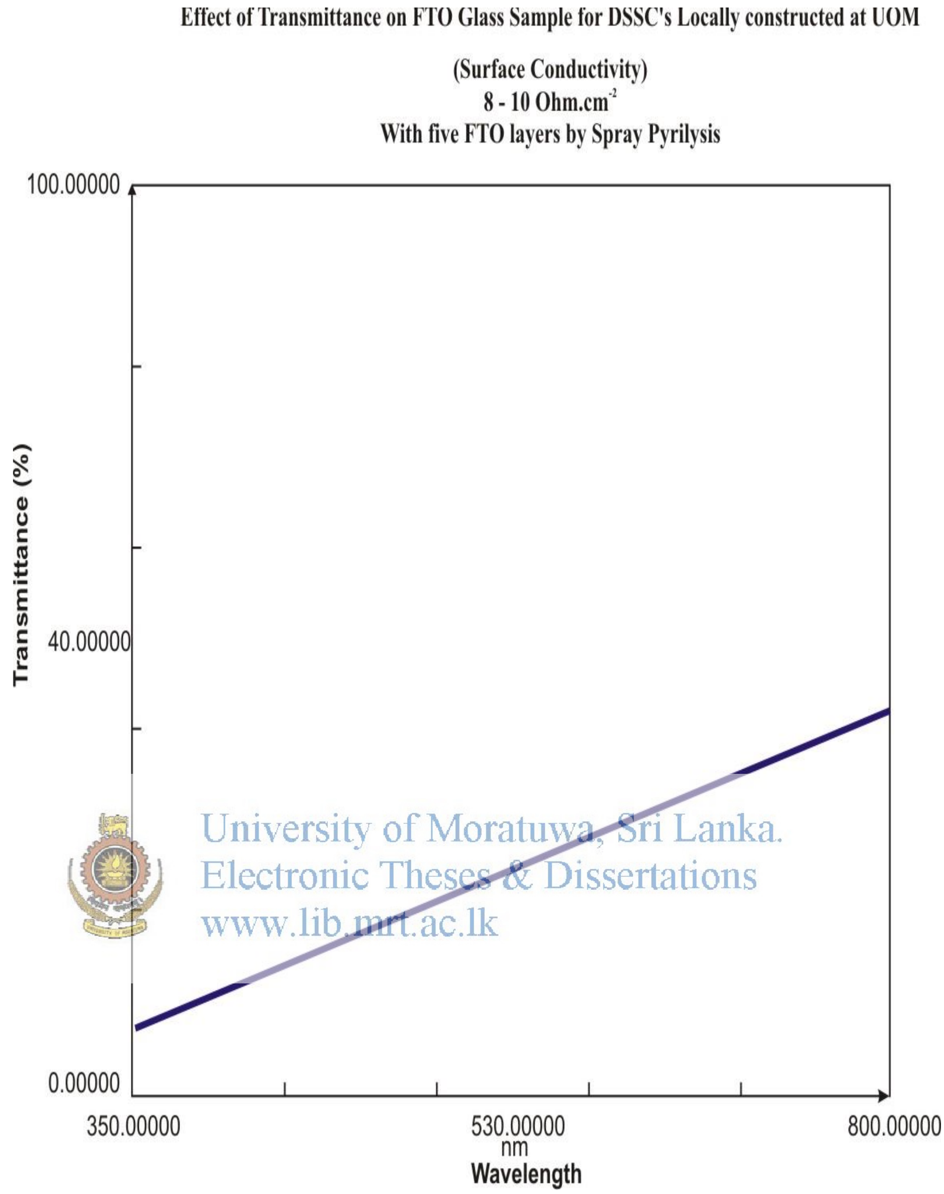


Figure 4.35 Effect on Transmittance on FTO glasses for DSSC's locally constructed at University of Moratuwa.

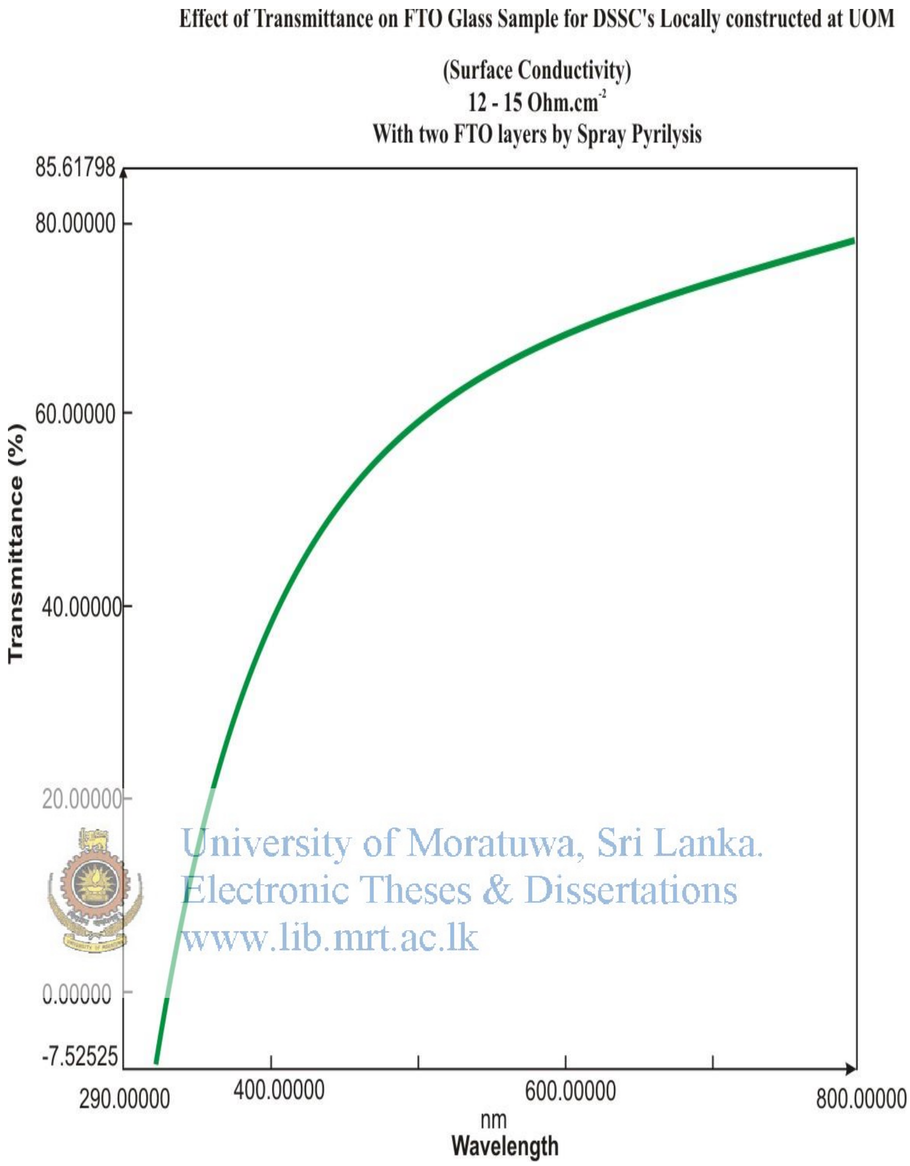


Figure 4.36 Effect on Transmittance on FTO glasses for DSSC's locally constructed at University of Moratuwa.

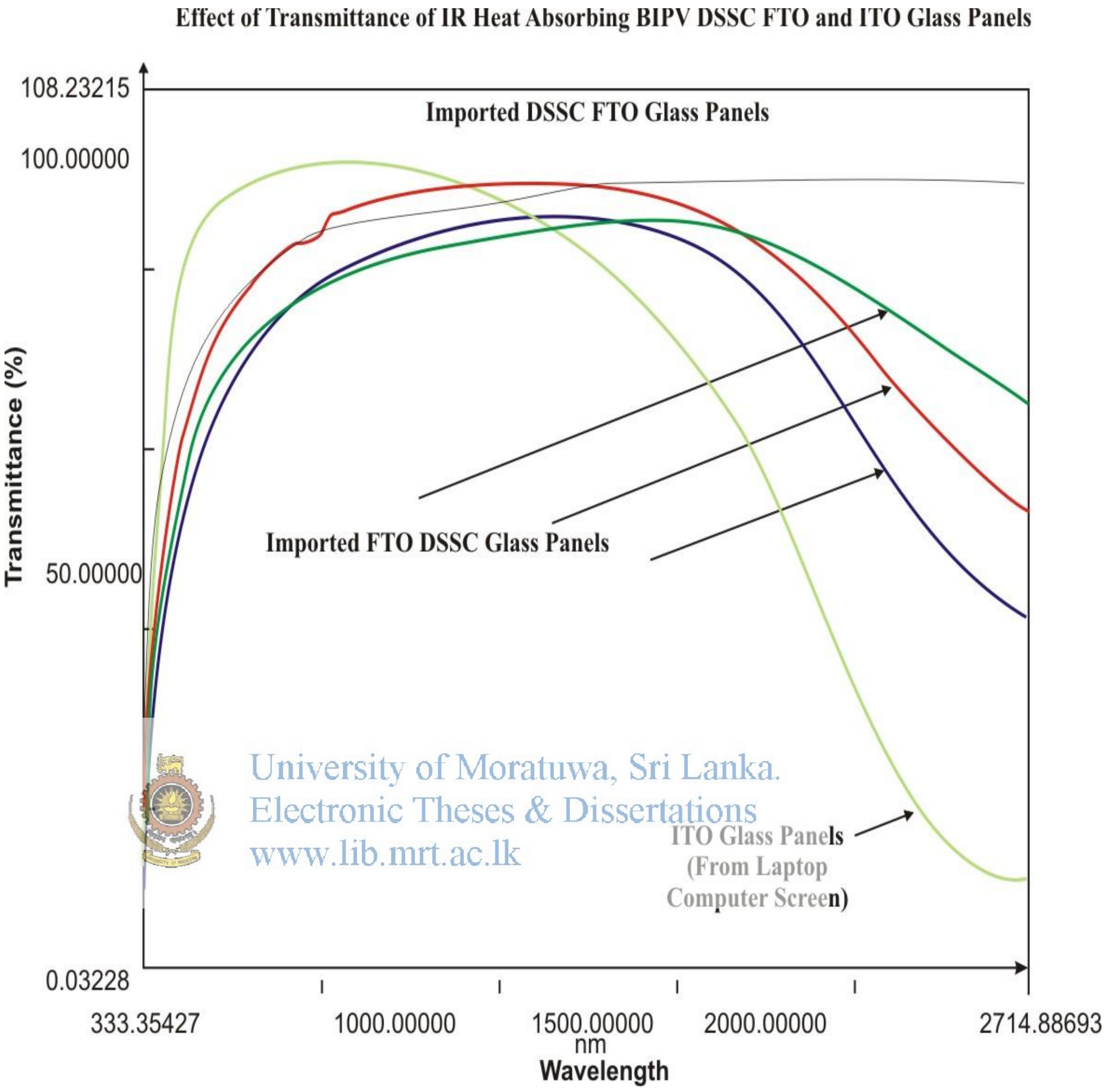


Figure 4.37 Effect on Transmittance on Imported FTO glasses for DSSC's and BIPV Panels for current and Voltage generation as well as IR heat absorption minimization.

Effect of Exfoliated Graphene Nanoplated Oxide on FTO Glass

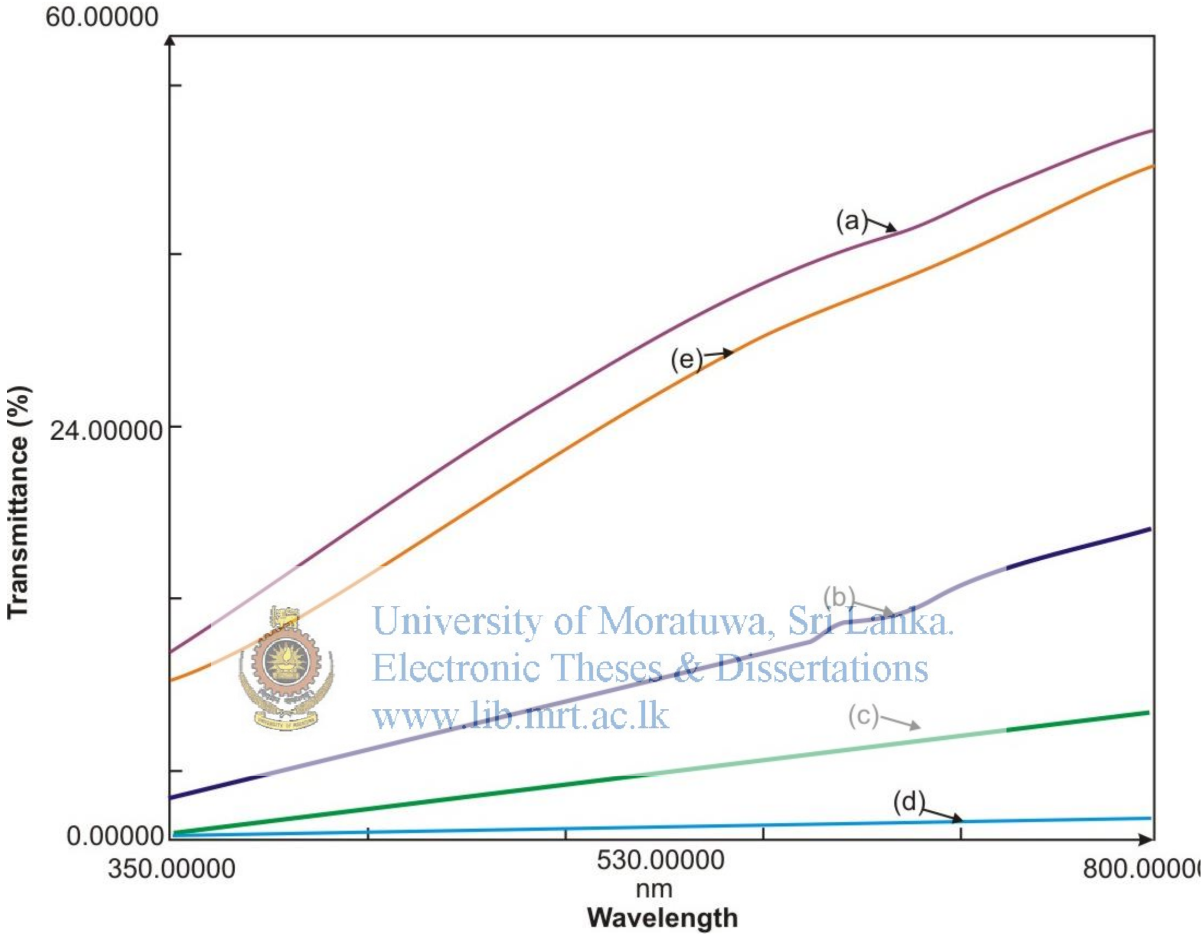


Figure 4.38 Effect of Exfoliated Graphene Oxide on FTO Glass at varying concentrations

(a) 5mg.mL (b) 10 mg.mL (c) 15 mg.mL (d) 20 mg.mL (e) untreated

4.4.4 Improvement of conductivity of Fluorine doped Tin Oxide (FTO) coated glass with Exfoliated Graphene Nanoplate solution in Hydrazine

The photovoltaic process of DSSC's could be enhanced by using FTO coated glass with Exfoliated Graphite Nanoplate solution in Hydrazine by a novel in situ simultaneous reduction – hydrolysis technique to produce Graphene – Titanium dioxide counter photo electrodes.

Reduction of Graphene oxide (GO) could be achieved by an in situ photo electro chemical method in a DSSC assembly, in which the semi conductor behavior of the reduced Graphene oxide (RGO) in controllable. It has been found that the GO film which assembled in a DSSC on the counter electrode has been partly reduced. An optimized assembly is promising for modulating the reduction degree of RGO and controlling the band structure of the resulting RGO. Moreover this method appears to be a green pathway for the production of RGO electrodes.

Graphene is a new carbon material with diverse properties being suitable for energy conversion and storage. Graphene oxide (GO) produced by exfoliation of Graphite oxide has been traditionally considered to be a precursor for Graphene. It has variable optical, mechanical, and electronic properties that can be tuned by controlling the degree of oxidation. Reduced Graphene oxide characterized as an incompletely reduced product of GO, is the intermediate state between graphene and GO. Because the oxygen bonding forms the Sp^3 hybridization on RGO and oxygen atoms have a large electro negativity than carbon atoms, RGO becomes a doped semiconductor where the charge flow creates negative oxygen atoms and a positively charged carbon grid. However understanding the controllable semiconductor behavior is still a big challenge.

Normally the bond gap of RGO increases with the oxidation level. Controlling the ratio of Sp^2 carbon atoms by reduction chemistry is a powerful way to tune the band gap. Therefore RGO can be controllably transformed from an insulator (GO) to a conductor (graphene). Owing to these characteristics, RGO could be used as very low conductivity electrodes in Dye-Sensitized Solar Cells. The reduction of GO is typically achieved by thermal annealing and exposure to Hydrazine.

4.4.4.1 Fabrication of a DSSC with GO

GO was synthesized from about 100µm particle diameter natural Graphite powder (1gm) and $NaNO_3$ (0.5gm), concentrated H_2SO_4 (25mL) in an ice bath. $KMnO_4$ (3gm) was added gradually under stirring to prevent rapid temperature rise, and the temperature of the mixture was kept below 20°C. The mixture was then stirred at 35°C for 4 hours. Then deionized water (45mL) was slowly added to the solution, followed by stirring the mixture at 98°C for 15 mins. The reaction was terminated by adding deionized water (140mL) and H_2O_2 (1mL, 30% wt%) under stirring at room temperature . The resulting graphite oxide was washed with de ionized water by filteration. Graphene oxide was obtained from the graphite oxide solution by ultrasonification at room temperature for 30 mins. Exfoliated graphite oxide in suspension after ultrasonification was removed by centrifugation at 3,000 rpm for 5 min.

Preparation of GO counter electrodes for DSSC's

The GO test electrodes were prepared by drop casting the above mentioned GO solution of 0 mg/mL, 5 mg/mL, 10 mg/mL, 15 mg/mL and 20 mg/mL concentrations on clean locally made FTO glass substrate of 12 - 15 ohm.cm^{-2} conductivity , and dried at room temperature. The measured conductivities of the treated FTO glass surface was then measured with a SANWA VX390 TH Multimeter and is at Table 4.15. The relevant graph of Conductance Vs. Coating Concentration of the Exfoliated Graphine oxide treated surfaces is at Figure 4.16. It is noted that the best conductivity of 4 Ohm.cm^{-2} obtained with a coating concentration of 20 mg/mL Exfoliated Graphine Oxide.

Fabrication of a Test DSSC

A test DSSC of 1cm x 1cm was then prepared using above mentioned FTO glass substrate coated with Exfoliated Grapheme oxide for counter electrode having a surface conductivity of 4 Ohm.cm^{-2} according to literature described at Chapter 3.3.3 sensitized with Mangoostein fruit rind extract .

Also the Transmittance Vs. Wavelength Spectra were also observed for imported DSSC FTO glass panels and ITO glass panels and these are depicted at Figure 4.13.

Experiments were also done at the SLINTEC to reduce the surface conductivity if the (--)ve FTO glass electrodes by coating with Exfoliated Graphite nanplated solutions in hydracine with varying concentration. The Transmittance Vs Absorbance Spectra obtained for these samples are presented at Figure 4.14. The relevant improvements to the surface conductivity of FTO glasses is noted at Table 4.11.

Table 4.11 Results of Improvements to Exfoliated Graphene Nanoplated solution coated on FTO Glass

Coating Concentration (mg.mL)	Surface Resistance(Ohms.cm-2)
(a) 0	12
(b) 5	20
(c) 10	16
(d) 15	11
(e) 20	08
(f) 22	6.8
(g) 25	6.0

(h) 26	6.0
(i) 27	6.2
(j) 28	6.3
(k) 29	6.4
(l) 30	7.0
(m)31	7.3
(n) 32	7.7

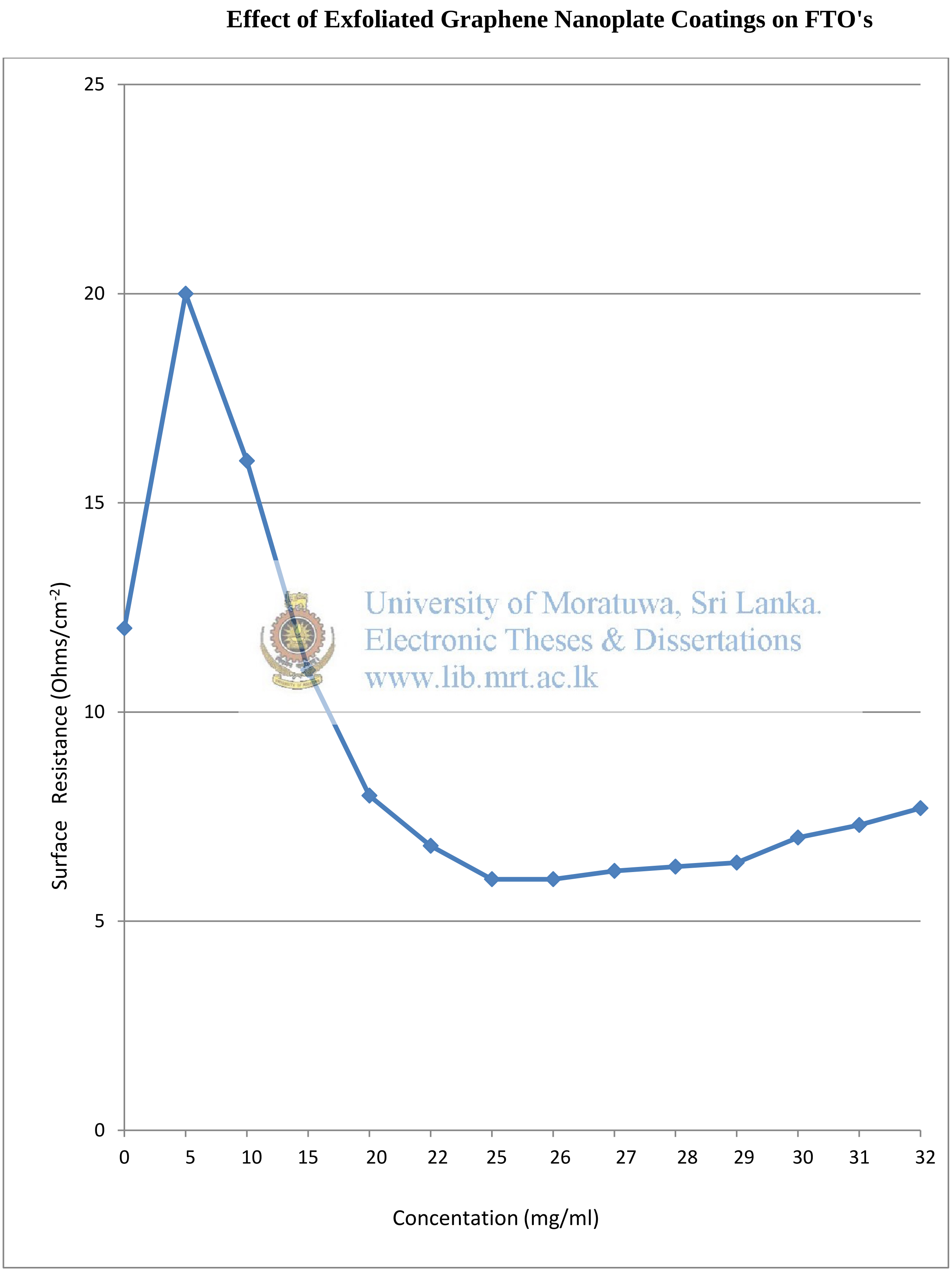


Figure 4.39 Effect of surface resistance on Exfoliated Graphene Nanoplate concentration on FTOs

4.4.4.1 Fabrication of a Test DSSC with Exfoliated Graphene oxide Counter Electrode.

A test DSSC of size 1cm x1cm was then prepared using above mentioned FTO glass substrate coatedwith Exfolitated Graphene oxide for the counter electrode having a surface resistance of 6-8 Ohms.cm^{-2}. According to literature described in Chapter 3.3.3 for DSSC sensitized with Mangoostein fruit rind dye which yielded a best conversion efficiency of 1.317%.

The following observations at **Table 4.12** below noted.

Cell Description	Cell No.1	Cell No.2	Cell No.3	Cell No.4
Voc(mV)	615.6	614.5	615.2	615.3
Isc (mA)	0.803	0.792	0.791	0.874
Jsc(mA.cm^{-2})	3.212	3.168	3.134	3.136
ff(%)	62.65	62.5	62.66	62.85
η(%)	1.317	1.295	1.298	1.291

This surpasses the highest conversion efficiency of 1.17 % obtained for DSSC's sensitized with Mangoostein fruit rind dye vide research paper titled " Dye- Sensitized Solar Cells using 20 natural dyes as sensitizers" published by Huzhi Zhou et al of School of Chemical Engineering, Dalian University of Technology, Dalian ,Peoples Republic of China in February 2011 in the Journal of Photochemistry and Photobiology A. Chemistry [215],[218].

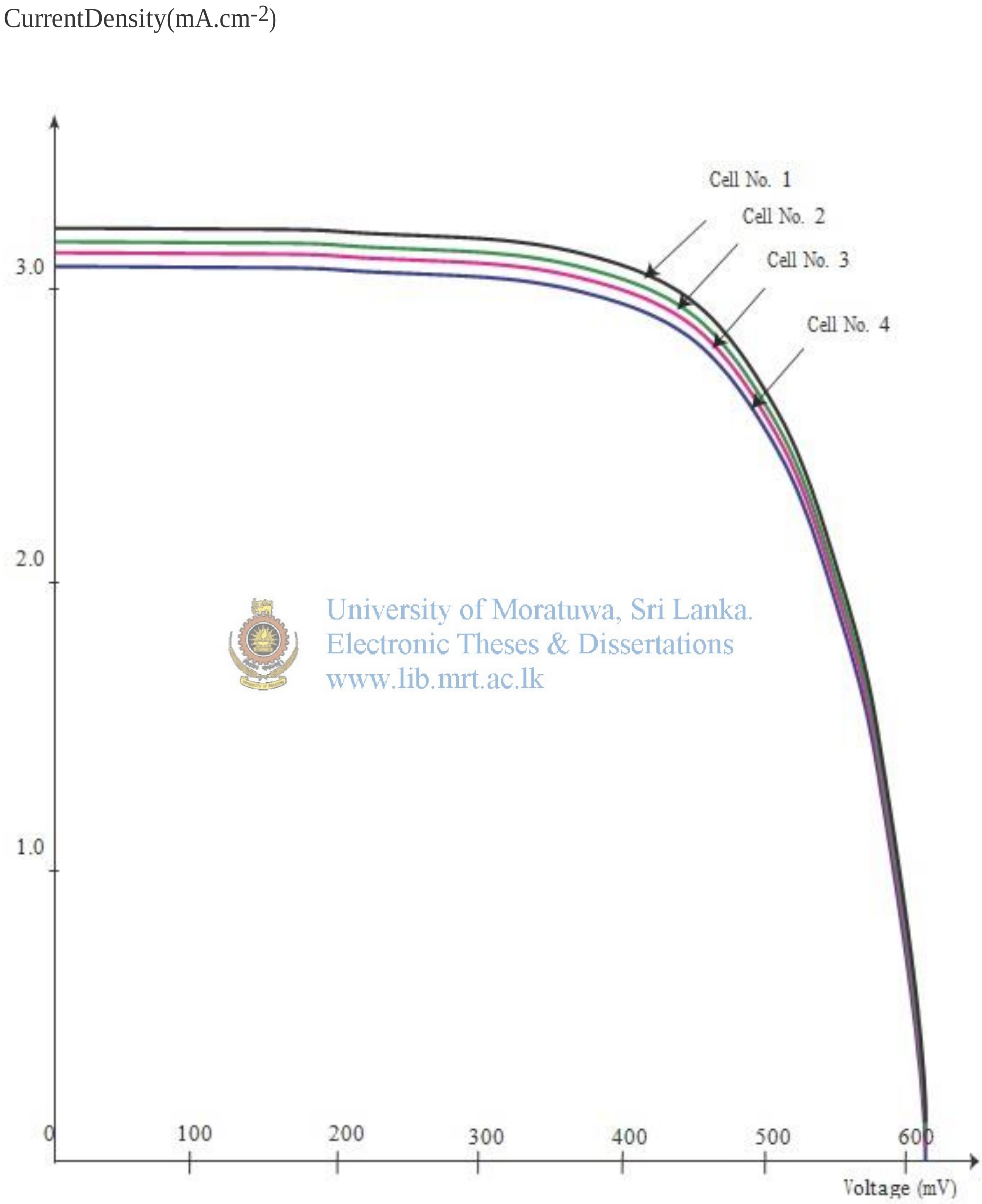


Figure 4.40 Current – Voltage characteristics of DSSC sensitized with Mangoostein dye with Exfoliated Graphene oxide nanoplate counter electrode.

4.4.5 Impedance Characteristics of a DSSC sensitized with Mangoostein dye having Exfoliated Graphene oxide nanoplate counter electrode

The impedance measurements of a test DSSC of size 1cm x1cm was carried out at the IFS,Hantana, Sri Lanka using the METROHM AUTOLAB Model AUT 8534 FRA Impedance Potentiostat Analyser. Subsequently , these measuremenats were carried out for DSSC's sensitized with Mangoostein , Fire fern, Banana flower and Tumeric dye at the Department of Physics,Spectro photometric Laboratory at the University of Kelaniya, Kelaniya using the Potentiostat/ Galvanostat/ ZRA GAM RY Instruments Inc-Series G300 with Hewlett Packard PRO Computer Processor.

At the SLINTEC,Pitipana, Exfoliated Graphene oxide nanoplate solution in Hydrazine was drop-casted as described in literature on 1cm X 1cm FTO glass substrates of 10-12 Ohms.cm^{-2} surface resistance prepared by the Author at the Industrial Chemistry Laboratory,University of Moratuwa. The influence of Exfoliated Graphene oxide coating on the electrochemical performance was investigated by Electrochemical Impedance Spectroscopy and Cyclic Voltammetry. These substrates exhibited high interconnected network structure with high electrical conductivity (low surface resistance) and good catalytic activity.

The effect of drop- casting Exfoliated Graphene oxide nano plate solution in Hydrazine could be seen at Table 4.15. It is observed at Fig 4.16 that when the concentration of this solution increased from 5mg /ml to 25mg/ml, the surface resistance of the coated substrate decreased in almost a linear manner to 6.00 Ohms.cm^{-2}and further increase of the coating concentration yielded no increment. An optimum concentration of 20mg/ml yielded a substrate glass surface resistance of approximately 6.5 Ohms.cm^{-2}.

These subsratives were thereafter heat- treated (sintered) in an electric oven at 600 ° C for 30 min and yieleded substrates with a surface resistance of about 6 - 8 Ohms.cm^{-2} for the preparation of counter electrodes of DSSC's [217].

4.4.6 Electochemical Impedance Spectroscopy of DSSCs

There afeter the Electrochemical Impedance Spectroscopy of test DSSC's of glass substrates of size 1cm x 1cm sensitized with Mangoostein fruit rind dye. (counter electrode coated with Exfoliated Graphene oxide nano plate solution and the photoelectrode of TiO_2 nanopowder paste coated on to glass sensitized with Mangoostein dye). This was done by using the Electrochemical Workstation – METROHM AUTO LAB AUT 85343 Impedance Potentiostat at IFS Hantana.Testing conditions were initial potential 600m V, high frequency 100,000 Hz, low frequency 10 Hz, amptitude 0.005V.The test data was fitted with computer software methods for Cyclic Voltammetry for the indentification of kinetic process,and Impedance Spectroscopy for the characterization of electron and kinetics and mass transport. The following Nyquist Plot and Cyclic Voltammetry analysis were carried out as shown below.

It is believed that when the concentration of Exfoliated Graphene oxide nanoplate solution is optimum (25mg/ml),the surface resistance of the coated glass substrate counter electrode is a minimum (approximately 6.5 Ohms.cm^{-2}as measured) and the highest catalytic reduction ability is obtained with highest possible values for Voc ,Isc ,Id ,ff as seen at Table 4.12.

4.4.7 Analysis of the Performance of DSSC's with CV, Bode , Nyquist and Mott Schottkey Plots

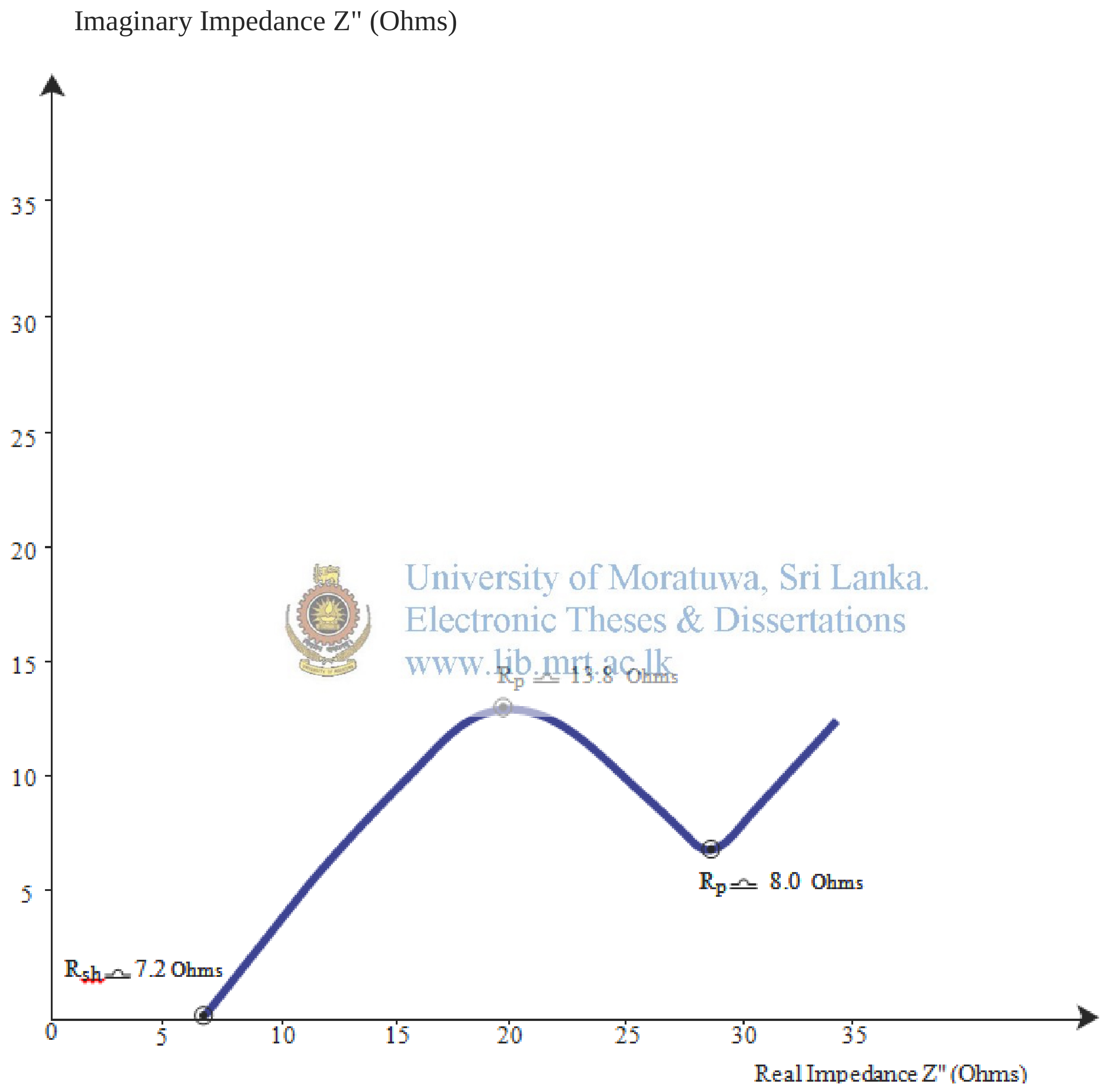


Figure 4.41 Nyquist Plot of Exfoliated Graphene oxide Counter Electrode of test DSSC (with TiO$_2$ photo electrode sensitized with Mangoostein dye.)

4.4.8 Investigating Catalytic activity of ExGO coating using CV

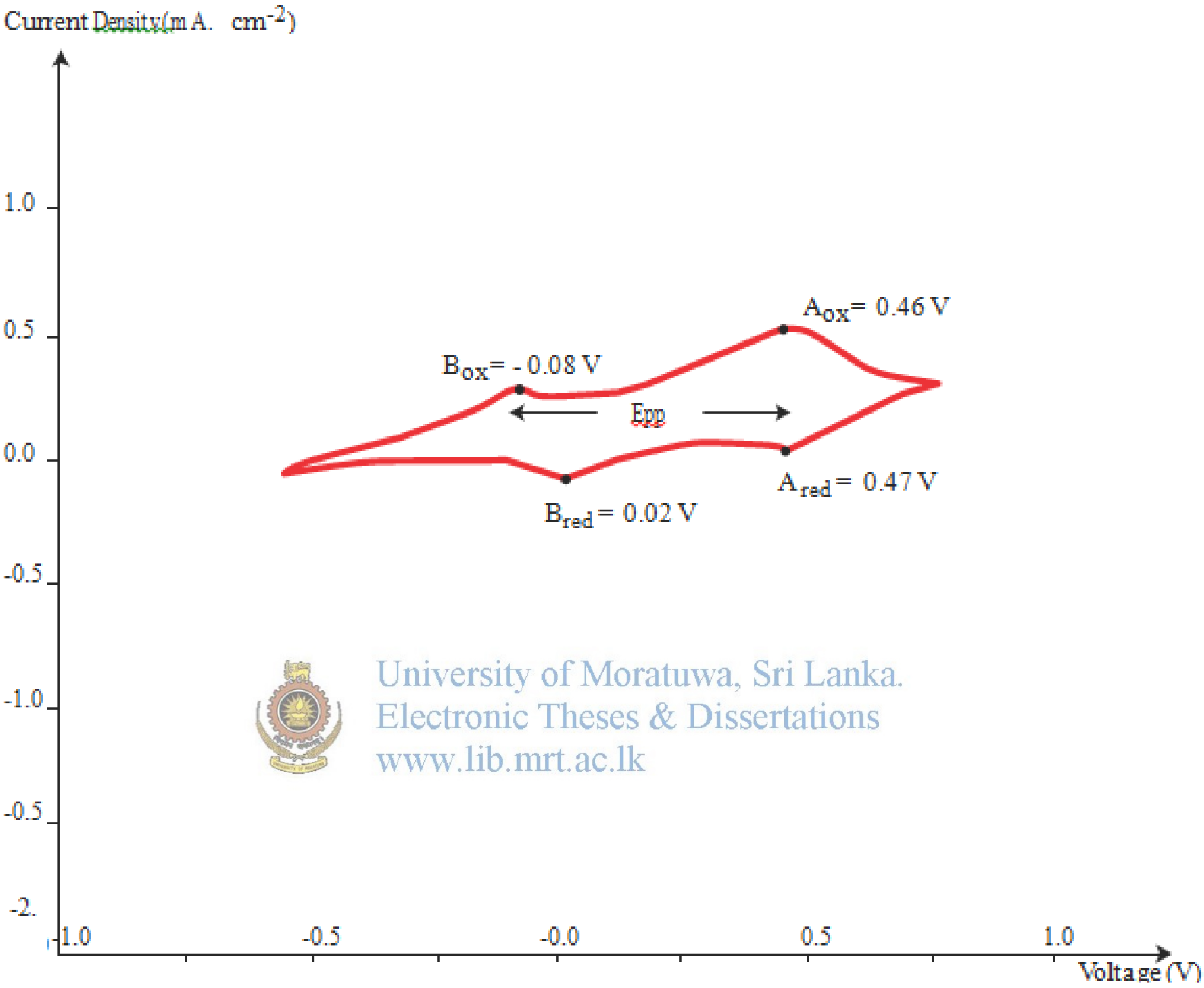


Figure 4.42 Cyclic Voltametrogram of Exfoliated Graphene oxide Counter Electrode of test DSSC (with TiO_2 Photoelectrode sensitized with Mangoostein dye)

Aox = 0.46V, Ared =0.48 , Box = -0.47V , Bred = -0.02V

The oxidation potential together with the absorption edge of the dye detrmined from the UV-vis absorption spectra are use to calculate HOMO and LUMO levels in electron Volts. Therefore the TiO_2 semiconductor of the DSSC sensitized with Mangoostein dye is capable of transferring electrons to its conduction band upon photo excitation from the LUMO of the dye. Thus the usual practice is to calculate the energy level of LUMO from the energy level of HOMO an adding to it the energy of the absorbed light calculated from the UV-vis absorption spectra of the dye .

Actual Calculation of HOMO, LUMO and Band Gap Energy Levels in a DSSC

$E_{(HOMO)} = e.\ E_{ox}$ (vs vacuum)

$E_{(LUMO)} = E_{(HOMO)} + h/\lambda$

$E_{(HOMO)} = -e\ (E_{OX} + 4.40).e\ V$---------------------(1)

$E_{(LUMO)} = -e\ (E_{red} + 4.40).\ e\ V$--------------------(2)

$E_g = 1243/\lambda_{onset}$ --(3)

where,

f= Frequency (Hz)

E= Energy (eVolts)

C= Speed of Light ($3x10^{8}\ ms^{-1}$)

h = Planks Constant ($6.625x10^{-36}\ Js^{-1}$)

e = Electron charge($1.602x10^{-19}$Coulombs)

λ_{onset}= Onset waveleghth of dye (nm)

$E_{LUMO} = E_{HOMO} + E_g$

$E = hv$

$C = f\lambda$

$\mathbf{E = hc / \lambda_{onset} .e}$

For Mangoostien dye the onset wavelength $\lambda_{onset} = 414$ nm

Band Gap = 1243 / 414 = **3.00e V**

$E_{(HOMO)} = e.\ E_{ox} = (1.602\ x10^{-19}\ x\ 0.46) = 0.737x10^{-19}\ e\ V$ = **$7.37\ X\ 10^{-21}\ e\ V$** (too low hence neglect).

$E_{(LUMO)} = (\ E_{HOMO} + h\ /\ \lambda) = (1.602\ x10^{-19}\ x\ 0.46) + 6.625x\ 10^{-34} / 192\ x10^{-9}) = 0.025x10^{-44}\ eV$
= **$2.5\ x10^{-46}\ e\ V$** (too low hence neglect)

$E = h.\ C\ /\ \lambda_{onset}\ .e = (6.625x10^{-34})x\ (3x10^{8}) / (414x10^{-9})\ x\ (1.602x10^{-19}) = 0.064x10^{2}\ e\ V$

E = 6.64 e V (Energy level of a DSSC sensitized with Mangoostein dye)

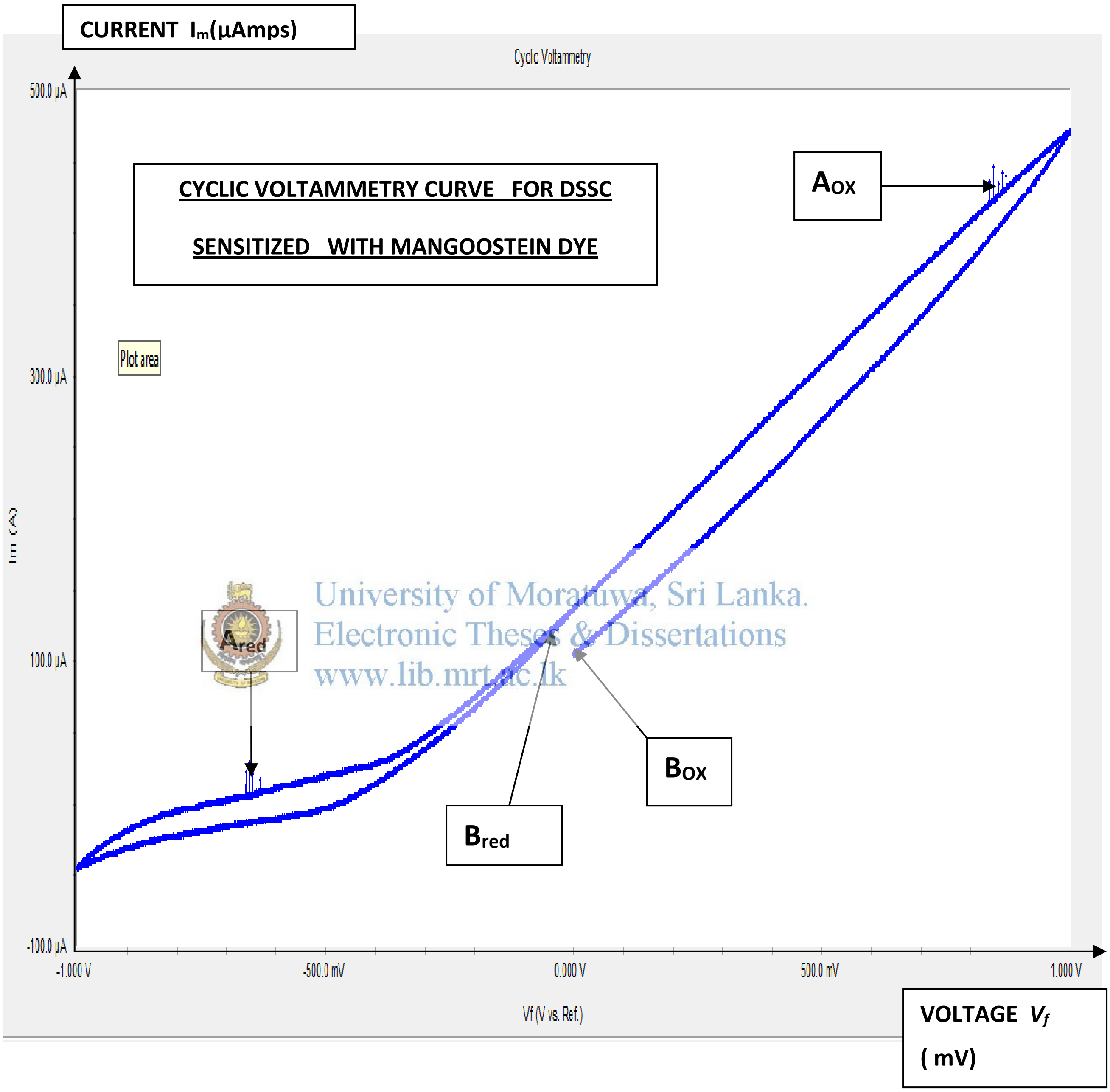


Figure4.43 CyclicVoltammetry curve for DSSC sensitized with Mangoostein dye .

This represents the Current against Voltage behaviour of the DSSC sensitized with Mangoostein dye where two pairs of oxidative and reductive peaks are observed . It is believed that Aox and Ared are due to the oxidation and reduction of I_2 / I_3, and peaks B ox and Bred to the oxidation and reduction of I / I_3. Since the counter electrode of a DSSC is responsible for catalyzing the reduction of I_3 / I the characteristics of the peak Box and Bred are the focus of this analysis .

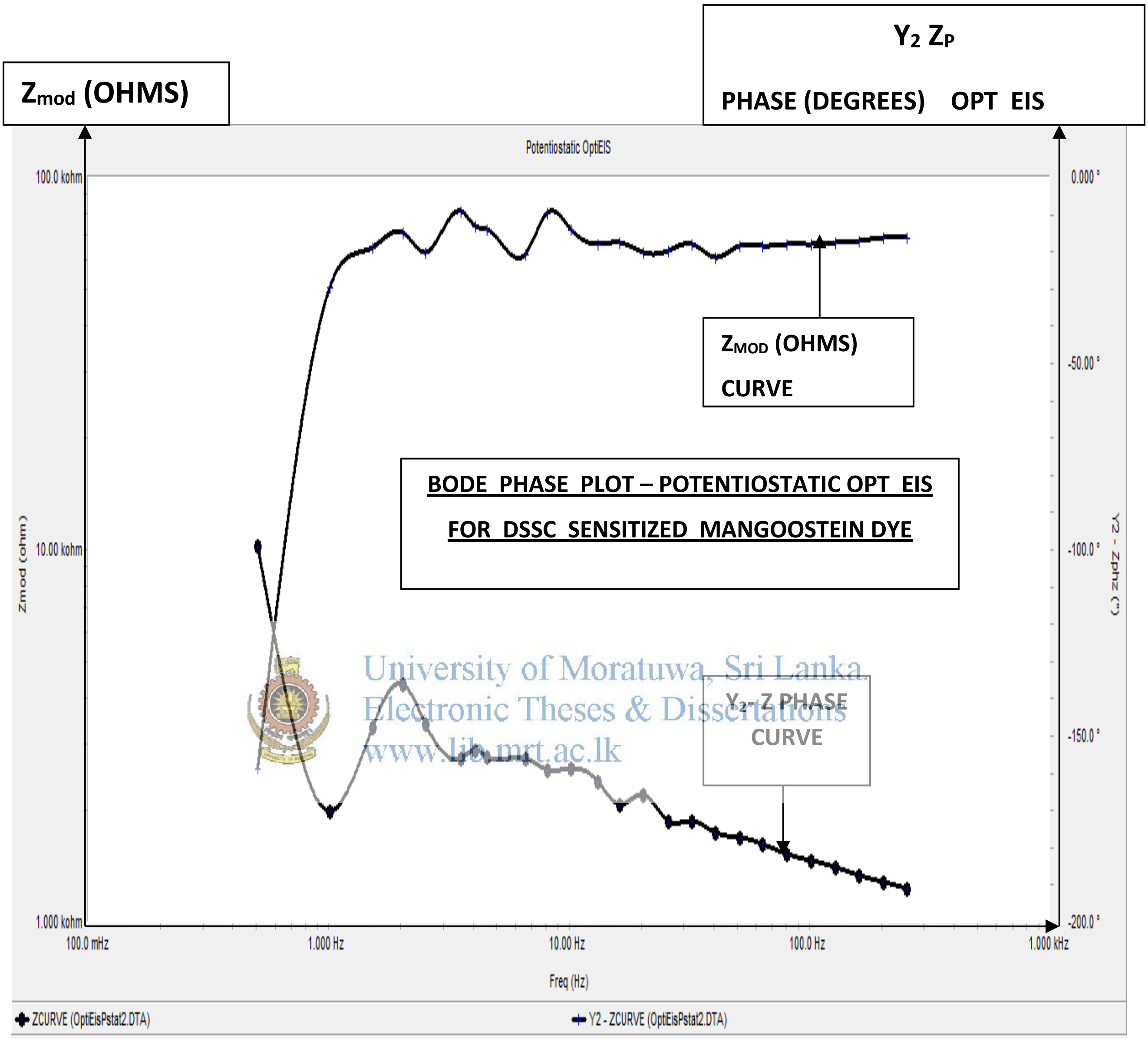


Figure 4.44 Bode Phase plot for DSSC sensiitized with Mangoostein dye

Generally the impedance spectrum of an electrochemical system like a DSSC sensitized with Mangoostein dye can be represented as a Bode plot , which represents the impedance of the device as a function of frequency . There are two types of Bode plots , log l Z 1 vs log ω or 1 Z 1 vs. log ω and Ө vs. log ω , describing the frequency dependencies of of the modulus and phase respectively . A Bode plot is normally depicted logarithimically over the measured frequency range because the same number of points is collected at each decade . It usually starts at a high frequency and end at a low frequency . This Bode plot depicts the Z_{mod} vs. Frequency (top curve) , and Y_2 – Z phase vs. Frequency (bottom curve) for DSSC sensitized with Mangostein dye . Almost parallel horizontal two lines of curves represents fairly good performance.

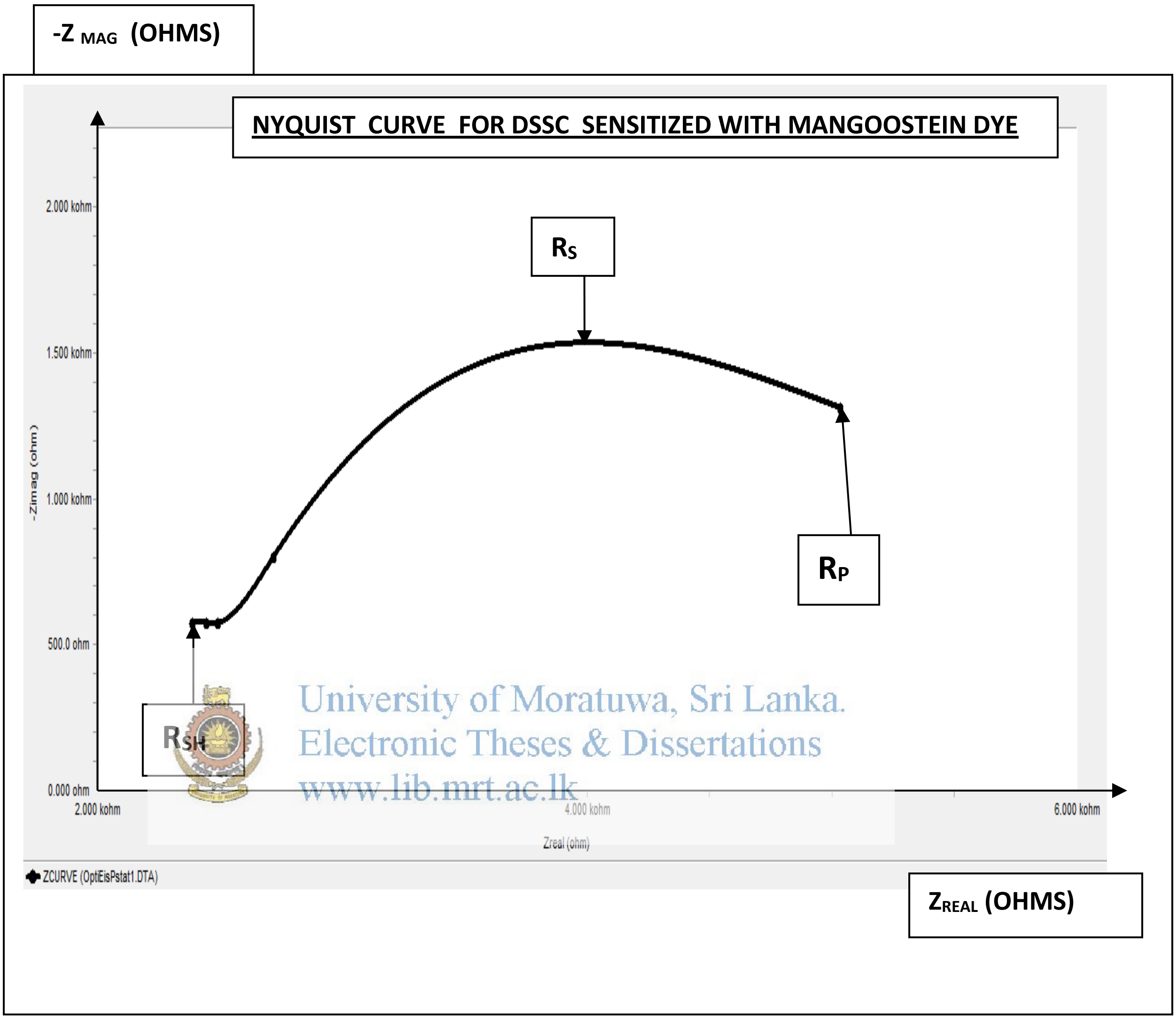


Figure 4.45 Nyquist curve for DSSC sensitized with Mangoostein dye .

Generally , the impedance spectrum of an electrochemical system like a DSSC sensitized with Mangostein dye can also be presented as a Nyquist plot , which is a representaion of the impedance as a function of frequency . Nyquist plot is displayed for a data set of Z impedance values for n points measured at different frequencies with each point representing the real and imaginary parts of the impedance .

The prominent semicircle of this plot indicates that a Mangostein dye sensitized solar cell has good capacitance between its two electrodes , and hence has good potential for the production of relatively high conversion efficiency devices .

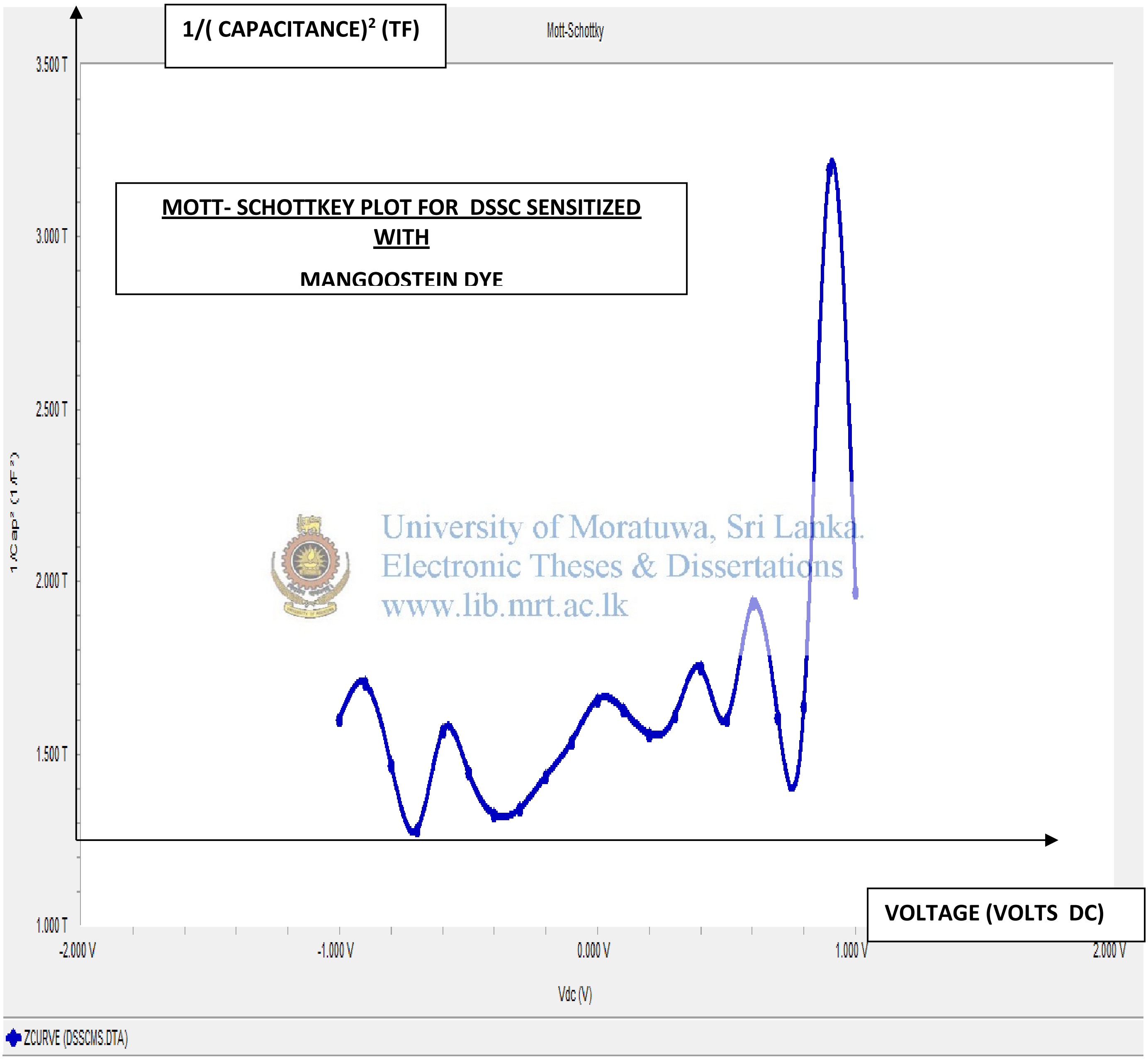


Figure 4.46 Mott Schottkey plot for a DSSC sensitized with Mangoostern dye .

In Mott Shottkey plot of a DSSC sensitized with Mangoostein dye with 1 / (Capacitance)^2 vs. Frequency depicts a prominent inverse linear relationship for a frequency of above 20 KHz , and increasing quadratic curves for a frequencies of 50 KHz and 200 KHz for a typical dye sensitized DSSC .

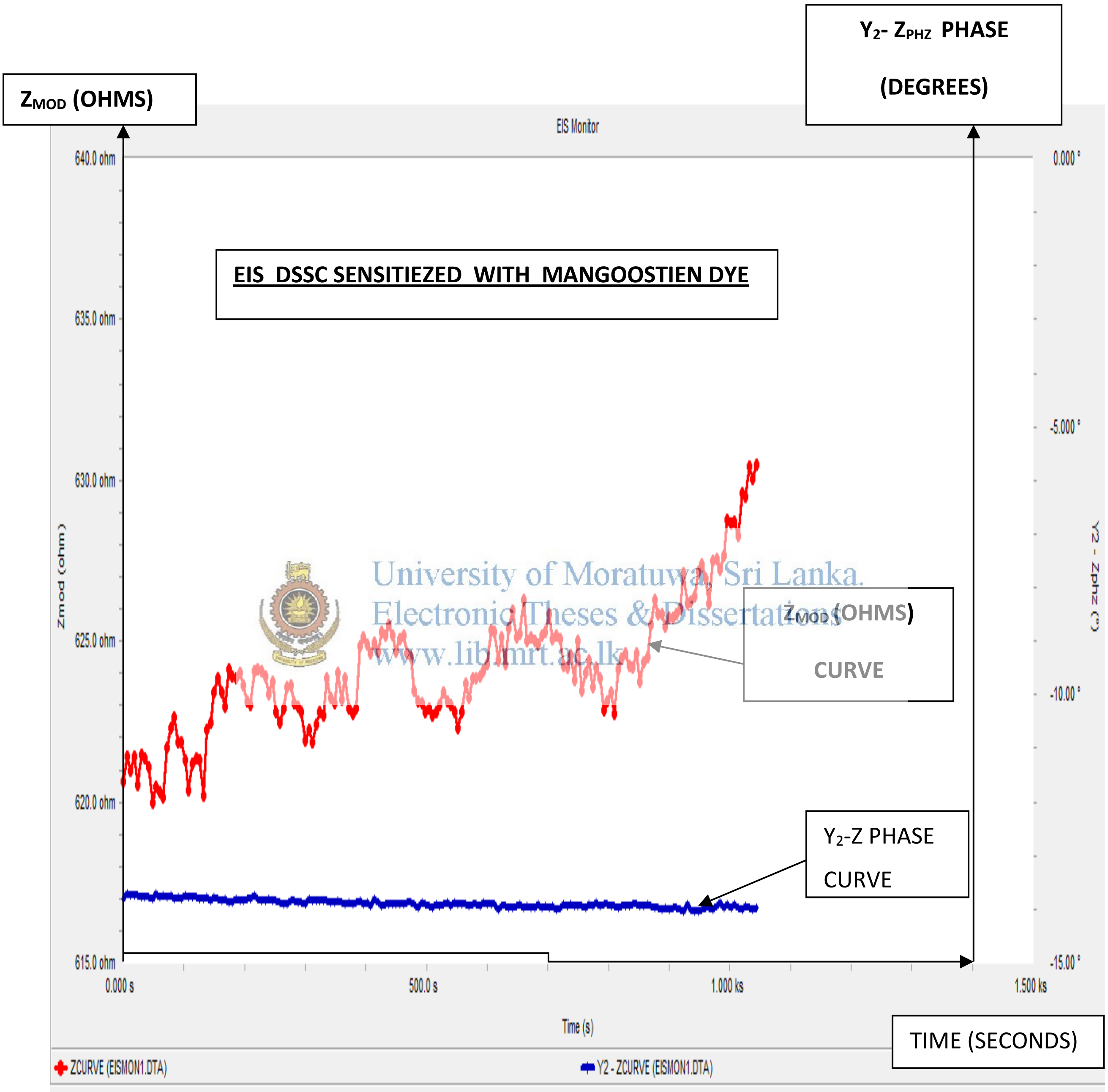


Figure 4.47 EIS Monitor Impedance plot for DSSC sensitized with Mangoostein dye .

The modulus of the impedance values against elapsed time depicts a sinusidually increasing values as shown above for a DSSC sensitized with Mangostein dye as seen in the red graph (the sharp peaks are due to noise).

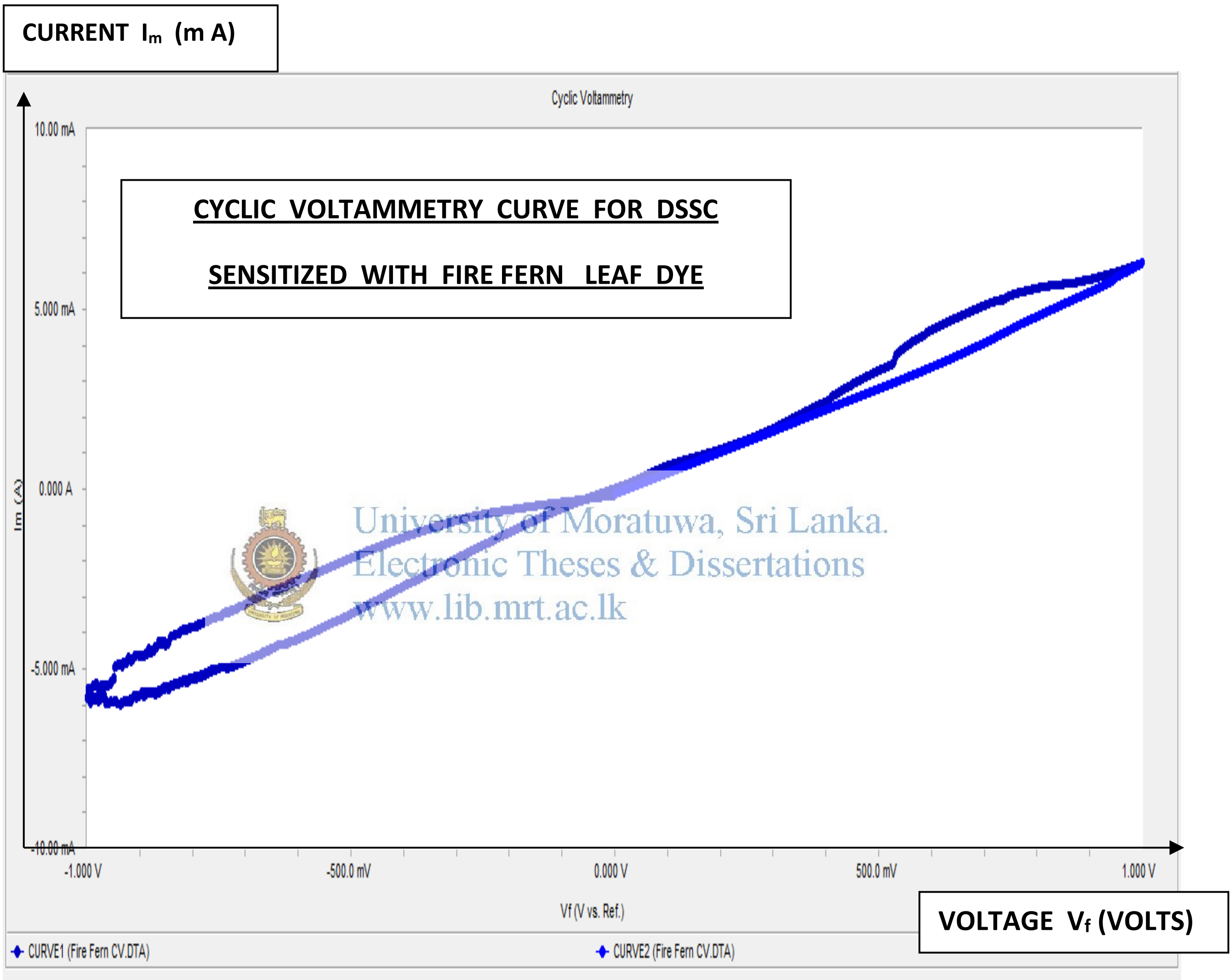


Figure 4.48 Cyclic Voltammetry curve for DSSC sensitized with Fire fern leaf dye.

In this graph the oxidation and reduction values for the DSSC sensitized with Fire fern leaf dye are not clear. Otherwise the CV curve seems satisfactory .

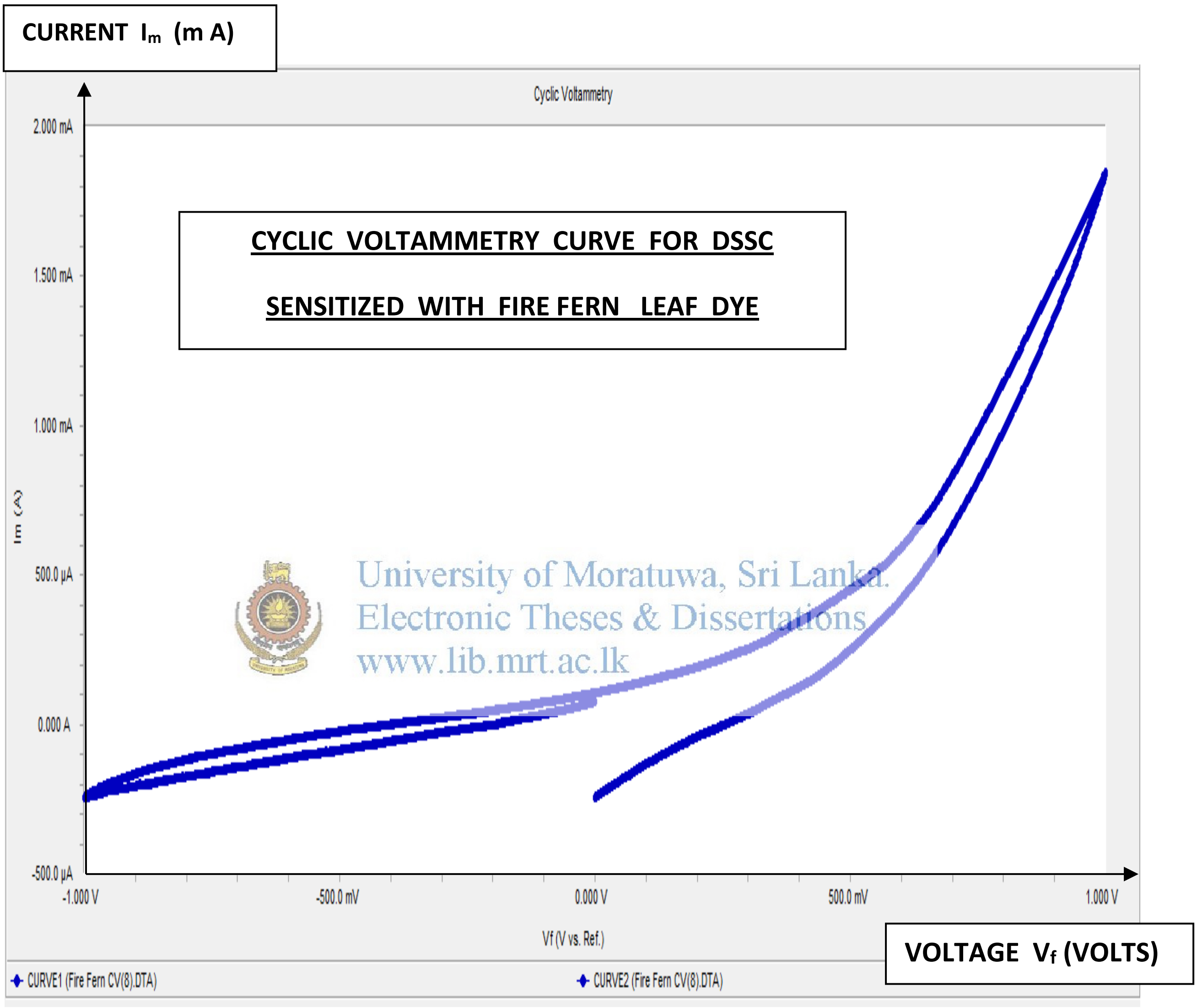


Figure 4.49 Cyclic Voltammetry curve for DSSC sensitized with Fire fern leaf dye.

In this CV curve also for DSSC sensitized with Fire fern leaf dye , the oxidation and reduction values are not clear . Otherwise this graph seems to be satisfactory .

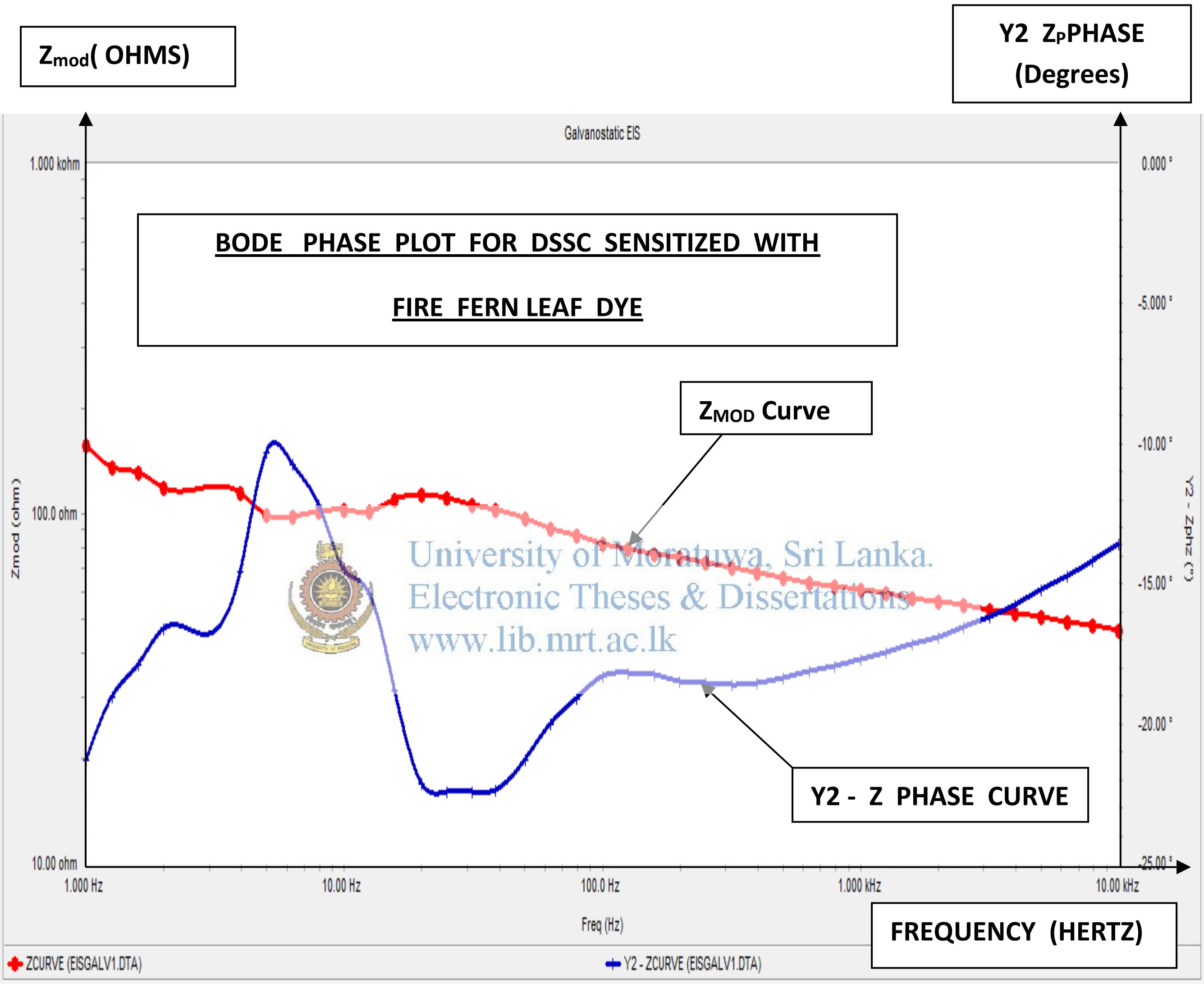


Figure 4.50 Bode phase plot for DSSC sensitized with Fire fern leaf dye.

In this plots the the modulus of the Impedance and Phase angle over Frequency converge around 5 KHz , where as ideally they should be parallel to each other .

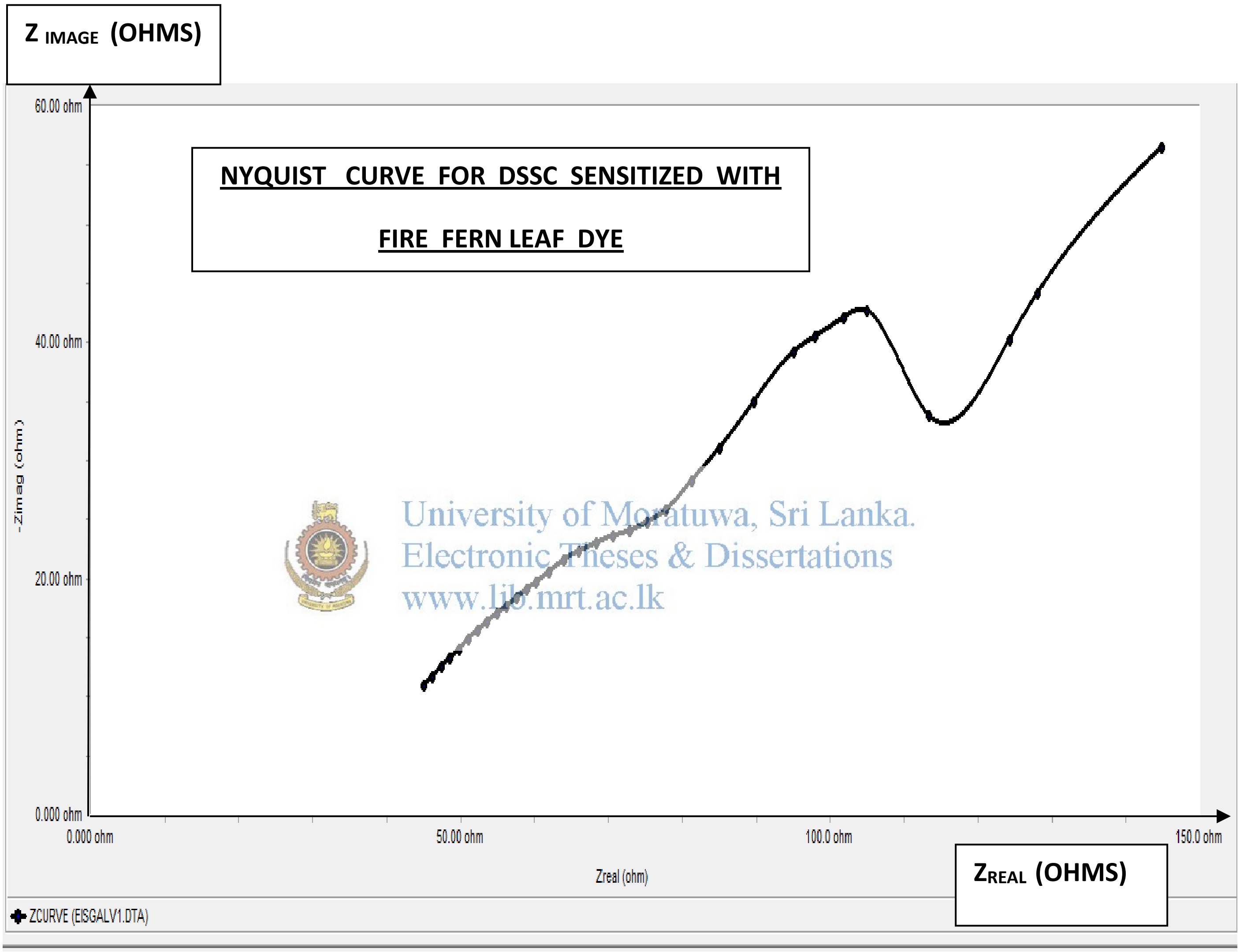


Figure 4.51 Nyquist curve for DSSC sensitized withFire fern leaf dye .

In this plot the required semicircle has got distorted from Z_{real}(real impedance) of 50 Ohms to about 110 Ohms .

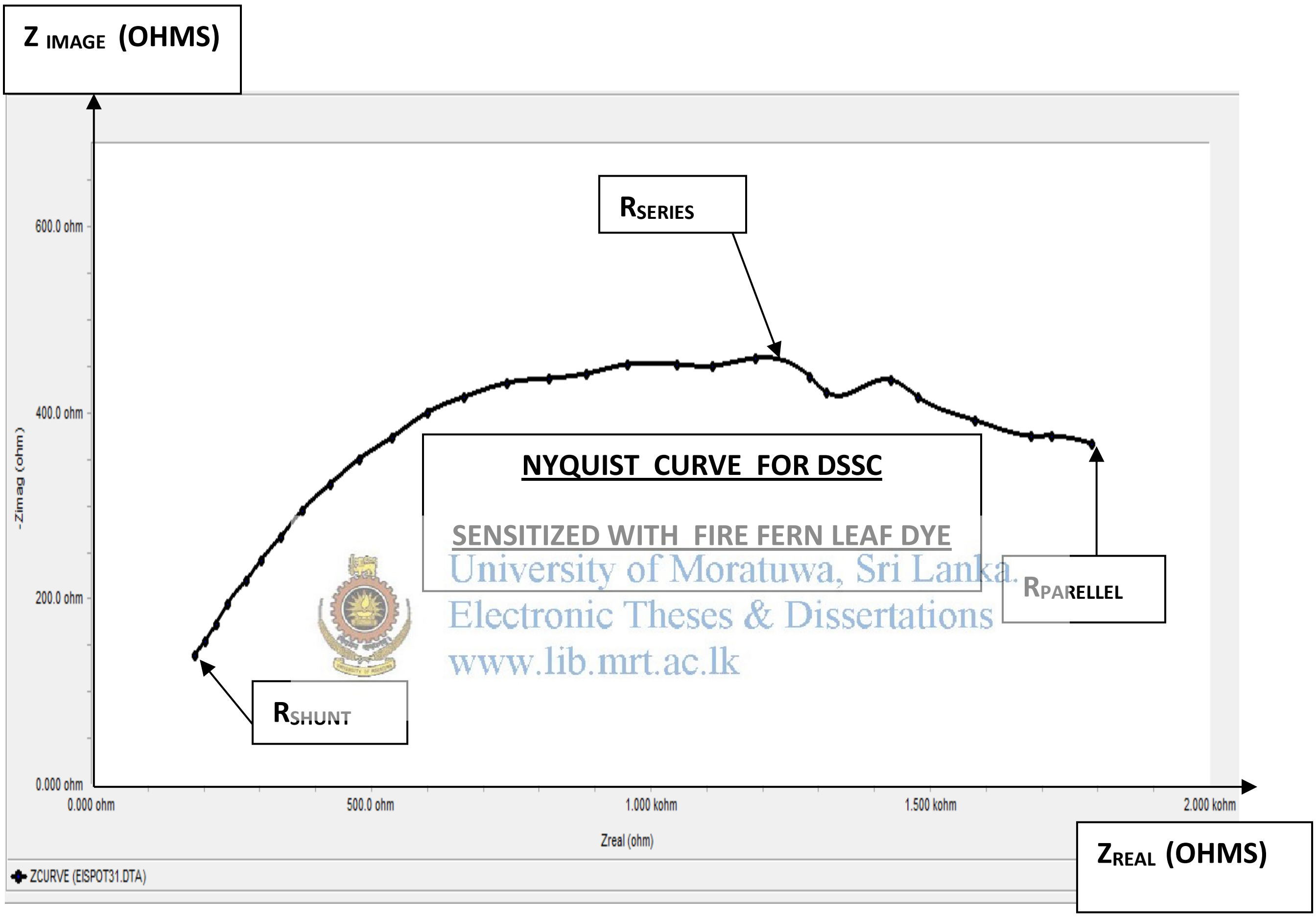


Figure 4.52 Nyquist curve for DSSC sensitized with Fire fern leaf dye .

In this graph the semi circle for a real Impedance of 200 Ohms to about 1300 Ohms has reduced to about 50% of this value .

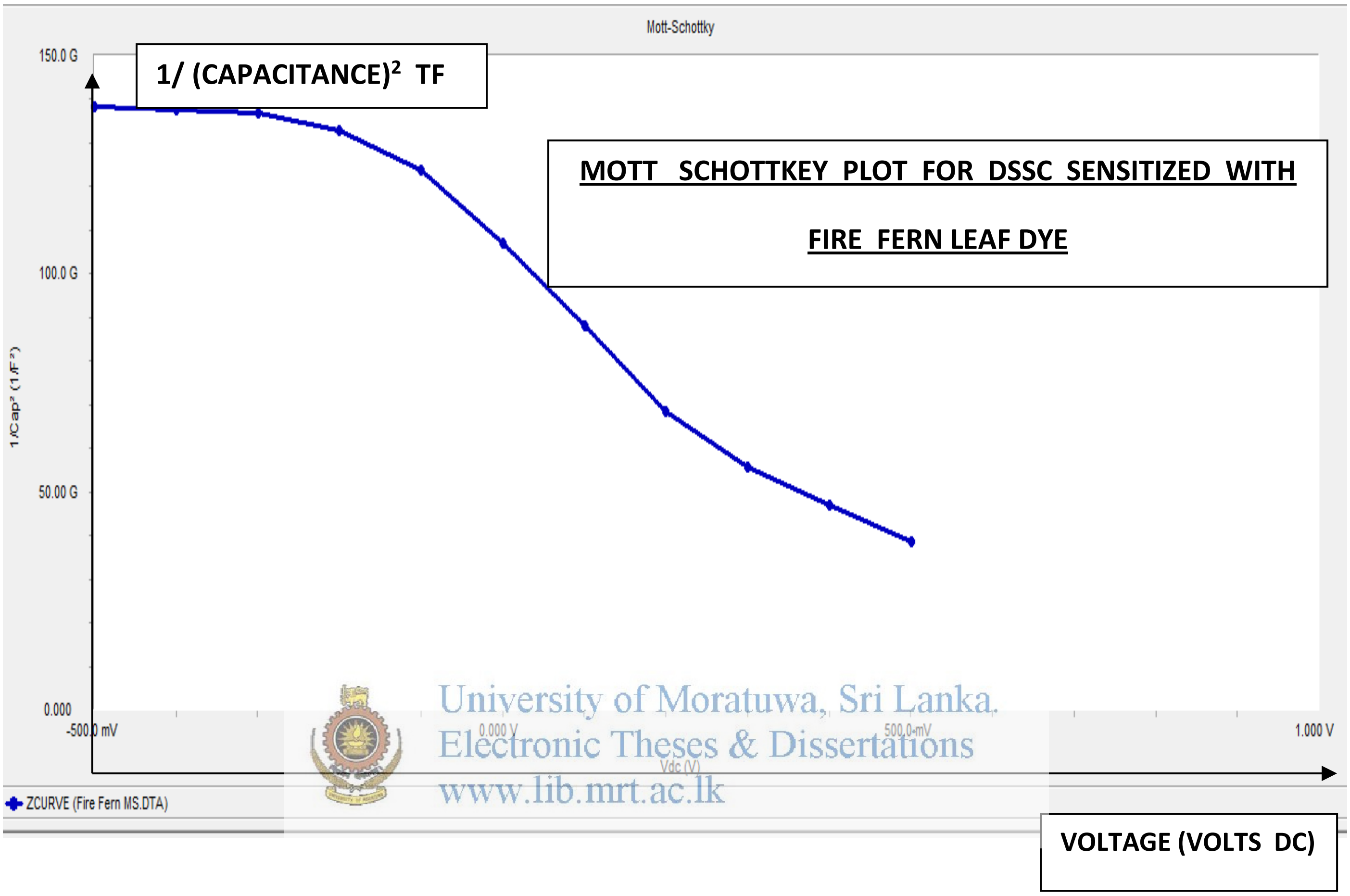


Figure 4.53 Mott Schottkey plot for DSSCsensitized with Fire fern leaf dye.

This plot displays almost linearly decreasing 1/ (Capacitance)^2 values against Voltage from 125 GF to 35 GF .

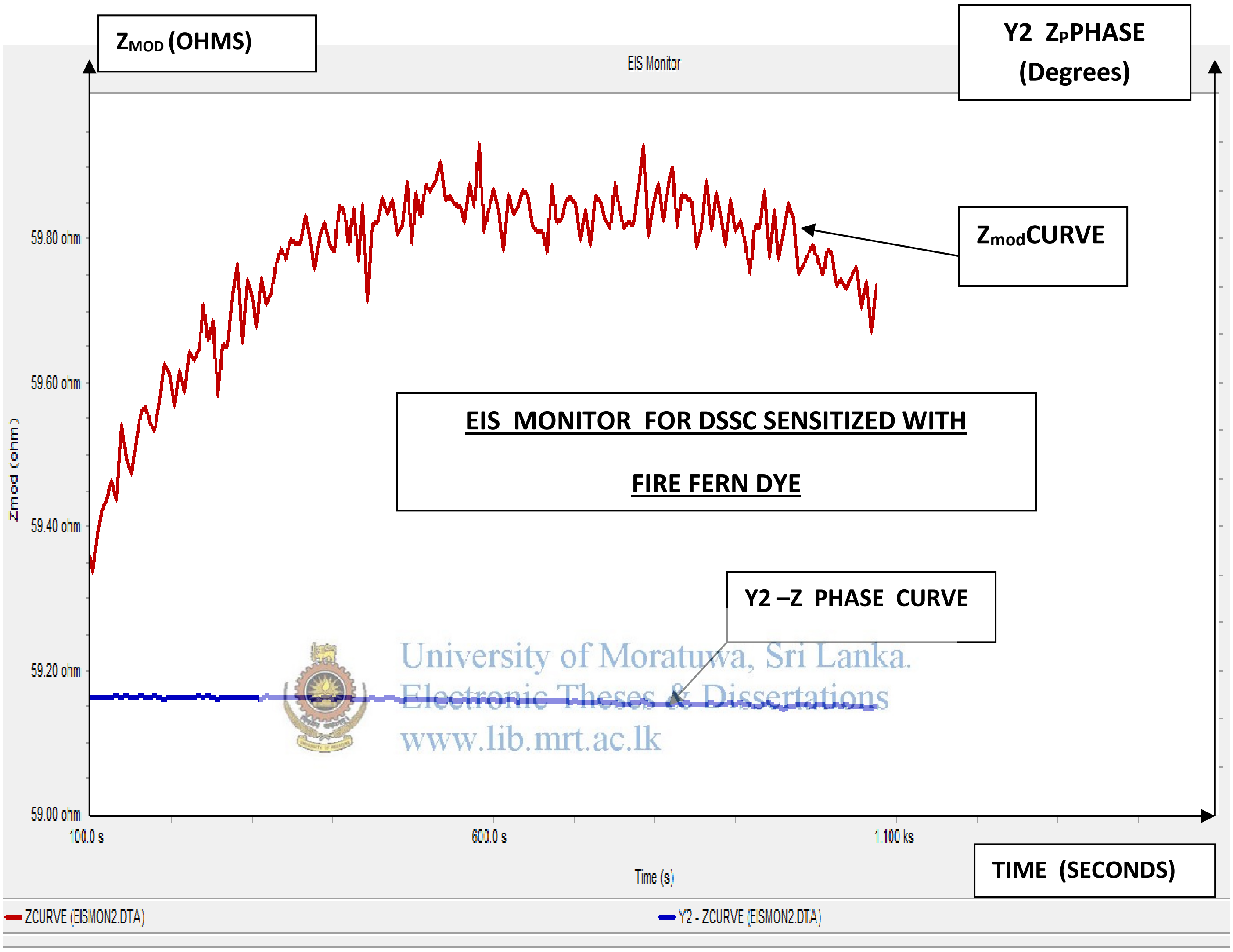


Figure 4.54 EIS Monitor Impedance plot for DSSC sensitized with Fire fern leaf dye .

This depicts an EIS Monitor Impedance plot of almost semi circular increment of the modulus of the Impedance against Time (the red spikes due to picked up noise). The lower Y_2 Impedance (blue) plot is almost linearly constant against time .

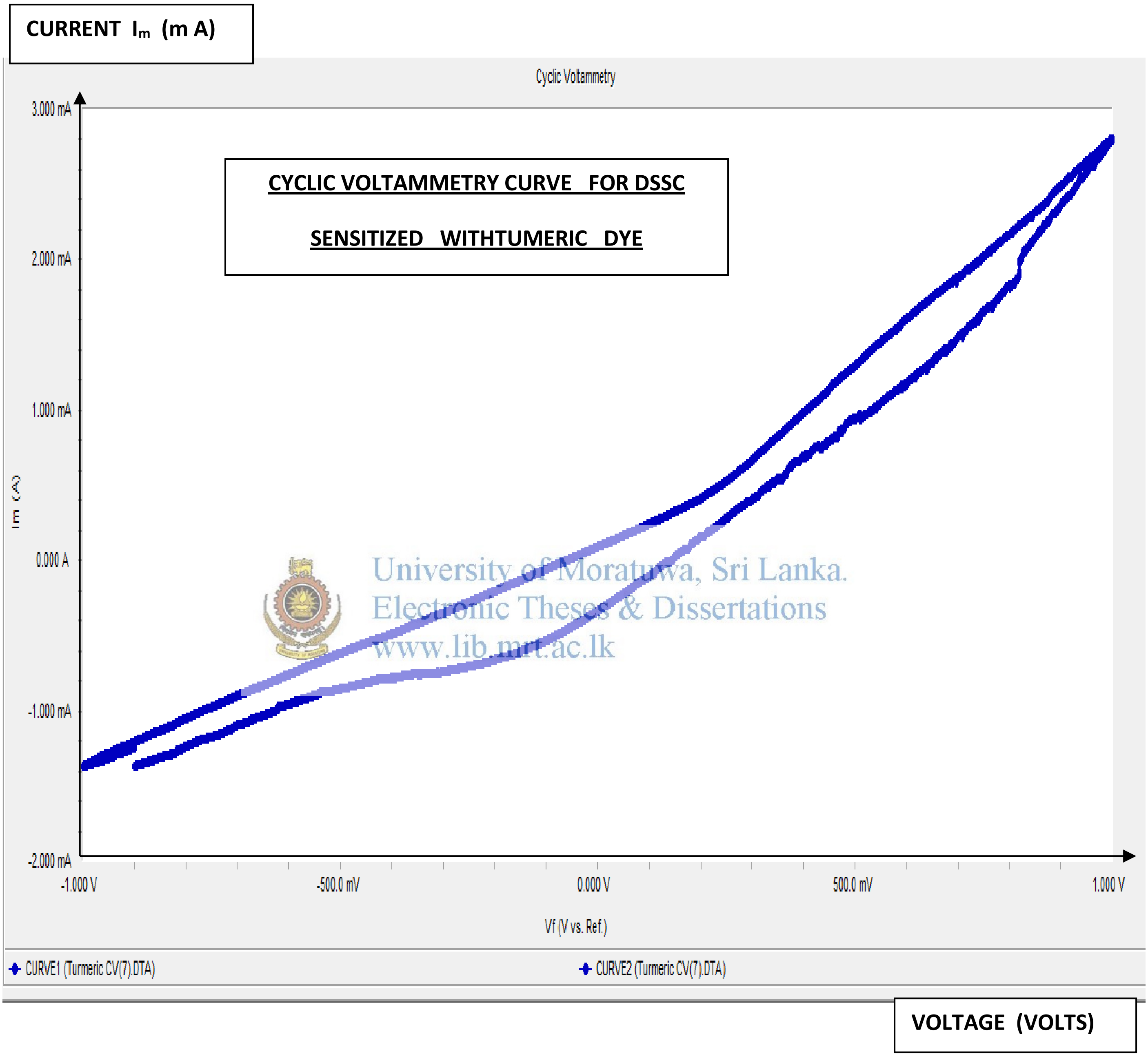


Figure 4.55 Cyclic Voltammetry curve for DSSC sensitized with Turmeric dye.

The oxidation and reduction values of the two curves are not clearly visible in this plot . However, the CV plot for DSSC sensitized with Turmeric dye seems to be satisfactory .

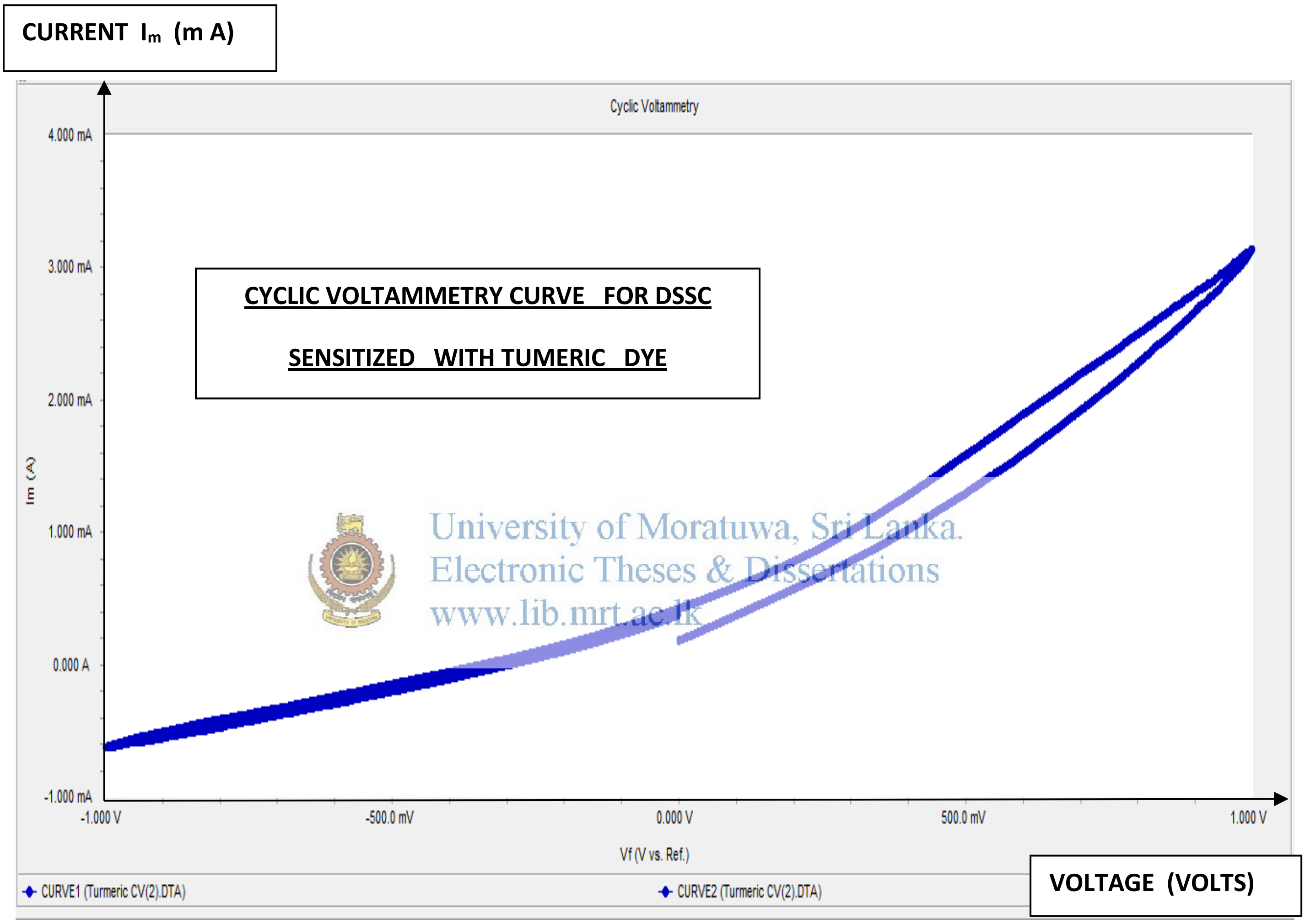


Figure 4.56 Cyclic Voltammetry curve for DSSc sensitized with Turmeric dye .

This CV seems to be satisfactory except for the left side reduction curve line at the bottom which has merged with top reduction curve .

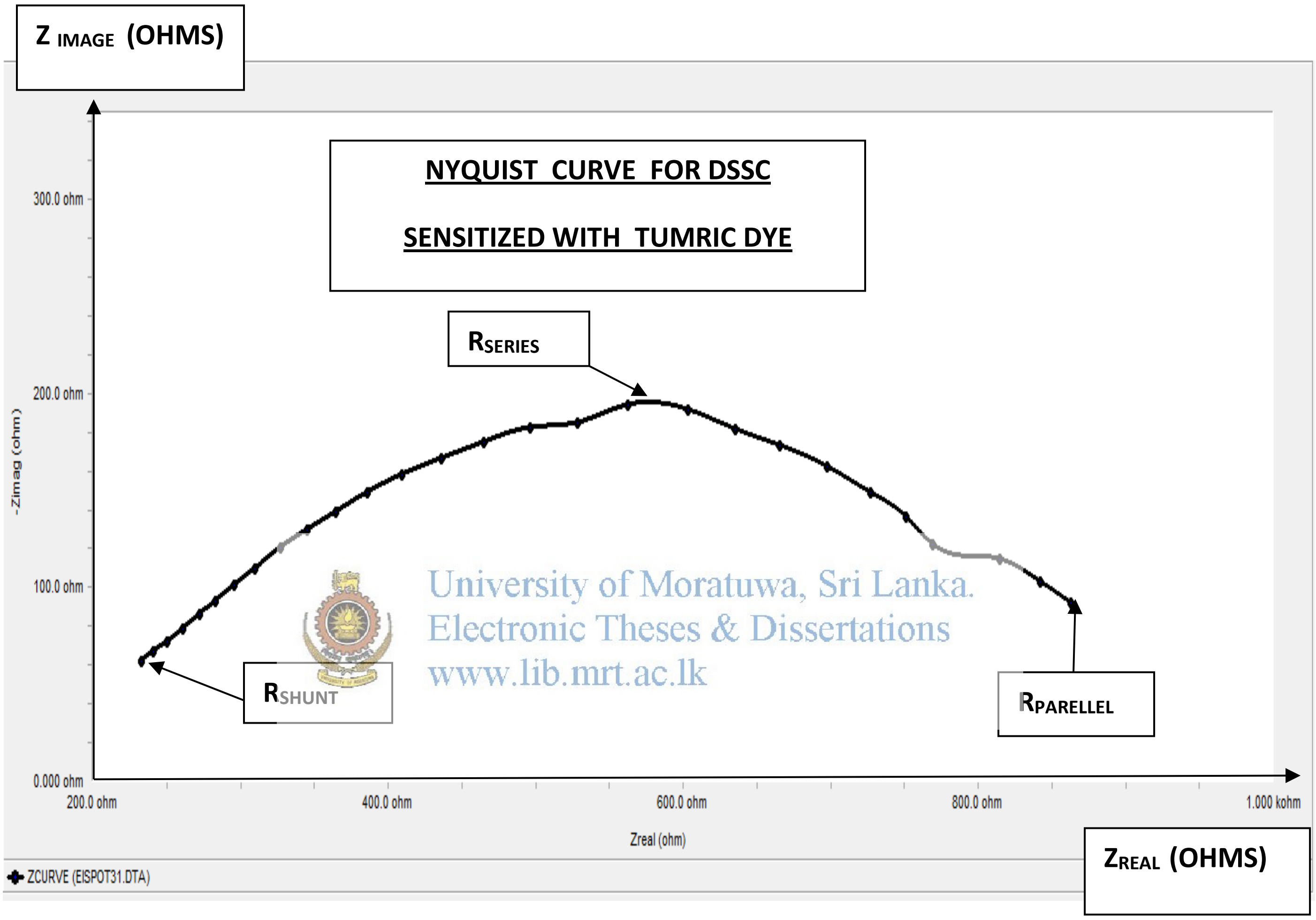


Figure 4.57 Nyquist curve for DSSC sensitized with Turmeric dye .

The required semi circular Z_{imag} vs Z_{real} curve has got somewhat distorted .

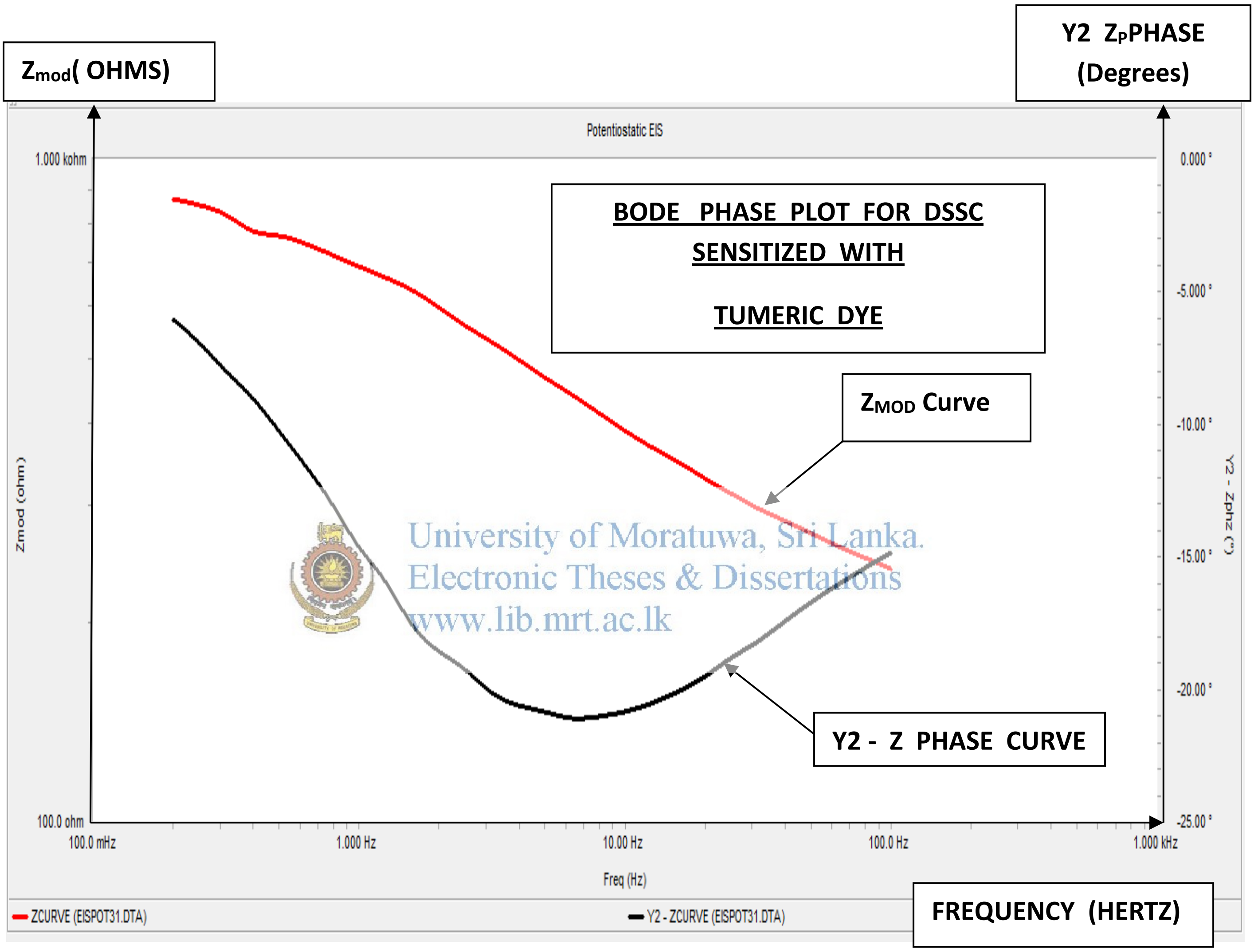


Figure 4.58 Bode phase plot for DSSc sensitized with Turmeric dye .

The Impedance and Phase plots against Frequency should be parallel to each other , but not so .

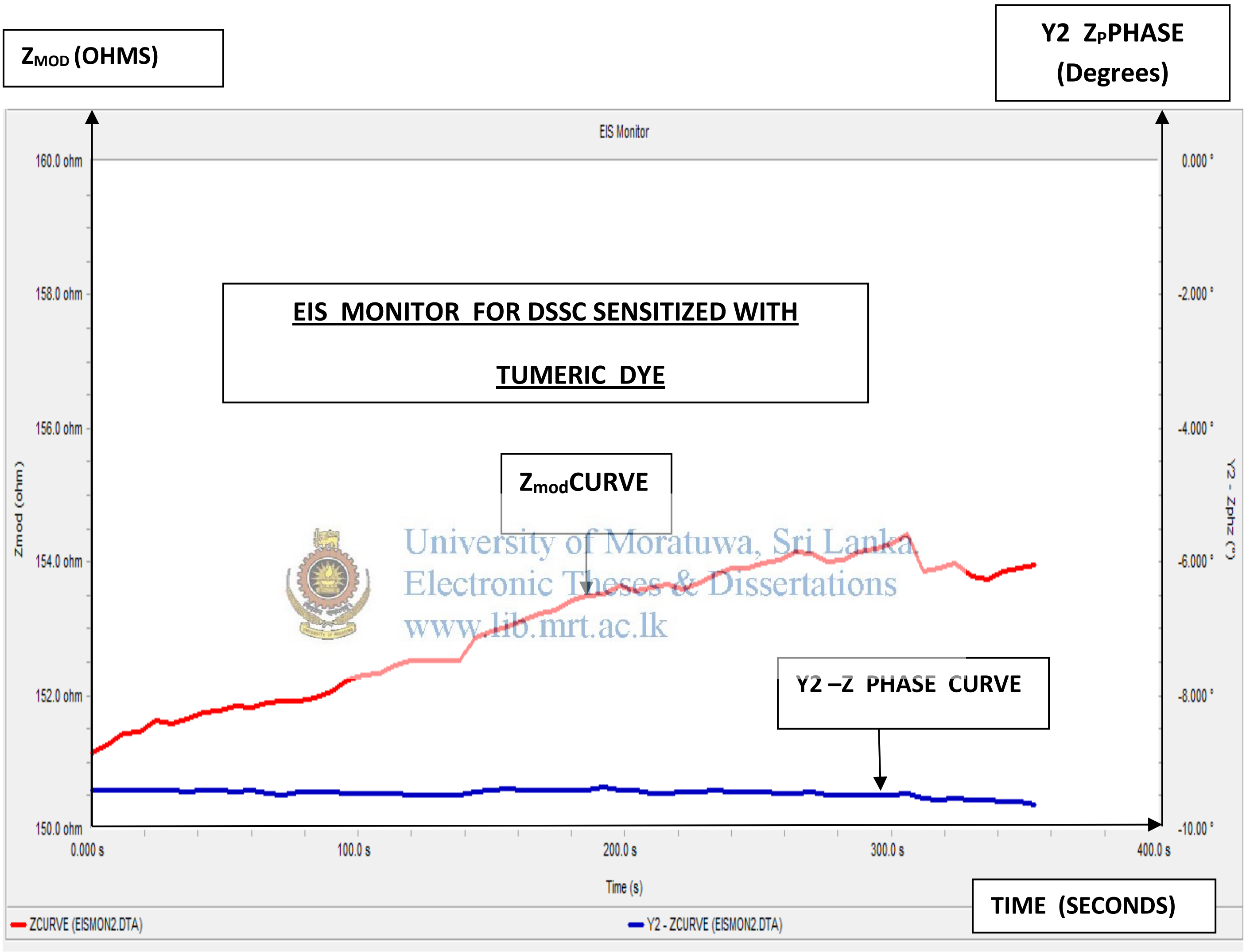


Figure 4.59 EIS Monitor for DSSC sensitized with Turmeric dye.

The modulus of the Impedance over Time for DSSC sensitized with Turmeric dye increases almost linearly, where as the Phase angle over Time is almost constant .

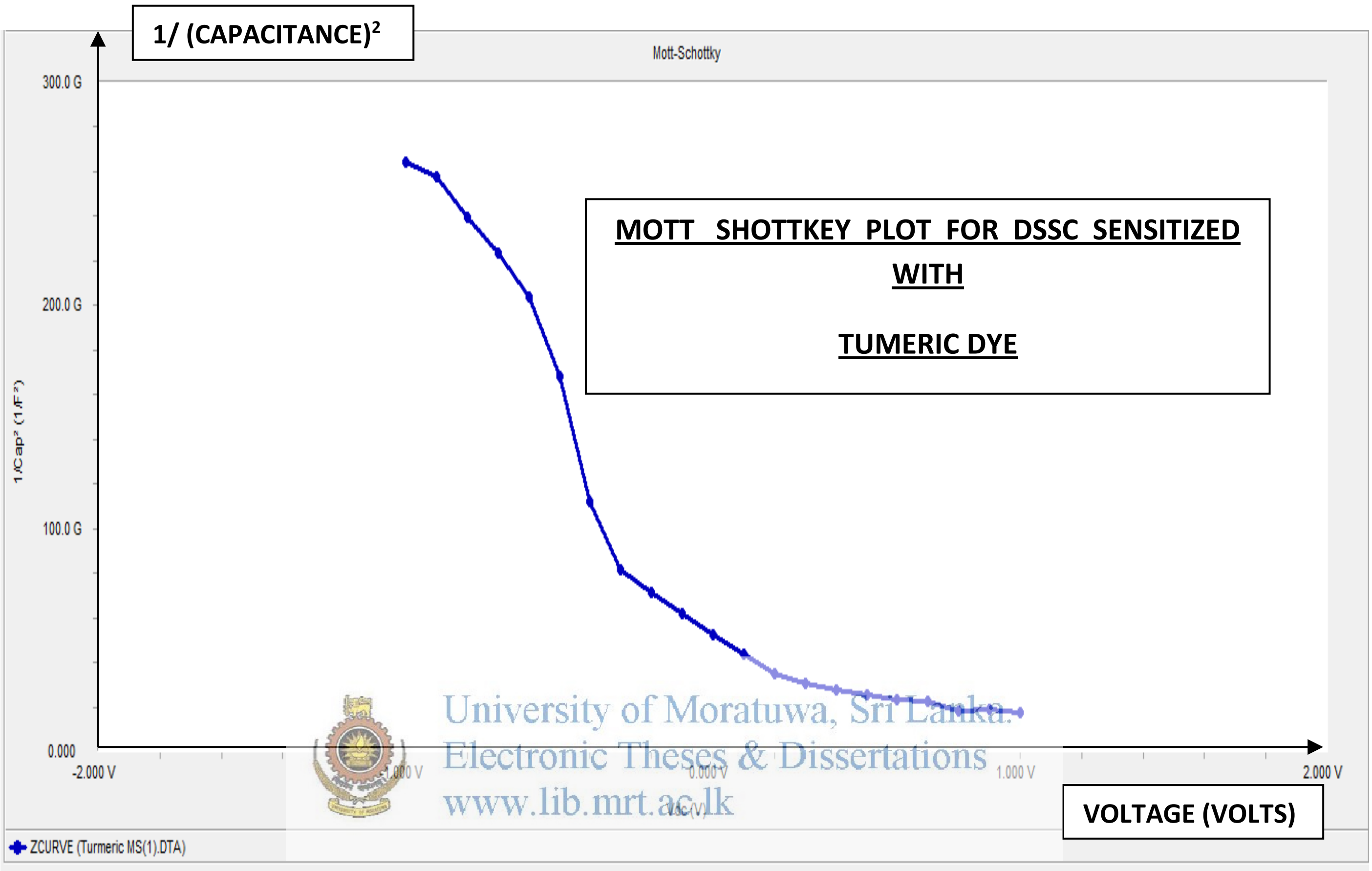


Figure 4.60 Mott Shottkey plot for DSSc sensitized with Turmeric dye .

The 1/ (Capacitance)^2 vs Voltage plot decreases almost linearly from -- 1.000 Volt to – 0.250 Volt, and again from – 0.250 Volt to 1.000 Volt in two segments .

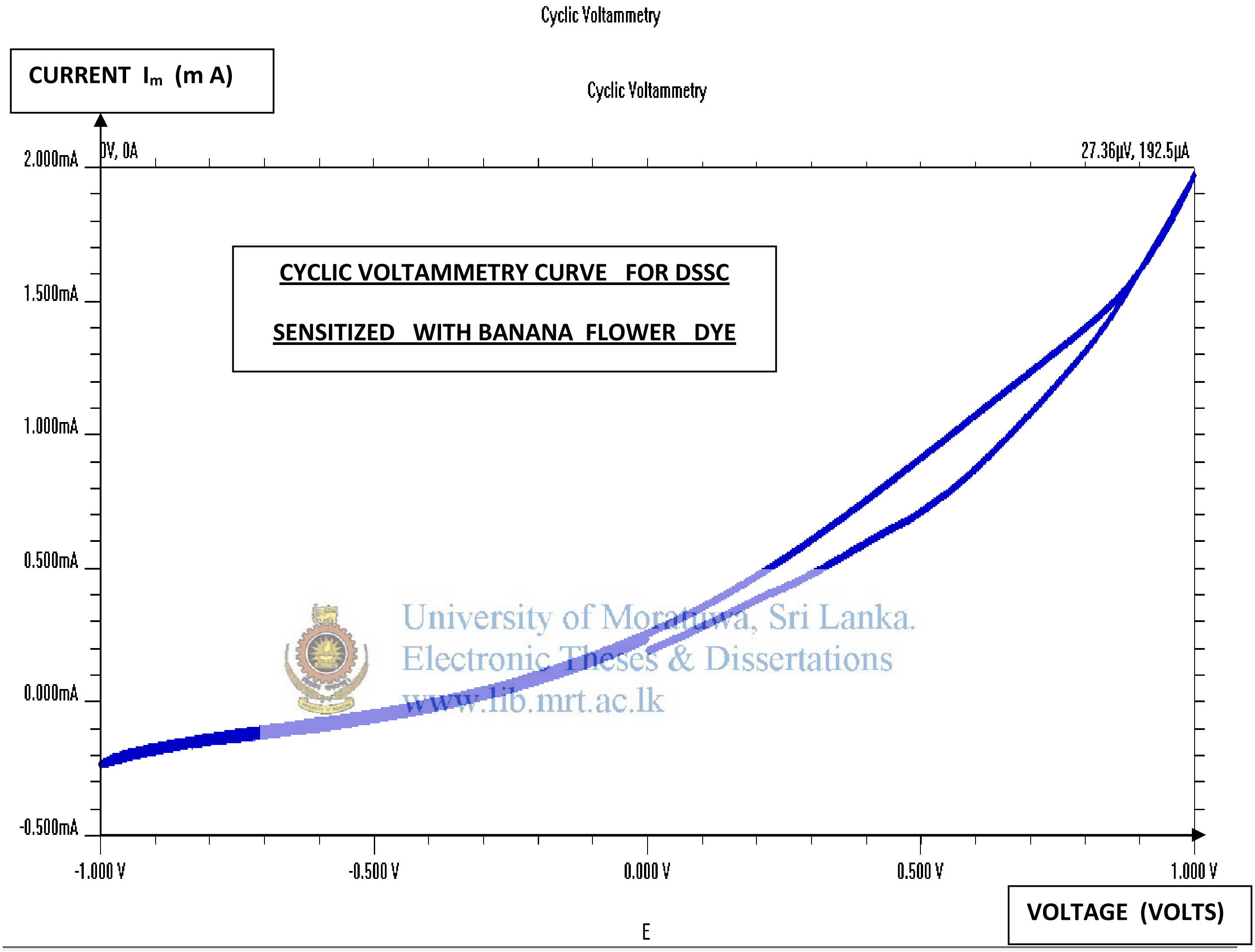


Figure 4.61 Cyclic Voltammetry curve for DSSC sensitized with Banana flower dye.

This CV curve seems to be satisfactory except that the bottom left reduction curve has merged with the top left reduction curve .

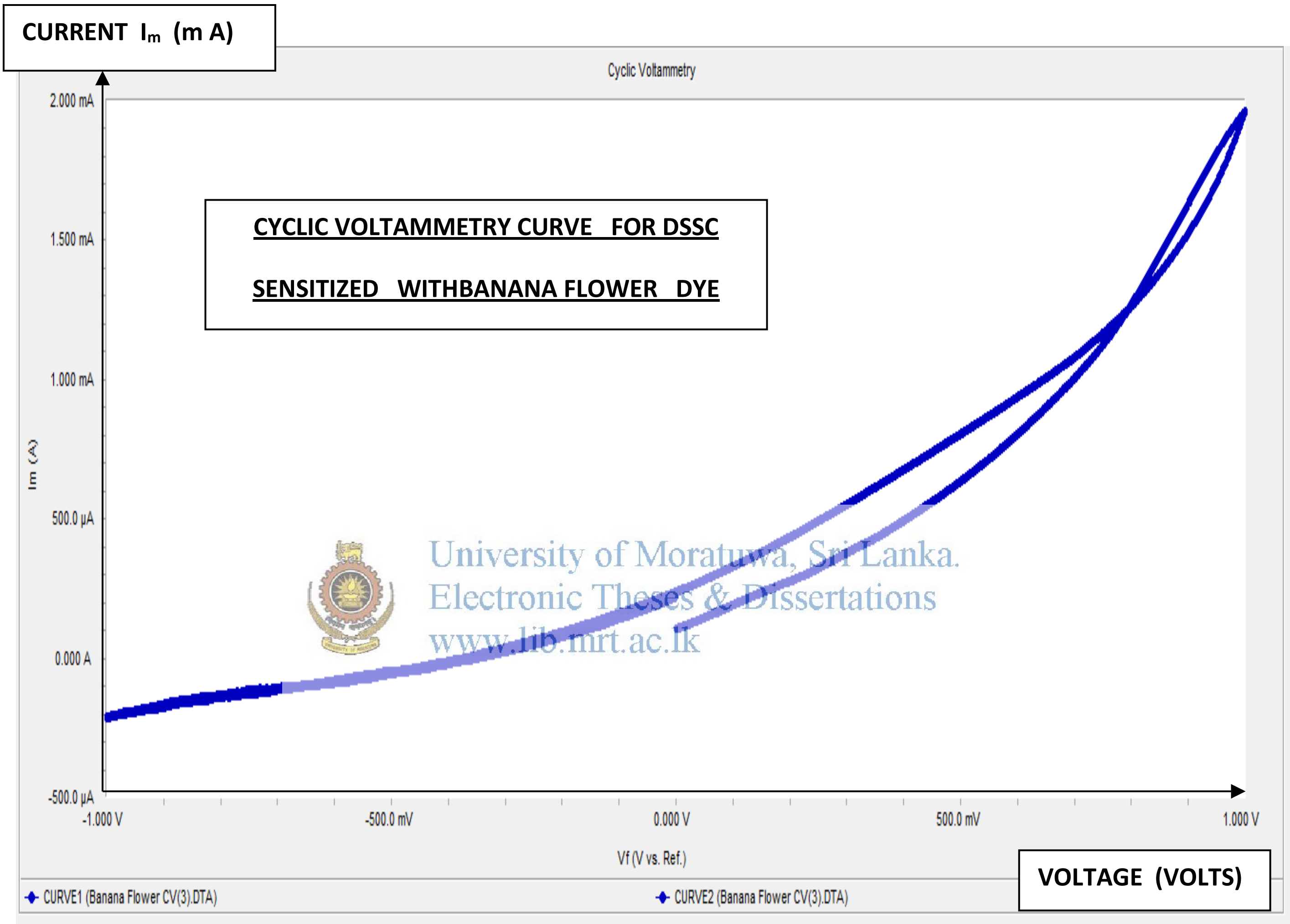


Figure 4.62 Cyclic Voltammetry curve for DSSC sensitized with Banana flower dye .

The bottom left reduction curve has merged with the top left reduction curve .

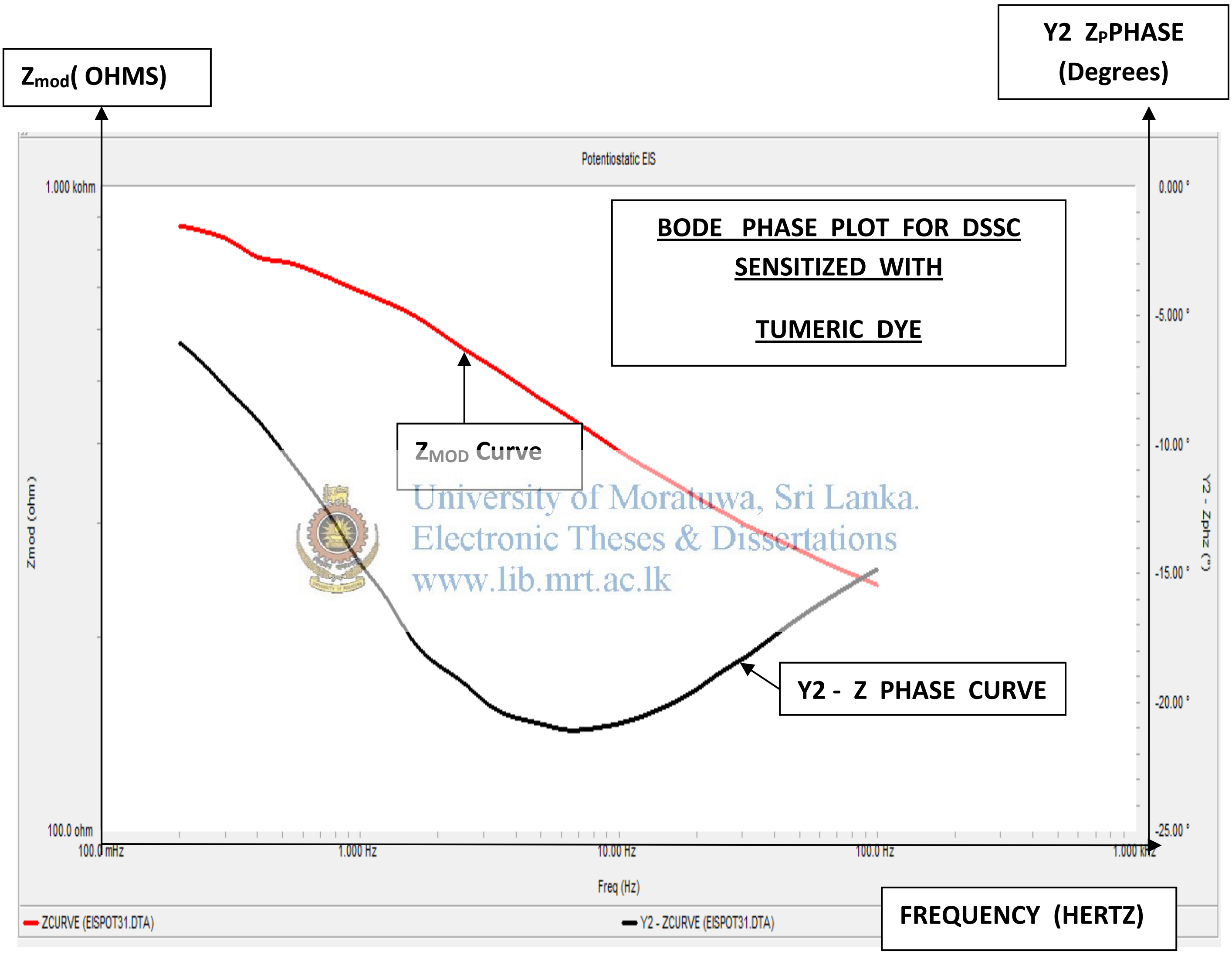


Figure 4.63 Bode Plot for DSSC sensitized with Tumeric dye

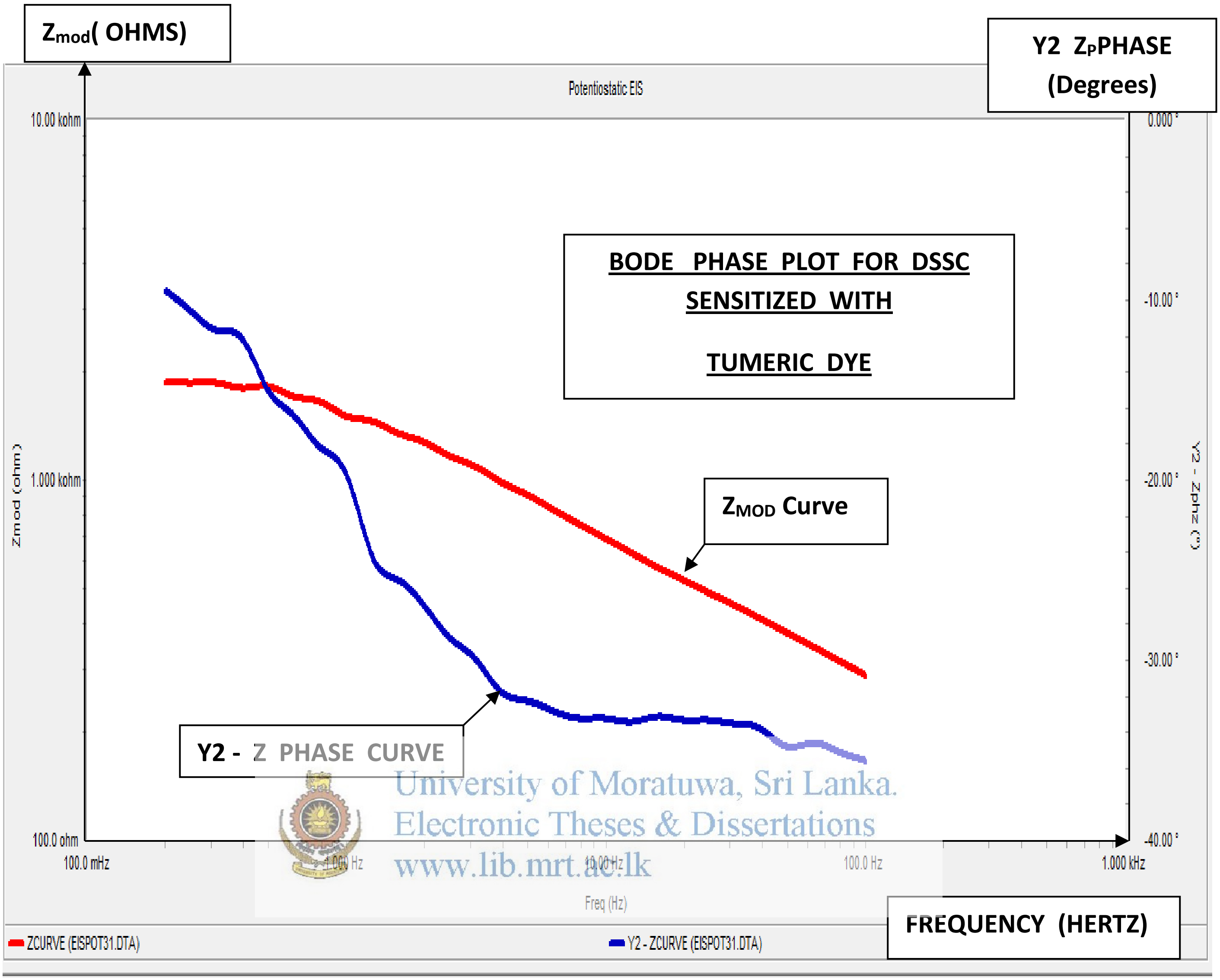


Figure 4.64 Bode phase plot for DSSc sensitized with Banana flower dye .

These two curves should be parallel to each other .

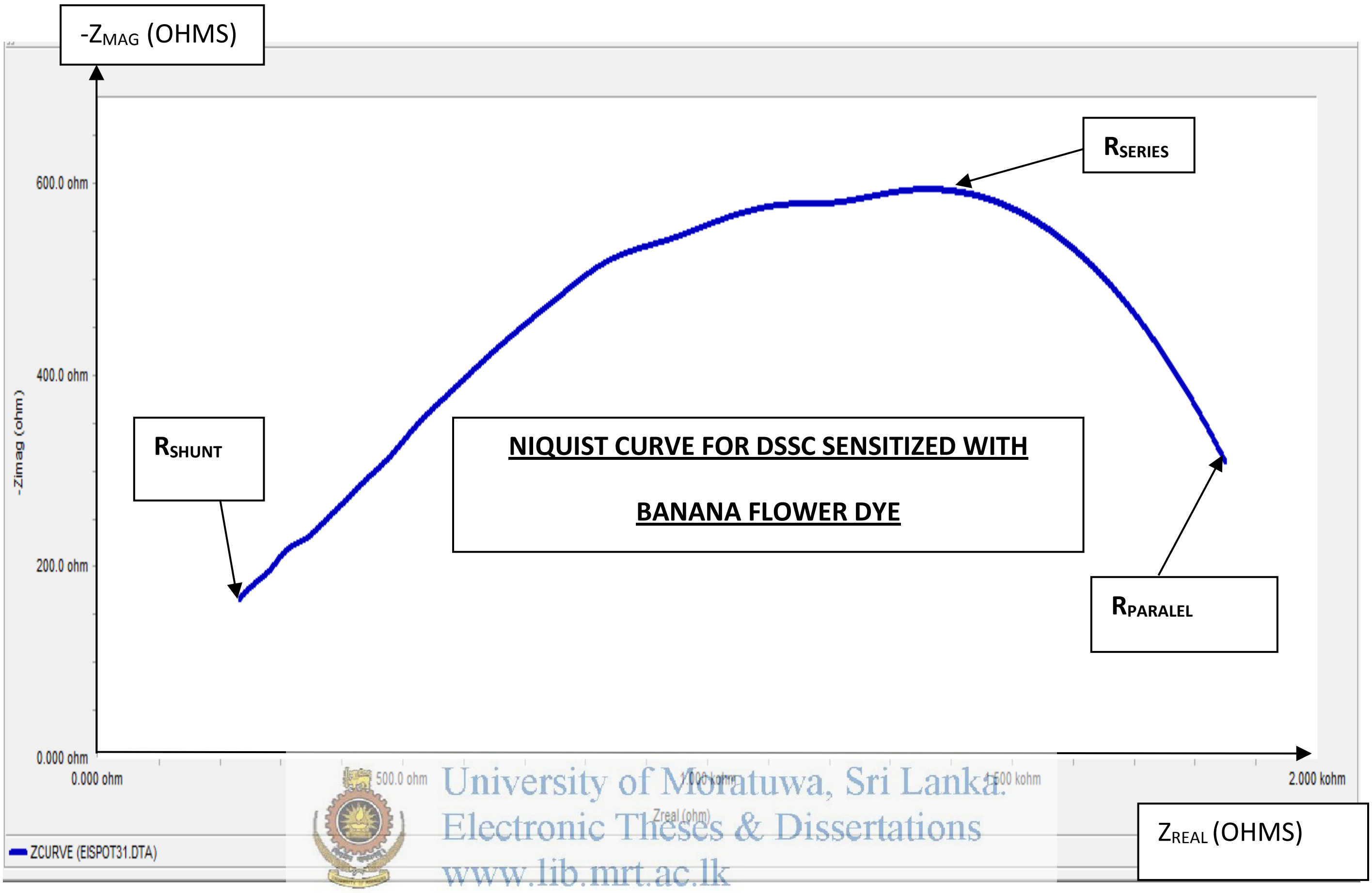


Figure 4.65 Nyquist curve for DSSC sensitized with Banana flower dye .

This curve should be ideally semi circular .

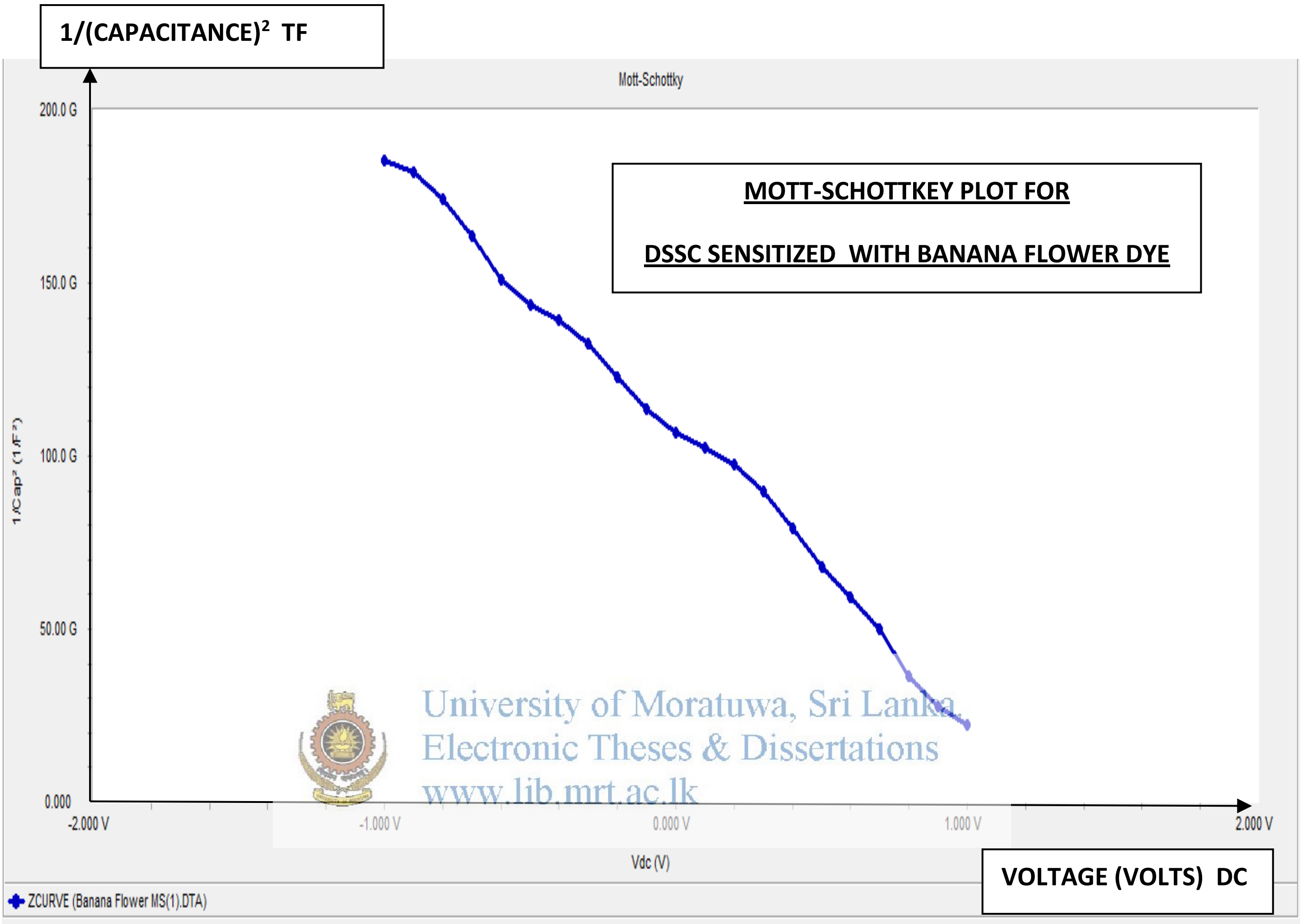


Figure 4.66 Mott Schottkey plot for DSSC sensitized with Banana flower dye .

Ideally this plot should be inversely linear for 1/ (Capacitance)^2 vs. Voltage .

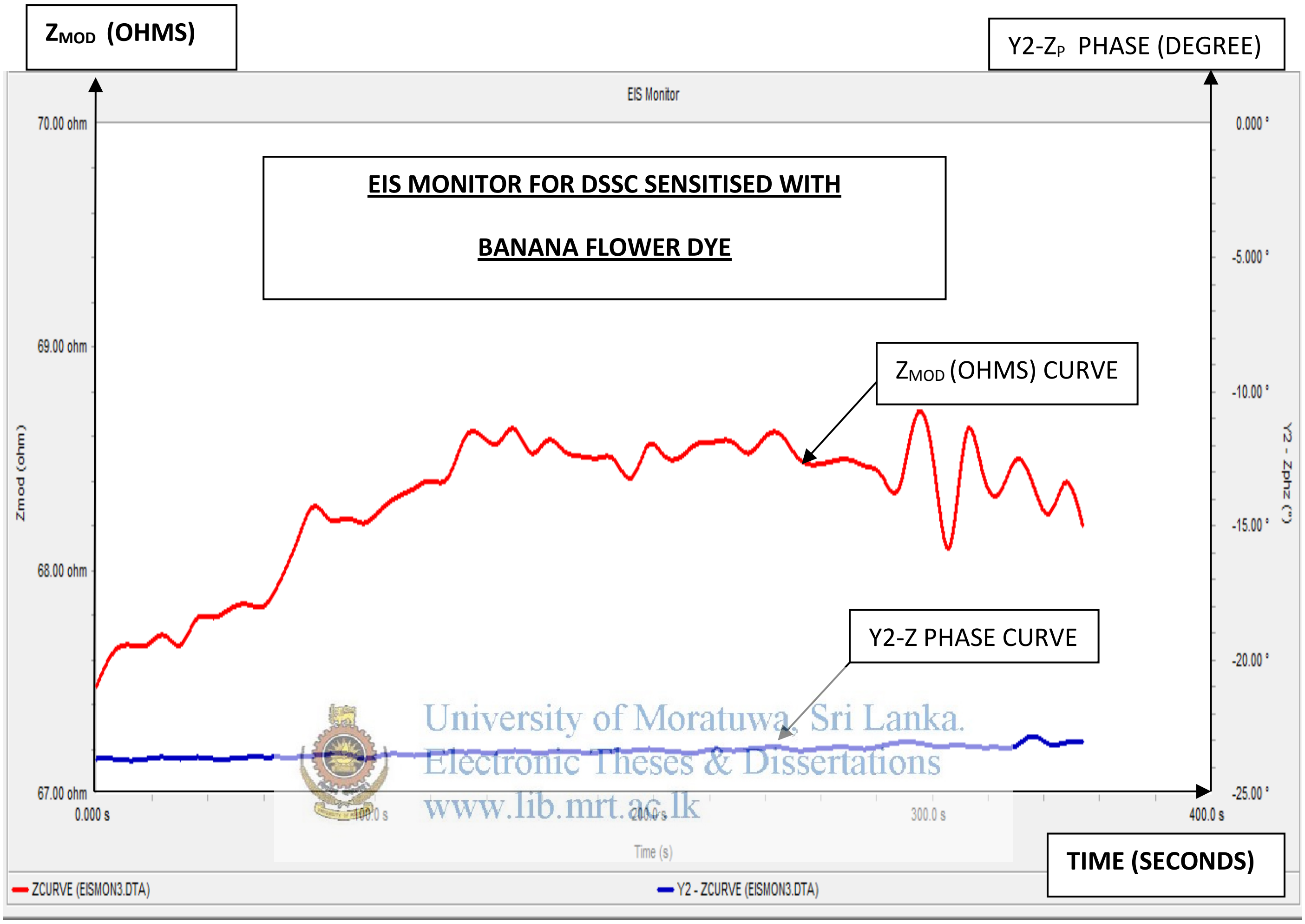


Figure 4.67 EIS Monitor for DSSC sensitized with Banana flower dye.

The top red curve of the modulus of Impedance vs. Time should increase almost linearly where as some what sinusoidally increasing and decreasing curve is seen , and the bottom blue curve of Phase vs. Time should be constant as seen .

It is pertinent to note that by carefully scrutinizing all the Cyclic Voltammetry curves , Bode plots , Nyquist curves , Mott Schottkey plots and MIS Impedance plots of DSSC's sensitized with ripe Mangoostein fruit rind dye extracts, and a cross- section of other best natural dyes of plants and trees growing in Sri Lanka identified , the former dye holds the potential to produce DSSC's with relativelygood conversion efficiency using cheap , freely available and environmentally natural dyes .

The detailed analysis of the Nyquistand Bode plots of DSSC’s mentioned above is as

follows :

Generally , the impedance spectrum of an electrochemical system like a DSSC can be presented in Nyquist and Bode plots, which are representions of the impedance as a function of frequency.

A Nyquist plot is displayed for the data of real and imaginary impedance values (Z_{real} , Z_{img}) measured at different frequencies with each point representing the real and imaginary parts of the impedance .There are two types of Bode plots , log 1 Z 1 vs. log ω or 1 Z 1 vs. log ω or [Z] vs. log ω and Ө vs log ω , describing the frequency dependence of the modulus and phase respectively .

[Z]= Impedance in Ohms, ω= 2∏ f where f is frequency in Hertz, Ө= Phase angle in degrees , $Z_{img =}$ Imaginary impedance , $Z_{real =}$ Realimpedance] .

A Bode plot is normally depicted logarithimically over the measured frequency range because the same number of points is collected at each decade . Both plots usually start at a high frequency and end at a low frequency .

Therefore the Nyquist plot of a DSSC with FTO coated glass electrodes depicts Z_{img} vs Z_{real} values for electrochemically affected counter and photo electrodes enclosing an electrolytic medium between them (usually KI / I redox electrolyte). By inclined and near inclined (-- 90 degrees) sloping lines , impedance spectra in Nyquist plots of these DSSC’s show almost capacitive responses for these systems differing only in impedance .

Significant decrease in impedance magnitudes would be observed at higher frequencies for DSSC’s containing counter electrodes of FTO (Fluorine doped Tin oxide) coated with Exfoliated Graphene oxide nanoplate . These would show an apparent lowering of slopes owards – 45 degrees above 10 Hz , and also some shifts of all curves towards higher Z_{real} values .

According to the definition of impedance as a vector with magnitude [Z] and phase angle Φ, these plots show impedance spectra of these systems in the form of Bode plots of log 1Z1 and Φ vs . log ω .

Indiference to Nyquist plots that show only low frequency parts of capacitive impedance responses , Bode plots allow comparison of impedance spectra at all measured frequencies . For these systemsBode magnitude plots show almost resistive response – related plateaus at broad range of higher frequencies (10^{5} --10^{2} Hz) . Below 100 Hz , the slopes are changed towards near – 1 sloping t curve characterizing almost capacitive electrode responses . Not ideal capacitive responses for all Graphene electrodes are however indicated by phase angles lower than – 90 degrees at low frequency part of Φ vs. log ω dependencies .

Generally, the complex capacitive presentations allow clear presentation of dissipative processes for otherwise capacitive electrode responses. The diameter of the circle is increased due to increase of capacitance values for Graphene oxide coated electrodes modified by higher number of cycles .

The influence of potential charge in impedance spectra of modified Graphene electrodes in a DSSc are in the form of Bode plots seen above , where impedance spectra of modified Graphene electyrodes measured at different potential values can be compared .

It is pertinent to note that Nyquist plot and Bode plot canj give an indication of the selective efficiencies of DSSC's . The higher the value of the phase shift , the lower the conversion efficiency of a DSSC.

Effect of Permittivity on the DSSC Conversion Effciency

The Resistance is a measure of the opposition of a circuit to the flow of a steady current , while Impedance takes into account not only the resistance but also dynamic effects (known as Capacitive and Inductive Reactance)

Admittance is ameasure of how easily a circuit or device will allow a current to flow . It is defined as inverse of Impedance . $Y = 1 / Z$ where Y= Admittance in Siemens , and Z = Impedance in Ohms .

Also $Y = G + jB$, where G= Conductance in Siemens, and B = Suceptance in Siemens and $j^2 = -- 1$

Also $Z = R + jX$, where impedance is composed of real (resistive from resistors), and imaginary parts (from inductors producing inductive reactance , and capacitors producing capacitive reactance) .

Thus $Y = Z^{-1} = 1/(R+jX) = (1 / R^2 + X^2) (R – jX)$

The permittivity is directly related to electric suceptibility . For example, in a capacitor an increased permittivity allows the same charge to be stored with a smaller electric field (and thus a smaller voltage) leading to an increased capacitance . As the capacitance is increased (AC voltage) , a larger number of electrons charge plates every cycle and therefore the current is increased . The following equations show the relationship between permittivity and impedance .

$C = \text{€} A / d$

[d = distance between the plates , C= Capacitance, €= Permittivity , V = Voltage ,I = Curent]

$C = V/ I = -- \check{j} / 2\prod f Z$

$\text{€} A / d = --\check{j} / 2\prod f Z$

Z = --ǰ d / 2∏ f € A

An increase in permittivity (increase in capacitance will result in lower impedance). This could be depicted in the Mott Shottkey plots of DSSC’s of $1 / (\text{Capacitance})^2$ vs. frequency, where a prominent inverse linear relationship is observed for high frequencies

(about 20 KHz), and increasing quadrative function above this frequency .

Effects of the Impedance parametres on I - V curves

An important practical application of the parameters obtained fromimpedance is the interpretation of the I – V curves of the solar cells. Since the solar cells operate at steady state , it is essential to determine the cause of the current density – potential response , which describes the solar cell performance .

Effect of Series Resistance

The rise in series resistance reduces the Fill Factor (ff) ande consequently the Efficiency (ɳ) of the solar cell . If it is too large , also I_{sc} and J_{sc} become affected . The same effect occurs with large photogenerated currents : the higher the current crossing the cell , greater is the drop in potential due to the series resistance corrections , and thus also drops in the fill Factor and Efficiency .

The series resistance is a very important limiting factor in the solar cells , esoecially if the objective is to scale them up to large area cells or to use dyes with enhanced injection properties . in such cases , a correct choice of the geometric design and materials employed for collecting the charge and regenerating the dye is crucial in order to minimize this resistance .

Effects related to Recombination Resistance

In a DSSC , the charge regeneration is determined by the dye and its interaction wit6hy the holes and electrons – conducting media , providing the maximum current density attainable by the solar cell . Since the recombination resistabnce is the element determining how the generated charge may be lost , this is the particular parameter that will limit the maximum performance attainable fror the solar cell . the maximum Efficiency is then modulated by the seriesw resistance effect as mentioned above .

Effect of increasing the Temperature

Increasing the temperature upto about 60 degrees Centigrade reduces both the charge transfer at the counter electrode and the diffusion resistance in the electrolyte , thus reducing the series resistance of the cell , and thereby contribute to raise the Fill Factor of the solar cell .

Use of Impedance Spectroscopy for identification of Performance Improvement of DSSC’s

In summary, the advantage of using Impedance Spectroscopy is that it becomes possible to distinguish the individual electrical contributions influencing the performance of the working cells without destroying them. One can thus identify the limiting processes in the cells , and direct research efforts at enhancing the solar cell efficiency in the specific physico – chemical and material properties that need to be improved .

However, it is understood that Mangoostein dye is one of the best natural dyes available in the world at present for use in DSSCs , and if concerted research is done by a group of dedicated multidisciplinary Scientists on DSSCs sensitized with Mangoostein dye , it should be possible to obtain a conversion efficiency of 5 – 6 % if the performance of all constituent components of a DSSC are optimized and made stable . Once this is achieved and these cells are made stable and long lasting (with a lifetime of about 20 years), these DSSCs would pose a serious threat to present day crystalline and amorphous Silicon - based solar cells for low power and even medium power applications in the field .

4.4.9 New Developments-- Continued

Operating a Model Catamaran Wooden Sail boat of 4 feet length

The operation of this boat in a 6 feet diameter rubber inflatable water pond was demonstrated at the Renewable Energy Exhibition held at the University of Moratuwa in March 2010. This Catamaran boat was mechanically coupled to a 8 inch long toy radio controlled boat operating on 4.5 Volts DC which was provided by 06 Nos. 4" x 3" x 0.3" series connected Mangoostein dye sensitized DSSC's (mounted on the cloth sail of Catamaran boat) using fluorine doped Tin oxide (FTO) transparent glasses provided by Dr. Upul Wijayantha, Senior Lecturer Department of Chemistry, University of Loughborough, England. These DSSC's were supplemented by a commercial organic solar panel providing 4.5 volts DC to the radio – controlled toy boat. A photograph of this system is attached at photograph 4.1below .

Photograph 4.1 4 feet long Solar Powered Catamaran Sail Boat

4.4.10 Scale up of above Boat , Construction and Operation of a Fibre Glass Catamaran Sail Boat of 18 feet length

This boat was constructed at the University of Moratuwa with the assistance of a Fishing Boat Builder. This was done in order scale – up the previously mentioned model Catamaran Boat, and to demonstrate the concept of solar powered Catamaran Sail Boat operating on Mangoostein dye-sensitized DSSC's supplemented by a commercial organic Polyethylene napthalate solar panel. This renewable solar power source provides propulsion power to this boat instead of expensive and fast depleting petrol/diesel/fossil fuels.

This boat is powered by 24 Nos series connected Mangoostein dye sensitized DSSC's of size 4" x 3" x 0.3" constructed at the University of Moratuwa using locally assembled FTO glasses described. These DSSC's would trickle charge a 12 Volts DC 24 Ampere Hour Motor Cycle battery, supplemented by a 15 Volts DC 3.5 Ampere output commercial organic polyethylene napthalate solar panel when exposed to sunlight .

Photograph 4.2 18 feet long Solar Powered Catamaran Sail Boat

Power Requirements of Catamaran Boat

The solar panels which would provide charging current during periods of sunlight to the 12 Volts DC 24 AH motor cycle battery , would provide propulsion to a 12 Volts DC Reversible Induction Trolling Motor (available) at 2 Amps on the boat (24 Watts) to travel forward, turn to starboard and port and to go astern.

Power generated by one commercial organic & DSSC panel

15 Volts DC at 3.3 Amps (approx) = 50 Watts

Power Consumption of vessel :

a. For propulsion 12 Volts DC
1 No Induction motor at 2 Amps = 12 x 2 Watts
= 24 Watts

b. For navigational lights
12 Volts DC at 5 Watts x 3 = 15 Watts

Total power requirements of vessel = 24 + 15
= **39 Watts**

The designed safety margin of vessel on full load (worst conditions)

= 50 – 39 Watts
= **11 Watts**

Estimated maximum speed of Boat = 1.34 x sq.root Length at waterline in Feet

= 1.34 x sq. root 10 = 1.34 x 3.162

= **4.237 Knots**

Please see attached photograph of Organic / DSSC Powered Catamaran Boat.

Also please see the photographs of the Basin Trials carried out on this Catamaran Boat at Appendix M.

The average maximum charging current from the combined solar panel was measured at 14.2 Volts DC at 2.82 Amperes in diffused sunlight, experienced during period 12 - 17 November 2014 when Basin Trials were done on the Catamaran Boat. This was found to be an adequate to trickle charge the 12Volts DC 48AH Lead Acid Battery, to ensure efficient conversion of solar power to propulsion power by the 12Volts 32 Pounds thrust Electric Propulsion Unit. The maximum average speed of the Boat in calm water was assessed at 4 - 4.5 Knots. The dynamic stability of the Boat was also tested whilst carrying out two “figure of 8” maneuvers in quick succession, turnings to port and staboard, travel forward and astern (at 3 variable speeds) were tested with a crew of 4 men and found to be satisfactory. Also the total endurance of about 6.5 - 7.0 hourswas assessed for use during simulated silent mode operation of the Boat for covert, amphibious, military operations in inland waters when closing- on to enemy territory.

4.4.11 Construction of a DSSC Powered Battery Charging Unit for i Pods and Mobile Radio Telephones

These were constructed at the Industrial Chemistry Laboratory of the University of Moratuwa as described at Chapter 3.3.6 was utilized with capacitors to prevent damage due to overcharging and transient voltages picked up from nearby mains power outlets. The entire circuit could be enclosed in a suitable plastic enclosure with outlets for input and output each.

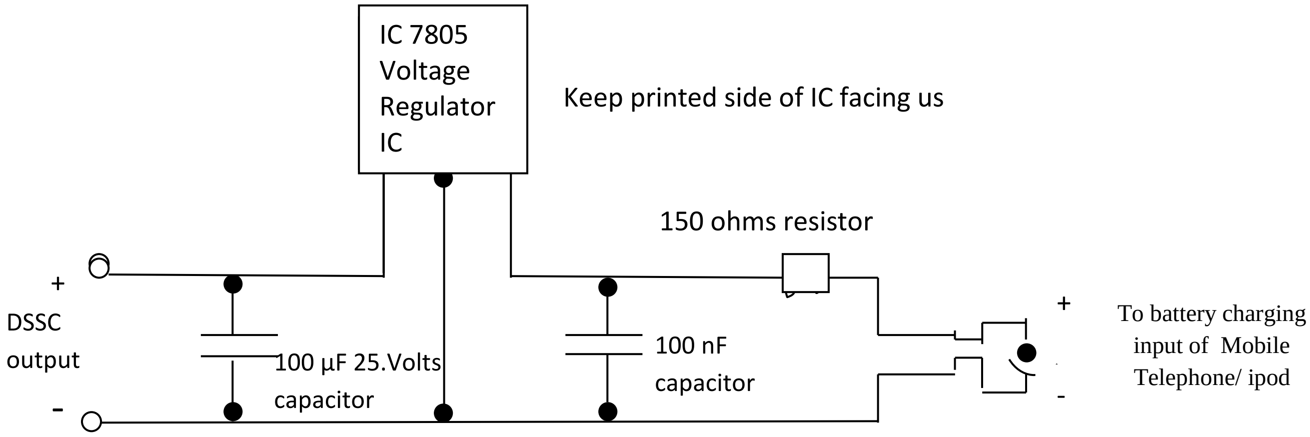


Figure 4.68 Power regulator and protection circuit for DSSC battery charger.

The salient features of DSSC Cell Phone Charger are:

- Excellent voltage /current regulation
- Current limited to safe value
- Cell Phone battery can never be overcharged
- The IC 7805 is thermally and short circuit protected thus the entire circuit is virtually inductible.

The batteries usually used in cell phones are 3.7 Volt Lithium Ion type, hence 8 Nos. Mangoostein dye sensitized DSSC's producing approx 500 mV each V_{OC} in series would provide (500 mV x 8) = 4 Volts DC for charging of these batteries.

4.4. 12 Construction of DSSC powered LED operated low cost Multi-coloured Garden Night Units for Hotels / Tourist Promotion

This was also constructed by the Author at the Industrial Chemistry Laboratory of the University of Moratuwa as described at Chapter 3.3.7.

The average open circuit voltage and short circuit current measurements made with this device in direct sunlight is shown below.

Voc = 565.4 mV

Isc = 0.422 mA

After a period of 3 months these measurements were repeated as follows :

Voc = 563.6 mV

Isc = 0.377 mA

This low cost, environmentally friendly Mangoostein dye sensitized DSSC powered LED operated multi coloured Garden Night Lighting unit has been found to be functioning satisfactory after one month of exposure to direct sunlight.

Please see the photograph at Appendix N.

4.4.13 Construction of Building Integrated Photovoltalic (BIPV) System for highrise buildings to provide diffused lighting with multi coloured LED operated Lighting System to demonstrate its concept of operation

Two 4 feet x 3 feet locally constructed FTO conducting glass sheets were used to construct a Mangoostein dye sensitized DSSC having a surface conductivity of 12 – 15 Ohm.cm^{-2} prepared .in the Industrial Chemistry Laboratory of the University of Moratuwa is being investigated for use with coloured lights to provide diffused lighting in thes buildings is being investigated. These prototype DSSC panels have been found to operate satisfactorily even in diffused sunlight conditions and cloud cover when the energy generated from photons of sunlight arestored in a 12 Volts DC Lead Acid Battery. Also the FTO conducting glasses used for the vertical window panes of these high rise buildings to be built especially in tropical countries would prevent / minimize the absorption of heat in the form of IR radiations emitted at the upper end of the visible electromagnetic spectrum of sunlight.

These aspects are being studied vide graphs at Figure 4.13 to minimize undesired heat absorption from sunlight whilst permitting maximum possible voltages and currents to be generated by DSSC's sensitized with Mangoostein fruit rind extract sensitized natural dyes.

Please see the relevant photograph at Appendix N.

4.4.14 Use of Building Integrated Photovoltaics (BIPV) FTO glasses for DSSC's

This technique could be used for the preparation of BIPV FTO glasses for DSSC's using natural dyes FTO glasses for DSSC's using natural dyes to provide diffused LED lighting of high rise buildings.

Two soda lime test BIPV FTO glass slides of dimensions 4 feet x 3 feet were prepared . Thereafter , (-)ve photo electrode was prepared by pasting 1 cm width of sellotape adhesive tape strips vertically to prepare vertical individual cell DSSC's with this electrode The surface areas not covering with sellotape was coated with TiO_2 paste by Doctor blade method prepared in the usual manner, and air-dried with a hair dryer warm air blast. The sellotape strips were then removed and this electrode was sintered in an electric oven at 450^{o}C for 30 mins. and allowed to cool down to room temperature overnight. Then the TiO_2 coated surface areas were dipped in Mangoostein fruit rind dye solution for 12 hours, excess liquid drained off and air dried.

The (+)ve counter electrode was then prepared from the other FTO glass by evenly rubbing the FTO glass treated surface with Graphite powder. The excess powder was washed with distilled water and then with Ethanol.

Thereafter the two electrodes width their treated surfaces facing each other were sandwiched and firmly held in place with insulated steel clips. The redox KI/I electrolyte was then introduced between the two glass slides using a nanopipette in order to cover the entire internal surface areas of glass slides facing each other. The outer four sides of the composite DSSC was sealed with Silicone glue by evenly applying it with a small paint brush, avoiding any air bubbles. The sealed edges of the DSSC was blown with hot air from an electric hair dryer at 140^{o}C for 2 mins for the sealant to melt evenly and adhere firmly between the two glass slides, in order to prevent the leakage of the redox electrolyte.

The individual cells of this DSSC was connected in series to increase the open circuit voltage of each DSSC individual cell a required. On top of the TiO_2 coated areas small 0.5 cm x 0.5 cm very thin cut Copper foil pieces which have been soldered to thin Copper wires were placed firmly by applying pressure with the nose end of a plier and their outer edges covered with 'Superglue' quick- drying and sealing adhesive. These wires constitute the connections electrical for the (--)ve electrodes. Similar electrical connections were made with the Graphite coated (+)ve electrodes with Copper with wire soldered Copper foil pieces. (In order to increase the current output of these individual DSSC cells, they need to be connected in parallel). After making the electrical contact connections the output voltage of the BIPV test DSSC cell was measured at room temperature with different sunlight as follows:

V_{OC} = 584.6 mV
I_{SC} = 0.587mA

After a period of 6 months, these measurements repeated were as follows:
V_{OC} = 567 . 3 mV
Isc = 0. 496 mV

4.4.15 Use of FTO coated DSSC's sensitized with Mangoostein fruit rind extract for provision of propulsion power for Catamaran Sail Boat

Arrangements were made construct 48 Nos. 4" x 3" FTO conducting glasses for the preparation of 24 Nos. Mangoostein fruit rind extract sensitized DSSC's for installation on the 18 feet long Catamaran Sail Boat to demonstrate the concept of operation of Sail Boats powered by DSSC / Organic Solar Cells. These DSSC's are supplemented with a commercial Organic Solar Panel of Polyethylene napthalate to provide propulsion power to this boat instead of expensive and fast depleting petrol/diesel /fossil fuels.

This boat is powered by 24 Nos. series connected Mangoostein dye sensitized DSSC's of size 4" x 3" x 0.3" constructed at the University of Moratuwa using locally assembled FTO glass as mentioned above and at Chapters 3.3.4, 6.3 and Table 11. These DSSC's, would trickle charge a 12 Volts DC 24 Ampere Hour Motor Car Lead Acid Battery, supplemented by a 15 Volts DC 3.5 Ampere Commercial Organic Polyethylene napthalate solar panel.

Initially 48 Nos. Soda lime glass slides of dimension 4" x 3" x 0.3" (10 cm x 7.6 cm x5.mm) were washed in Teepol detergent solution in distilled water, dilute Sulphuric acid, and rinsed with Ethanol and left to dry at non temperature.

Thereafter the 24 Nos. individual DSSC's sensitized with Mangoostein were prepared as follows. The (-)ve photo electrodes were prepared by pasting Nos. 0.25 cm witdh sellotape strips vertically to prepare 24 Nos. individual cell DSSC's with this electrode. The surface areas not covered with sellotape were coated with TiO_2 paste by the doctor blade method, prepared in the usual manner, and air dried with a hair dryer hot air blast. The sellotape strips were then remove and these electrode were then sintered in an electric over at 450^{o}C for 30 mins, and allowed to cool down to room temperature overnights. The TiO_2 coated surface areas were then dipped in Mangoostein fruit rind dye extract for 12 hours, excess liquid drained off and air dried.

The (+) ve counter electrodes were then prepared from the other 24 Nos. FTO glasses by evenly rubbing the FTO glass treated surfaces with fine graphite powder. The excess powder was washed off with distilled water and then with Ethanol.

Thereafter the (+ve) and (--ve) electrodes with their treated surfaces facing each other were sandwiched and firmly held in place with insulated steel clips. The redox KI/I electrolyte was then introduced between the two glass slides using a micropipette in order to cover the entire intend surface areas of the two glass slides facing each other. The outer four sides of the composite DSSC was sealed with Silicone glue by evenly applying it with a small paint brush, avoiding any air bubbles. The sealed edges of the DSSC', were blown with hot air from an electric hair dryer at 140 degrees C for 2 min for the sealant to melt evenly and to adhere firmly between the two glass slides, in order to prevent the leakage of the redox electrolyte.

The individual cells of the DSSC's were connected in series to increase the circuit voltage of the individual DSSC's as required. On top of the TiO_2 coated areas small 0.25 cm x 0.25 cm very thin cut Copper foil pieces which have been soldered to thin Copper wires were placed firmly by applying pressure with the nose end of a long nose pliers and their outer edges covered with 'Superglue' quick drying and sealing adhesive. These wires constitute the connection for the (--ve) electrodes. Similar electrical connections were made with the Graphite coated (+) we electrodes with Copper wires soldered Copper foil pieces. (In order to increase the current output of these individual cells, they need to be connected in parallel). After making the electrical connections, the output voltage of the DSSC's was measured at room temperature with diffused sunlight.

This low-cost, environmentally friendly DSSC powered motor cycle battery trickle charging unit has been found to be working satisfactorily after about 6 months' of exposure to diffused sunlight, and also in direct sunlight.

Please see the Catamaran Boat photographs at Appendix M.

4.4.16 Construction and development of DSSC- Fabric Integrated small Battery Chargers

This was attempted in the Industrial Chemistry Laboratory , Textile technology Laboratory of the University of Moratuwa and the Spectrocopy Laboratoryof the Sri Lanka Institute of Nanotechnology (SLINTEC) at Biyagama in order to provide battery charging facilities for portable i pod and Mobile Radio Telephones .
A mixture of Succinic acid (6 % . w / v) and Sodium phosphate (SHP, 4 % o.w.f) was prepared in distilled water . 2 Nos of 4 // X 4 // cotton fabric sheet were dipped in that mixture for one hour at room temperature . Here the used material liquor ratio was 1 : 20 . then the fabric sheet was taken out , oven dried at 85 degrees c and cured at 180 degrees C, Nanocrystalline TiO2 powder was dispersed in distilled water and loaded to the cured fabric sheet .

Thereafter the UV-vis Absorption Spectra for the treated cotton fabric sheet and the untreated cotton fabric sheet was observed on a Spectrophotometer and Energy Dispersive X ray Spectroscopy (EDX) equipment at the Sri lanka Institute of Nanotechnology (SLINTEC), Biyagama through courtesy of Mr. Ruchira Wijesena .

The (--) ve electrode of the test fabric integrated DSSC was prepared by rubbing a Graphite block on one surface , and attaching a tiny Copper strip soldered to Copper wire . The (+) electrode of the test DSSC was prepared with the other treated cotton fabric by spraying with a small plastic garden water spray bottle TiO2 nanocrystalline powder (Deguzza – P 25) dissolved in Ethanol with one drop of Triton , 12 drops of dilute Acetic acid ground in an agate mortar for 30 min, and subject to an ultrasonic oscillator for 15 mins. The fabric sheet was drained of excess liquid and a hair dryer used fror vertical drying .thereafter it was cured at 180 degrees C for 30 mins in an electric oven , cooled to room temperature , and dipped on side facing downwards in Mangoostein fruit rind extract dye in Ethanol for 12 hrs. Redox electrolyte (KI : I in 10 : 1 by weight ratio)was sprayed on to the dye treated side of the fabric sheet , and a copper4 strip with a copper wire attached to the surface of the treated fabric for use as the (+)ve electrode . The two treated pieces of the fabric was then evenly stitched with an electric sewing machine and the open circuit voltage and short circuit current at the two electrodes were measured with KEITHLEY 2000 Electronic Multimeter .

The following average measurements made on a 4 // X 4 // cotton treated fabric sheets were as follows :

Voc = 367 .5 milli Volts
Isc = 225 micro Amps

CHAPTER 5

CONCLUSIONS

It has been observed that after detailed analysis of about 150 natural dyes of photosynthetic plants growing in Sri Lanka, that they are a cheap, abundant usually non toxic and environmentally friendly alternative to very expensive and scare synthetic organic dye available for the construction of practical DSSC's .

During this study various components of plants were tested electrically and electronically for use as suitable sensitizers for DSSC's . It was noted that plant pigmentation occurs due to the electronic structure of the pigment interacting with sunlight to alter the wavelengths that are either transmitted or reflected by the plant tissues..

In DSSC's attempts are made to mimic the photosynthetic process of plants absorbing carbon dioxide gas in the green chloroplasts of leaves in the presence of sunlight and water drawn from the ground through the roots, and thus converting them to carbohydrates and releasing oxygen to the atmosphere. Thus in DSSC's the solar energy of photons in sunlight is converted to direct electrical energy in the form of voltage and current. During this study it was observed and concluded that the maximum conversion efficiency of solar energy to electrical energy of natural dyes of plants growing in Sri Lanka is around 1% especially for natural dyes of deep purple colour. Also it is concluded that generally darker the colour of the natural dye, greater would be their conversion efficiency. It has been found that this efficiency may be increased to around 2 -3% (comparable to conversion of solar energy to chemical energy by photosynthesis) by the addition of trace amounts of various chemicals such as conc. Hydrochloric / Acetic and etc to alter the chemical structures of these natural dyes, here their colours .It is also noted that various coloured pigments of plants consisting of chlorophylls, carotenoids, flavonoids, anthrocyanins, betalanins and their antioxidants contribute to reasonably good solar energy to electricity conversion efficiencies. It has observed that especially the purified ethnolic extracts of Mangoostein fruit rind of Garcinia mangostana endemic to Sri Lanka comprising xanthones, flavanoids and rutin contribute to a relatively good conversion efficiency of around 1% due to the synergestic effect of these individual dyes.

The use of DSSCs in low power applications have been demonstrated .

CHAPTER 6

RECOMMENDATIONS AND FUTURE WORK

It is recommended that further research on the design and development of stable, durable DSSC's for commercial outdoor applications using natural dyes of plants growing in Sri Lanka be done by a team of multi disciplinary group of competent and eminent Scientists and Engineers at a suitable research Institute / University in Sri Lanka in order to increase the conversion efficiencies of relatively good natural dyes such as Mangoostein fruit rind, Ekirriya wood, Egg Plant fruit peel, Karawala kabilla fruit berry, Banna flower inflorescence, Beetroot, Turmeric and Fire fern leaf (not endemic to Sri Lanka) etc to possibly increase their conversion efficiencies to about 2% -- 3% or even higher upto 5 – 6 % (with Mangoostein dye). Then it would be commercially viable to manufacture practical DSSC's sensitized with these low - cost, abundant and environmentally friendly natural dyes of plants. These DSSC's could be developed for low power applications such as recharging of Mobile Radio Telephone batteries , i pods, Portable Manpack Radio Communications and Navigational Equipment, LED operated multi coloured Garden Night Lamps for Hotels / Tourist Promotion . Also the construction of Building Integrated Photovoltaic (BIPV) Systems with DSSC - Integrated Vertical Glass Windows for high – rise Hotel and Business Complex Buildings of major cities in Sri Lanka should be done in order to provide low power diffused lighting with multi -colored LED operated lighting systemsto reduce the dependency on the ever increasing costly national grid – based Electricity supplies, and also for provision of propulsion power to Small Boats , Three Wheel Vehicle Taxis etc .

6.1 Areas recommended

Future DSSC works initiated and under development

The scale – up and development of DSSC – related projects initiated for possible operational use is being further studied , developed and test trials are vbeing pursued for practical implementation . These include :

(a) Further developments of the 18 feet long Catamaran Fibre Glass Sail Boat operating on Mangosteen fruit rind dye sensitized DSSC's .Attempts are being made to demonstrate the concept of operation of this boat with DSSC's sensitized with natural dyes of plants (Mangosteen fruit rind, Turmeric root) instead of using fast depleting fossil fuels like petrol, diesel, kerosene oil etc.

(b) Futher improvements to the construction of DSSC powered small Battery Chargers for ipods, Mobile Radio Telephones, and portable Radio Communications Equipment etc.

(c) Futher improvements to the construction of DSSC powered muticolour LED garden lights.

(d) Construction of a prototype Building Integrated Photovoltaic (BIPV) System using LED lights for a high rise building to demonstrate the concept of operation of BIPV Battery Charging Systems. A simple DSSC BIPV panel sensitized with Mangoostein dye will be tested with a LED lighting system of 12 V DC to observe its functioning , and further improvments will be made to ensure that that it could be used in the field and to make it a commercial viability .

(e) Construction and development of Fabric -Intergrated DSSC’s.

One of the most promising renewable energy technologies is photovoltaics (PV). It is a truly elegant means of producing electricity on site, directly from the Sun without concern for energy supply or environmental harm. These solid-state devices simply make electricity out of sunlight, silently with no maintenance, no pollution and no depletion of materials.

There is a growing consensus that distributed PV systems that provide electricity at the point of use will be the first to reach widespread commercialization. Chief among these distributed applications are PV power systems for individual buildings.

Interest in the building integration of PV’s where the PV elements actually become an integral part of the building often serving as the exterior weather skin is growing worldwide. A whole new new vernacular of Solar Electric Architecture is beginning to emerge.

A Building Integrated Photovoltaic (BIPV) system consists of integrating PV modules into the building envelope, such as the roof or the façade. By simultaneously serving as building envelope material and power generator, BIPV Systems can provide savings in materials and electricity costs, reducing use of fossil fuels and emission of ozone depleting gases and architectural interest to the building.

While the majority of BIPV systems are interfaced with available utility grid, BIPV may also be used in standalone off-grid systems. One of the benefits of the grid-tied BIPV system is that with a cooperative utility policy, the storage system is essentially free. It is also 100% efficient and unlimited in capacity. Both the building owner and the utility benefit with grid tied BIPV. The on site production of solar electricity is typically greatest at or near the time of a building and the utilities peak loads. The solar contribution reduces energy costs for the building owner while the exported solar electricity helps support the utility grid during the time of its greatest demand.

A complete BIPV system includes:

a. PV modules (crystalline, thin film or DSSC’s).
b. Charge controller to regulate the power into and out of the battery storage bank (in stand-alone systems)
c. Power storage system generally comprised of the utility grid in utility-interactive systems or a number of batteries in stand-alone systems.
d. Power conversion equipment including inverter to convert the PV modules output to AC compatible with the grid.
e. Backup power supplies such as diesel generators (optional-typically employed in stand alone systems).
f. Appropriate support and mounting hardware, wiring and safety disconnects.

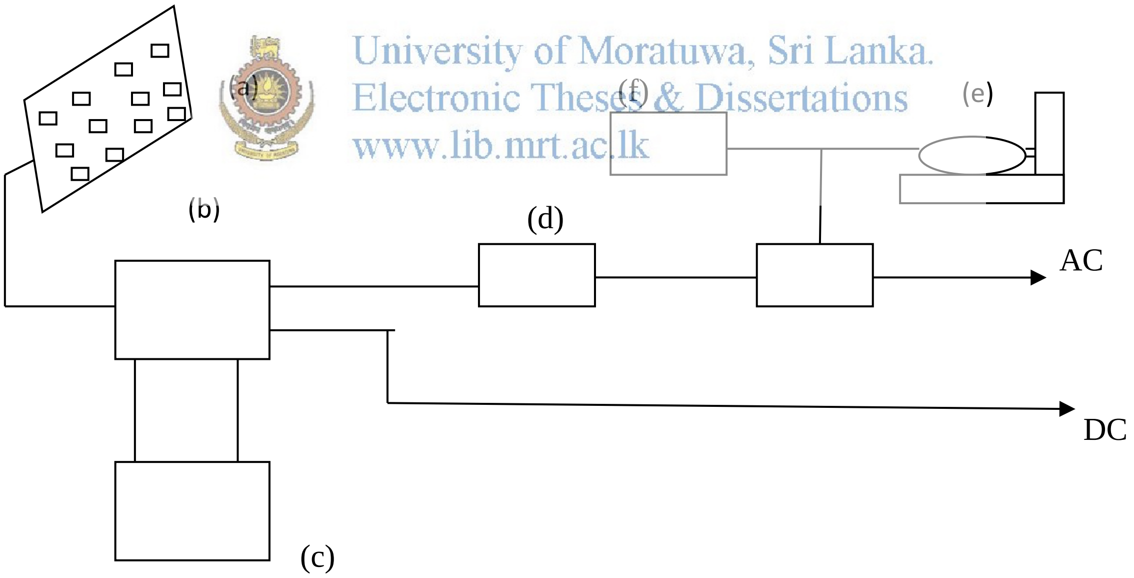


Figure 4.69 Typical BIPV System

Photovoltaic may be integrated into many different assemblies within a building envelope:

- Solar cells (DSSC’s /Films / Silicon) can be incorporated into the façade of a building complementing or replacing traditional view or spandrel glass. Often these installations are vertical reducing access to available solar resources compensate for the reduced power.

- PV’s may be incorporated into awnings and saw tooth designs on a building facade. These increase access to direct sunlight while providing additional architectural benefits such as passive shading.

- The use of PV in roofing systems can provide a direct replacement for batter and seam metal roofing and traditional 3-tab asphalt shingles.

- Using PV for sunlight systems can be both an economical use of PV and an exciting design feature.

- The 4” x 3” x 0.3” Flourine doped Tin oxide (FTO) coated glass slides could also be developed using Mangoostein fruit rind dye sensitized extract to provide electrochromic windows (ECW) of high-rise buildings, and for energy harvesting (EH). These ECW’s would also substantially reduce cooling /heating loads and increase human comfort. Thus EH-ECW technology could combine the merits of electrochromic windows and dye-sensitized solar cell technologies for dimming control of multi-coloured LED operated diffused lighting system, and to generate power to operate not only the ECW’s but also other electrical systems. The integration of EH-ECH systems into an autonomous building system would be the basis for a new concept called “locally harvesting and locally used”.

- Also research could be done to investigate the use of EH-ECW’s to generate a substarial portion of the energy used by buildings, thus reducing the impacts of central energy generation, and to increase visual comfort and building envelope performance resulting in healthier, more productive indoor environments, as well as to smooth the transfer of the above integrated technology to residential and commercial building design.

(e) Development of Fabric-integrated DSSC’s

This is being attempted in the Industrial Chemistry Laboratory, Textile Technology Laboratory of the University of Moratuwa and the Spectroscopy Laboratory of the Sri Lanka Institute of Nanotechnology (SLINTEC) at Biyagama

In order to provide battery charging facilities for portable iPods and Mobile Radio Telephones (and possibly for Manpack Mobile Radio Communications and SATNAV Navigational System)

A mixture of Succinic acid (6%W/V) and Sodium phosphate (SHP, 4% o.w.f) was prepared in distilled water. 2 Nos. of 4” x 4” cotton fabric sheet were dipped in that mixture for one hour at room temperature. Here the used material to liquor ratio was 1:20. Then the fabric sheet was taken out, oven dried at 85ºC and cured at 180ºC.

Nanocrystalline TiO_2 powder was dispersed in distilled water and loaded to the cured fabric sheet.

Thereafter the UV-Vis Absorption Spectra for the treated cotton fabric sheet and the untreated cotton fabric sheet was observed on a Spectrophotometer and Energy Dispersive Xray Spectroscopy (EDX) equipment at the Sri Lanka Institute of Nanotechnology (SLINTEC), Biyagama . The (-) ve electrode of the test fabric integrated DSSC was prepared by rubbing a graphite block on one surface, and attaching a tiny copper strip soldered to a copper wire. The (+)ve electrode of the test DSSC was prepare with the other treated cotton fabric by spraying with a small plastic garden water spray bottle TiO2 nanocrystalline powder (DEGUZZA-P25) dissolved in Ethanol with 1 drop of Triton, 12 drops of dilute Acetic acid, ground in an agate mortar for 30 min, and subject to an ultrasonic oscillator for 15 mins. The fabric sheet was drained of excess liquid and a hair dryer used for vertical drying. Thereafter it was cured at 180ºC for 30 mins. In an electric oven, cooled to room temperature, and dipped one side facing downwards in Mangoostein fruit rind extract dye in Ethanol for 12 hrs. Redox electrolyte (KI:I in 10:1 by weight ratio) was sprayed onto the dye treated side of the fabric sheet, and a copper strip with a copper wire attached to the surface of the treated fabric for use as the (+)ve electrode. The two treated pieces of the fabric was then evenly stitched with an electric sewing machine and the open circuit voltage and short circuit current at the two electrodes were measured with KEITH 2000 Electronic Multimeter.

The following gaverage measurements made on a 4” x 4” cotton treated fabric sheets were as follows:

Open Circuit Voltage (V_{OC}) =452 .2mV

Short Circuit Current I_{SC}) = 0.56 mA

(Connecting these fabric integrated DSSC’s in series will increase V_{OC} and in parallel will increase I_{SC}).

BIBILIOGRAPHY

1. Dharmadasa, I.M.2009. A Future Dominated by Solar Energy. Sheffield Hallam University, Sheffield, U.K.

2. Dharmadasa, I.M.2009. Solar Energy Technologies: A Status Report. Sheffield Hallan University, Sheffield, U.K.

3. Gratzel, Michael, O'Regan Brian. 1991. A low cost, high efficiency solar cells based on Dye Sensitized colloidal Ti O_2 film, Institute of Technology CH1015, Lausane, Switzerland, Letters to Nature, Magazine, Nature 359 (737-740).

4. Gratzel, Michael.2005.Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells, Inorganic Chemistry. Vol 44, P 6841-6851.

5. Guo, Ying., Huang, Lu., Portar, Alan L., 2009. Profiling Research Patterns for a New and Emerging Science and Technology: Dye-Sensitized Solar Cells, Beijing Institute of Technology, Beijing, Peoples Republic of China and Georgia Institute of Technology, Atlanta, U.S.A., sma.tech.edu/bitstream/handle/1853/3237/22-656-PB.pdf

6. Grätzel, M., 2003. Dye-sensitized solar cells. Journal of Photochemistry and Photobiology C: Photochemistry Reviews (4), 145-153.

7. Smested, G.P., 1998. Education and solar conversion:
Demonstrating electron transfer. Solar Energy Materials & Solar Cells 55, 157-178.

8. Hao, S., Wu, J., Huang, Y., Lin, J., 2006. Natural dyes as photo sensitizers for dye-sensitized solar cells. Sol. Energy 80, 209-214.

9. Kudagamage, K., 2008. Botanical Names and Sinhala Names of plants grown in Sri Lanka.Horticultural Crop Research & Development Institute, Gannoruwa, Sri Lanka.

10. Weerasinghe, A. Botany of Crops. Rajarata University, Sri Lanka.

11. Hasan,M.S., Roy,S., Corkish,R., 2010. Sustainable Energy in Asia and the Pacific:Emerging Technologies and Research Priorities in Solar Energy (DSSC"s), 28- 33.

12. Chmiel, G., Gehring, J., Uhlendorf, I., Jestel, D., 1998. Dye-Sensitized solar cells: Progress towards applications. Proceedings for the 2nd World Conference PVSEC, Vienna, Austria, 53-57.

13. Jihuci, Wv., Zhang, Lan., Sanachu, Hao., Pingziang, Li., Jia, Ming, Lin., Huang, M., Huang, Y., 2008. Progress on the Electrolytes for DSSC's. Pure Applied Chemistry Vol 80, No 11, 2245 – 2258.

14. Cambell, R., Wayne. D.R., 2007.Taking Natures' use of cheap Solar Power.Massey University, Nanotechnology Research Centre, New Zealand. Science Direct 6 April 2007.

15. Tennakone, K., Kumara, G.R.R.A., Kottegoda, I.R.M., Perera, V.P.S., Weerawardana, P.S.R.S., 1998. Sensitization of nanoporous film of TiO_2 with Santalin (red sandalwood pigment) and construction of dye sensitized solid-state photovoltaic cells. Journal of Photochemistry & Photobiology, 117(1998), 137-142.

16. Tennakone, K., Perera, V.P.S., Kottegoda, I.R.M., Kumara, G.R.R.A., 1998. Dye-sensitized solid state photovoltaic cell based on composite Zinc oxide/Tin oxide film. Journal of Physics., 32 (1999), 374-379.

17. Tennakone, K., Kumara, G.R.R., Kottagoda, I.R.M., Perera, V.P.S., 1999. An efficient dye-sensitized photoelectrochemical solar cell made from oxide of Tin and Zinc. Chemical Communication, 1999,15-16.

18. Tennakone, K., Kottagoda, SenadheeraG.K.R., Perera, V.P.S., Kottagoda, I.R.M., de Silva, L.A.A., 1999. Dye-Sensitized photoelectrochemical cells based on porous. SnO_2/ZnO composite and TiO_2 film is a Polymer electrolyte. American Chemical Society, Chen. Mater 1999, 2474 – 2477.

19. Tennakone, K., Kottagoda, I.R.M., de Silva, L.A.A., Perea, V.P.S., 1999. The possibility of ballistic electron transport in dye-sensitized semiconductor nano-crystalline particles aggregates. Semiconductor Science & Technology 14 (1999), 975 – 978.

20. Tennakone, K., Bandara, J., Photocatalytic activity of dye-sensitized Tin oxide nanocrystalline particles attached to Zinc oxide particles: Long distance electron transfer via ballistic transport of electrons across nanocrystallites. Applied Catalysis A: General 208 (2001) 335-341.

21. Tennakone., K., Senadheera, G.K.R., de silva, D.B.R.A., Kottagode, I.R.M., 2000. Higly Stable Solid- State Solar Cell with the semiconductor 4 CuBr3S$(C_4H_9)_2$ as the hale collector. Applied Physics Letters, American Institute of Physics, Vol.77, No.13.

22. Kumara, G.R.R.A, Konna, A., Senadheera, G.K.R., Jayaweera, P.V.V., de Silva, D.B.R.A., Tennakone, K., 2000. Dye-sensitized solar cells with the hole collector P-Cu SCN deposited from a solution in n-propyl sulphide. Solar Energy Materials & Solar Cells 69 (2001), 195-199.

23. Kumara, G.R.A., Konno, A., Tennakone, K., 2000. Photoelectrochemical cells made from SnO_2/ ZnO film sensitized with Eosin Dyes. The Chemical Society of Japan, Chemistry letters 2001, CL-001086.

24. Kumara, G.R.R.A., Tennakone, K., Perera, V.P.S., Konno., 2000. Suppression of recombination in a Dye sensitized photo electrochemical cell made from a film of Tin IV oxide crystallites coated with a thin layer of Aluminum oxide. Institute of Physics, Journal of Physics D (Applied Physics) 34 (2001) 864-873.

25. Tennakone, K., 2000. Dye sensitized solar cells: New ideas for their improvement. Proceedings of 5th workshop on low cost electronic materials, Solar Cells and Renewable Energy Sources, Colombo 22-25: Feb 2000: 78-80.

26. Senadheera, G.K.R., Tennakone, K., 2000. Fabrication of solid state dye sensitized TiO_2 photovoltaic cells with CuCNS. Proceeding of 5^{th} workshop on Low Cost Electronic Materials, Solar Cells and Renewable Energy Sources, Colombo. 22-25, Feb 2000: 81-85.

27. Kumara, G.R.A., Konno. A., Shiratsuchi. K., Tsukahara, T., Tennakone, K., 2001. Dye-Sensitized Solar State Solar Cells: Use of crystal growth Inhibitors for deposition of the Hole Collector. American Chemical Society, Chem. Mater 2002, 14, 954 – 955.

28. Senadhera,,G.K.R., Jayaweera, P.V.V., Perera, V.P.S., Tennakone, K., 2001. Solid State dye sensitized photocell based on pentacene as a hole collector. Solid Energy Material & Solar Cells, 73 (2002), 103-108.

29. Tennakone, K., Bandara, J. Bandaranayake, P.K.M., Kumara, G.R.A., Konno, A., 2001. Enhanced Efficiency of a Dye Sensitized Solar Cell made from MgO coated NanocrystallineSnO_2. Japan Society of Applied Physics, Vol.40 (2001), PP.L 732-734.

30. Tennakone, K., Senadheera, G.K.R., Jayaweera, P.V.V., 2001. Enhancement of the energy and quantum conversion efficiencies of a photo electrochemical cell sensitized with a combination of cationic and anionic dyes. Current Science, Vol. 81, No.1.

31. Tennakone, K., Perera, V.P.S., Kottegoda, I.R.M. de Silva, L.A.A., Kumara, G.R.R.A., 2001. Dye-Sensitized Photovoltaic Cells: Suppression of Electron – Hole Recombination by deposition of the Dye on Thin Emulating Films, Journal of Electronic Materials, Vol.30, No.8.

32. Bandara, J., Tennakone, K., Binduhewa, P., 2001. Probing the tunneling of electrons from SnO_2 to Zno in dye-sensitization of composite SnO_2/ZnO by use of generated H_2O_2 via reduction of O_2. Royal Society of Chemistry, U.K., Journal of Chemistry, 2001, 25, 1303 – 1305.

33. Bandara, J., Tennakone, K., Kiwi, J., 2001. Surface mechanism of Molecular Recognition between Amuirophenols and Iron oxide surfaces. American Chemical Society. U.S.A., Langmuir 2001, 3964 – 3965.

34. Bandara, J., Tennakone, K. 2001. Interparticle charge transfer in Dye-Sensitized Film composed of two kinds of semiconductor crystalline. Journal of Colloidal & Interface Science 236, 375-378.

35. Jayaweera, P.M. Palayangoda, S.S., Tennakone, K., 2001.,NanoporousTiO_2 Solar Cells Sensitized with bromopyrogallol red ligands. Journal of Photochemistry & Photobiology A: Chemistry 140 (2001), 173-177.

36. Kumara, G.R.A., Kaneko, S., Okuya, M., Tennakone, K., 2002. Fabrication of Dye-Sensitized Solar Cells using Triethylamine, Hydrothiocynate as a Cu I crystal growth inhibitor. Langmuir 2002, 18, 10493 – 10495.

37. Jayaweera, P.M., Palayangoda, S.S, Tennakone, K., Gamage, R.G.C.R., 2002. Cobolt (11) - bis (1, 10 – Phenanthroline) triphenyl methane dye complexes and their photo sensitization properties in nonoporous photovoltaic devices. Current Science Vol.83.,No.11.

38. Tennakone, K., Jayaweera, P.V.V., Bandara, P.K.M., 2002. Dye-Sensitized photo – electrochemical and solid state solar cells: Charge separation, transport and recombination, mechanism. Journal of Photochemistry & Photobiology, 158 (2003), 125-130.

39. Bandara, J. Tennakone, K., Jayathilake, P.P.B., 2002. Composite Tin and Zinc oxide nano crystalline particles for enhanced charge separation in sensitized degradation of dyes. Chromospheres 49 (2002), 439-445.

40. Bandara, P.K.M., Jayaweera, P.V.V., Tennakone, K., 2002. Dye-sensitization of Magnesium oxide coated cadmium sulphide. Solar Energy Materials and Solar Cells, 2002, Solmat : 298, 1-8.

41. Tennakone, K., Bandaranaayke, P.K.M., Jayaweera, P.V.V., Konno, A., Kumara, G,R.R.A., 2002. Die-Sensitized composite Semiconductor nanostructures. Physics E 14 (2002) 190 – 196.

42. Kumara, G.R.A., Kaneko. S, Okiya, M., Konno, A., Tennakone, K., 2002. NonocrystallineTiO$_2$ film for Dye-Sensitized Solar Solid State Cells. Publication of Chemical Society of Japan, Key Engineering Materials Vol.228 – 229 (2002), 119 – 124.

43. Tennakone, K., 2002. Dye-Sensitized semiconductor nanostructures for solar energy conversion. Ceylon Journal of Science 9(1), 1-8 (2002).

44. Perera, S., Senadheera, G.K.R., Tennakone, K., 2002. The Effect of MgO on the Enhancement of the Efficiency in Solid State Die-Sensitized Photocells Fabricated with SnO$_2$ and Cul. The Chemical Society of Japan, 76, 659 – 662 (2003).

45. Tennakone, K., 2002. Dye sensitized semiconductor nanostructures for solar energy conversion. Ceylon Journal of Science (Physical Science). 9 (1) : 1 – 8.

46. Jayaweera, P.M., Kumarasinge, A.R., Tennakone, K., 2002. NanoporousTiO$_2$ photovoltaic triphenylmethane dyes. Journal of Photochemistry and Photobiology A: Chemistry 126:111 – 115.

47. Perera, V.P.S., Tennakone, K., 2003. Surface trop mediated recombination in dye sensitized solid state solar cell with CuI as the hole collector. Proceedings of the 19th Technical Session March 2003. Institute of Physics. 51-57.

48. Perera, V.P.S., Tennakone, K., 2003. Recombination processes in Dye-Sensitized Solid State Solar Cells with Cu I as the hole collector. Solar Enegry Materials & Solar Cells. 79 (2003), 249 – 255.

49. Perera, V.P.S., Senadheera, G.K.R., Tennakone, K., 2003. Sensitization of Aluminum Chloride adsorbed Tin (IV) oxide nanocrystalline film with Rose Bengal. Journal of Colloidal and Interface Science 265 (2003). 428-431.

50. Tennakone, K., Jayaweera, P.V.V., 2003. Depleted semiconductor Quantum Naowire in a electrolytic medium. Superlattices and Microstructures 33 (2003) 23-28.

51. Perera, V.P.S., Pitigale, P.K.D.P., Jayaweera, P.V.V. Bandaranayeke, K.M.P., Tennakone, 2003. Dye Sensitized Solid State Photovoltaic Cells based on dye mutilayer semiconductor nanostructures. American Chemical Society Journal of Physical Chemistry, B 2003, 107, 13758 – 13761.

52. Bandara, J. Disaratne, C.M., Nanayakkara, S.D., 2003. Fabrication of n-p junction electrodes made of n-type SnO_2 and P-type NiO_2 for control of charge recombination in DSSC's. Solar Energy Materials & Solar Cells, Science Direct 81 (2004), 429 – 437.

53. Perera, V.P.S., Jayaweera, P.V.V., Pitigale, P.K.D.D.P., Bandaranayake, P.K.M., Hasting, G., Perera, A.G.V., Tennakone, K., 2003. Construction of Photovoltaic device by deposition of thin film of conducting polymer polythiocyanogens. Science Direct, Synthetic Metal 143 (2004), 283-287.

54. Pitigala, P.K.D.D.P., Seneviratne, M.K.I., Perera, V.P.S., Tennakone, K., 2004. Sensitization of nanostructured TiO_2 by Electrostatic coupling of Ionic Dyes to Ionic Absorbents. American Chemical Society, Langmuir 2004, 20, 5100-5103.

55. Bandaranayake, K.M.P., Senavirathne, M.K.I., Weligamuwa.,P.M.G.M., Tennakone, K., 2004. Dye-Sensitized Solar Cells made from TiO_2 film coated with outer layers of different oxide materials. Science Direct, Solar Energy Materials & Solar Cells 85 (2005), 91-98.

56. Perera, V.P.S., Pitigale, P.K.D., Seneviratne, M.K.S., 2004. A solar cell sensitized with three different dyes. Science Direct, Solar Energy Materials & Solar Cells 85 (2005), 91-98.

57. Konno, A., Kittagawa, T., Kida, H., Kumara, G.R.A., Tennakone, K., 2004. The effect of particle size and conductivity of Cu I layer on the performance of solid state DSSC's. Science Direct, Current Applied Physics 3 (2005) 149-151.

58. Seneviratne, M.K.I., Pitigala, P.K.D.D.P., Perera, V.P.S., Tennakone, K., 2004. American Chemical Society, Langmuir 205, 21, 2997-3001.

59. Kumara, G.R.A., 2004. Dye sensitized solid state solar cell made from Magnesium oxide coated nanocrystallineTiO_2 films: Enhancement of Efficiency. Journal of Photochemistry and Photobiology A: Chemistry, MFN 4195, 164, 183.

60. Bandara, J., Jayasundera, A., 2005. Solid State dye sensitized solar cell with P-type NiO as a hole collector. Solar Energy Materials and Solar Cells, 85 (3), 385 – 390.

61. Jayaweera, P.V.V., Pitigala, P.K.D.P., Tennakone, K., 2005. Dye sensitized rear infrared room temperature photovoltaic photon detectors. Applied Physics Letters 85 (3), 5754-5756.

62. Bandara, J., Jayasundera, A., Weerasinghe, H.C., 2005. Enhancement of photovoltage of dye sensitized solar cells by introducing high band gap oxide layers. Solar Energy Materials and Solar Cells 85 (4), 341-350.

63. Senadheera, G.K.R., Kitamura, T., Wade, Y., Yanagida, S., 2005. Photosensitized of nanocrystallineTiO$_2$ film by a polymer with two carboxylic groups, poly2 – thiopheremalonic acid. Solar Energy Materials and Solar Cells, 88(3), 315-322.

64. Bandara, J., Pradeep, V.W., Bandara, R.G.S.T., 2005. The role of n-p junction electrodes inminimizing the charge recombination and enhancement of photocurrent and photovoltage in dye sensitized solar cells. Journal of Photovoltage in dye sensitized solar cells. Journal of photo chemistry and Photobiology A: Chemistry, 170(3), 273-278.

65. Senadheera, G.K.R., Kobayashi, S., Kitamura, J., Wade, Y., Yangida, S., 2005. Versatile preparation method for mesoporousTiO$_2$ electrodes suitable for solid state dye sensitized photo cells. Bulletin of Material Science MFN 5149.

66. Kumara, G.R.R.A., Kawaguchi, T., Katoh, Y., Tennakone, K., 2005. Dye sensitized solid state cells sensitized with Coumarinderivaties Pacific Chemistry Congress, Honululu, Hawaii, U.S.A., 15-20 Dec 2005, MFN 5523.

67. Kumara, G.R.A., Koneko, S., Konno, A., Okya, M., Murakam, K., Tennakone, K., 2006. Large area dye sensitized solar cells :Meterial aspects of fabrication. 14(7), 643-651.

68. Kumara, G.R.A., Okye, M., Konno, A., Tennakone, K., 2006. Shinso Leaf pigment for dye sensitized solar solid state solar cells. 90 (9), 1220-1226.

69. Perera, V.P.S., Seneviratne, M.K.I., Pitigala, P.K.D.D.P., Tennakone, K., 2005. Doping of Cu SCN film for enhancement of conductivity : Application in solid state DSSC's. Science Direct, Solar Energy Materials & Solar Cells. 86 (2005), 443-450.

70. Kumara, G.R.A., Kanno, A., Okuyo, M., Tennakone, K., 2005. Dye-Sensitized Solar Cells with extremely thin liquid film as the Redox Electron Mediator. The Chemical Society of Japan, Chemistry letters, Vol. 34, No.4 (2005).

71. Dharmadasa, I.M., Robers, J.S., Hill, G., 2005. Third generation multi layer graded bandgap solar cells for achieving high conversion efficiencies: Experimental results. Science Direct, Solar Energy Materials & Solar Cells, 88 (2005) 413-422.

72. Agenman, B.O., Kaneko, S., Kumara, A., Okuya, M., Murakami, K., Konno, A., Tennakone, K., 2005. Sensitization of NanocrystallineSnO_2 Film with Indoline Dyes. Japanese Journal of Applied Physics, Vol.44, No.23, 2005, 731-733.

73. Jayaweera, P.M., Rajapakse, R.M.S.P., Tennakone, K., 2005.,TiO_2nanoporous photo electrochemical cells (PEC's) sensitized with mixed cationic/anionic dye systems : Role of the second cationic fluorescent dye on photocurrent enhancement. Science Direct, Chemical Physics Letters 412 (2005) 29-34.

74. Seneviratne, M.K.I., Pitigale, P.K.D.D.P., Tennakone, K., 2005., Chromospheres linked conducting polymers attached to semiconductor surfaces : A strategy for development of DSSC's. American Chemical Society, Journal of Physical Chemistry B, 2005, 109, 16030-16033.

75. Sirimanne, P.M., Seneviratne, I., Tennakone, K., 2005. An enhancement of photo properties of solid state TiO_2/dye/CuI type cells by coupling mercurochrome with natural juice extracted from pomegranate fruits. The Chemical Society of Japan, Chemistry Letters Vol.34, No.11.

76. I/F Novic and DSSC's. Tennakone, K., Jayaweera, P.V.V., Pitigala, P.K.D.D.P., Perera, A.G.I., Tennkone, K., 2005. Semiconductor Science & Technologies. 20 (2005), L1-L3.

77. Senadheera, G.K.R., Silva, N.S., 2006. Efficient Quasi Solid Solar Cells employing molten salt electrolyte. Sri Lanka Journal of Physics, Vol.7 (2006) 15-22.

78. Fernando, T.M.R.C., Senadheera, G.K.R., 2008, Synthetic and Characterization of carboxylatedthiophere co polymers and their photo-voltaic cells. Current Science Vol.95, No.6.

79. Fernando, J.M.R.C., Senadheera, G.K.R., 2008. Natural Anthrocyoni..as photosensitizes for DSSC's. Current Science Vol.95, No.5.

80. Bandara, J., Pradeep, U.W., 2008. Turning of flet band potentials of nanocrystallineTiO_2 and SnO_2 particles with an outer shell of MgO layer. MFN 5913, 517(2), 952 – 956.

81. Bandara, T.M.W.J., Dissanayake, M.A.K.L., 2008, Polyethylene oxide PEO – based anion conducting solid polymer electrolyte for PEC solar cells. Journal of Solid State Chemistry, 12(40003), 913-920.

82. Ariyasinghe, Y.P.Y.P., Wijayarathna, T.R.C.K., Kumra, I.G.C.K., Jayaratne, I.P.L.,Thotawatthage, C.A., Gunathilake, W.S.S., Senadheera, G.K.R., Perera, V.P.S., 19th October 2010. Efficient possivation of SnO_2nano crystallites by Indoline D-149 via dual chelation. Journal of Photochemistry & Photobiology A, Chemistry xxx (2010) xxx-xxx (Article in Press.)

83. Bandara,T.,Dissanayake,M.A.K.L.,Somasundaram, L.R.A.K.,Illeperuma,O.A.,Varaprathan, K.,Mellander, S.C., Postgraduate Institute of Science,University of Peradeniya, Peradeniya. 1994.
    a. Quasi Solid State DSSC's
    b. Solid State DSSC's.

84. Bandara, L.R.A.K., Dissanayake, M.A.K.L., Ekanayake, G.V.K., Illeperuma, O.A., Weeraman, T.T.K., Department of Chemistry, University of Peradeniya. 1998. Dye-Sensitized photoelectrochemical solar cells with PEO based solid polymer electrolytes. Proceedings of the workshop on renewable Energy Sources, Colombo 10-11 Feb. 1998, 11 PR 2937, 541.14: 541.13.

85. Fernando, C.A.N., Weththasinghe, S.K., Department of Physics, University of Ruhuna. 2000. Phtocurrent generation of a dye sensitized solid state photovoltaic cell made from n-Cu_2O and P – Cu SCN thin' film. Proceedings of the 5th Workshop on low cost Electronic Materials, Solar Cells and Renewable Energy Sources. Colombo, 22-25 Feb.2000: 86-93.

86. Fernando, C.A.N., Kumarawadu, I., Kiyagawa, A., Suzuki, M., Department of Physics, University of Ruhuna, Matara. 1999. Crystal Violet dye-sensitized photocurrent by participation of surface sates on P. Cu SCN photocathode. Solar Energy Materials. 629.7.064.535.215 semi conductor materials.

87. Fernando C.A.N., Weththasingha, S.K., Department of Physics, Ruhuna, Matara. 2001. Improved photocurrent quantum efficiency and kinetics of photocurrent generation of a dye sensitized solid state solar photovoltaic cell made from n Cu2O and P-Cu SCN thin film. Japanese Journal of Applied Physics. 40:1-7.

88. Fernando, C.A.N., Takashi, K., Kitagawa, A., Suzuki, M., Wethasinghe, M., Kunarawadu, I., Department of Physics, University of Ruhuna, Matara. 2001. Remarkable stability of the enhanced sharp photocurrent in netyhlinolet – C18 and Solar Energy Materials. 629.7. 064: 535.215.

89. Fernando, C.A.N., Kumarawadu. I., Department of Physics, University of Ruhuna, Matara. 2001. Colloidal P-CuI sensitized double dye system. Semiconductor Science and Technology: 214 – 218, PR 3905.

90. Fernando, C.A.N., Priyankara, W.TC.,Dharmadasa, I.M., Department of Physics University of Rhuna, Matara. 2002. Photocurrent of Ruhuna, Matara. 2003. Photocurrent enhancement of interlocked LB film dye layers in a P-Cu SCN sensitized photoelectrochemical cell. Renewable Energy. 25:69-79.

91. Fernando, C.A.N., Department of Physics, University of Ruhuna, Matara. 2002. Hydrogen production from photoelectrochemical cells using low cost semiconductor film, and dye sensitized solar cell production with ordered and disordered molecular arrangement.

92. Jayaweera, P.M., Department of Chemistry, University of Colombo, Colombo. 2003. Photocurrent conversation efficiency of solar cells sensitized with a combination of ationic and anionic materials.

93. Ravirajan, P., David, T.R., Department of Physics, University of Jaffna, Jaffna. 2005. Controlling recombination kinetics of hybrid, polymer/ metal oxide solar cells.

94. Premalal, E.V.A., Perera, V.P.S., Open University of Sri Lanka, Nugegoda. 2005. Photovoltaic effects of dye-deposited metal electrodes in electrolytic media. Proceedings of the 21st Technical Session – Institute of Physics, March 2005: 57-61.

95. Director, National Energy Research and Development (NERD) Centre, J-Ela. 2006. Cheaper ways to produce Dye-Sensitized Solar Cells.

96. Hussain, F.M., Sirakumar, V., Department of Physics, University of Peradeniya, Peradeniya. 2007. Structural studies of plant pigments used in dye sensitized solar cells. Proceedings of the University of Peradeniya Research Sessions ,Purse 2007. 12 (ii): 275 - 277. PR6160.

97. Bandara, T., Dissanayake, M., Illeperuma, O.A., Varaprathen, V., Vignarookan, K., Mellander, P.E., 2008. Postgraduate Institute of Science, University of Peradeniya, Peradeniya. Polyethylene oxide based anion conducting solid polymer electrolyte for PRC solar cells.

98. Siripala, W.P., University of Kelaniya, Kelaniya. 2008. Solid state dye sensitized solar cells.

99. Aponsu, G.L.M.P., De Silva, R.C.L., Perera, V.P.S., Open University of Sri Lanka, Nugegoda. 2008. Enhanced photovoltaic effects of dye sensitized solar cells of SnO_2surface modified with gold nanoparicles. PR 6207.

100. De Silva, R.C.L., Liyanage, L.S.G., Perera, V.P.S., Open University of Sri Lanka, Nugegoda. 2008. Electron Kinetics of Dye Sensitized Solar Cells made from Al_2O_3 coated SnO_2nano crystalline films. PR 6214.

101. Aponso, G.L.M.P., Premalal, E.V.A., Liyanage, L.S.G., Perera, V.P.S., Open University of Sri Lanka, Nugegoda. 2008. Deposition of P_t and An Quantum Dots on TiO_2 nanoparticles: study of ballistic electron transport with dye sensitization

102. Solar Electric Light Fund Report. 1991. Solar Power and light for Developing World.

103. Solar Electric Light Fund Report. 1991. Energy Environment and Economic Development.

104. Dharmadasa, I.M.2009. A Future Dominated by Solar Energy. Sheffield Hallan University, Sheffield, U.K.

105. Dharmadasa, I.M.2009. Solar Energy Technologies: A Status Report. Sheffield Hallan University, Sheffield, U.K.

106. Manil, G.Gap Analysis Product standards of Solar PV. Arizona State University, Arizona, U.S.A.

107. United States Department of Energy.2009. The Solar America Board for Codes and standards (Solar ABC) GAP Analysis process for Solar PV's.

108. Clacerie, A., ADME, France, Joyce, A, INETI Portugal, Rantil M., Formas, Sweden, Ahm, P.PA Energy, Denmark, Passiniemi, P., NAPS, Finland.2009. A SWOT Analysis of PV RTD in Europe.

109. Nanotechnology Developments in India – A status Report. April 2009.

110. Guo, Ying., Huang, Lu., Portar, Alan L., 2009. Profiling Research Patterns for a New and Emerging Science and Technology: Dye-Sensitized Solar Cells, Georgia Institute of Technology, Atlanta, U.S.A., sma.tech.edu/bitstream/handle/1853/3237/22-656-PB.pdf

111. Berger, Frank.,Loeffler, Jonathan., September 2005. SWOT Analysis concerning the use of Nanomaterials in the Solar Energy Sector.

112. Report from nanoform. Cum: Nanotechnology helps solve the world's energy problems – April 2004.

113. Report from VTT Technology Studies, Nano Road Map project October 2004.

Expert interview, Mr. Ken FraumhoflerISE Freiberg, Department of Solar Cells, Germany.

114. Dye-Sensitized Solar Cells, European Institute for Energy Research, 2005.23 April 2006<http:www.either.um_karlsrule_ de>

115. Gratzel, Michael, O'Regan Brian. 1991. A low cost, high efficiency solar cells based on Dye Sensitized colloidal Ti O_2 film, Institute of Technology CH1015, Lausane, Switzerland, Letters to Nature, Magazine, Nature 359 (737-740).

116. Campbell, R. Wayne.2007.taking Nature cue for cheap solar power, Massey University, Nanotechnology Research centre, New Zealand, Science Direct.

117. Bryan, R. 2008. A new ingredient for solar cells – Raspberries.

118. Amonbitbamy, V.2008.Die-Sensitized solar cells based on Titanium dioxide sensitized with natural dyes, Department of Physic and Integrated Nanotechnology Research centre, Faculty of Science, Khonikaen, University of KhaKha 4002, Thailand.

119. Gratzel, Michael.2005.Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells, Inorganic Chemistry. Vol 44, P 6841-6851.

120. Botanical Names and Sinhala Names of Plants grown in Sri Lanka.

121. Kudagamage, Horticultural Crop Research & Development Institute, Gannoruwa, Sri Lanka.

122. Weerasinghe, A. Botany of Crop. Rajarata University, Sri Lanka.

123. Corkish, Richard. Solar Energy.2010. Australian Academy of Science, School of Photovoltaic & Renewable Energy, University of New South Wales, Sydney, Australia.

124. Graph of Best Research Cell Efficiencies on DSSC's from 1975 to 2010. National Renewable Energy Laboratory Boulder, Colorado, U.S.A.

125. Main Research Organizations and Established Companies in the world carrying out R & D on Dye-Sensitized solar cells. PV Industry Note # PV1-0302.01 8 August 2005. Prometheus Institute for sustainable Technologies, 1420 North Lake Shore Drive # 9A, Chicago, Illinois 60610, U.S.A.

126. Mukhergee. D andChackravathi. S : ‘Fundamentals of Renewable Energy Systems’, New Age International Ltd. Publishers, New Delhi, India, Reprint 2005.

127. Sawatsuk.T: 'Green Photosynthesis for Dye-sensitized Solar Cells', National Nanotechnology Center (NANOTEC) , NSTDA, 111 Thailand Science Park, Phathuthani 12120, Thailand, December 2008.

128. Chindaduang. A : ‘Polymer Assisted Degeneration of Zinc Oxude for Dye-sensitized Solar Cells’ National Nanotechnology Center, NSTDA, 111 Thailand Science Park, Phathuthari 12120, Thailand, December 2008.

129. Amonbitbamy. V : 'Dye-sensitized Solar Cells Based on Titanium Dioxide, sensitized with natural dyes', Department of Physics and Integrated Nanotechnology Research Center, Faculty of Science, Khonikaen University, Khan Khan 4002, Thailand, December 2008.

130. Ammsakihan.T : 'Development of Low Temperature Slurry' for Dye-sensitized Solar Cells Flexible Photo electrodes’, Department of Chemistry and Center of Excellence for Innovations in Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand, December 2008.

131. Fernando.J.M.R.C. andSenadheera. G.K.R.: Natural Anthrocyanins as Photosynthesis for Dye-sensitized Solar Devices’, Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka, Current Science Vol. 95, No.5, 10 September 2008.

132. Fernando. J.M.R.C. and Senadheera.G.K.R: ‘Synthesis and Characterization of CarboxylatedThiophene Co-polymers and their use in Photovoltaic cells’, Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka, Current Science Vol. 95, No.6, 25 September 2008.

133. Kamat. Prashant, Professor : ‘Meeting the Clean Energy Demand’, University of Notre Dam, Department of Chemistry and Bio Chemistry, Indiana 46566 – 5674, U.S.A., Journal of Physics C 2001, 111, 2834 – 2800, 6 December 2006.

134. New Energy News: 'Planning Molecular Antennae to convert light photons to electrical power', <http:// www.podrak.com/ire/ine9.html>.

135. Exploring the Nanowaorld : <http:// mrsec.misc.edu /edate/index.html>.

136. Yamazoki.E and Murayama. M: ‘Utilisation of Natural Carotenids as Photosynthesizers for Dye-Sensitized Solar Cells,' Industrial Research Division, Prefectural Science and Technology Promotion Center, Takachaya 5-5-45, Japan, Science Direct, 3 August 2006.

137. Hitoshi. K and Hideki. S : ‘Theoritical Studies of 1:1 Charge Transfer complexes between Nitrogen containing Heterocycles and I_2 Molecules and Implications on the, Performance of Dye-Sensitized Solar Cells’, Energy Technology Research Institute, National Institute of Advanced Science and Technology (AIST), Tsukuba Central 5-1-1, Higashi, Tsukube, Japan, Science Direct, 5 December 2005.

138. Kazuliom. S, Yamaguoh. M, Kumagen. M., Tanabo N, Yonagid, S: 'Dye-Sensitized Solar Cells with Ionic gel electrolyte prepared from Imidazcilian Salts and Agarose', Photonics and Materials Research Department, Institute of Research and Innovation, 1201 Takode, Kashima, Chibo 227-0861, Japan, Science Direct, 14 April 2005.

139. Perera. V.P.S., Pitigala. P.K.D.D.P., Seneviratne. M.K.I, Tennakone, K: 'A Solar Cell sensitized with three different dyes', Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka, Science Direct, 2 June 2004.

140. Seneviratne. M.K.I, Pitigala. P.K.D.D.P., Perera. V.P.S., Tennakone. K : ‘Molecular Rectification: Applications in Dye-Sensitized Solar Cells’, Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka, 9 December 2004.

141. Garcia C.G., Polo. A.S., IheN.Y.M.: 'Fruit Extracts and RuthaniumPolypryndime Dyes for sensitizations of TiO_2 in Photoelectrochemical Solar Cells', Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka, Science Direct, Journal of Photo Chemistry, 10 April 2003.

142. Battacharya. K.G., Sarme. A : ‘Adsorption characteristics of the Dye Brilliant Green on Neem Leaf Powder’, Department of Chemistry, Gauchati University, Gawachati 781014, Assam, India, Science Direct- Dyes & Polymers, 6 January 2003.

143. Chigurupati. N, Saiki. L, Gayser. C., Dash A.K: 'Evaluation of Red Cabbage Dye as a potential natural colour for, pharmaceutical use', Department of Pharmacy, Sciences, School of Pharmacy and Allied Health Professions, Craghtm University 2800, California Plaza, Omaha NE6878, U.S.A., International Journal of Pharmeceutics, 30 April 2002.

144. Tennakone. K, KuroG.R.R.A., Kottegoda. RM, Perera. V.P.S. WeerasundaraP.S.R.S.: ‘Sensitization of Nanoporous films of TiO_2 with Santalin (Red Sandlewood pigment) and construction of Dye-Sensitized Photovoltaic Cells’, Institute of Fundamental studies, Hantana Road, Kandy, Sri Lanka, Science Direct, Journal of Photo Chemistry and Photo Biology, 9 June 1998.

145. PVNET European Roadmap for PV R & D, AmulfJager – Walden Office for Publications of the European Union 2004.

146. Nanocrystalline Dye–Sensitized Solar Cell Kit. http://www.solidem. com/solarcell/ cellkit.html.

147. National Renewable Energy Laboratories (NREL), Colorodo, U.S.A., Feature Storage-Photovoltaic Innovations, Win 2 R & D 100 Awards.

148. Luguear. Antonio : ‘Handbook of Photovoltaic Science & Engineering’, John Wiley and Sons, ISBN 0471491969.

149. Cheng Hsiao Wu, Williams Richard: ‘Limiting efficiencies of multiple energy - gap quantum devices’, Journal of Applied Physics, U.S.A., 54-674(1983).

150. ASTM International G173-03, 'Standard Tables for Reference, Solar Spectral Irradices.'

151. Winfel Peter (2005): ‘Physics of Solar Cells’ Weinheim. Wiley-VCH, ISBN 3-527-40438.

152. Green. D, Martin A : ‘Third generation photovoltaics – Solar Cells for 2020 and beyond.’

153. Solar Cells: Wikipedia, 25 April 2006 ,<http;//ea.wikipedia. org/wiki.solar.cell>.

154. LovgreStephen : ‘Spray-on Solar Power Cells are true break throughs’, National Geographic News, 14 January 2005, 18 April 2006, <http://news. nationalgeographic.com>.

155. Gratzel. Michael: 'Solar Cells for cheap – 2006', Interview with the Inventor of DSSC’sPolytechniquesFederales de Lausame, Switzerland at MIT Technology Review, 12 September 2006 , http://www.technologyreview.com/read–article.aspx? id = 17490&ch = biztech&sc=&pg=1.

156. Bryan R : ‘A new ingredient for solar cells – Raspberries', 9 January 2008.

157. Campbell R. Wayne Dr: ‘Taking Nature’s cue for Cheap Solar Power,’ Massey University, Nanotechnology Research Centre, New Zealand, Science Direct, 6 April 2007.

158. LenzmanF.O., Kroon J.M.: 'Recent Advances in Dye-sensitized Solar Cells', Energy Research Centre of Netherlands(ECN), Westerduinweg 3, Petten 1725, Netherlands, 13 September 2008.

159. Huijser, AnmarieDr: ‘Around the world with Dye-Sensitized Solar Cells’ Technical University of Delft, Netherlands, 27 May 2008.

160. TakenakaK : ‘SONY develops cost – efficient Solar Cells’, SONY Corporation, Tokyo, Japan, 25 May 2008.

161. Solaronix S.A., Rue de Louriette 129 CH-1170, Anborne, Switzerland, ‘Dye Solar Cell Assembly Instructions.’

162. Wan H: ‘Dye-Sensitized Solar Cells’, Department of Chemistry, University of Alabama, Alabama,U.S.A.

163. University of Karlsruhe, European Institute for Energy Research: ‘Dye- Sensitized vs Thin Film Solar Cells’, 30 June 2006.

164. Gratzel Michael, O’Regan Brian: ‘A Low cost, High efficiency Solar Cells based on Dye – Sensitized colloidal TiO_2 films’, Institute of Physical Chemistry, Swiss Federal Institute of Technology CH1015, Lousane, Switzerland, Letters to Nature Magazine, Nature 359 (737-740) 24 October 1991.

165.. CherepyN.J, SmestadG.P., Gratzel Michael, ZhonyJ.N: ‘Ultra Fast Electron Injection Implications for a Pphotoelectrochemical Cell utilizing an Anthrocyanin Dye Sensitized TiO_2Nanocrystalline Electrodes’ Department of Chemistry, University of California, Santa Cruz, California 95064, U.S.A., Journal of Physics B1897, 101-9342-9342-9351, 7 September 1997.

166. GratzelMichael : ‘Photoelectrochemical Cells’ , Nature, Volume 414, 15 November 2001.

167. GratzelMichael : 'Solar Energy Conversion by Dye – Sensitized Photovoltaic Cells', Inorganic Chemistry, 2005 Vol. 44, p6841-6851.

168. GratzelMichael : ‘A high molar Extintion coefficient charge transfer sensitizer and its implications in Dye-Sensitized Solar Cells’, Journal of Photochemistry and Photobiology 185, 28 June 2006.

169. RossierI.N. GratzelMichael : 'Solid Hybrid Dye – Sensitized Solar Cells – New Organic Materials, Charge recombination and stability', EcolePolytechniqueFederale Lausanne, Switzerland, 5 February 2009.

170. Kruger J : 'Interface Engineering in solid state Dye – Sensitized Solar Cells', EcolePolytechniqueFederale , Lausanne, Switzerland, 2003.

171. Gratzel Michael, Kalyanasunderam K: ‘Dye-Sensitized Cells (DYSC) based on Nano crystalline Oxide semiconductor Films', Laboratory for Photonic’s and Interfaces, Swiss Federale Institute of Technology, CH 1015, Lausanne, Switzerland, 2 February 1997.

172. TennakoneK : ‘Dye-Sensitized Semiconductor Nanostructures for Solar Energy Conversion’, Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka, Ceylon Journal of Science.

173. SenadheeraG.K.R., JayasuriyaP.V.V., PereraV.P.S. Tennakone K: ‘Solid State Dye-Sensitized Photocell based on Pentacene as a hole collector’, Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka, Solar Energy Material and Solar Cells Journal 73 (2002) 103-108, 8 October 2001.

174. SubramniamV.R.: 'Nanostructured Semiconductor components for Solar Cells’, Department of Chemical and Materials Engineering, University of Navada, Navada, Reno, U.S.A., Electro Chemical Society Interface Journal, Science Direct, 2007.

175. Dye-Sensitized Solar Cells, European Institute for Energy Research, 2005. 23, April 2006 <http://www.either.um-kalsruhe-deEl-Agez, T.M.Tayayan, A.E., Al-Kalour, A., Jaya, S.A., Abdel Latif, M.S. Dye Sensitized Solar Cells Based on ZnO Film and Natural Dye. Internation Journal of Materials and Chemistry. 2012. Vol.3, pp 105-110.

176. Calogero, G. DiMarco, G., Caramon, S. Cazzanti, S and Argazzi and Bignozzi, C.A. Natural dye sensitizers for photoelectrochemical cells, Energy & Environment Science, 2009, Vol.2, pp1162-1172.

177. Moon, J., Tuominen, A., and Suominen, A. Forecasting a change in technology: Are Dye-sensitized solar cells a source of ubiquitos energy? International Journal of Technology, Policy Management, Vol.12, Nos 2/3, 20/2, pp 177-194.

178. Zhon, H. Wu L., GaO, Y. and Ma, T. Dye sensitised solar cells using 20 natural dyes as sensitizers. Journal of Photochemistry and Photobiology A. Chemistry 2011,pp 188-194.

179. Narayan, R.M., Review: Dye sensitized solar cells based on natural photosensitizers. Renewable and Sustainable Energy Reviews 16 (2012), pp208-215.

180. Buraidah, M. H., Teo, L.P., Yusuf S.N.F., Noor, M.M., M.Z., Careem, M.A., Majid, S.R., and Araf, A.K. TiO2/Chitosan – NH4I (+I2)-BMII-Based Dye-Sensitized Solar Cells with Anthrocyanin Dyes Extracted from Black Rice and Red Gabbage. International Journal of Photoenergy Vo.2011 (2011), pp1-9.

181. Nuwanya, A.C., Ezeno, F.I., and Ejikme, P.M. Dye Sensitized Solar Cells: A technically and economically alternative concept to p-n junction photovoltaic devices. International Journal of Physical Sciences, 2011, Vol.6 (22), PP 5190-5201.

182. Hardin, B.E., Snaith, H.J. and McGhee, M.D. The renaissance of dye sensitized solar cells. Nature Phototonics 2012 Vol., pp162-169.

183. El-Agez, T.M., Tayyan, A.E., Al-Kalaur, A., Jaya, S.A., Abdel Latig, M.S. Dye Sensitized Solar Cells Based on ZnO Films and Natural Dyes. International Journal of Materials and Chemistry. 2012 Voll.3, pp105 – 110.

184 Harrey, J.P., Toan, S., and Rochford, J.Artificial Photosynthesis: A workshop in Solar Cell Design. Department of Chemistry, University of Manachusetts, Boston, U.S.A. 2011, pp 1-6.

185. Dumbrava, A., Enoche, I., Opera, C.I., and Georgexn Towards a more efficient utilization of Betalians as pigments for Dye-Sensitized Solar Cells. Digest Tournal of Nanomaterials and Biostructures.. 2012. Vol.7, No.1, pp 339-351.

186. Cruz, R., Alfredo, D., Tanaka, P., and Mendes, A. Reduced graphene oxide films as transparent counter -electrodes for dye sensitized solar cells ,Science Direct, Elsevier, Solar Energy, 2011. Vol. 86, pp 716 - 724.

187. Chen, C., Long, M., Xia, Min., Zhang, C., and Cai, W. Raduction of graphene oxide by an in-site photoelectro chemical method in a dye sensitized solar cell assembly.

Springer Open, Nanoscale Research Letters. 2012 .Vol.7(1):101, pp 1-5.

188 De Silvestro, H., What physical Factors Affect Current - Voltage Characterisitcs of Dye Solar Cells? Chief Scientist Dyesol Ltd., New South Wales, Queensburg Australia. 2008. Dyesol Newsletter, February 2008. pp 1-16.

189. Gordon, R.G. Criteria for choosing Transparent Conductors. www.mrs. org/publications/bulletin, Augst 2000. 20000. pp52-57.

190. Halme, J., Toivola, M.Tolvanen, A., and Lund, P. Charge transfer resistance of spray deposited and compressed counter electrodes for dye-sensitized solar cells on plastic substrates. Elsevier, Science Direct, Solar Energy Materials & Solar Cells. 2006. Vol.90, pp 872 -886.

191. Fleischer, K., Area, E., and shvets, I.V.Alternative Flourine Precursor for synthesis of SnO2: F by spray pyrolysis. Thin Solid Films. Cleaner Energy Laboratory, School of Physics, Trinity College Dublin, Dublin , Ireland. 2011. pp 1-23.

192. Hirunlabh, J., Suthateetanet, S. Kirtikara, K., and Pyrn, R. D. School of Energy & Materials, King Mongbut; Univeristy of Technology, Bangkok, Thailand. DSSC's with natural dyes.Thammasat International J.Sc. Tech. Vol 3 Nos, 1998. pp 10-20.

193. Stathatos, E., and Dionysion, D.D. Comparative Studies on Dye Sensitized Solar Cells with nanostructured TiO2 film prepared inroom or in high temperature. Technological Educational Institute of Patras, Greece. 2009. pp 1-4.

194. Yousaf, S.A., and Ali, S. Effect of Flourine doping an Optoelectronic properties of Tin dioxide. Department of Physics University of Lahore, Pakistan. 2008. Coden-JNSMAC PK ISSN 0022-2941,Vol.. 48,No.1 & 2, PP 43-50.

195. Zhang , Q., and Cad, G. Nanostructured photoelectrodes fo dye-sensitized solar cells. 2011. Elsevier, Science Direct, Nanotoday, Vol,6, pp 91-109.

196. Mertinson, A.B.F., McGrarrah, J.E., Parpia, M.O.K., and Hupp, J.T.Dynamics of charge transport and recombinationin ZnO nanorod array dye-sensitized solar cells. Physical Chemistry Chemical Physics. Journal. 2006.pp 4655 -4659.

197. Senadhera, G.K.R.. Spray painted nanostructured TiO2 electrodes for solid-state dye sensitized photocells. Sri Lanka Journal of Physics, Institute of Physics, Sri Lanka. 2004. Vol.5, pp 17-25.

198. Gratzel, M., and Durrant, J.R.Dye-Sensitized Mesoscopic Solar Cells. Chapter 8.2008. pp 503-536.

199. National Solar Technology Roadmap. National Renewable Energy Laboratory, Colorado, U.S.A. Sandia National Laboratories, U.S.A, and U.S. Department of Energy. 2007. NREL/MP 520-41739.

200. Durr, M., Schmid, A., Obermeuier, M., Rosselli, S., Yasuda, A., and Nelles. Low temperature fabrication of dye-sensitized solar cells by transfer of composite porous layer. Nature Materials 2005. Vol.4, pp 607-611.

201. Li, N., Pan, N., Li, D., and Lin, S. Natural Dye-Sensitized Solar Cells based on highly ordered TiO2 Nanotube Arrays. International Journal of Photoenergy. 2013. Vol. 2013, 5 pages.

202. Nishantha, M.R., Yapa, Y.P.Y.P., and Perera, V.P.S. Sensitization of Photoelectrochemical. Solar Cells with a natural dye extracted from Kopsia flavida fruit. Proceedings of Technical Sessions, Institute of Physics, Sri Lanka. Department of Physics, Open University of Sri Lanka. 2012. Vol.28, pp 54-58.

203. Kelvin, O.O., and Ekpunobi. Fabrication and characterisitcs of Dye Sensitized Solar Cell using Anarcardium Occidentale Sensitizer. Advances in Applied Science Research. Department of Physics, Nmamdi Azikriwe University , Nigeria. 2012. Vol.3(5), pp 3390 - 3395.

204. Moustofa, K.F., Tekaby, M.Shenany, E.T., and Khattab, N.M.Green Dyes as Photosensitizers for Dye-Sensitized Solar Cells. Solar Energy Department, National Reserch Centre, Dokki, Giza , Egypt. Journal of Applied Sciences Research 2012. Vol.8(8), pp 4393-4404.

205. Lai, W.H., S.Y.H., Teoh, L.G., and Hon, M.H.Commercial and natural dyes and photosensitizers for a water - based dye sensitized solar cell loaded with gold particles. Department of Materials Science and Engineering National Cheng kung University, Tainan, Taiwan. Science Direct. Journal of Photochemistry and Photobiology Chemistry. 2005. Vol 195, pp307-313.

206. Cramer , H.E., Griep, M.H.., Choi, D.S., and Kama, S.P. Green Nanochemistry Approach to Titanium Dioxide nanoparticle Dye-Sensitized Solar Cells. United States of America, Army Research Laboratory, Aberdeen Proving Ground, Maryland, U.S.A. 2012. ARL-TR-6033, 22 pages.

207. Mamide, T., Mandhe, S.B., and Mishra, A. Study and Analysis of Dye -Sensitized Solar Cells. Department of Mechanical Engineering, M.B.E.Society College of Engineering, Nagpur, India. International Journal of Modern Engineering Research, Vol. 2, Issue 5. 2012. PP 3597 - 3601.

208. Chen, Y.S., Lee, J.N., Tsai, S.Y., and Ting, C,C, Manufacture of Dye, Sensitized Nano Solar Cells and their I - V Curve Measurements. Institute of Mechatronic Engineering, National Taipei University of Technology, Taiwan. Proceedings of ICAM 2007. 2007. 7 pages.

209. Puspa, S. Natural Dye Sensitized Solar Cells - A Review. Ingertaconnect, Publishing Technology, Advanced Science Letters. 2012.pp1- 10.

210. Narayen, M.R. Investigation of some common Fijian flower dyes as photosensitizers for dye sensitized solar cells. School of Engineering and Information Technology, Charles Darwin University, Darwin, Australia. Renewable and Sustainable Energy Reviews. 2012. Vol.16,pp 208 - 215.

211. Alhamed, M., Issa, A.S., and Doubal W. Studying of Natural Dyes properties as photosensitizer for Dye Sensitized Solar Cells (DSSC). Department of Physics, Faculty of Sciences, Alleppo University, Syria. 2012. Journal of Electron Devices, Vol. 16, pp1370-1383.

212. Nataraj , N.M. A Comparative Study of the Photovoltaic Response of Anthrocyanin Dyes from Different Natural Sources. United States Army Research Laboratory, Composites and Hybvrid Materials Branch. 2012. pp1-17.

213. Kumara, N.T.R.N.Ekanayake, P., Lim, a., Liew, L.Y.C., Iskonder, M., Ming, L.C., Senadheera, G.K.R. Layered Co-sensitization for enhancement of conversion efficiency of natural dye sensitized solar cells. Faculty of Science, University of Brunei, Bovneo and Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka. 2013. Journal of Alloys and Compounds 581 (2013 186-191.

214 US State Market Insight, Quarterly Publication (Q2 – 2013) of GTM Research & Solar EnergyIndustries Association (SEIA), U.S.A

215 Huizhi Zhou, Liqiong Wu, Yurong Gao , Tingli Ma . Dye – Sensitized Solar Clls using 20 Natural Dyes as Sensitizers . School of Chemical Engineering , Dahlian

216. MonishkaRita Narayan. Review : Dye-Sensitized Solar Cells based on natural photosensitizers .School of Engineering and Information Technology , Faculty of Engineering , Technology ,Science and environment , Charles Darwin University , Darwin , Australia . 2012. Renewable and Sustainable Energy Reviews. 16, (2012), 208 – 215 .

217. Yiming , Chen., Haiyan ,Zhang., Yuting, Chen., and Jaiapeng, Lin. Study of Carbon Nanocomposite Counter Electrodes for DSSC's , Faculty of Materials 7 Energy , Guandang University of Technology , Guanzhou , China. Journal of Nanomaterials . 2013. 6 pages .

218. Huang, S., Moon, J., Lee, S., Kim,D.H., Lee, D., Choi,W., and Jeon, M. Carbojn Nanotubes as Counter electrodes for DSSC's , Department of Nanosystem Engineering , Inje University ,Gimhoe,Gyeongnam , South Korea . 2007 . Electronics Letters , Vol. 43, No. 25,2 pages.

219. Photovoltaics : Thin Film Technology about to make it's breakthrough . Solar Server .2008.

220. Grama,S. A Survey of Thin Film Solar Vopltaic Industry and Technologies . Massechusettes Institute of Technology , Massechsettes , U.S. A. 2008 .

221. Green, M.A. Recent Developments in Photovoltaics .Solar Energy Vol. 76, No. 1 – 3 , 3 – 8 . 2004 .

222. Chopra, K.L., Paulson, P.D., and Dutta, V. Thin Film Solar Cells an Overview . progress in Photovoltaics Research and Applications . Vol. 12, No. 2 – 3 . 2004, pp 69 -- 92.

223. Cadmium telluride Solar Cells . Encyclopedia Britanica Inc, U.K. 2014.

224. Cadmium telluride (Cd te) Photovoltaics .What Is .com . 2014.

225. Pontmons, J., and Von Roederm , B. Thin Film CIGS and Cd Te Photovoltaic Technologies :Comercializat6ion , Critical Issues and Applications . Vol. 14 , No. 5. 2006. Pp 393 – 411 .

226. Stamberg, B.J. Copper indium gallium selenide and related materials for Photovoltaic Devices . A Critical Review in Solid State and Materials Science , Vol. 27 (2) : 73 . 2002 .

227 Charaacterization of Efficient CIGS Absorbers . National Renewable Energy Laboratory, Boulder , Colorado, U.S.A. May 2008.

228. Jorgenson, M.C., Norrman, K., and Knebas, F.C. Stability / Degradation of Polymer Solar Cells . Solar Energy Materials & Solar Cells .2008. Vol. 92, (7), 686.

229. Sharker, M.C., Muhlbacher , D., Koppe , M., Waluf, C. Design Rules inj Bulk Heterojunction Polymer Solar Cells . Advanced Materials . 2006. Vol. 18 (6), 789.

230. Heywang, W., and Zainger , K.H. Silicon the Semiconductor Material . Springer verlog 2004.

231. Whenham, S.R., Green, M.A., Watt, M.E., Corkish, R. Applied Photovoltaics . Earthscan . 2007. Chapter 2.

232. Polycrystalline Thin Film Solar Cell Technologies . National Renewable Energy Laboratory , Boulder, Colorado, U.S.A. 10 February 2011.

233. Nakayashiki, K., Rawanville , B., Yelundur , V., and Hanoko , J,I. Fabrication and Analysis of High efficienjcy String Ribbon Silicon Solar Cells . Solid State Electronics . 2006. Vol.50, 1406.

APPENDIX- A

Table 1. All Research Papers on DSSC's Published by the IFS, Hantana, Sri Lanka with their salient analysis

(also included in the Bibiliography Section)

SR. NO	RESEARCH PAPER	AUTHOR / S	PUBLISHED DATE & MEDIA	RESEARCH AREA
1	Sensitization of nano porous films of TiO_2 with santalin (red sandle wood pigment) and construction of dye-sensitized solid-state photovoltaic cells	K.Tennakone, G.R.R.A.Kumara I.R.M.Kottegoda, V.P.S.Perera, P.S.R.S. Weerawardana	9 July 1998 Journal of Photochemistry & Photobiology 117(1998) 137-142.	Dye-Sensitized solid state photovoltaic cells of santalin constructed by depositing p-Cul or P-CuCNS on santalin coated with nano porous TiO_2 films. Observed effects of light absorbed by the dye-molecules injecting electrons into TiO_2 and holes into Cul (or CuCNS) generating short-circuit photocurrent of ~ 6mA/cm^2 and photo voltage of ~450 mV at 800 W/m^2 simulated sunlight.
2	Dye-sensitized solid state photovoltaic cell based on composite zinc oxide / tin oxide films.	K.Tennakone V.P.S.Perera I.R.M.Kottegoda G.R.R.A.Kumara	29 September 1998 Journal of Physics 32 (1999) 374-379.	In Dye-sensitized fully solid state cells having the structure of rough n-type semiconductor film comprising Zinc and Tin (IV) Oxide/Ruthenium-bipridyl Complex / p-Cul are found to generate high short circuit currents and open circuit voltages.
3	An efficient dye-sensitized photo electrochemical solar cell made from oxides of Tin and Zinc.	K.Tennakone G.R.R.A.Kumara I.R.M.Kottagoda V.P.S.Perera	19November 1999 Chem. Communications, 1999, 15-16.	A photo electrochemical solar cell made from a porous film consisting of a mixture of Ruthenium bipridyl complex suppresses recombination of photo generated electrons and dye cations generating a short

				circuit photocurrent of 22.8 mA/cm^2 and open circuit voltage 670mV in direct sunlight 900W/m^2) with an efficiency of ~ 8%
4.	Dye-Sensitized Photo electrochemical Cells based on Porous SnO_2/ZnO composite and TiO_2 films with a Polymer electrolyte.	K.Tennakone G.K.R.Senadheera V.P.S.Perera I.R.M.Kottagoda L.A.A.de Silva	13 August 1999 American Chemical Society Chem. Mater 1999, 2474 - 2477	Polyacrylonitrile polymer electrolyte based photo electrochemical cells have been fabricated with Ruthenium bipridyl complex as the sensitizer using porous films of SnO_2/ZnO and TiO_2 films. For both types short circuit currents and efficiencies obtained.
5.	The possibility of ballistic electron transport in dye-sensitized semiconductor nano crystalline particle aggregates.	K.Tennakone I.R.M.Kottagoda L.A.A.de Silva V.P.S.Perera	17August 1999 Semiconductor Science & Technology. 14(1999) 975-978	A dye sensitized photo electrochemical cell made from nano-porous composite film consisting of Tin and Zinc oxides generates exceptionally high photo currents at an optimum mixing ratio of the two oxides.
6	Photocatalytic activity of dye-sensitized Tin oxide nano crystalline particles attached to zinc oxide particles: Long distance electron transfer via ballistic transport of electrons across nano crystallites	K.Tennakone J. Bandara	7 July 2000 Applied Catalysis A: General 208 (2001) 335-341	A catalyst comprising chains of dye-sensitized SnO_2 nano crystallite (10-15nm) attached to larger ZnO (~600nm) particles is found to photogenerate hydrogen from water with visible light in the presence of a hole scavenger.
7.	Highly stable dye-sensitized solid-state solar cell with the semi	K.Tennakone G.K.R.Senadheera	1 August 2000 Applied Physics Letters, American	Construction of a dye sensitized solid state solar cell with the semiconductor

	conductor 4 CuBr $3S(C_4H_9)_2$ as the Hole collector)	D.B.R.A.de Silva I.R.M.Kotagoda	Institute of Physics Vol.77 No.13	4 CuBr $3S(C_4H_9)_2$ as the hole collector is reported. Cell delivered a short circuit photo current of ~ $43mA/cm^2$ and open circuit voltage of 400 mV at 1.5 air mass,1000 Wm^{-2} sunlight.
8	Dye-sensitized solar cells with the hole collector p-CuSCN deposited from a solution in n-propyl sulphide	G.R.R.A.Kumara, A.Konno, G.K.R.Senadheera P.V.V.Jayaweera D.B.R.A.de Silva K.Tennakone	30 September 2000 Solar Energy Materials & Solar Cells 69(2001) 195-199.	DSSC formed with CuSCN on Ruthanium complex dye coated nano crystalline TiO_2 films found to yield higher short circuit current, open circuit voltage and efficiency compared to cells made with CuSCN by other deposition techniques.
9	Photoelectrochemical cells made from SnO_2 / ZnO films sensitized with Eosin Dyes	G.R.A.Kumara A.Konno, K.Tennakone	29 November 2000 The Chemical Society of Japan Chemistry Letters	DSSC constructed with SnO_2/ZnO, SnO_2 and TiO_2 film sensitized with Eosin Y dye observed to yield high short circuit photocurrent and efficiency compared to cells made from SnO_2, ZnO or TiO_2.
10.	Suppression of recombination's in a Dye-Sensitized Photo electrochemical Cell made from a film of Tin IV Oxide crystallites coated with a thin layer of Aluminium Oxide.	G.R.R.A.Kumara, K.Tennakone, V.P.S.Perera A.Konno	5 December 2000 Institute of Physics, Journal of Physics D (Applied Physics) 34 (2001), 868-873	DSSC consisting of a film of SnO_2 coated with ultra fine particles of Al_2O_3 generates exceptionally high open circuit voltages as compared to a cell made only from SnO_2.
11.	Dye sensitized solar cells : New ideas for their improvement .	K. Tennakone	December 2000 Proceedings of the 5th workshop on low cost electronic materials, Solar cells and renewable energy sources, Colombo 22-25 Feb 2000 : 78 - 80	Instructions for improvement of efficiency, stability.
12.	Fabrication of solid state dye sensitized TiO_2 photo	G.K.R. Senadheera,	December 2000. Proceeding of	Investigation of Solid State Solar cells to prevent

	voltaic cells with Cu CNS.	K. Tennakone V.P.S. Perera	5th workshop on Low Cost Electronic Materials, Solar Cells and Renewable Energy Sources, Colombo 22 – 25, Feb 2000; 81-85	leakage of liquid electrolyte (stability enhancement)
13.	Dye-Sensitized Solid-State Solar Cells: Use of Crystal Growth Inhibitors for deposition of the Hole Collector.	G.R.A.Kumara A.Konno K.Shiatsuchi T.Tsukalara K.Tennakone	31 December 2001 American Chemical Society 14, 954-955	Solid State DSSC characteristics investigated are reported.
14.	Solid State Dye-Sensitized Photocell based on Pentacene as a hole collector	G.K.R.Senadheera P.V.V.Jayaweera V.P.S.Perera K.Tennakone	8 October 2001. Solid Energy Materials& Solar Cells 73 (2002) 103 - 108	Solid State dye sensitized photovoltaic cell with Pentacene deposited onto Ruthenium dye coated $Ti0_2$ electrode doped with Iodine fabricated and evaluators
15.	Enhanced Efficiency of a Dye-Sensitized Solar Cell made from MgO coated Nano crystalline SnO_2	K.Tennakone J.Bandara P.K.M.Bandaranayake G.R.A.K.Kumara A.Konno	23 May 2001 Japan Society of Applied Physics Vol. 40 (2001) pp.L732-L734.	Nano crystalline SnO_2 dye sensitized photo electro chemical solar cells coated with SnO_2 crystallites with thin film of MgO observed to enhance voltage and efficiency to 650-700 mV and approx 6.5% respectively.
16.	Enhancement of the energy and quantum conversion efficiencies of a photo electrochemical cell sensitized with a combination of cationic and	K.Tennakone G.K.R.Senadheera P.V.V.Jayaweera	17 May 2001 Current Science Vol. 81, No.1	Dye bromopyrogallol red surface complexes to TiO_2 adsorbs electron donating cationic dye, binding it to anionic sulphonate site. Resulting double dye film

	anionic dyes.			shows enhanced current and energy conversion efficiencies and a broad spectral response owing to charge transfer.
17.	Dye-Sensitised solid state Photovoltaic cells: Suppression of Electron - Hole Recomb-inations by deposition of the Dye on Thin Insulating Film in contact with a semiconductor.	K.Tennakone V.P.S.Perera I.R.M.Kottagoda I.A.A.de Silva G.R.R.A.Kumara A.Konno	15. May 2001. Journal of Electronic Materials, Vol.30, No.8, 2001	Heterojunction n-SnO_2/ Ru-dye/ p-CuI prepared by depositing ruthenium bipridyl dye on a mesoporous film of SnO_2 coated on a thin film of Al_2O_3 behaved as a DSSC
18.	Probing the tunneling of electrons from SnO_2 to ZnO in dye- sensitization of com-posite SnO_2/ZnO by use of generated H_2O_2 via reduction of O_2	J.Bandara K.Tennakone P.Binduhewa	5 September 2001 Royal Society of Chemistry, U.K. Journal of Chemistry 2001,25, 1303-1305	A composite system of SnO_2/ZnO semiconductor found to generate higher H_2O_2 yield than individual oxide semiconductor when sensitized with various dyes.
19.	Surface mechanism of Molecular Recognition between Aminophenols and Iron oxide surfaces	J.Bandara K.Tennakone J.Kiwi	29 January 2001. American Chemical Society, USA Langmuir 2001, 3964-3965.	The degradation of 2-aminophenol on hematite proceed more favourably than the degradation of 3 and 4 aminophenol because of the formation of a strong surface complex between 2 aminophenol and hematite that facilitates charge transfer to oxide surface.
20.	Interparticle charge transfer in Dye-Sensitized Films composed of two kinds of semiconductor crystallites.	J.Bandara K.Tennakone	22 January 2001 Journal of Colloidal & Interface Science 236, 375-378 (2001)	Interparticle charge transfer between different types of semiconductor crystallites in band gap excitation or dye sensitization was analysed
21.	Nanoporous TiO_2 Solar Cells Sensitized with Iron (II) complexes of brompyrogallol red ligands.	P.M.Jayaweera S.S.Palayangoda K.Tennakone	16 January 2001. Journal of Photochemistry & Photobiology,	Complexation of bromo pyrogallol ligand with di (aqua) bis (oxalate) iron (II) moiety $[Fe(II)\ H_2O_2\ C_2O_4]^2$ shows enhanced

			Elsevier, 140 (2001), 173-177	photovoltaic properties.
22.	Fabrication of Dye-Sensitized Solar Cells using Triethylamine Hydrothiocyanate as a CuI crystal Growth Inhibitor.	G.R.A.Kumara S.Kaneka M.Okuya K.Tennakone	2 October 2002. American Chemical Society, USA. Langmuir 2002, 18,10493-10495.	The hole mobility in the hole collector of a DSSC investigated.
23.	Cobolt (II) - bis(1,10-phenanthroline) triphenyl methane dye complexes and their photo sensitization properties in nanoporous photovoltaic devices.	P.M.Jayaweera, S.S.Palayangoda, K.Tennakone, R.G.C.R.Gamage	21 September 2002 Current Science Vol83, No.11	Bromopyrogallol red pryocatechol violet the two tripheryl methane type ligands can be readily complexed with $Cu[(1,10\text{-}phen)_2]^2$ moiety. The resulting complexes were found to be capable of enhancing photovoltaic properties when compared with corresponding ligands
24	Dye-sensitized photo electrochemical and solid state solar cells: Charge separation, transport and recombination mechanisms.	K.Tennakone P.V.V.Jayaweera P.K.M.Bandara	1 July 2002 Journal of Photochemistry & Photobiology, 158 (2003), 125 – 130.	Experimentation of dye sensitized photo electro chemical cells made from SnO2, ZnO and comparison with similar cells based on TiO_2 gives insight into the nature of charge separation, transport, and recombination.
25.	Composite Tin and Zinc oxide nano crystalline particles for enhanced charge separation in sensitized degradation of dyes.	J. Bndara K.Tennakone, P.P.B.Jayatilake	10 June 2002 Chemosphere 49 (2002), 439-445	Composite ZnO / SnO_2 degradation has been studied with sensitized degradation of dyes eg. Eosin Y in relation to efficient charge separation properties of the catalyst.

26.	Die-Sensitization of Magnesium oxide coated Cadmium sulphide	P.K.M.Bandara P.V.V.Jayaweera K.Tennakone	10 April 2002 Solar Energy Materials and Solar Cells	Nano crystalline films of CdS sensitized with ruthenium N_3 dye show a feeble photo-response, but when an ultra thin outer shell of magnesium oxide is deposited on CdS, photo-response greatly enhanced.
27.	Effect of Imidazolium Salts on the performance of solid state Dye-Sensitized photovoltaic cells using Copper Iodide as Hole Collector	A.Konno G.R.A.Kumara R.Hata K.Tennakone	7 February 2002 Electrochemistry, 70, N0.6 (2002)	DSSC'S in general have problems of long term Photostability. Addition of several 1-ethyl 3 methylim-idazolium (Im) salts improved the performance and stability.
28.	Die-Sensitized Composite Semi conductor nano structures	K.Tennakone P.K.M.Bandaranyake P.V.V.Jayaweera A.Konno G.R.R.A.Kumara	Physics, Physics E 14 (2002), 190-196	Deposition of ultra thin shells of insulators or high band gap semiconductors on crystallites, a dramatic increase in open circuit voltage and quantum conversion efficiencies observed.
29.	Nanocrystalline TiO_2 films for Dye-Sensitized Solid State Solar Cells.	G.R.A.Kumara S.Kaneko M.Okiya A.Konno K.Tennakone	Publication of Ceramic Society of Japan, Key Engineering Materials Vol. 228-229 (2002) pp 119-124	A special type of TiO_2 film that is less porous but factually rough is used to prevent short circuiting when preparing films to overcome difficulties in sealing of liquid electrolyte type DSSC's
30.	Dye-Sensitized Semiconductor Nanostructure for solar	K.Tennakone	Ceylon Journal of Science, Physical Science	Insight gained from experimental and theoretical studies on DSSC's made from different

	energy conversion		9(1), 1-8(2002)	semiconductors and its composites summarized.
31.	Dye sensitized semiconductor nanostructures for solar energy conversion.	K. Tennakone	October 2002 Ceylon Journal of Science (Physical Science). 9 (1) : 1 - 8	Structural analysis of TiO_2 film.
32.	Nanoporous TiO_2 photo voltaic cells sensitized with metalchromic triphenylmethane dyes	P.M. Jayaweera A.R. Kumarasinghe K. Tennakone	December 2002, Journal of Photo Chemistry and Photobiology A: Chemistry. 126: 111-115	
33.	Surface trap mediated recombination in dye sensitized solid state solar cell with CuI as the hole collector.	V.P.S. Perera K. Tennakone	March 2003. Proceedings of the 19th Technical Session – March 2003, Institute of Physics 51-57	
34.	The effect of MgO on Enhancement of Efficiency in solid state Dye sensitized Photo Cells fabricated with SnO_2 and CuI.	S.Perera G.K.R.Senadheera K.Thennakone S.Ifo T.Kitamura Y.Wade S.Yanogide	9 September 2002 The Chemical Society of Japan 76,659–662 (2003)	In DSSC's made for SnO_2 and MgO enhancement of photocurrent and voltage found when percentage of MgO to SnO_2 was around 4 wt %, due to formation of a thin energy barrier which suppresses the recombination of photo electrons
35.	Efficient Die Sensitized Photo Electrochemical Cells made from nano crystalline Tin (IV) oxide – Zinc Oxide Composite	G.R.A.Kumara K.Tennakon. I.R.M.Kottagoda	7 January 2003 Institute of Physics Semiconductor Science	This paper explains in detail how a thin shell of ZnO on SnO_2 could effectively counteract recombination of electrons with acceptors in

	films	P.K.M.Bandara A.Konno, M.Okuya S.Kanebu, K.Murakam	&Technology, UK. 18(2003),312-318	electrolyte (eg. 1_3^-) and increase efficiency of DSSC's based on nano crystalline films of TiO_2.
36.	Recombination processes in Dye-sensitized Solid State Solar Cells with CuI as the hole collector	V.P.S.Perera K.Tennakone	30 March 2003 Solid Energy Materials & Solar Cells 79(2003),249-255	In solid state DSSC's stoichiometrically excess Iodine molecules adsorbed at the CuI surface acts as hole trapping site that mediate recombination.
37.	Sensitization of Aluminium chloride adsorbed Tin (IV) oxide nanocrystalline film with Rose Bengal	V.P.S. Perera G.K.R.Senadheera K.Tennakone	29 April 2003 Journal of Colloidal and Interface Science 265 (2003),428-431	DSSC's made from anionic dye Rose Bengal exhibits enhanced quantum and energy conversion efficiencies.
38.	Depleted semiconductor Quantum Nanowire in an electrolytic medium	K.Tennakone P.V.V.Jayaweera	27 May 2003 Superlattices and Microstructures, Elsevier Ltd. 33(2003), 23-28	It is shown that electron lateral confinement leading to sub bands can be readily achieved by surrounding a doped semiconductor nanowire in an electrolytic medium.
39.	Dye-Sensitized Solid State Photovoltaic Cells based on dye multilayer semiconductor nanostructures	V.P.S.Perera P.K.D.P.Pitigala P.V.V.Jayaweera, K.M.P.Bandaranayake K.Tennakone	29 October 2003. American Chemical SocietyJournal of Physical Chemistry, B 2003,107,13758-13761	Attempts made to improve efficiency of DSSC's if ways are found to broaden the spectral response resolving fundamental issues involved.
40.	Fabrication of n-p junction electrodes made of n-type	J.Bandara	10 November 2003 Solar Energy	The n-P junction electrode fabricated coating nano

	SnO_2 and p-type NiO_2 for control of charge recombination in DSSC's	C.M. Divaratne S.D.Nanayakkara	Materials Solar &Cells, Science Direct 81 (2004), 429-437	crystalline SnO_2 thin film with a thin layer of p-type NiO found to increase photocurrent and photo voltage.
41.	Construction of photovoltaic device by deposition of thin films of conducting polymer polythio cyanogens.	V.P.S.Perera P.V.V.Jayaweera P.K.D.D.P.Pitigala P.K.M.Bandaranayake G.Hastings A.G.U.Perera K.Tennakone	18 December 2003 Science Direct, Synthetic Metals 143 (2004) 283 - 287	A method is developed for electrode position of conducting polymer polythiocyanogen on conducting Tin Oxide glass or other conducting substrate by anodic discharge of SCN ions from a solution of KSCN in propylene carbonate.
42.	Sensitization of nano structured TiO_2 by Electrostatic coupling of Ionic Dyes to Ionic Absorbates.	P.K.D.D.P.Pitigala M.K.I.Seneviratne V.P.S.Perera K.Tennakone	5 April 2004 American Chemical Society Langmuir 2004, 20, 5100 - 5103	DSSC's of configuration n-TiO_2/X- Y/p – CuSCN where, X=trihydrobenzonic acid mercurochrome Y=methyl violet were constructed. These cells found to be more efficient and delivered higher short circuit currents and open circuit voltages compared to cells based on methyl violet or mercurochrome, by extending their spectral response.
43.	Dye-sensitized solar cells made from nano crystalline TiO_2 films coated with outer layers of different oxide materials.	K.M.P.Bandaranayake M.K.I.Seneviratne P.M.G.M.Weligamuwa K.Tennakone	23 May 2004 Science Direct, Coordination Chemistry Review 248(2004)	Higher efficiencies obtained from DSSC's of TiO_2 type when these crystallites in the film coated with different oxide materials of varying thickness.

			1277-1281.	
44.	A Solar Cell sensitized with three different dyes	V.P.S.Perera P.K.D.Pitigala M.K.S.Seneviratne	2 June 2004 Science Direct, Solar Energy, Materials & Solar Cells 85(2005),91-98	In order to broaden the spectral response and to enhance the efficiency to DSSC's. construction of a semiconductor dye hetero structure of configuration n-TiO_2/D_1/ P-CuSCN/D_2/ P-CuSCN/D_3/ P-CuSCN where, D_1=Fast Green D_2 = Rhodamine 6 G D_3 = Acridine Yellow effected and evaluated.
45.	The effect of particle size and conductivity of CuI layer on the performance of solid state DSSC's	A.Konno T.Kitagawa H.Kida G.R.A.Kumara K.Tennakone	6 July 2004 Science Direct, Current Applied Physics 3 (2005) 149-151	Conductivity of CuI film greatly increased by addition of thiocyanate salts and efficiency improved.
46.	Molecular Rectification application in Dye-Sensitized Solar Cells	M.K.I.Seneviratne P.K.D.D.P.Pitigala V.P.S.Perera K.Tennakone	9 December 2004 American Chemical Society Langmuir 2005 21, 2997-3001	A DSSC hetero junction configuration of n-TiO_2/PD-Cu PC-MV/P-CuSCN (where PD=3,4, pyridine dicarboxylic acid anchored to TiO_2, CuPC=Copper (IF) Phthallcyamn tetrasulphonic ionicaly linked to PD, MV=methyl violet complexed to CuPC) developed to demonstrate applicability of molecular

				rectification of DSSC's as a strategy to suppress recombination.
47.	Doping of CuSCN films for enhancement of conductivity: Application in DSSC's	V.P.S.Perera M.K.I.Seneviratne P.K.D.D.P.Pitigala T.Tennakone	29 December 2004 Science Direct, Solar Energy Materials & Solar Cells 86 (2005), 443-450	Construction of solid state DSSC's requires high band gap (therefore transparent)hole collectors which can be deposited on a dye coated nano crystalline semiconductor surface without denaturing the dye presented.
48.	Dye sensitized Solid State solar cells made form magnesium oxide coated nano crystalline TiO_2 film, : Enhancement of the efficiency.	G.R.R.A. Kumara	2004 Journal of Photobiology and photo chemistry A: Chemistry MFN 4195 164, 183	
49.	Solid State dye sensitized solar cell with P-type NiO as hole collector.	J. Bandara A. Jayasundera	2005 Solar Energy Methods and Solar Cells 85(3), 385 - 390	
50.	Dye sensitized near infra red room temperature photo voltaic photon detectors.	P.V.V. Jayaweera P.K.D.P. Piyadasa K. Tennakone	2005 Applied Physics letters 85 (23), 5754 - 5756	
51.	Enhancement of photo voltage of dye sensitized solid state solar cells by introducing high band gap oxide layers.	J. Bandara A. Jayasundera H.C. Weerasinghe	2005 Solar Energy Materials and Solar Cells 85 (4), 341-350	
52.	Photosensitization of nanocrystalline TiO_2film by a polymer with two carboxylic groups, poly3 thiophenemalonic acid.	G.K.R. Senadheera T.Kitamura Y. Wade Yanaside	2005 Solar Energy Materials and Solar Cells 88(3), 315 - 322	
53.	The role of n-p junction electrodes in minimizing	J. Bandara	2005 Journal of	

	the charge recombination of and enhancement of photo current and photo voltage	V.W. Pradeep R.G.S.T. Bandara	Photochemistry and Photobiology A: Chemistry 170(3), 273 - 278	
54.	Versatile preparation methods for mesoporous TiO_2 electrodes suitable for sold state dye sensitized photocells	G.K.R. Senadheera S. Kobayashi J. Kitamura Y. Wade S. Yongido	2005 Bulletin of Material Service MFN 5149	
55.	Dye sensitized Solid State Solar Cell sensitizedwith Coumarin derivatives	G.R.R.A. Kumara T. Kawaguchi. Y. Ketoh K. Tennakone	2005 Pacific Chemistry Congress, Honolulu, Hawaii, U.S.A. 15-20 Dec 2005, MFN 5523	
56.	Large area dye sensitized solar cells : Material Aspects of Fabrication	G.R.A. Kumara S. Kaneko A. Konno M. Okyo K. Tennakone	2006 Solar Energy Materials and Solar Cells 14 (7), 643 - 651	
57.	Shinso Leaf Pigment for dye sensitized solid state solar cells	G.R.A.Kumara S.Kanko A.Konno	2006 Solar Energy Materials and Solar Cells 90 (9) 1220 - 1126	
58.	Dye-Sensitized Solar Cells with extremely thin liquid film as the Redox Electron Mediator	G.R.A.Kumara S.Kaneko A.Kanno M.Okuya K.Tennakone	14 January 2005 The Chemical Society of Japan, Chemistry letters, Vol. 34, No.4, (2005)	A hybrid DSSC with a thin film of liquid is interposed between the dye coated nano crystalline semiconductor surface and a solid hole collector demonstrated.
59.	Sensitization of nano crystalline SnO_2 films with Indoline dyes	B.O.Agyeman S.Kaneko	27 May 2005 Japanese Journal of Applied Physics	Using Indoline dyes as sensitizers for DSSC's based on SnO_2. Efficiency of 2.8% achieved, compared to 1.2%

		A.Kumara M.Okuya K.Murakami A.Konno K.Tennkone	Vol. 44, No. 23, 2005,731-733	for rutherium bipiridyl dye (N-719) under same experimental conditions.
60.	TiO_2 nano porous photo electrochemical cells (PEC's) sensitized with mixed cationic /anionic dye systems: Role of the second cationic florescent dye on photocurrent enhancement	P.M.Jayaweera R.M.S.P.Rajapakse K.Tennakone	22 Jane 2005 Science Direct, Chemical Physics Letters 412 (2005) 29-34	Bromopyrogallol red (BPR) an anionic dye material used in DSSC's as the sensitizer in conjunction with a fluorescent dye rhodomine B and acridine orange enhanced photovoltaic properties.
61.	Chromopore linked conducting polymers attached to semiconductor surfaces: A strategy for development of DSSC's	M.K.I.Seneviratne P.K.D.D.P.Pitigala K.Tennakone	24 June 2005 American Chemical Society Journal of Physical Chemistry B, 2005 109,16030-16033	Attaching chromopores to a conducting polymer chain anchored to semiconductor surface found to be a good strategy for development of DSSC's
62.	As enhancement of Photo properties of solid state TiO_2/dye/CuI type cells by coupling mercurochrome with natural juice extracted from pomegranate fruits.	P.M.Sirimanne I.Seneviratne K.Tennakone	24 June 2005 The Chemical Society of Japan Chemistry letters Vol.34, No.11	Electrostatic coupling of mercurochrome with an anthrocyanin pigment extracted from pomegranate fruits result on enhancement of photovoltaic properties of TiO_2/dye/CuI solid state solar cells.
63.	1/f Noise and DSSC's	P.V.V.Jayaweera P.K.D.D.P.Pitigala A.G.I.Perera K.Tennakone	28 June 2005 Semiconductor Science and Technologies Institute of Physics U.K. Doi:10,1088/0268-	The adsorbed molecular species such as H_2O and I_2 that produce electron acceptor states on TiO2 surface found to generate $\frac{1}{f}$ noise in the electric current through nano crystalline films of TiO_2 due to trapping and de-trapping

			124/20/0/000	of electrons at the surface states.
64.	Efficient Ouasi Solid Solar Cells employing , molten salt electrolytes	G.K.P. Senadheera N.S. Silva	July 2006 Sri Lanka Journal of Physics Vol. 7 (2006) 15-22	Use of molten salt electrolyte to enhance long term stability.
65.	Synthesis and characterization of carboxylated thiophene co polymers and their use in photovoltaic cells	T.M.R.C. Fernando G.K.R.Senadheera	25 September 2008. Current Science Vol.95, No.6	Several 3 substitute thiophene and pyrole bearing co polymers were chemically synthesized and their possible usage as sensitizers investigated.
66.	Tuning of flat band potentials of nanocrystalline TiO_2 and SnO_2 particles with an outer shell of Mg O layer.	T. Bandara U.V. Pradeep	2008 Science Citation Index, MFN 6399 517(2) 952 - 956	
67.	Polyethylene oxide PEO-based anion conductivity solid polymer electrolyte for PEC Solar Cells	T.M.W.J. Bandara M.A.K.L. Dissanayake	2008 Science Citation Index MFN 6579 12 (4002) 913-917	Use of Solid polymer electrolytes for enhance long term stability.
68.	Natural Anthrocyanins as photosensitizers for DSSC's	J.M.R.C.Fernando G.K.R.Senadheera	30 July 2008 Current Science Vol.95, No.5	Different natural pigments containing anthrocyanins extracted from tropical flowers studied as possible sensitizers for DSSC's. Overall efficiency of these cells varied from 0.2. to 1.1%. Hibiscus surothenin (magenta flower) gave best photosensitized effect
69.	Efficient passivation of SnO_2 nanocrystallites by Indoline D-149 via via dual	Y.P.Y.P. Ariyasinghe T.C.K. Wijayarathne I.G.C.K. Kumara I.P.L. Jayantha	19 October 2010 Journal of Photochemistry & Photobiology A	An efficiency exceeding 3% reported for the first time in SnO_2 based dye solar cells consisting of Indoline D 149

	chelation	C.A. Thtawattage W.S.S. Gunathilake G.K.R. Senadheera V.P.S. Perera	Chemistry xxx (2010) xxx – xxx (Article in press)	dye.
70.	Nanocrystalline TiO_2 photo excited with natural dyes	P.A,Abeygunawardena S.Palakubura C.A.Thotawattage M.A.K.L.Dissanyake G.K.R.Senadeera	28 July 2011 Solar Asia 2011 International Conference Proceeding	Natural dye sensitizationof nanocrystalline TiO_2 photocrodes
71.	Utilization of Natural pigments excited from Henna leaf in combination with Gelatine as sensitizer in photoelectro chemical solar cells.	C.N.Nuperachchi T.R.C.K.Wijayaratna V.P.S.Perera	28 July 2011 Solar Asia 2011 International Conference Proceeding	Natural dye sensitization with steno leaf in Geletine of DOC's
72.	Comparison of Natural pigments in Black Tea and Green Tea with DSSC's	C.N.Nuperachchi C.A.Thotawattage G.K.R.Senatheera V.P.S.Perera	28 July 2011 Solar Asia 2011 International Conference Proceedings	Natural dye sensitization with Black and Green Tea
73.	Evaluation of Dyes from Melastrom Malabothium: A native plant of Borneo as a poterial natural dye for DSSC's	P.Ekanayake R.Zain M.Iskander K.Tennakoon S.Yoshikawa G.K.R.Senadheera	28 July 2011 Solar Asia 2011 International Conference Proceedings	Analysis of natural dyes from plants grown in Borneo.

74.	Flourence based organic dyes for DSSC’s	K.R.J.Thomas	28 July 2011 Solar Asia 2011 International Conference Proceeding	Sunthesis and analysis of Flourine based organic dyes for DSSC’s

APPENDIX –B

Research Papers on DSSC's published by Institutions / Universities in Sri Lanka other than at the IFS (also included in the Bibiliograpy Section)

1. Bandara, T., Dissanayake, M.A.K.L., Somasundaram, Bandara, L.R.A.K., Illeperuma, O.A., Varaprathan, K., Mellander, S.C., Postgraduate Institute of Science,University of Peradeniya, Peradeniya. 1994.

2. Bandara, L.R.A.K., Dissanayake, M.A.K.L., Ekanayake, G.V.K., Illeperuma, O.A., Weeraman, T.T.K., Department of Chemistry, University of Peradeniya. 1998. Dye-Sensitized photoelectrochemical solar cells with PEO based solid polymer electrolytes. Proceedings of the workshop on renewable Energy Sources, Colombo 10-11 Feb. 1998,

3. Fernando, C.A.N., Kumarawadu, I., Kiyagawa, A., Suzuki, M., Department of Physics, University of Ruhuna, Matara. 1999. Crystal Violet dye-sensitized photocurrent by participation of surface sates on P. Cu SCN photocathode. Solar Energy Materials - Semi conductor materials.

4. Fernando, C.A.N., Weththasinghe, S.K., Department of Physics, University of Ruhuna. 2000. Phtocurrent generation of a dye sensitized solid state photovoltaic cell made from n-Cu_2O and P – Cu SCN thin' film. Proceedings of the 5th Workshop on low cost Electronic Materials, Solar Cells and Renewable Energy Sources. Colombo, 22-25 Feb.2000: 86-93.

5. Fernando C.A.N., Weththasingha, S.K., Department of Physics, Ruhuna, Matara. 2001. Improved photocurrent quantum efficiency and kinetics of photocurrent generation of a dye sensitized solid state solar photovoltaic cell made from n Cu_2O and P-Cu SCN thin film. Japanese Journal of Applied Physics.

6. Fernando, C.A.N., Takashi, K., Kitagawa, A., Suzuki, M., Wethasinghe, M., Kunarawadu, I., Department of Physics, University of Ruhuna, Matara. 2001. Remarkable stability of the enhanced sharp photocurrent in netyhlinolet – C18 and Solar Energy Materials.

7. Fernando, C.A.N., Kumarawadu. I., Department of Physics, University of Ruhuna, Matara. 2001. Colloidal P-CuI sensitized double dye system. Semiconductor Science and Technology.

8. Fernando, C.A.N., Priyankara, W.TC., Dharmadasa, I.M., Department of Physics University of Rhuna, Matara. 2002. Photocurrent of Ruhuna, Matara. 2003. Photocurrent enhancement of interlocked LB film dye layers in a P-Cu SCN sensitized photoelectrochemical cell. Renewable Energy.

9. Fernando, C.A.N., Department of Physics, University of Ruhuna, Matara. 2002. Hydrogen production from photoelectrochemical cells using low cost semiconductor film, and dye sensitized solar cell production with ordered and disordered molecular arrangement.

10. Jayaweera, P.M., Department of Chemistry, University of Colombo, Colombo. 2003. Photocurrent conversation efficiency of solar cells sensitized with a combination of ationic and anionic materials.

11. Ravirajan, P., David, T.R., Department of Physics, University of Jaffna, Jaffna. 2005. Controlling recombination kinetics of hybrid, polymer/ metal oxide solar cells.

12. Premalal, E.V.A., Perera, V.P.S., Open University of Sri Lanka, Nugegoda. 2005. Photovoltaic effects of dye-deposited metal electrodes in electrolytic media. Proceedings of the 21st Technical Session – Institute of Physics, March 2005: 57-61.

13. Director, National Energy Research and Development (NERD) Centre, J-Ela. 2006. Cheaper ways to produce Dye-Sensitized Solar Cells.

14. Hussain, F.M., Sirakumar, V., Department of Physics, University of Peradeniya, Peradeniya. 2007. Structural studies of plant pigments used in dye sensitized solar cells. Proceedings of the University of Peradeniya Research Sessions ,Purse 2007. 12 (ii): 275 - 277.

15. Bandara, T., Dissanayake, M., Illeperuma, O.A., Varaprathen, V., Vignarookan, K., Mellander, P.E., 2008. Postgraduate Institute of Science, University of Peradeniya, Peradeniya. Polyethylene oxide based anion conducting solid polymer electrolyte for PRC solar cells.

16. Siripala, W.P., University of Kelaniya, Kelaniya. 2008. Solid state dye sensitized solar cells.

17. Aponsu, G.L.M.P., De Silva, R.C.L., Perera, V.P.S., Open University of Sri Lanka, Nugegoda. 2008. Enhanced photovoltaic effects of dye sensitized solar cells of SnO_2 surface modified with gold nano paricles.

18. De Silva, R.C.L., Liyanage, L.S.G., Perera, V.P.S., Open University of Sri Lanka, Nugegoda. 2008. Electron Kinetics of Dye Sensitized Solar Cells made from Al_2O_3 coated SnO_2 nano crystalline films.

19. Aponso, G.L.M.P., Premalal, E.V.A., Liyanage, L.S.G., Perera, V.P.S., Open University of Sri Lanka, Nugegoda. 2008. Deposition of P_t and An Quantum Dots on TiO_2 nanoparticles : study of ballistic electron transport with dye sensitization.

20. Attanayake C.I.F., Premachandra, BAJK' Alwis., AAP., Senadheera, G.K.R., Univeristy of Moratuwa, Sri Lanka and Institute of Fundamental Studies, Sri Lanka. 2008. Design and Development of Dye-Senitized Organic Semiconductor Based Photo Electric System utilizing Nanotechnology for Low cost and Efficient Conversion of Solar Energy to Electricity, Proceedings of 13th ERU Symposium, 6 NOV. 2008 16-17.

21. Attanayake, C.I.F. Premachandra, B.A.J.K., Alwis, A.A.P., Senadheera, G.K.R., University of Moratuwa, Sri Lanka and Institute of Fundamental Studies, Sri Lanka. Solar Powered Naval

Patrol Boat operating Dye-Sensitized Solar Cells (DSSC's) utilizing Fruit and Spice Extracts 2011. National Energy Symposium 2011 of Sri Lanka Sustainable Energy Authority , Ministry of Power and Energy, 13th& 14th August 2011. 71-78.

22. Attanayake, C.I.F., Premachandra, B.A.J.K., Alwis, A.A.P. Senadheera G.K.R., University of Moratuwa and Institute of Fundamental Studies Hantana Open University of Sri Lanka, Palgolla, Sri Lanka. Study of Novel Dyes to support DSSC Research. Confenerence Proceedings of First National Nanotechnology Conference 2012, National Science Foundation of Sri Lanka, 24-25 August 2012. 48-52.

23. Attanayake, C.I.F., Premachandra, B.A.J.K., Alwis, A.A.P., Senadheera, G.K.R., University of Moratuwa and Institute of Fundamental Studies, Hantana and Open University of Sri lanka, Polgolla, Sri Lanka. Dye-Sensitized Solar Cells utilizing over 100 Natural Dyes as Sensitizers. American Institute of Chemical Engineers (AICHE) Annual Meeting , 3 – 8 November 2013 , Global Challenges for Engineering – a Sustainable Future , Hilton, San Fransisco, Union Square , California, U.S.A.

24. Review of Dye Sensitized Solar Cells Research in Sri Lanka . 01 November 2011. Department of Chemical & Process Enginering , University of Moratuwa, Katubedda, Sri Lanaka . C.I.F.Attanayake, B.A.J.K. P remachanadra A.A.P.De Alwis and G.K.R.Senadheera.

25. Comparison of Characteristics and Properties of Rutin and Mangoostein Dye Sensitized Solar Cells . 5 May 2015. Submitted for publication in the Journal of National Science Foundation , Sri Lanka. C.I.F.Attanayake, B.A,J.K.Premachandra, A.A.P. De Alwis and G.K.R.Senadheera.

APPENDIX - C

Construction of DSSC’s

Cleaning of conducting glasses with flourine - Doped Tin Oxide Layer

1. First cut conducting glasses into dimensions of 2 cm x 0.5 cm x 0.25 cm with glass cutter.

2. Clean conducting glasses in a beaker filled with Teepol (Soap). Carefully wash them by shaking beaker with Electronic Ultrasonic Cleaner (BRANSON 200) for about 5 minutes.

3. Wash with clean a water.

4. Clean with dilute Sulphuric Acid (1 part by volume acid to 3 parts by volume water. Add acid to water).

5. Wash with clean tap water in an Sulphuric Acid bath of size approximately 2 feet diameter, 8 inches high plastic bucket where about 15 drops of dilute Sulphuric Acid has been added to the bucket containing clear tap water up to about 5” high.

6. Wash with distilled water by inserting a beaker containing Teepol cleaned glasses. Then wash with fresh water and distilled water.

7. Fill beaker containing glasses with Propane 2 OL and boil it by keeping it in a hotplate (100°C). Remove glasses with a Tweezer and keep with conducting side on top (use Multimeter) on a tissue paper.

Preparation of Titanium Dioxide (TiO_2) Nano Paste

1. Use a porcelain mortar and pestal by first washing as before at Sr. Nos. 1 to 6 above.

2. Dry it using an electric hair drier to remove moisture.

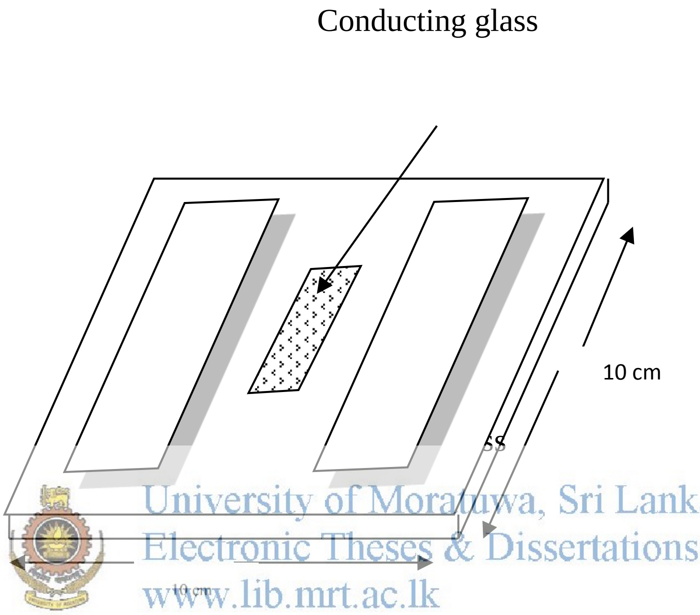
3. Insert 200 mg of TiO_2 nanopaste (DEGUSSA powder) (25nm – 30nm) into a plastic boat.

3 &4. Put about 12 drops of Analytical grade Acetic Acid (CH_3COOH) using a glass dropper and mix it with the pestal. Mix well into a paste. ($TiO_2 + CH_3COOH$ = Ti Acetate) add 3 mL Ethanol and grind for 30 mins.

5. Add 1 drop of TRITON X-100 to make the mixture porous, and mix well.

6. Add 3 ml of ETHANOL (Repack) and mix well for about further 30 minutes by hand.

7. Apply one drop of this liquid from the pestal onto the top of conducting glass placed on a glass plate with two slightly higher glass slides on either side parallel to it. Brush with a glass slide to remove excess liquid.(Doctor Blade method)

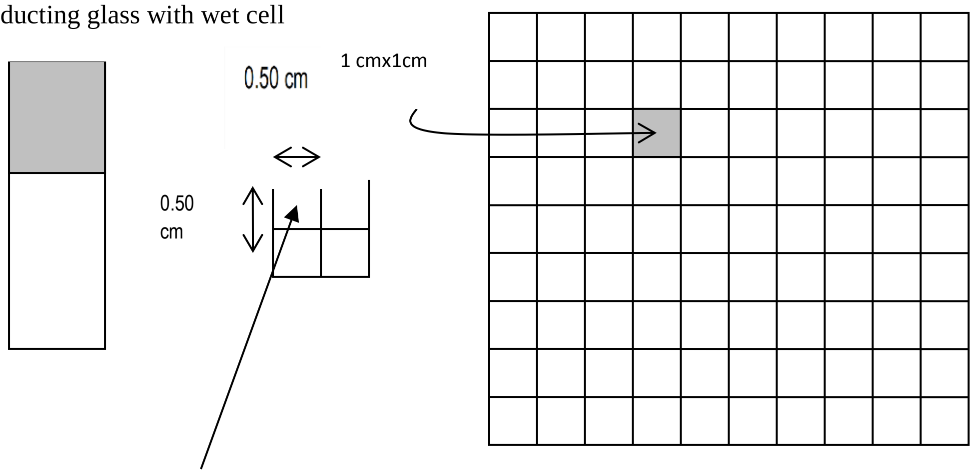


8. Remove conducting glass and place it on a tissue with liquid side on top.

(Ehanol will evaporate)

9. Remove glass plate with a Tweezer and place it on a graph paper with polythene sheet on top of it.

Conducting glass with wet cell



0.25 Sq,cm each square.

Synter in a oven for 30 mins.

10. Prepare Dye solution with a natural pigment from flowers or fruits with Ethanol in a test tube. (Cut pieces washed with Ethanol and filtered)

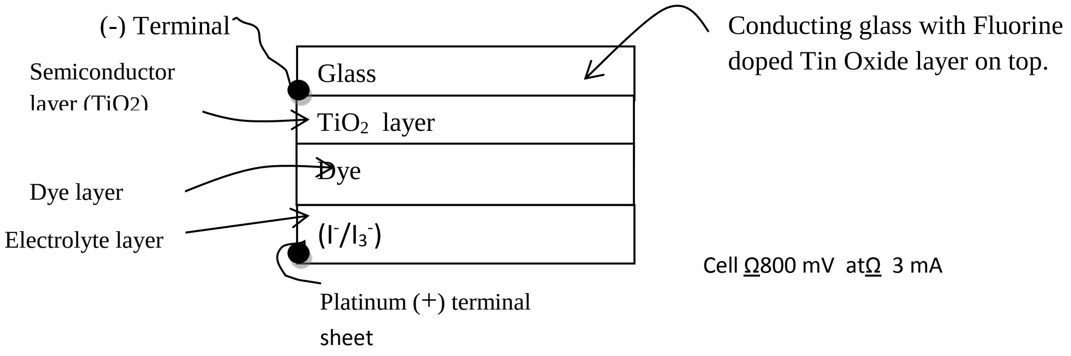
11. Drip the prepared glass conductor into the dye solution in a test tube and keep for about 12 hours.

12. Add Repack EHANOL into the test tube containing conducting glass and wash it.

13. Remove conducting glass and dry it with a hair a dryer till the liquid evaporates.

14. Get a glass plated with PLATINUM (10 μm) on one side and place prepared film to touch the PLATINUM and clip it with a metal crocodile clips to hold it in place.

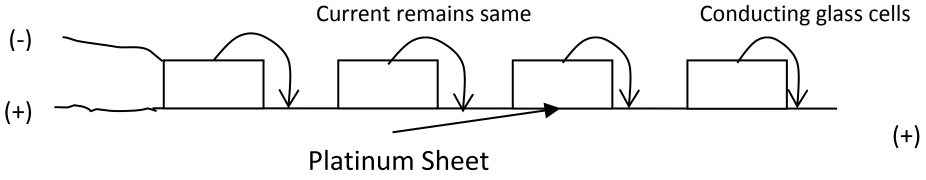
15. Add IODINE Electrolyte (I^-/I_3^-) REDOX into capillary space between PLATINUM plate and prepared film with a dipper. (Wet Cell)



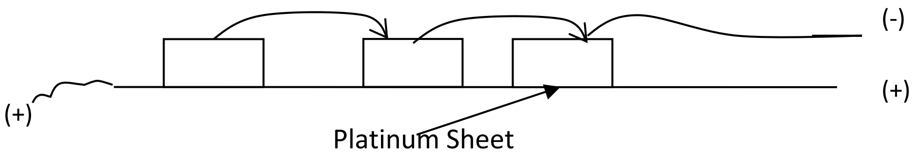
Cell Ω800 mV atΩ 3 mA

This cell may be sealed with SULAN paper heated to 150°C by placing on a hot plate.

16. To increase the voltage, add these cells in series.\

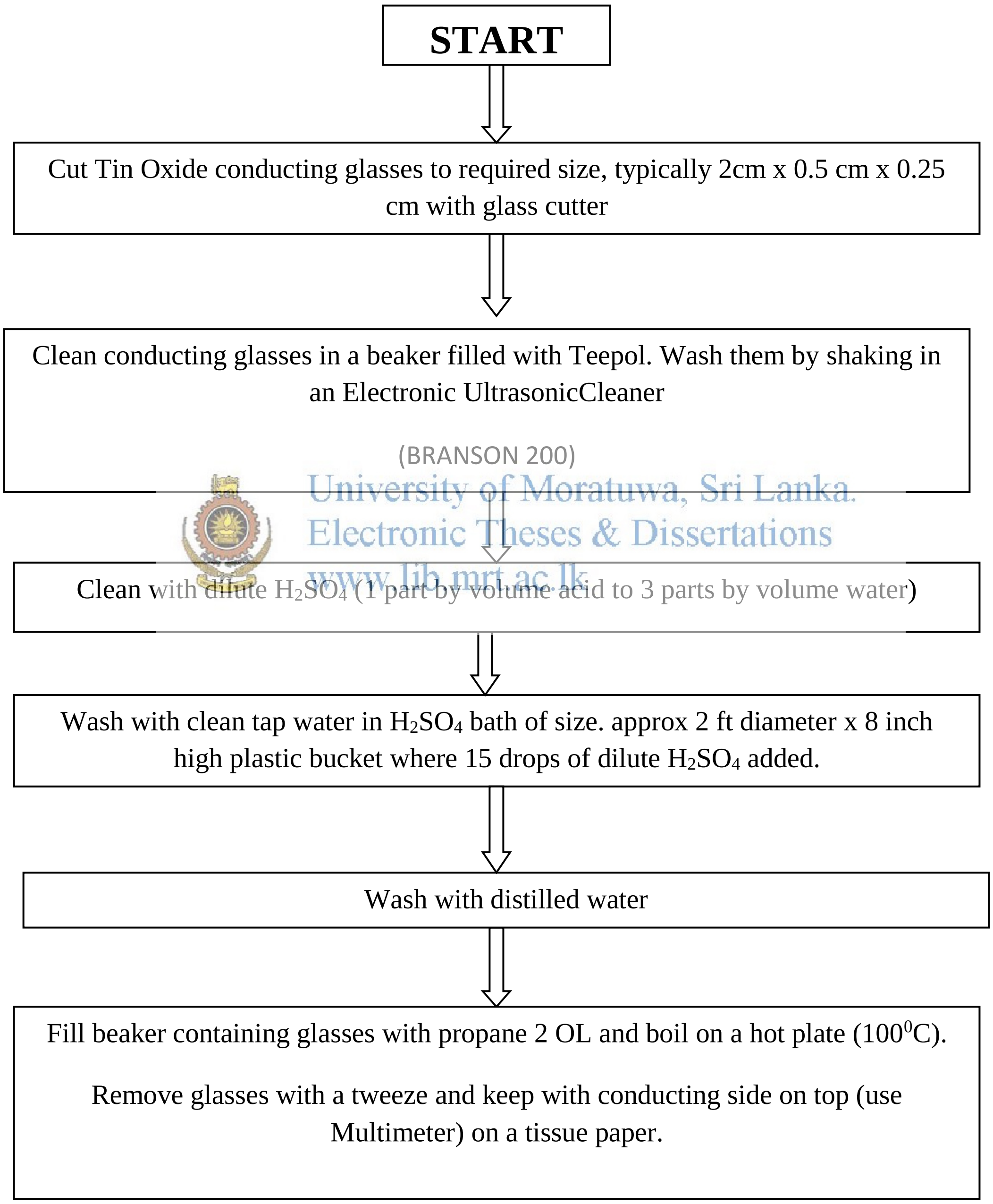


17. Connect in parallel to increase current or increase area.



Flow chart for Preparation of DSSC's

Cleaning of Conducting Glasses with Fluorine - doped Tin Oxide Layer



START

Cut Tin Oxide conducting glasses to required size, typically 2cm x 0.5 cm x 0.25 cm with glass cutter

Clean conducting glasses in a beaker filled with Teepol. Wash them by shaking in an Electronic UltrasonicCleaner

(BRANSON 200)

Clean with dilute H_2SO_4 (1 part by volume acid to 3 parts by volume water)

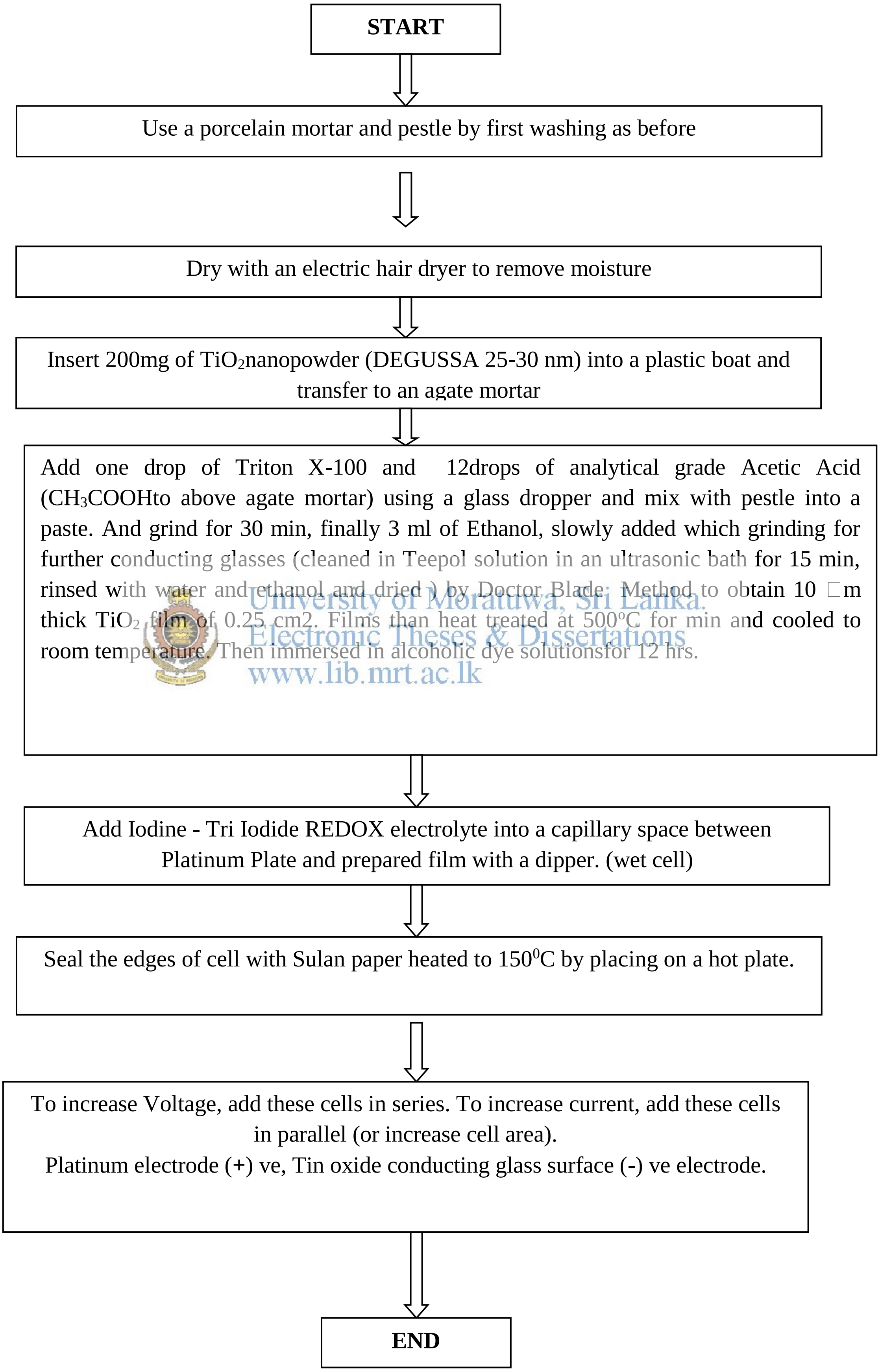
Wash with clean tap water in H_2SO_4 bath of size. approx 2 ft diameter x 8 inch high plastic bucket where 15 drops of dilute H_2SO_4 added.

Wash with distilled water

Fill beaker containing glasses with propane 2 OL and boil on a hot plate (100^0C).

Remove glasses with a tweeze and keep with conducting side on top (use Multimeter) on a tissue paper.

Preparation of Titanium dioxide (TiO_2) Nanopaste and Assembly Of DSSC's



START

Use a porcelain mortar and pestle by first washing as before

Dry with an electric hair dryer to remove moisture

Insert 200mg of TiO_2nanopowder (DEGUSSA 25-30 nm) into a plastic boat and transfer to an agate mortar

Add one drop of Triton X-100 and 12drops of analytical grade Acetic Acid ($CH_3COOH$to above agate mortar) using a glass dropper and mix with pestle into a paste. And grind for 30 min, finally 3 ml of Ethanol, slowly added which grinding for further conducting glasses (cleaned in Teepol solution in an ultrasonic bath for 15 min, rinsed with water and ethanol and dried) by Doctor Blade; Method to obtain 10 µm thick TiO_2 film of 0.25 cm2. Films than heat treated at 500°C for min and cooled to room temperature. Then immersed in alcoholic dye solutionsfor 12 hrs.

Add Iodine - Tri Iodide REDOX electrolyte into a capillary space between Platinum Plate and prepared film with a dipper. (wet cell)

Seal the edges of cell with Sulan paper heated to 150^0C by placing on a hot plate.

To increase Voltage, add these cells in series. To increase current, add these cells in parallel (or increase cell area).
Platinum electrode (+) ve, Tin oxide conducting glass surface (-) ve electrode.

END

APPENDIX – D

NATURAL DYES FROM PLANTS

GROWN IN SRI LANKA

Sr.No.	Name	Botanical name	Parts used
1.	Thekka (Teak)	*Tectona grandis Linn*	Leaves, Bar, Root
2.	Dan pothu	*Syzygium cumini*	Stem, Bark
3.	Kohomba	*Azadirachtin indica*	Bark
4	Rambutan	*Nephelium lappaceum*	Fruit Skin
5	Bulath	*Piper Betle*	Leaves
6	Kos (Jack)	*Artocarpus hetorophyllus*	Saw dust
7	Venivel	*Coscinium fenestratum*	Stem
8	Kurundu	*Cinnamomum verum*	Bark
9	Kothala Himbutu	*Salicia reticulate*	Bark
10	Delum	*Punica granatum*	Fruit skin
11	Rath Handun	*Pterocarpus Santalinus*	Stem
12	Ranawara	*Gassia auriculata*	Flowers
13	Aralu	*Terminalia Chebula*	Fruit
14	Bulu	*Terminalia Belerica*	Fruit
15	Munamal Pothu	*Mimusop elengi*	Stem
16	Welmadata	*Rubia Cardifolia*	Root and Stem
17	Mangoosteen	*Garicnia mangostana*	Fruit Skin
18	Daspethiya	*Tegetus erecta*	Petals
19	Loku Luunu	*Allium cepa*	Skin

20	Wada	*Hibiscus rosa-sinensis*	Used leaves
21	The (Tea)	*Camellia Sinensis*	Used leaves
22	Katarou	*Clitoria ternated*	Flowers
23	Kuppamenia	*Acalypa indica*	Leaves
24	Kopi	*Coffea arabica*	Leaves, seeds
25	Kottamba	*Terminalia catappa*	Riped leaves
26	Devadara	*Erithroxylum manogynum*	Stem
27	Beet root	*Beta vulgaris*	Rysome
28	Kaippu	*Acacia catechu*	Wood
29	Pethangi	*Caesalpinia sappan*	Wood
30	Marathondi	*Lawsonia intermis*	Wood, leaves
31	Seyum wel	*Oldeulandia umbellate*	Roots and tubers
32	Rasandun	*Berberis aristate*	Roots and tubers
33	Ahu Dumbu	*Morinda citrifolia*	Roots and tubers
34	Kudu miris	*Toddalia asiatica*	Roots and tubers
35	Kaha	*Curcuma domestica*	Roots and tubers
36	Kela gas	*Butea monosperma*	Flowers
37	Sepalika	*Nyctanthus arbo-tristis*	Flowers
38	Maliththa	*Woodfordia fruitticosa*	Flowers
39	Anaththa	*Bixa Ovellana*	Seeds
40	Nil awariya	*Indigofera tinctora*	Leaves and stem
41	Hamparilla	*Mallotus phillipiueses*	Stem
42	Welikaha	*Memecyloa capitellatua*	Rhysome
43	Sen kottan	*Semecarpus anacardium*	Seed
44	Kumbuk	*Terminalia arjuna*	Bark
45	Hik	*Lannea coromandelica*	Bark

46	Ipil Ipil	*Leucaena leucocephala*	Bark
47	Gas Penela	*Sapindus trifoliatus*	Seed
48	Wal inguru	*Zingiber cylindricum Moon*	Rhysome
49	Puwak	*Areca catechu*	Seed
50	Kothala Himbutu	*Salicia reticulata*	Wood and root
51	Bowitia	*Osbekia aspera*	Bark
52	Mal ehela	*Cassia fistula*	Bark
53	Mahogani	*Swietenia mahagoni*	Bark, Saw dust
54	Bulu	*Terminalia berelia*	Bark
55	Madan	*Syxgium cumini*	Bark
56	Rath mal	*Ixora coccinea*	Flowers
57	Kaju	*Anacardium occidentale*	Bark and fruit
58	Sera	*Cymbopogon cutratus*	Rhysome
59	Inguru	*Zingiber cylindricum Moon*	Rhysome
60	Rata kaha	*Bixa orellana*	Seed
61	Alisarin	*Hydrorcy anatharaquinones*	Stem
62	Masakka	*Quercus Infectoria*	Rhysome
63	Pipigngna	*Cucumis sativusl*	Stem
64	Gammalu	*Pterocarpus marsupium Roxb.*	Stem
65	Rata-embilla	*Morus Tinctoria*	Fruit
66	Annasi	*Ananas Comosus*	Leaves
67	Kesel	*Musa Sapientum*	Muwa
68	Goraka	*Garcinia Cambogia*	Fruit
69	Nelum	*Nelumbo Nucifera gaerin*	Flowers

70	Carrot	*Daucus carrota*	Fruit
71	Daisiya	*Chrysanthemum Leucanthemum*	Flowers
72	Grass	*Zingiber cylindricum Moon*	Leaves
73	Rosa	*Rosa Indica*	Flower
74	Suriyakantha	*Helianthus Annuus*	Flowers
75	Thakkali	*Solanum Lycopersium*	Fruit
76	Eucalyptus	*Eucalyptus globules*	Bark
77	Lemon grass	*Zingiber cylindicum Moon*	Leaves
78	Nivithi	*Basella alba*	Seed
79	Kadalu	*Impatiens flaccida*	Flower
80	Canas	*Canna ediulis*	Flower
81	Boganvila	*Bougainvilla spectabilis*	Flower
82	Beligeta	*Aegle marmelos*	Fruit
83	Kaduru	*Cerbera manghas*	Fruit
84	Katakaluwa	*Myrica nagai*	Fruit
85	Thembili	*Eugenia bracteata*	Husk
86	Mulberry	*Morus alba*	Fruit
87	Mango	*Mangifera indica*	Fruit, leaves, bark
88	Blackberries	*Rubus Fruitcoses*	Fruit
89	Raspberries	*Rubus Edaem*	Fruit
90	Blueberries	*Vaccinum angustifolium*	Fruit
91	Star Fruit	*Averrhoa Carambola*	Fruit
92	Bankoro	*Morinda Citrifolia*	Bark of roots
93	Annato	*Bixa ovellana*	Dried seed
94	Bayok	*Petaro Spermum*	Bark

95	Jack Fruit	*Artocarpus heterophyllus*	Sawdust
96	Bread Fruit	*Artocarpus affilis*	Inflorescence
97	Shoe Flower	*Hibiscus surattensis*	Flower petals
98	Pokuru Wada	*Hibiscus rocacinesis*	Flower petals
99	Kaneru	*Nerium oleander*	Flower petals
100	Rathu Kathuru murunga	*Sesbania grandiflora*	Flower petals
101	Maha ratmal	*Rhododendron arboretum*	Flower petals
102	Red Sandalwood	*Pterocarpus santalinus*	Wood
103	Big Onion	*Allium Cepa*	
104	Brazlin	*Nephelium Lappaceum*	Wood
105	Tumeric	*Curcuma domestica valet*	Rhizome
106	Walmadata	*Rubia coxdiflora*	Root, stem
107	Mery Gold	*Targets erectra*	Flower petals
108	Rathadin		Stem
109	Kekum pothu		Bark

Best Research - Cell Efficiencies Table at IFS, Kandy
(since inception to –date)

SR. NO.	DATE	DYE	BEST EFFICIENCY (%)
1.	July 1998	Santalin red	3
2.	September 1998	Ruthenium (metallic dye complex)	7.8
3.	August 1999	Ruthenium	8
4.	August 1999	Ruthenium	4.1
5.	August 1999	Ruthenium	6
6.	July 2000	Ruthenium	1.53
7.	September 2000	Ruthenium	1.5
8.	November 2000	Eosin	3.2
9.	December 2000	Ruthenium	3.2
10.	January 2001	Metallochromic	0.3
11.	May 2001	Ruthenium	10
12.	May 2001	Bromopyrogallol red	0.8
13.	May 2001	Ruthenium	0.25
14.	October 2001	Ruthenium	0.8
15.	December 2001	Ruthenium	3.0
16.	February 2002	Ruthenium	2.7
17.	April 2002	Ruthenium	2.1
18.	July 2002	Ruthenium	6.0
19.	September 2002	Bromopyrogallol red and Pyrocatechol violet	1.4
20.	September 2002	Ruthenium	6
21.	September 2002	Ruthenium	3.7
22.	September 2002	Ruthenium	6.9
23.	September 2002	Ruthenium	0.5
24.	January 2003	Ruthenium	0.8
25.	April 2003	Rose Bengal	1.5
26.	October 2003	Fast green and Acridine Yellow	1.67
27.	November 2003	Ruthenium	2.7
28.	December 2003	Polythiocyanoglen conducting polymer	0.3

29.	April 2004	Methyl violet and Mercurochrome	1.37
30.	June 2004	Ruthenium	8.2
31.	June 2004	Fast green, Rhodomine and Acridine Yellow	1.67
32.	July 2004	Ruthenium	2.3
33.	December 2004	Methyl violet	1.4
34.	December 2004	Ruthenium	2.3
35.	January 2005	Ruthenium	3.7
36.	May 2005	Indoline	2.8
37.	June 2005	Acridine orange, Rhodomine B and Bromopyrogallol red	0.82
38.	June 2005	Mercurochrome	2.4
39.	June 2005	Mercurochrome	1.0
40.	July 2008	Hibiscus surottensis flower (natural dye)	1.14
41.	September 2008	Ruthenium	1.21

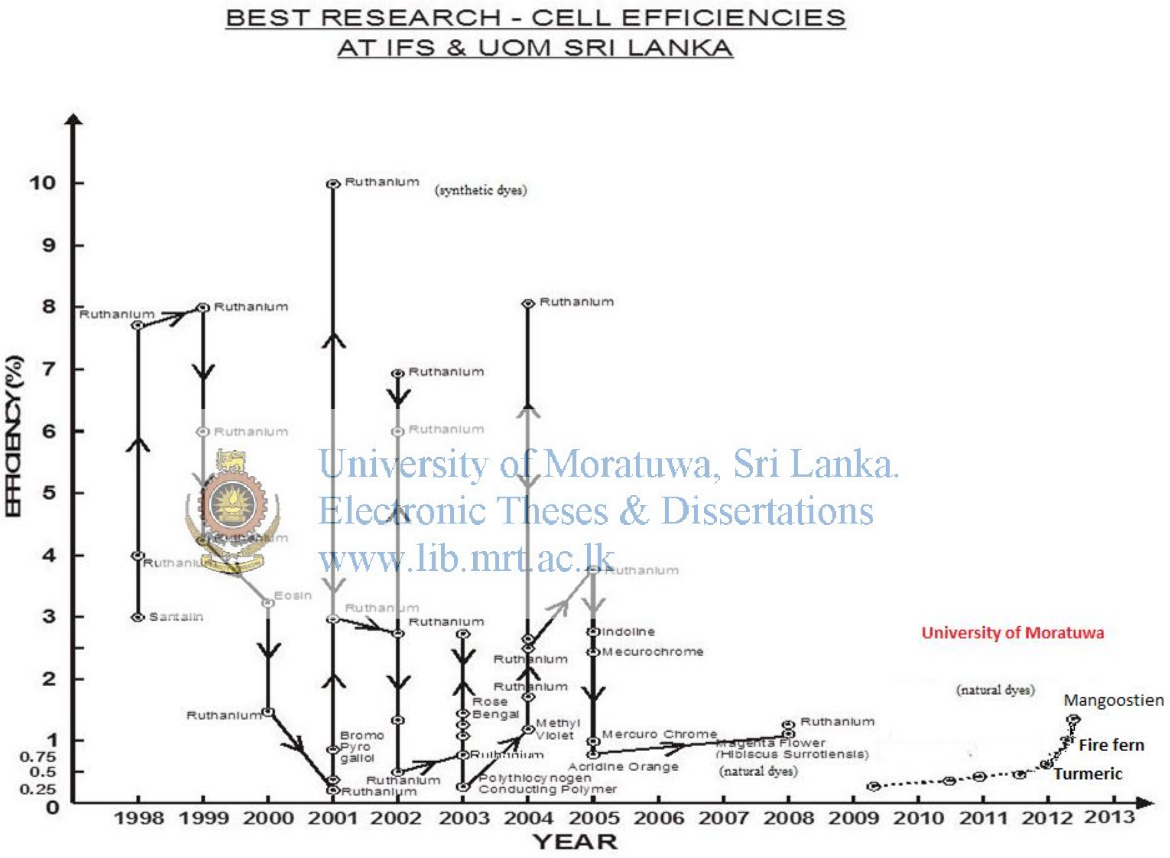
By University of Moratuwa Research Staff at IFS (Author)

1.	June 2009	Mangoostein (Natural dye) Turmeric (Natural dye)	0.111 0.210
2.	January 2010	Mangoostein (Natural dye) Turmeric (Natural dye)	0.165 0.223
3.	October 2010	Mangoostein (Natural dye) Turmeric (Natural dye	0.271 0.241
4.	February 2011	Mangoostein (Natural dye) Turmeric (Natural dye)	0.340 0.252
5.	December 2012	Mangoostein (Natural dye) Turmeric (Natural dye) Fire fern (Natural dye)	1.053 0.264 0.802

APPENDIX- F

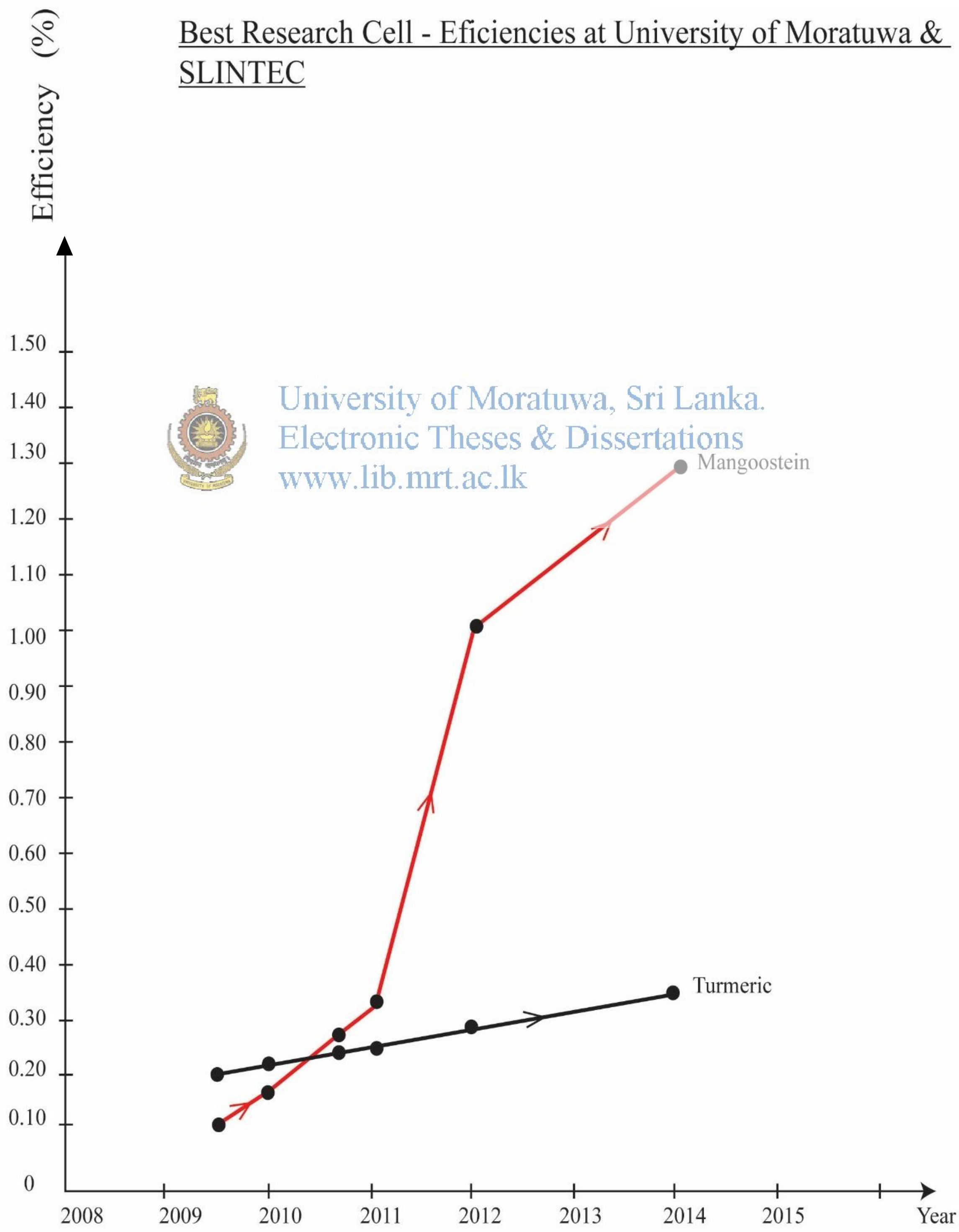
BEST RESEARCH – CELL EFFICIENCIES

AT IFS AND UNIVERSITY OF MORATUWA , SRI LANKA

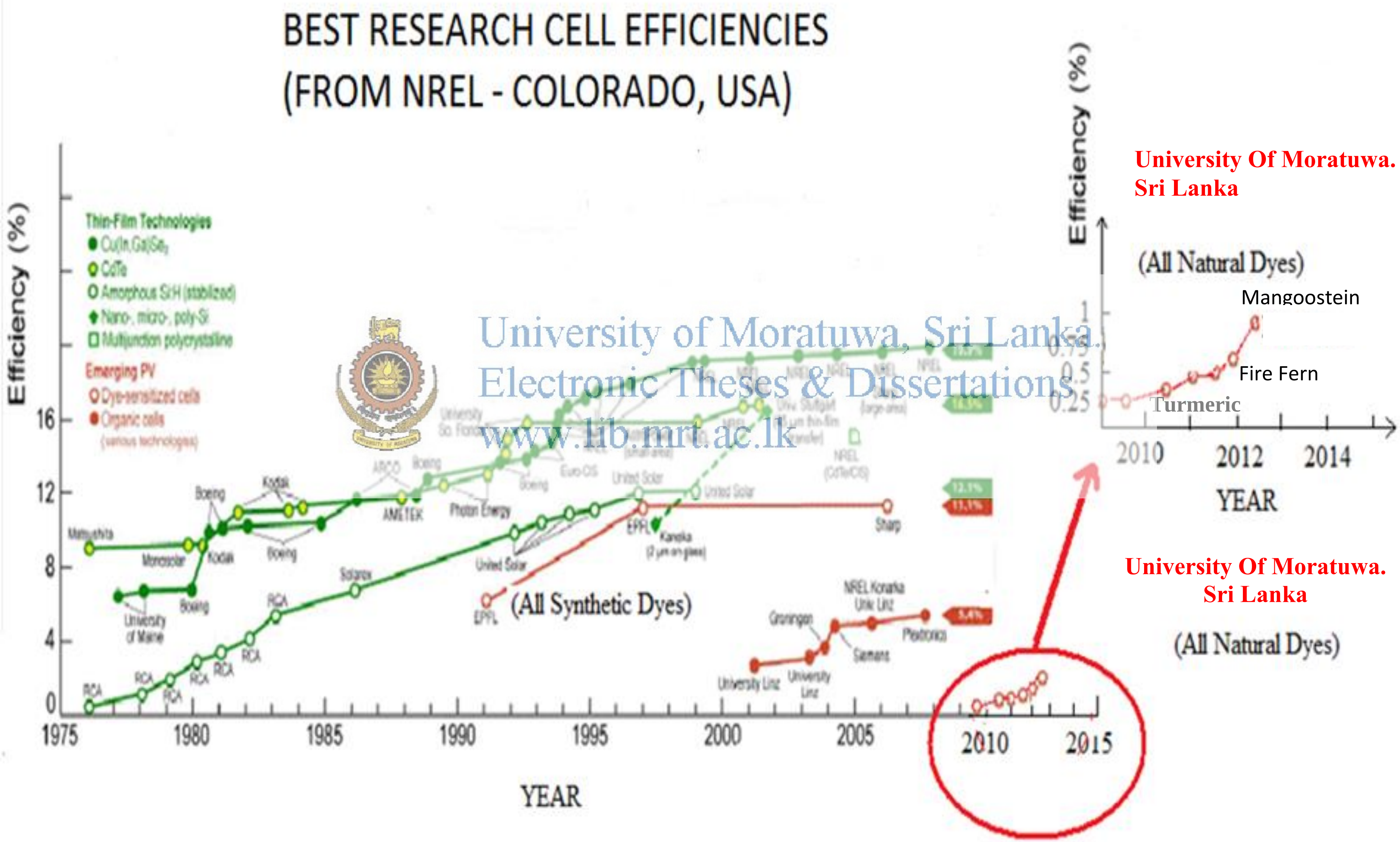


BEST RESEARCH – CELL EFFICIENCIES

AT IFS AND UNIVERSITY OF MORATUWA , SRI LANKA

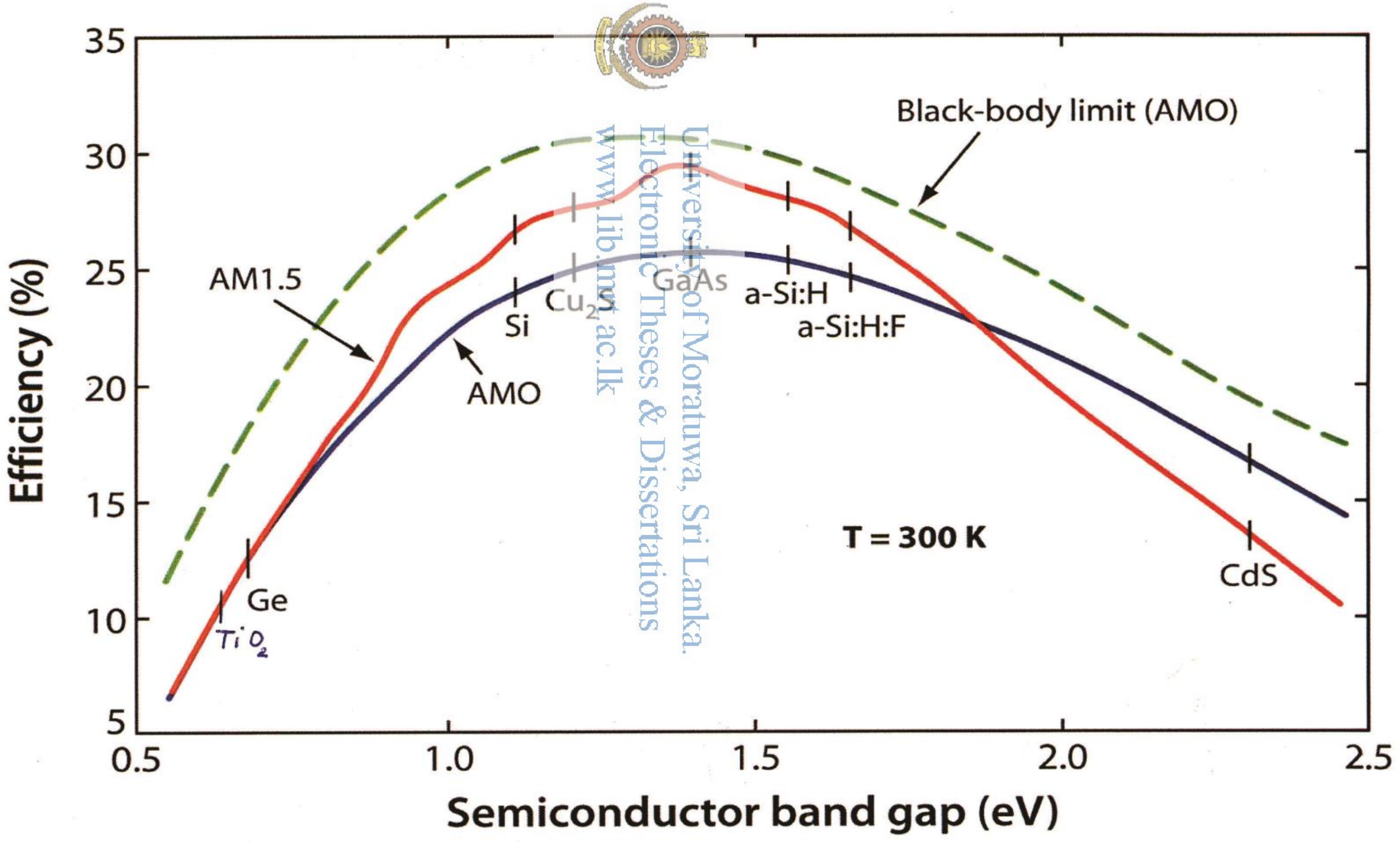


APPENDIX H

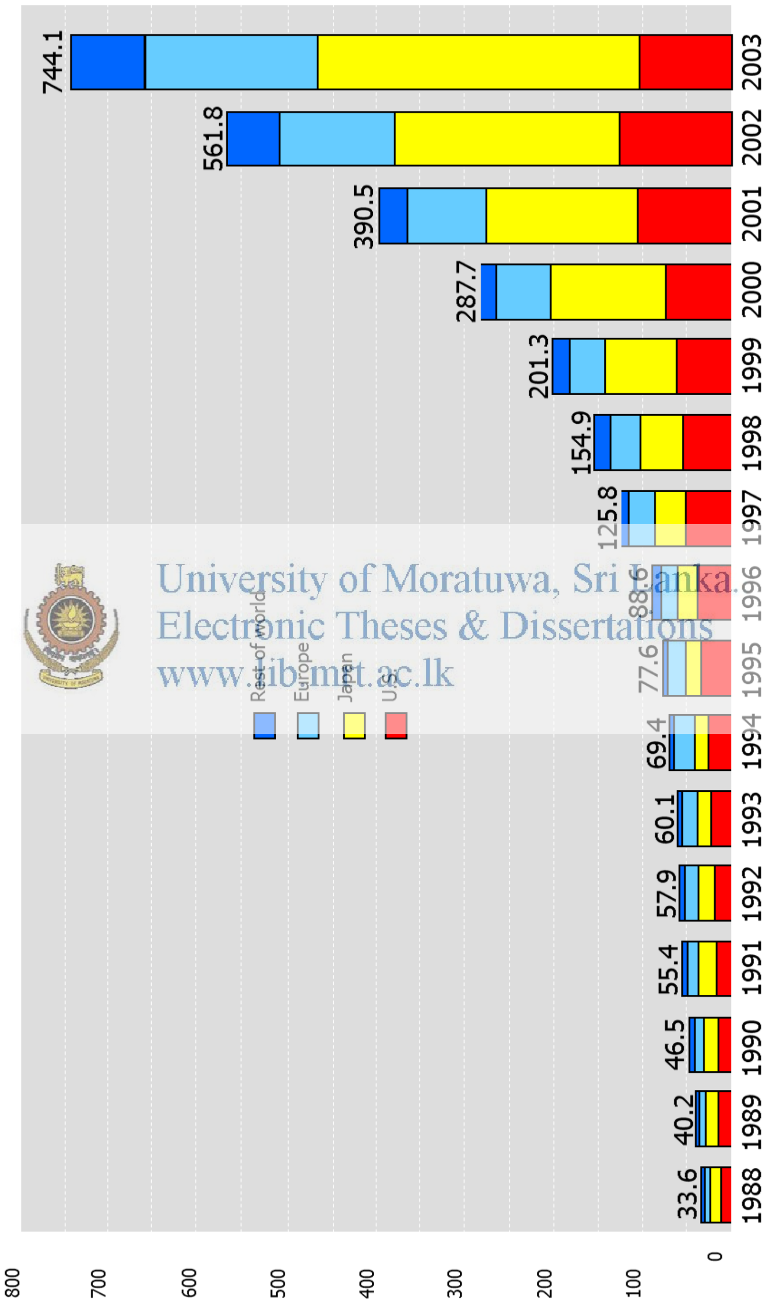

BEST RESEARCH CELL EFFICIENCIES
(FROM NREL - COLORADO, USA)
Efficiency (%)
Thin-Film Technologies
Cu(In,Ga)Se2
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Multijunction polycrystalline
Emerging PV
Dye-sensitized cells
Organic cells (various technologies)
0
4
8
12
16
1975
1980
1985
1990
1995
2000
2005
2010
2015
YEAR
(All Synthetic Dyes)
Matsushita
Monosolar
Kodak
Boeing
University of Maine
RCA
Solarex
AMETEK
Photon Energy
ARCO
United Solar
EPFL
Kaneka (2 µm on glass)
Sharp
NREL
Euro-CIS
University Linz
Groningen
NREL Konarka Univ Linz
Siemens
Plextronics
12.1%
11.1%
5.4%
Efficiency (%)
University Of Moratuwa. Sri Lanka
(All Natural Dyes)
Mangoostein
Fire Fern
Turmeric
1
0.75
0.5
0.25
2010
2012
2014
YEAR
University Of Moratuwa. Sri Lanka
(All Natural Dyes)

APPENDIX I

BAND GAPS OF VARIOUS SOLAR CELL MATERIAL AND CONVERSION EFFICIENCIES OF VARIOUS TYPES OF SOLAR CELLS



Commercialization & Market Potential of Solar PV's

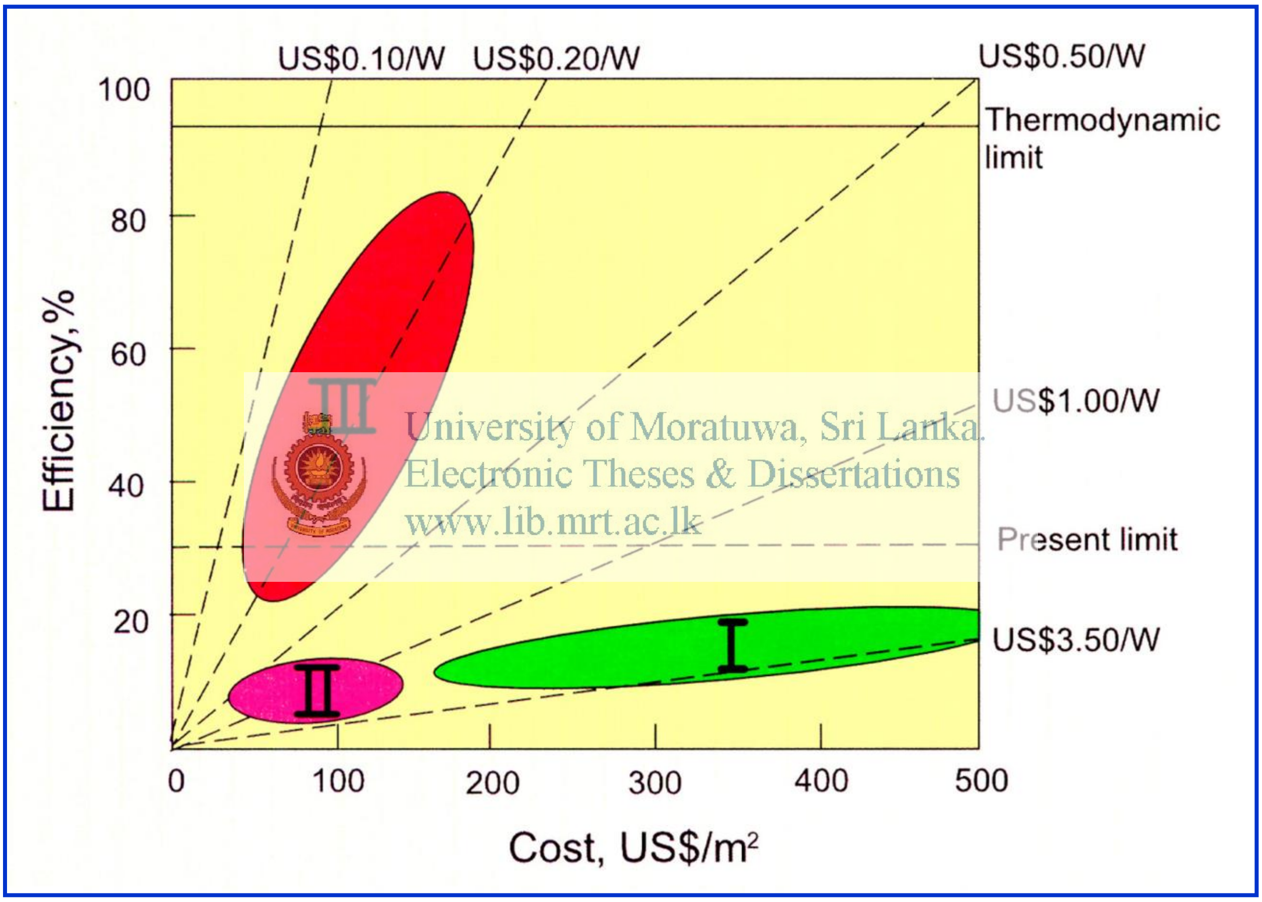


Amount of solar photovoltaic systems accumulated in the world by major producers for period 1981 to 2003

PV Power Costs as Function of Cell Efficiency and Module Cost

APPRENDIX -K

EFFICIENCY VS COST FOR I, II AND III GENERATIONS OF SOLAR CELLS



For PV or PEC to provide the level of C-free energy required for electricity and fuel—power cost needs to be 2-3 cents/kWh ($0.40 – $0.60/W)

APPRENDIX - L

List of Major Solar PV Cell Manufacturing Companies in the World

1 Sustainable Technologies International, Queensbayan, NSW, Australia
2 BP Solar, Burstadt, Germany
3 BP Solar, Sydney NSW, Australia
4 Ersol Solar Energy AG, Germany, Wilhelms
5 Eni Power S.P.A. Australia
6 GE Energy, Atlanta Georgia U.S.A.
7 Pecell Technologies, Santa Babara California, U.S.A.
8 Global Solar Energy Inc, Arizona U.S.A.
9 Suntech, Betzville, Mayland U.S.A.
10 Yingili Green Energy, Baoding, Hebei, China
11 Isofotan, Madrid, Spain
12 UPV Solar, Coimbatore, Tamil Nadu, India
13 Kyocera Solar Corporation, San Diego, California, USA
14 Mitsubishi Electric, Chiyoda, Tokyo, Japan
15 Photowatt International, Hilboro, Oregon, U.S.A.
16 Q-Cell AG, Thalheim/Wolfen, Saxany, Germany
17 Schott Solar, Alyenau, Germany
18 Sanyo Electric Company, Shija, Japan
19 Sharp Corporation, Osaka, Japan
20 Solar World AG, Bonn, Germany
21 United Solar Ovonic LLC, Leiester, Leiestershire, U.K.
22 Dyesol, Queensbayan, NSW, Australia
23 Toshiba, Tokyo, Japan
24 Fuji Electric, Osaka, Tokyo, Japan
25 Nippon Electric, Chiyoda, Tokyo, Japan
26 Motech, Delaware, Florida, U.S.A.
27 Schott Solar, Albuguerque, NM, U.S.A.
28 Sanyo, Shija, Japan
29 Shell Solar, Colorado, U.S.A.
30 Unisolar, Michigan, U.S.A.
31 Company Greatcell, Lausanne, Switzerland
32 Greatcell Company, Wekdinweg, Netherlands
33 Company Mansolar, Pettan, Netherlands
34 Free Energy Europe, Hague, Netherlands
35 Solarian GmbH, Berlin, Germany
36 Ersol Solar AG Balion, Germany
37 Eurosolaro, Rome, Italy
38 Deutsche Solar, GmbH, Munich, Germany
39 Central Electronics, New Delhi, India
40 Bharat Heavy Electicals, Banglore, India
41 Euro Multisession, Mumbai, India
42 Microsol Power, Hydrabad, India
43 Biztech Power, Karachi, Pakistan
44 Solar Power Systems, Karachi, Pakistan
45 Solar Power, Rawlpindi, Pakistan
46 Gorosabel Solar, Mendro, Spain
47 Mandrajon Assembly, Gipuzkoa, Spain
48 Advanced Dicing Technologies, Hifa, Israel
49 Amcor Solar Energies Ltd, Ashod, Israel
50 Arava Power Company, Ketura, Israel
51 Bangkok Solar, Chachoengao, Thailand
52 Alpha Synergies, Bangkok, Thailand
53 Photovoltaic Manufacturing Company, Teheran, Iran
54 Canadian Solar, Ontario, Canada
55 Allesun Solar, Richmond, BC, Canada
56 Aquatech Solar, Auckland, New Zealand
57 Electro IO, Veniseux, France
58 Sharp Energia, Paris, France
59 Solaraire, Paris, France
60 SVS Sra, Brno, Czechoslovakia
61 SCR Energy, Radihastem, Czechoslovakia
62 G24 Innovations Ltd, Cardiff, Wales,

APPENDIX - M

Main Research Organizations and Established Companies in the world carrying out R& D on Dye-Sensitized Solar Cells

1. Georgia Institute of Technology, USA

Location : Georgia, Atlanta, USA

Research highlights: The centre for organic Photonics and Electronics (COPE) in the School of Electrical and Computer Engineering at Georgia Tech does research on improving efficiencies and design structures of light-weight organic solar cells. This centre works with the University Centre for Excellence in Photovoltaic (UCEP) for improving conventional silicon and organic solar cells. Led by Prof. Bernard Kippeler, COPE has designed cells using crystalline organic films called Pentacene that results more efficient and lightweight solar cells.

2. Korea Institute of Energy Research

Location: Daejeon, South Korea

Research Highlights: The Institute specializes in energy research and works on developing new technologies supporting energy policies. It has carried out research on improving organic solar cell technology with TiO2, and integrating this with other solar based technologies.

3. Center for Photonics and Optoelectronic Materials.

Location: New Jersey, USA.

Research highlights: This center, affiliated with the Department of Electrical Engineering does research on technologies for making organic solar cells more efficient and cheaper. This Center has recently developed techniques for manufacturing organic solar cells at higher efficiencies about 5%.

4. United States Air Force Research Laboratories

Location : Ohio, USA

Research highlights: The scientists and researchers at the materials and manufacturing Directorate have been involved in developing advanced, flexible organic based solar cells. The research has focused on all-polymer and organic material approach, and Dye sensitized organic and inorganic material hybrid approach. This research is expected to yield versatile used of PV, especially for military operations and applications Present studies have resulted in efficiencies of over 10%.

Established Companies producing Die-Sensitized Solar Cells

5. Sustainable Technologies International Dyesol Australia Pty Ltd.

Location: Queenbeyar, NSW, Australia

Company Profile: This company was the world's first company to start commercial production of dye sensitized solar cells which are based on organic cell technology. It also produces photovoltaic components using nanotechnology. The company started its pilot production line in 2001 and had an annual production capacity of .5 MW for organic solar cells by 2008. This Company is now owned by Dyesol Australia Pty Ltd.

6. Global Photonic Energy Corporation

Location : New Jersey, U.S.A.

Company Profile: Global photonics is a renewable energy technology development company. It has also carried out research on enveloping technologies for producing organic solar cells. The company targets designers and product innovators to accelerate the development of this technology.

7. General Electric Global Research Company

Location: GE Offices worldwide

Company Profile: This company has a research unit at GE works on developing flexible substrates without silicon and optimized organic solar cells for energy conversion. The focus is on making use of technology and OLED device architecture in photovoltaic technology. It also develops roll - to - roll organic plastic sheets that can substitute conventional silicon panels and be used in a variety of applications.

8. Toshiba Research Europe Ltd.

Location : Cambridge, U.K.

Company Profile: Toshiba Company research centre works on developing organic solar cells, and has developed technologies that generate organic solar cells with efficiencies around 7%, with higher lifetimes. The centre has produced a technique for manufacturing plastic based solar cells using dyes suitable for varieties of applications.

9. Siemens Research and Development

Location : Germany

Company Profile: The Siemens Research group of this company works on developing efficient printed organic solar cells that can be scaled up for commercial use. The efficiencies of the cells developed exceed 5%, more than regular levels of commercial cell production. They are also lightweight and flexible. This technology has been sold to companies like Konarka.

10. Konarka Technologies Inc.

Location: Lowell, Masschusetts, USA.

Company Profile: Konarka Technologies Inc has worked on developing technologies for commercial production of low-cost cells on flexible material, with a focus on combining organic and nanotechnologies and polymer electronics. The company has had US$ 32 million financing by various investor agencies since 2001, and acquired the organic solar cell research group at Siemens in September 2005. Pilot - Scale production of organic solar cells began in 2005 and production is expected to scale up to commercial levels in 2009 / 2010. The Company diversified into manufacturing photovoltaic material adaptable for various applications, like spray-on plastic photovoltaic panels, solar fabric that generate power etc.

11. Solar AMP LIC

Location: Raleigh, North Carolina, U.S.A.

Company Profile: This company focuses on research and development of renewable technologies, and organic photovoltaic components. As part of a recent joint effort with BP, the start-up company has started to conduct test for developing commercially viable organic molecular based cells without using dye-sensitized solar cells with efficiencies targeted at 10-15% with lifetimes of 25 years.

12. Greatcell Company

Location: Lausanne, Switzerland

Company Profile: This company focuses on dye - sensitized solar cells using organic technology., It was brought by Tulloch Management Pty Ltd. which also owns sustainable Technologies International (STI) and Dyesol Australia Pty Ltd., but carried out research on organic solar cells, and assembles STI's outdoor facade modules.

13. AIXTRON AG

Location: Aachen,Germany

Company Profile: AIXTRON is a manufacture and supplier of equipment for compound semiconductor devices. In continuation of its Organic Vapour Phase Deposition (OVPD) business, the Company has expanded research on organic solar cells in association with other companies, and is sponsored by the German Company Halin Meitner-Institute HMI.

APPENDIX – M

Basin Trials of Organic / DSSC Powered Catamaran Boat


INORGANIC SOLAR CELL POWERED BOAT
SOORIYA – C 120


ORGANIC SOLAR CELL POWERED BOAT
SOORIYA – C 120


P 475


ORGANIC SOLAR CELL POWERED BOAT
SOORIYA – C 120


SOLAR CELL POWERED BOAT
SOORIYA – C 120


SOORIYA – C 120
BOAT

APPENDIX – N

Design and Development of PV – DSSC Devices and Systems at University of Moratuwa

Herbert Arnold Gmbh, Germany – Electric Oven 440Volts, 3Phase for Spray Pyrolysis of FTO Glasses at 580°C

Spray Pyrolysis of FTO Glasses at 580°C

Preparation of FTO Glasses for Catamaran Boat

Design & Development of DSSC Operated Battery Charger for Mobile Phones, iPods etc.

DSSC Operated Garden Lights for Hotels

Prototype DSSC – BIPV Window Panels for High – Rise Buildings

DSSC Solar Panel for Catamaran Boat

Design & Development of Electrically Operated Natural Dye Extraction Unit

Portable DSSC Testing Spin Coating Machine