

**FABRICATION AND CHARACTERIZATION OF TITANIUM
DIOXIDE - ROSELLE (ZOBO) DYE SENSITIZED SOLAR
CELL**

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(M.Sc. PHYSICS)**

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DECLARATION

I hereby declare that this work is the product of my research effort undertaken under the supervision of Prof. Garba Babaji and has not been presented anywhere for the award of a degree or certificate. All sources have been duly acknowledged.

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CERTIFICATION

This is to certify that the research work for this thesis on Fabrication and Characterization of Titanium Dioxide - Roselle (Zobo) Dye Sensitized Solar Cell was written by (BALA ISMAIL ADAMU, SPS/12/MPY/00044) were carried out under my supervision.

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ABSTRACT

This work presents the fabrication of a Titanium dioxide Roselle dye sensitized solar cell under different annealing temperatures. Doctor-Blade method was used in the fabrication and Keithley 2400 source meter under A.M 1.5 illumination from Newport class A solar simulator was used in testing the fabricated TiO₂-Roselle dye sensitized solar cell. Maximum values of open circuit voltage of V_{oc} , short circuit current density J_{sc} , fill factor FF, and the Energy conversion efficiency η were found to be 0.78V, $45.8\mu Acm^{-2}$, 0.45 and 0.0056 respectively. The efficiency obtained in this work of 0.0056 is more than one reported recently.

CHAPTER ONE INTRODUCTION

1.0 INTRODUCTION

In today's society, it is becoming ever important to find alternative sources of energy that are both cheap and efficient. Solar cells have become one of the most widely-researched methods of obtaining energy in "greener" ways than burning fossil fuels, etc. One of the new variants on the solar cell that is currently being researched is the dye-sensitized solar cell (DSSC), which was invented by (Gratzel and O'Regan, 1991), where conventional systems take advantage of the semiconductor to absorb light and transport charge carriers, DSSCs separate these two functions. A sensitizer, which is anchored to the surface of a wide band semiconductor, absorbs sunlight. When light is incident on the dye, electrons are injected from the dye into the conduction band of the solid, accounting for the charge separation. The electrons are then transported in the conduction band of the semiconductor to the charge collector. Using sensitizers with a broad absorption band along with nanocrystalline oxide films (most commonly titanium dioxide) allows for the efficient capture of a large fraction of sunlight over a large spectral range (Luk, 2010).

TiO₂ was one of the most widely studied semiconductor materials due to its favourable physical, optical and electrical properties and its many important applications, such as photocatalyst, solar cells, gas sensors and even biomaterials. It had excellent optical transmittance in the visible range, electronics properties and good stability in adverse environment, It also has wide band gap energy and it is a kind of semiconductor that is transparent to visible light and has excellent optical transmittance. Additionally TiO₂ films have potential uses for a number of electronic device applications such as dye-sensitized photovoltaic cells as well as antireflective (AR) coatings, gas sensors, electrochromic displays, and planar waveguides. The high dielectric constant of TiO₂ allows its consideration as an alternative to silicon dioxide for ultrathin gate oxide dielectrics used in memory and logic devices. Several methods have been used to prepare TiO₂ films, and these include chemical vapour deposition (CVD), pulsed laser deposition, reactive sputtering and sol-gel deposition. The sol-gel technique has emerged as one of the most promising techniques as this method produces samples with good homogeneity at low cost (Muhamad, 2009).

The current-voltage (I-V) measurement is common measurement technique used to investigate the current-voltage (I-V) curve of thin films. From this curve the electrical properties of the thin films can be studied.

1.1 STATEMENT OF PROBLEMS/ JUSTIFICATION

Nigeria is among the fast growing country in Africa in both infrastructures and population. This means that the existing electrical power supply is strained because the electrical demands in the country overweight the electrical power supply. Solar radiation are much available in Nigeria, especially the northern part of the country. Nowadays most of the research groups and industries in Nigeria used the silicon based solar cell to generate the electricity. The third generation DSSC provide effective solution to energy problem due to its nanoscopic and mesoscopic character of its materials (Ricardo et al., 2011). DSSC is expected to be used for future clean energy. Among the DSSC ruthenium complex shows high energy conversion efficiency.

However, ruthenium is a rare metal so that the cost of the ruthenium complex is very high. In addition it contained heavy metals which make it becomes unpopular from environmental aspects. These attract the attention of the researchers in DSSC searching for the replacement of the rare and expensive ruthenium compounds. Many kind of natural dye have been actively studied and tested as low-cost materials. In nature some fruits

flowers, leaves, bacteria etc., shows various colours and contain several pigments that can be easily extracted for the fabrication of DSSC.

Therefore, natural harvestable Roselle (Zobo) dye are available in Nigeria, easy to prepare, low-cost, non-toxic and environmentally friendly.

1.2 AIM AND OBJECTIVES

The aim of this work is to explore means of improving the performance of DSSC fabricated by the blade method using Roselle (Zobo) as the dye.

The objectives of this research are to:

- Improve the TiO₂ deposition process through the use of Gum Acacia.
- Investigate the fabricated DSSC performance.
- Investigate the effect of Annealing Temperature of fabricated DSSC.
- Investigate the effect of Degradation of fabricated DSSC

1.3 SCOPE AND LIMITATION

This work involves fabrication and J-V characterization of Titanium Dioxide-Roselle Dye sensitized solar cell using natural harvestable Roselle (Zobo) as dye. This work is limited to J-V characterization.

1.4 OVERVIEW OF SOLAR CELL TECHNOLOGY

A solar cell is an electronic device which convert direct solar energy into electricity using the process called photovoltaic effect. The process is achieved by shining light on the solar cell which creates an electrical current or voltage in the material that generate an electric power (Musa, 2010).

First and second generations photovoltaic cells are mainly constructed from semiconductors including crystalline silicon, III-V compounds, cadmium telluride, and copper indium selenide/sulphide (Khalil, 2011). Low cost solar cells have been the subject of intensive research work for the last three decades. Amorphous semiconductors were announced as one of the most promising materials for low cost energy production. However, dye sensitized solar cells DSSCs emerged as a new class of low cost energy conversion devices with simple manufacturing procedures. Table 1 summarizes the various types of solar cell and the challenges facing them.

Table 1: Solar cell category, types and their associated challenges (Agilent Technologies, 2009)

Category	Types	Challenges
Silicon	1. Single crystalline	1. Development of the device structure
	1 Polycrystalline	2. improvement on the crystal quality
	2 amorphous	3. multiplying the junction
Compound	3 GaAsInp 5. CdTe/Cds, Cu ₂ S/CdS, CIGS	4. Control of band gap 5. multiplying the junction
Organic	6. Pentacene 7. Phthalocyanine 8. merocyanine	6. Development of the device structure (including multi-junction) 7. structure (including multi-junction) 8. Development of the materials
Photochemical	9. Dye sensitized	9. Development of the materials

Basically a solar cell, SC, consists of a junction of p- and n-type semiconductors. At the interface the Fermi levels of both semiconductors are the same, generating depletion region, and therefore, a charge separation. When photons are absorbed in the p-type region, an electron-hole pair is created. Each electron is then injected in the n-type region and the hole goes across p-type region. In the case of TFSCs the amount of material for the SCs production is considerably less, thus it reduces costs. Some other advantages consist on the possibility of working with lighter materials and flexible substrates (Recardo et al., 2011).

Most solar cell characteristics can be obtained from simple I-V measurements. (Figure 1) shows the IV characteristics of a typical solar cell under forward bias and illumination. The short circuit current (I_{sc}) is the current through the solar cell when the voltage across the solar cell is zero. The open circuit voltage (V_{oc}) is the voltage across the solar cell when the current through the solar cell is zero and it is the maximum voltage available from the solar cell. The maximum power point (P_{max}) is the condition under which the solar cell generates its maximum power; the current and voltage in this condition are defined as I_{max} and V_{max} (respectively). The fill factor (FF) equation (2) and the conversion efficiency (η) equation (1) and (3) are metrics used to characterize the performance of the solar cell. The fill factor is

defined as the ratio of P_{max} divided by the product of V_{oc} and I_{sc} . The conversion efficiency is defined as the ratio of P_{max} to the product of the input light irradiance (E) and the solar cell surface area (A_c). (Agilent, 2009)

$$FF = \frac{P_{max}}{V_{oc} \times I_{sc}} \quad (1)$$

$$\eta = \frac{V_{oc} \times I_{sc} \times FF}{E \times A_c} \quad (2)$$

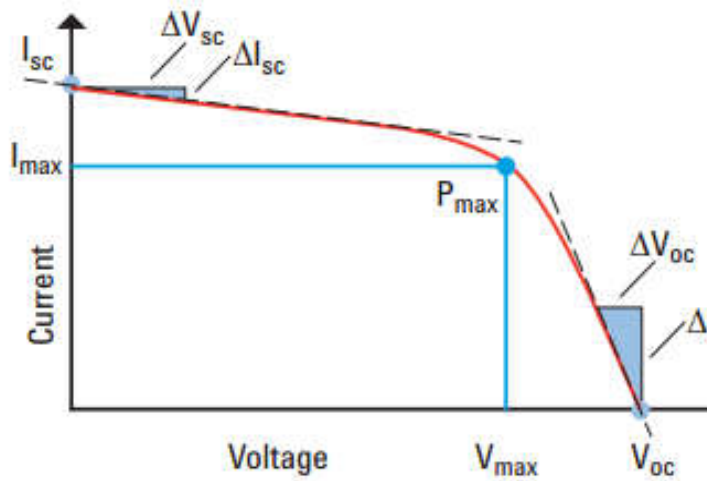


Fig.1: Typical I-V Forward Bias Characteristics of a Solar Cell

Although there are a variety of methods to obtain R_{sh} and R_s , one of the most straightforward techniques is to measure the slope of I-V characteristics as shown in Figure 1.

$$R_{sh} = \frac{V_{sc}}{I_{sc}} \quad (3)$$

$$R_s = \frac{V_{oc}}{I_{oc}} \quad (4)$$

R_{sh} and R_s can be obtained from Equation (3) and (4) respectively.

1.5 DYE SENSITIZED SOLAR CELL (DSSC)

Solar cell or photovoltaic cell is a semiconductor device that converts solar energy into electricity. This conversion is called the photovoltaic effect, and the field of research related to solar cells is known as photovoltaics. Photovoltaic cells have gained widespread acceptance as a source of clean and renewable energy. Although the cost of crystalline silicon solar cells has dropped significantly over the past decade, these devices are still too expensive to compete with conventional grid electricity (Udodiri, 2010). A promising alternative to conventional silicon cells is given by the Dye Sensitized Solar Cells (DSSC).

Dye-sensitized solar cells are a promising potential replacement for silicon-based solar cells. With advancements in nanostructured semiconductors, high efficiency sensitizers and robust electrolytes, the performance of

modern DSSCs is becoming more and more competitive. Simple processing, low-cost materials and a wide range of applications are all helping DSSCs to find a foothold in the marketplace (www.azonano.com).

1.5.1 Components Of Dye Sensitized Solar Cell (DSSC)

The current DSSC design involves a set of different layers of components stacked in serial, including glass substrate, transparent conducting layer, TiO₂ nanoparticles, dyes, electrolyte, and counter electrode covered with sealing gasket. The typical configuration is shown in (Figure 2).

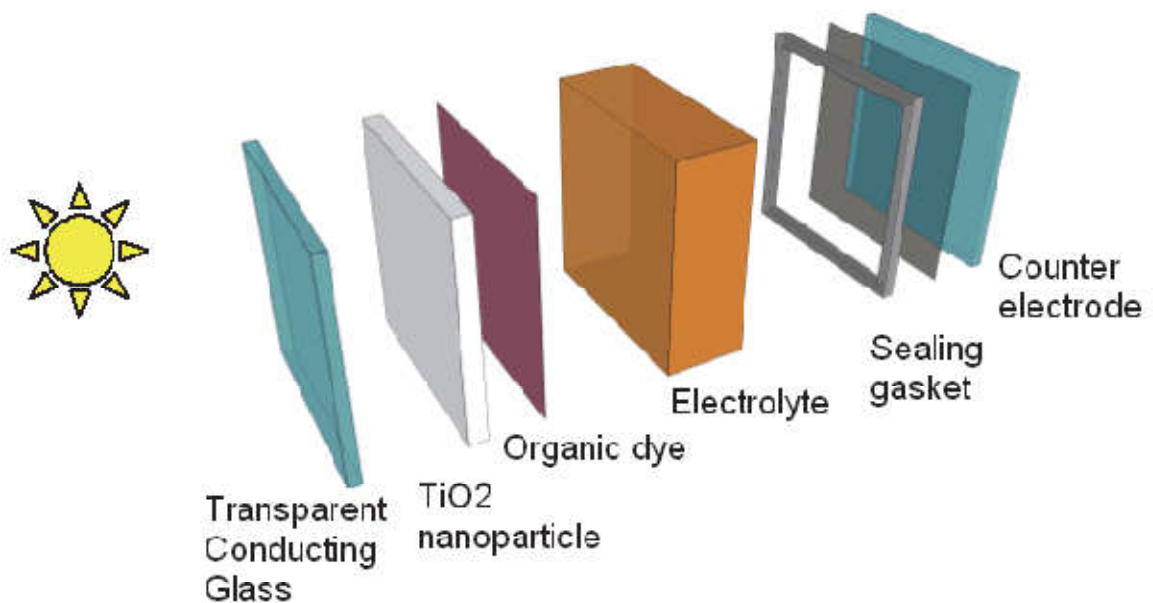


Figure 2: Typical Configuration of a DSSC (Yang Jiao, 2011)

1.5.2 Transparent Substrate For Both The Conducting Electrode And Counter Electrode

TCO is a layer of glass substrate, usually placed in the front of the DSSC. This layer is crucial since it allows sunlight penetrating into the cell while conducting electron carriers to outer circuit. Transparent Conductive Oxide (TCO) substrates are adopted, including F-doped or In-doped tin oxide (FTO or ITO) and Aluminium-doped zinc oxide (AZO), which satisfy both requirements. ITO performs best among all TCO substrates. However, because ITO contains rare, toxic and expensive metal materials, some research groups replace ITO with FTO. AZO thin films are also widely studied because the materials are cheap, nontoxic and easy to obtain.

The conductive film ensures a very low electric resistance per square. Typical value of such resistance is 10-20 Ω per square at room temperature. The nanostructured wide bandgap oxide semiconductor (electron acceptor) is applied, printed or grown on the conductive side. Before assembling the cell the counter electrode must be coated with a catalysing layer such as graphite layer to facilitate electron donation mechanism to the electrolyte (electron donor) as. One must bear in mind that the transparency levels of the transparent conducting electrode after being coated with the conductive film is not 100% over the entire visible and near infrared (NIR) part of the

solar spectrum. In fact, the deposition of nanostructured material reduces transparency of the electrode (Khalil, 2011).

1.5.3 TiO₂ Nanoparticles

DSSC has a low efficiency less than 1% until Professor (Grätzel, 2000) employs porous TiO₂ as the anode material. Usually a layer of negatively doped TiO₂ (n-TiO₂) nanoparticles is used. The advantages of TiO₂ include high photosensitivity, high structure stability under solar irradiation and in solutions, and low cost. The typical particle size is 8-30 nm in diameter, and the TiO₂ films thickness is 2-20µm, with the maximum efficiency located at a thickness of 12-14µm depending on dyes and electrolyte chosen (Ito et al., 2008). However, as a wide bandgap semiconductor (~3.2 eV), TiO₂ absorbs only UV light, which comprises only a small fraction (~5%) of solar spectrum (Khalil, 2011). As a result, dye molecules are employed for visible light capture.

1.5.4 Dye

The dye molecules are the key component of a DSSC to have an increased efficiency through their abilities to absorb visible light photons. Early DSSC designs involved transition metal coordinated compounds (e.g., ruthenium complexes) as sensitizers because of their strong visible absorption, long excitation lifetime and efficient metal-to-ligand charge transfer (Yang,

2011). However, high cost of Ru dyes ($> \$1,000/\text{g}$) is one important factor hindering the large-scale implementation of DSSC. Although highly effective, with current maximum efficiency of 11% (Grätzel, 2005), the costly synthesis and undesired environmental impact of those prototypes call for cheaper, simpler, and safer dyes as alternatives.

Organic dyes, including natural pigments and synthetic organic dyes, have a donor-acceptor structure called as push-pull architecture, thus improving short circuit current density by improving the absorption in red and infrared region. Natural pigments, like chlorophyll, carotene, and anthocyanin, are freely available in plant leaves, flowers, and fruits and fulfil these requirements. Experimentally, natural-dye sensitized TiO₂ solar cells have reached an efficiency of 7.1% and high stability (Campbell et al., 2007).

Synthetic organic dyes are the most promising. Various types have recently been developed, including indolic dyes (D102, D149) (Yang, 2011), and cyanoacrylic acids (JK, C209). The same as some natural dyes, they are not associated with any metal ions, being environmental benign and easily synthesized from abundant resources on a large scale. The efficiency has reached a high level of 10.0-10.3% (Wang et al., 2010). They are relatively cheap, at the cost of one-tenth of corresponding Ru dyes. Light soaking experiments have confirmed they possess long-time stability: 80% efficiency

has been maintained after 1,200 hours of light-soaking at 60 °C (~5 million turnovers). The commercialized production of these synthetic dyes has been established in China this year. A single dye usually has a limited adsorption spectrum, so some research groups use several kinds of dyes to relay energy transfer and compensate each other and have achieved good results (Hardin et al., 2010).

1.5.5 Electrolyte

Currently three different kinds of electrolytes have been used in real DSSCs with pros and cons of each kind: (i) the most common electrolyte is I/I₃⁻ in organic solvents, such as acetonitrile. Sometimes lithium ion is added to facilitate electron transport. This kind of electrolyte is good for ion diffusion and infiltrate well with TiO₂ film, keeping highest efficiency of all DSSCs. But limited long-term stability due to volatilization of liquid hinders its wide use. (ii) Inorganic ionic liquids made of salts or salt mixture. It looks like solid while it has properties of liquid and it performs well in conductivity. But after a long period of time, its efficiency declines. (iii) Solid electrolyte, such as spiro-MeOTAD or CuI (Konno et al., 2007). For CuI, its instability and crystallization makes it hard to fill in the porous TiO₂ films. The problem can be solved by adding ionic liquid into the electrolyte. Spiro-MeOTAD is a typical kind of organic hole conductor, which has been

developed for years and the DSSC based on this kind of electrolyte has reached the efficiency of 5% (Yu et al., 2009).

1.5.6 Operation of Dye Sensitized Solar Cell (DSSC)

Sunlight enters the cell through the transparent Indium-doped tin dioxide (SnO₂:I) top contact, striking the dye on the surface of the TiO₂. Photons striking the dye with enough energy to be absorbed create an excited state of the dye, from which an electron can be "injected" directly into the conduction band of the TiO₂. From there it moves by diffusion (as a result of an electron concentration gradient) to the clear anode on top (www.wikipedia.com). Meanwhile, the dye molecule has lost an electron and the molecule will decompose if another electron is not provided. The dye strips one from iodide in electrolyte below the TiO₂, oxidizing it into triiodide. This reaction occurs quite 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 triiodide then recovers its missing electron by mechanically diffusing to the bottom of the cell, where the counter electrode re-introduces the electrons after flowing through the external circuit.

1.5.7 Mechanism of Dye Sensitized Solar Cell (DSSC)

According to Wikipedia, the main processes that occur in a DSSC are;

The following primary steps convert photons to current:

Step 1: The incident photon is absorbed by Natural pigments photosensitizers adsorbed on the TiO₂ surface.

Step 2: The photosensitizers are excited from the ground state (S) to the excited state (S^{*}). The excited electrons are injected into the conduction band of the TiO₂ electrode. This results in the oxidation of the photosensitizer (S⁺).



Step 3: The injected electrons in the conduction band of TiO₂ are transported between TiO₂ nanoparticles with diffusion toward the back contact (TCO). And the electrons finally reach the counter electrode through the circuit.

Step 4: The oxidized photosensitizer (S⁺) accepts electrons from the I⁻ ion redox mediator leading to regeneration of the ground state (S), and the I⁻ is oxidized to the oxidized state, I₃⁻.



Step 5: The oxidized redox mediator, I_3 , diffuses toward the counter electrode and then it is reduced to I^- ions.



The efficiency of a DSSC is depends on four energy levels of the component: the excited state (approximately LUMO) and the ground state (HOMO) of the photosensitizer, the Fermi level of the TiO_2 electrode and the redox potential of the mediator (I^-/I_3) in the electrolyte.

CHAPTER TWOLITERATURE REVIEW

2.0 INTRODUCTION

This chapter highlight the general review on Titanium dioxide based dye sensitized solar cell, also a review on titanium dioxide Roselle dye sensitized solar was presented.

2.1 TYPES OF DYE SENSITIZED SOLAR CELL

Currently DSSC are of two types: Liquid electrolyte DSSCs and Solid-state DSSCs (SS-DSSCs), which use solid hole conductors instead of a liquid electrolyte, are also capable of delivering high voltages. The hole conductor is typically made from either wide band gap small molecules (such as spiro-MeOTAD) or semiconducting polymers (such as PEDOT or P3HT). These DSSCs are in principle more industrially compatible than standard DSSCs because they do not contain a corrosive liquid electrolyte, which requires careful packaging. The highest values of V_{OC} (>1 V) achieved so far have been demonstrated in devices that exploit a small-molecule hole conductor (Hagfeldt, 2010). In SS-DSSCs, hole transfer occurs directly from the oxidized dye to the HOMO level of the hole conductor, which then transports the charge to the (typically silver) counter electrode. Dye regeneration occurs over a period of tens to hundreds of picoseconds, several orders of magnitude faster than regeneration with the iodide/triiodide –

redox couple. We believe that an over-potential of only 200mV may be sufficient for hole regeneration, thus allowing for power-conversion efficiencies of more than 20%, again assuming a loss of 100 mV on the electron-transfer side. Although the first SS-DSSCs made with solution-processable small molecules achieved power-conversion efficiencies of less than 1%, researchers have recently increased this value to 7.1%⁵. Significant recombination rates, together with the difficulty in achieving high levels of pore-filling in thicker films, means that SS-DSSCs currently work best at thicknesses of only a few micrometres. The greatest issues facing SS-DSSCs are their incomplete light harvesting and lower internal quantum efficiency, which together result in current densities that are lower than liquid-based DSSCs (Brian et al., 2012).

2.2 RECENT DEVELOPMENTS ON DSSC

A recent report by Wikipedia on new developments on Dye Sensitized solar cells (DSSC) from 2003 to 2013 runs thus:

2.2.1 In 2003

A group of researchers at the Swiss Federal Institute of Technology has reportedly increased the thermostability of DSSC by using amphiphilic ruthenium sensitizer in conjunction with quasi-solid-state gel electrolyte.

The stability of the device matches that of a conventional inorganic silicon based solar cell. The cell sustained heating for 1,000 h at 80 °C.

The group has previously prepared a ruthenium amphiphilic dye Z-907 to increase dye tolerance to water in the electrolytes. In addition, the group also prepared a quasi-solid-state gel electrolyte with a 3-methoxypropionitrile (MPN)-based liquid electrolyte that was solidified by a photochemically stable fluorine polymer.

The use of the amphiphilic Z-907 dye in conjunction with the polymer gel electrolyte in DSSC achieved an energy conversion efficiency of 6.1%. More importantly, the device was stable under thermal stress and soaking with light. The high conversion efficiency of the cell was sustained after heating for 1,000 h at 80 °C, maintaining 94% of its initial value. After accelerated testing in a solar simulator for 1,000 h of light-soaking at 55 °C (100 mW cm²) the efficiency had decreased by less than 5% for cells covered with an ultraviolet absorbing polymer film. These results are well within the limit for that of traditional inorganic silicon solar cells.

The enhanced performance may arise from a decrease in solvent permeation across the sealant due to the application of the polymer gel electrolyte. The polymer gel electrolyte is quasi-solid at room temperature, and becomes a

viscous liquid (viscosity: 4.34 mPa·s) at 80 °C compared with the traditional liquid electrolyte (viscosity: 0.91 mPa·s). The much improved stabilities of the device under both thermal stress and soaking with light has never before been seen in DSSCs, and they match the durability criteria applied to solar cells for outdoor use, which makes these devices viable for practical application.

2.2.2 In 2006

The first successful solid-hybrid dye-sensitized solar cells were reported.

To improve electron transport in these solar cells, while maintaining the high surface area needed for dye adsorption, two researchers have designed alternate semiconductor morphologies, such as arrays of nanowires and a combination of nanowires and nanoparticles, to provide a direct path to the electrode via the semiconductor conduction band. Such structures may provide a means to improve the quantum efficiency of DSSCs in the red region of the spectrum, where their performance is currently limited.

On August 2006, to prove the chemical and thermal robustness of the 1-ethyl-3-methylimidazolium tetracyanoborate solar cell, the researchers subjected the devices to heating at 80 °C in the dark for 1000 hours, followed by light soaking at 60 °C for 1000 hours. After dark heating and

light soaking, 90% of the initial photovoltaic efficiency was maintained – the first time such excellent thermal stability has been observed for a liquid electrolyte that exhibits such a high conversion efficiency. Contrary to silicon solar cells, whose performance declines with increasing temperature, the dye-sensitized solar-cell devices were only negligibly influenced when increasing the operating temperature from ambient to 60 °C.

2.2.3 In April 2007

Wayne Campbell at Massey University, New Zealand, has experimented with a wide variety of organic dyes based on porphyrin. In nature, porphyrin is the basic building block of the hemoproteins, which include chlorophyll in plants and hemoglobin in animals. He reports efficiency on the order of 5.6% using these low-cost dyes.

2.2.4 In June 2008

An article published in Nature Materials demonstrated cell efficiencies of 8.2% using a new solvent-free liquid redox electrolyte consisting of a melt of three salts, as an alternative to using organic solvents as an electrolyte solution. Although the efficiency with this electrolyte is less than the 11%

being delivered using the existing iodine-based solutions, the team is confident the efficiency can be improved.

2.2.5 In 2009

A group of researchers at Georgia Tech made dye-sensitized solar cells with a higher effective surface area by wrapping the cells around a quartz optical fiber. The researchers removed the cladding from optical fibers, grew zinc oxide nanowires along the surface, treated them with dye molecules, surrounded the fibers by an electrolyte and a metal film that carries electrons off the fiber. The cells are six times more efficient than a zinc oxide cell with the same surface area. Photons bounce inside the fiber as they travel, so there are more chances to interact with the solar cell and produce more current. These devices only collect light at the tips, but future fiber cells could be made to absorb light along the entire length of the fiber, which would require a coating that is conductive as well as transparent. Max Shtein of the University of Michigan said a sun-tracking system would not be necessary for such cells, and would work on cloudy days when light is diffuse.

2.2.6 In 2010

Researchers at the École Polytechnique Fédérale de Lausanne and at the Université du Québec à Montréal claim to have overcome two of the DSSC's major issues:

- "New molecules" have been created for the electrolyte, resulting in a liquid or gel that is transparent and non-corrosive, which can increase the photovoltage and improve the cell's output and stability.
- At the cathode, platinum was replaced by cobalt sulfide, which is far less expensive, more efficient, more stable and easier to produce in the laboratory.

2.2.7 In 2011

Dyesol and Tata Steel Europe announced in June the development of the world's largest dye sensitized photovoltaic module, printed onto steel in a continuous line.

Dyesol and CSIRO announced in October a Successful Completion of Second Milestone in Joint Dyesol / CSIRO Project. Dyesol Director Gordon Thompson said, "The materials developed during this joint collaboration have the potential to significantly advance the commercialisation of DSSC in a range of applications where performance and stability are essential

requirements. Dyesol is extremely encouraged by the breakthroughs in the chemistry allowing the production of the target molecules. This creates a path to the immediate commercial utilisation of these new materials.

Dyesol and Tata Steel Europe announced in November the targeted development of Grid Parity Competitive BIPV solar steel that does not require government subsidised feed in tariffs. TATA-Dyesol "Solar Steel" Roofing is currently being installed on the Sustainable Building Envelope Centre (SBEC) in Shotton, Wales.

2.2.8 In 2012

Northwestern University researchers announced a solution to a primary problem of DSSCs that of difficulties in using and containing the liquid electrolyte and the consequent relatively short useful life of the device. This is achieved through the use of nanotechnology and the conversion of the liquid electrolyte to a solid. The current efficiency is about half that of silicon cells, but the cells are lightweight and potentially of much lower cost to produce.

2.2.9 In 2013

During the last 5-10 years, a new kind of DSSC has been developed the solid state dye-sensitized solar cell. In this case the liquid electrolyte is replaced by one of several solid hole conducting materials. From 2009 to 2013 the efficiency of Solid State DSSCs has dramatically increased from 4% to 15%. Michael Graetzel announced the fabrication of Solid State DSSCs with 15.0% efficiency, reached by the means of a hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ dye, subsequently deposited from the separated solutions of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 .

First architectural integration at EPFL's new convention center, in partnership with Romande Energie. The total surface will be 300 square meters, in 1400 modules of 50 cm x 35 cm. Designed by artists Daniel Schlaepfer and Catherine Bolle.

Now a day, many researchers group are still conducting series of experiments on DSSCs using different types of dyes. (Aldo, 2008) observed that there are four groups of dyes normally used in fabricating DSSCs namely Natural dyes, Industrial dyes, Organic dyes and Ruthenium-based dyes. He noted that natural dyes give DSSC with the lowest electric energy conversion efficiency of about 1%. This is followed by industrial dyes, organic dyes and finally ruthenium-based dyes which presently give the highest energy conversion efficiency of about 11%. In a bid to increase the

efficiency of DSSC with natural dye which is readily available and at a lower cost, (Bignozzi, 2008) reported that he used an anthocyanin dye extracted from eggplant to fabricate an optimized DSSC and obtained an efficiency of 1.74%. He also fabricated DSSC with Z-907 SSC with Co (DEA) as electron transfer mediator and obtained efficiency of 0.467%.

Waita *et al.* (2006), however, reported that he fabricated DSSCs with ruthenium dye, TiO₂ film and platinum counter electrodes using different film thicknesses and obtained a maximum efficiency of 3.3% on 10µm film thickness on the active area of 0.785cm². (Suri *et al.* 2007) on the other hand reported that he fabricated DSSCs using organic dye (Eosin-Y) with ZnO and Al-doped ZnO (AZO) films. He obtained electric energy conversion efficiency of 1.43% and 0.6% for undoped ZnO and Al-doped ZnO electrodes respectively.

2.2.10 In 2014

Finally, in 2014, a molecularly engineered porphyrin dye, coded SM315, which features the prototypical structure of a donor–p-bridge–acceptor and both maximizes electrolyte compatibility and improves light-harvesting properties. Linear-response, time-dependent density functional theory was used to investigate the perturbations in the electronic structure that lead to

improved light harvesting. Using SM315 with the cobalt(II/III) redox shuttle resulted in dye-sensitized solar cells that exhibit a high open-circuit voltage V_{OC} of 0.91 V, short-circuit current density J_{SC} of 18.1 mA cm⁻², fill factor of 0.78 and a power conversion efficiency of 13%.

2.3 CHALLENGES AND RECOMMENDATIONS ON DSSC

Even though DSSCs have demonstrated their potential for solid-state p-n junction devices with power conversion efficiencies over 11% they are still far from other technologies such as multi-junction collectors where efficiencies over 41% have been registered. These efficiencies differences are vast, so that the main advantage for the technological application of DSSCs should be based on the simplicity of the fabrication and the promise of a low cost technology (Ricardo et al., 2011). However, more research should be undertaken to improve the power conversion efficiencies in order to turn this technology into a very competitive option in worldwide photovoltaic solar cells market

Counter electrode progress has been mainly driven by the replacement of platinum. A key selling point of DSSCs is their low cost. At the current price of 1810\$/g, platinum substitution is an easy way to produce more economical solar cells. Recent examples of substitutes include carbon counter electrodes, metal counter electrodes as well as CoS counter electrodes. One of the advantages of platinum is that it can be applied in very thin films, allowing transparent counter electrodes to be made a valuable feature which may someday be used to allow for tandem cells or solar harvesting windows

Electrolyte solutions have for the most part remained quite unchanged over the past decade. Electrolytes are usually customized according to the valence band and conduction band of the sensitizers used and thus as new dyes keep emerging into the market, so do the electrolyte mixtures. Electrolyte solutions include Iodide and Iodine in Acetonitrile as well as additives such as lithium or pyridines which have been shown to prevent recombination as well as modify the redox potential of the electrolyte solution. Due to the volatile nature of the Acetonitrile electrolyte, there has been a push to use alternative electrolyte solutions including ionic liquids, eutectic melts, water and solid state charge transporters. Although ionic liquids have reached 7% efficiency, they have been shown to be unstable under prolonged thermal stress and light soaking. Eutectic melts have recently reached 8.2% (Arsenault, 2011) which has sparked a flurry of interest in this field.

Future research will have to focus on improving the short-circuit current by extending the light response of the sensitizers in the near-IR spectral region in order to reduce the effect of nonoptimised dark current. It is very important to achieve power conversion in this region as a regular technology since it would be a very remarkable difference in favour of DSSCs.

Several steps towards different dyes combinations, sensitive to different wavelength, should be taken in another effort to improve DSSCs efficiencies. For this reason, research should be carried out to find new and cheaper dyes suitable for this kind of cells, free of high-cost, non-toxic, environmentally friendly and low abundant materials. Design aspects in DSSCs should be drawn to attention since this is another potential advantage that this technology could offer compared to others with higher power conversion efficiencies.

An innovative work involving variations in the transparent electrodes and other components of the cells could be performed with the purpose of obtaining flexible and shape adaptable DSSCs. Hybrid cells based on solid-state inorganic and organic-hole conductors are an attractive option in particular for the flexible DSSCs embodiment. Mesoscopic dye-sensitised cells are well suited for a whole realm of applications ranging from the low-power market to large-scale applications. Their excellent performance in diffuse light gives them a competitive edge over silicon in providing electric power for stand-alone electronic equipment both indoors and outdoors. DSSCs are already being applied in building-integrated PV and this will become a fertile field of future commercial development.

According to Yun (2011), the nano-crystalline semiconductor anode is not only where the sensitizers adhere, but also where the charge transfer occurs. Consequently, it is acknowledgeable that the quality of the semiconductor electrode directly affects the efficiency of DSSC. Reducing charge recombination is the most direct means to improve DSSC efficiency, and the quality of TiO_2 film is one of the most important key. There are four fundamental requirements of the electrode materials: large surface area and roughness, sponge-like nano-crystalline structure with good electronic contact. The anode material structure should allow electrolyte redox couple regenerates the oxide dye and charge should also be able to rapidly inject into the semiconductor. These mechanics will determine the efficiency of the DSSC. TiO_2 electrode is one of the most important key to increase the efficiency because it is where sensitizers load and the electrons transfer happen. The requirements of the TiO_2 film is relate to these mentioned concepts. However, the efficiency and stability of DSSCs do not depend on a single factor. There must be trade off among different factors to improve the performance of DSSCs.

2.4 REVIEW ON ROSELLE (ZOBO)/ TiO₂DSSC

The use of solar cells is increasing very slowly. One of the reasons is that the most commonly used type, made from silicon is quite expensive to manufacture. That is why there has been a great deal of research into alternative solar cells over the past few years to identify a cheaper and more stable source of energy thus the introduction of DSSCs. (udodiri,2010) noted that “DSSCs are extremely promising, because they are made of low-cost materials and do not need elaborate apparatus to manufacture”.

The Roselle (*Hibiscus sabdariffa*) is known as zobo in Nigeria. It is a species of hibiscus native to the old world tropics, used for the production of blast fiber and as an infusion. It is an annual or perennial herb or woody-based subshrub, growing to 2-2.5m (7-8ft) tall. The leaves are deeply 3-5 lobed, 8-15cm(3-6in) long, arranged alternatively on the stems shown in **Plate 1**. The flowers are 8-10cm(3-4in) in diameter, white to pale yellow with a dark red spot at the base of each petal, and have a fleshy calyx at the base, 1-2cm(0.39-0.79in) wide, enlarging to 3-3.5cm(1.2-1.4in), fleshy and bright red as the fruit matures. It takes about six months to mature.



Plate 1: Roselle Plant

In Nigeria, Many researchers group are still conducting series of experiments on TiO_2 -Roselle DSSCs. According to (udodiri,2010),he fabricated the TiO_2 -Roselle DSSCwith incident solar light to electric energy conversion efficiency and fill factor of 0.6% and 56% respectively. Similarly, Baba, et al., (2012) found that the DSSC based on TiO_2 -Roselle generated photocurrent with short-circuit current, $I_{sc} = 0.14\text{mA}$; open-circuit voltage, $V_{oc} = 0.5$; fill factor, $ff = 0.652$ and a photo conversion efficiency of 0.08%. also, Adenike, et al.,(2013)investigate the performance of Hibiscuss sabdariffa (Roselle) and Azardirachta Indica (Nimtree) TiO_2 DSSC with solar energy conversion efficiency; 0.002 % and 0.00017 %, fill factor; 0.739 and 0.4, current density; $4.5\text{mA}/\text{cm}^{-2}$ and $2.5\text{mA}/\text{cm}^{-2}$ and

Voc; 0.0124mV and 0.0118mV respectively. Again, Jude et al., (2013) reports the photocurrent-voltage characteristics of DSSCs fabricated with the anthocyanin-dyed and un-dyed electrodes, he obtained an ; open circuit voltage of (0.33V) and (0.24V), short circuit photocurrent of (2.60mA/cm²) and (0.20mA/cm²), fill factor (0.68) and (0.63) and photoelectric conversion efficiency(0.58%) and (0.03%); respectively. On the other hand, Ahmed et al., (2013) reported an investigation on Hibiscus abdariffadye extracts as natural sensitizers of TiO₂ films for DSSC, he obtained the best overall solar power conversion efficiency and fill factor of 0.033% and 41% respectively, under AM 1.5 irradiation and a maximum current density of 0.17mAcm⁻².

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CHAPTER THREE MATERIALS AND METHOD

3.0 INTRODUCTION

This chapter outlines the materials and procedures for the fabrication of TiO₂-Roselle DSSCs with procedures employed in I-V Characterization of the fabricated TiO₂-Roselle Dye Sensitized Solar cells.

3.1 MATERIALS

Titanium Dioxide TiO₂ (79.89Mw, 99%), isopropanol, ethanol were procured from Tofel Ltd, Kano-Nigeria, Indium tin oxide coated (ITO) glass slide (25mm x 25mm with surface resistivity 10Ω/sq) obtained from Techinstro Ltd-India, silver paste from ENSON Japan Ltd. I/I³ was prepared as based on the Nanolab procedure. All these materials are analytical grade and used as received without any further purification.

3.2 EXPERIMENT

3.2.1 Source and Preparation of Gum Arabic

Gum acacia was obtained from Taura local government, Jigawa state, Nigeria. The samples were pulverized with the aid of mechanical blender (liquidizer). 20g of each pulverized sample was weighed using Adventure OHAUS Electronic weighing balance model AR2740 mixed with 50g of well blended powdered activated carbon soot and boiled with distil water for

3 hours. The extract of the sample were decanted to remove the residual part of the samples as shown in **Plate2**.

3.2.2 Source and Preparation of Roselle (Zobo) Extract

Roselle (Plate 1) was obtained from Gujugu, Jigawa state, Nigeria. The anthocyanin dye used in sensitizing the nanoscale TiO₂ film was extracted from hibiscus sabdariffa which is a common edible plant called Zobo by Nigerians. Dried leaves of Hibiscus Sabdariffa were crushed and boiled in 100ml of distilled water for 25minutes. The residue was then removed and filtered. The resulting extract was centrifuged to remove any solid residue and was used directly as prepared for the construction of DSSC's at room temperature.

3.2.3 Identifying the Conductive Side of The ITO Glass slides

The conductive side of the indium-tin coated oxide (ITO) glass slides was identified by continuity test. The resistance of ITO glass slides was determined using Digital Multimeter Model-DT9205A. The Multimeter was connected across the square edges of the ITO glass slide shown in **plate 3**.

3.2.4 Preparation of Tio₂ Paste

TiO₂ powder as much as 20 grams was transferred it into a beaker then added into it as much as 5 mL of vinegar and Mixed thoroughly until the mixture is uniform and free of lumps, 1-2 drops of gum acacia was added to the solution. The mixture was stirred until evenly distributed.

3.2.5 Cells Fabrication

The DSSCs were fabricated based on Doctor-blade method. Indium tin-coated oxide (ITO) glass plates were cleaned with isopropanol, ethanol, and then deionized water and dried in air. Sellotape was employed as a spacer to control the film thickness and to provide uncoated areas for electrical contact. An equal amount of well blended powdered activated carbon soot was mixed with Anionic surfactant (morning fresh) liquid was used as counter electrode material (carbon paste). The carbon paste which was prepared through Doctor-blading technique was applied at one of the edges of the conducting glass and distributed with a squeegee sliding over the tape-covered edges. The deposition of our counter electrode on indium doped tin oxide (ITO) glass substrate was enabled through the doctor- blading method. Titania paste (Qualikems, Ltd.) was spread over the spacer between the sellotape on the conducting glass substrate using the same Doctor-Blade technique. The TiO₂ coating was then dried in air at room temperature for 10 min and sintered at various temperature ranging from 250-450°C for 30 minutes to remove any organic matter. This process ensures electrical contact between particles and good adhesion to the TCO glass substrate. The thickness of the photoanode film was about 0.07mm and its area was 2 x 2cm². After cooling to 29°C the TiO₂ electrodes were immersed into purified

Roselle juice. After the dye adsorption the films were cleaned with pure ethanol to remove the excess Roselle-dye and dried for 20 minutes. The resulting nanoporous layer made from the sintered particles was stored in a sealed environment to avoid moisture absorption from ambient air. The binder clips was cleaned with ethanol before it was rightly placed on the dyed working electrode. The conductive side of the transparent electrodes was gently placed on top of conducting carbonized side of the counter electrodes. We introduced 0.5ml drops of the electrolyte (Iodide/triiodide) through one of the gap left between the two glasses of **plate 4** by capillary action. Electrical contacts were made by applying the silver paste ((ENSON, Ltd.) on the uncoated areas along the conducting side of electrode.



Plate2: Gum Arabic



Plate 3: continuity test of conductive and non-conductive side of ITO glass slides

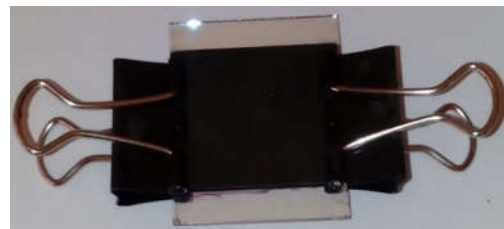
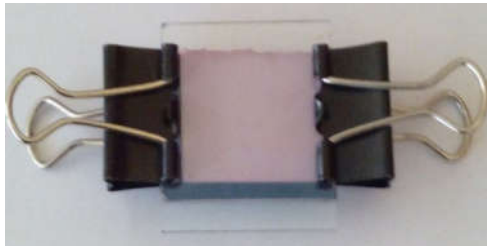


Plate 4: picture of front and back view Titanium Dioxide-Roselle DSSC

3.3 DYE SENSITIZED SOLAR CELL CHARACTERIZATION

3.3.1 Resistivity and conductivity of ITO glass slides

The resistivity and conductivity of the ITO glass slides was measured according to equation (10) and (11). Where R and t are the resistance and the thickness of the ITO glass slides respectively.

$$R = \rho \frac{L}{A} = \rho \frac{L}{W \times t}, \text{ for } L = W (\text{square}) \text{ we have} \quad (9)$$

$$\rho = R \times t \text{ and} \quad (10)$$

$$\sigma = \frac{1}{R \times t} \quad (11)$$

3.3.2 Photo Response of TiO₂ Electrode Surfactant DSSC

The photo response of the TiO₂-Roselle DSSCs fabricated with different surfactant was measured directly using analogue voltmeter (EDM-14, 0-2V) and ammeter (EDM-14, -20-100 μ A) under sunlight and under illumination. The test was conducted by exposing the active surface area of the cell under the sunlight and then under illumination of 100W filament bulb.

3.3.3 Photo Response of Silver Paste TiO₂-Roselle DSSC

The comparative photo response of the TiO₂-Roselle DSSCs fabricated with silver paste and crocodile clips was measured in the same way as in section 3.3.2.

3.3.5 Thickness Of The Film Deposited On The ITO Glass Slides

The thickness of the TiO₂ film deposited was measured using micrometer screw gauge. Each layer was deposited by doctor-blade method and annealed under 400⁰C for 30 minute. Additional layer was deposited on top of the former one.

3.3.6 J-V Characteristics

The performance of the DSSCs were measured using a calibrated AM 1.5 solar simulator Controller (Newport, Oriel instruments, Model: 69922) with a light intensity of 100 mWcm⁻² and a computer controlled digital source meter (Keithley, Model: 2400) at Sheda Science And Technology Complex, Abuja, Nigeria. The I–V measurements were carried out on the TiO₂-Roselle DSSCs after an aging period of seven (7) days. Thermally sealed cells were stored well and applied to electrochemical measurements every seven days in order to study their long term stability. The photoelectrochemical parameters, i.e., the fill factor (FF) and light to-electricity conversion efficiency (η), were calculated based on equation (1) and (2).

CHAPTER FOUR RESULTS AND DISCUSSION

4.0 INTRODUCTION

This chapter gives an outline of the results on the whole work with discussion were necessary. The result was presented in Five segments, the first segment contain the results of resistivity and conductivity of ITO glass slides, the second, third and fourth segments contain the results of Photo Response on TiO₂ Electrode Surfactant DSSC, Photo Response on Silver Paste TiO₂-Roselle DSSC and Results of Thickness of The Film Deposited On ITO Glass Slides. In the fifth segment the results of I-V characterization was presented.

4.1 RESULT OF RESISTIVITY AND CONDUCTIVITY OF ITO GLASS SLIDES

It can be seen that, the measured resistivity and conductivity of various glass slides (A-J) shown in Table 2. The resistance of the glass slides depend on the distance of separation between the two terminals of the multimeter. These result shows that the performance of the dye sensitized solar cell depends on the overlap area between the two conductive glass slides.

4.2 RESULTS OF PHOTO RESPONSE ON TiO₂ ELECTRODE SURFACTANT DSSC

The effect of surfactant was observed in Table 3, in which the vinegar + gum acacia happened to be the best surfactant with overall short circuit density and open circuit voltage of 0.41V and 80.06 μ A respectively.

4.3 RESULT OF PHOTO RESPONSE ON SILVER PASTE TiO₂-ROSELLE DSSC

Electrical contact happen to be one of the major problem of DSSC due to its photosensitivity properties, however silver paste was used to overcome this challenge for fixed electrical contact, Table 4 shows the average effect of silver paste as a counter electrode material.

Table 2: Measured Resistivity And Conductivity Of Various ITO Glass Slides Of 1.1mm Thickness

Sample	Resistance (Ω)	Resistivity (Ωm)	Conductivity (Ωm) ⁻¹
A	67.7	0.07447	13.42823
B	67.6	0.07436	13.44809
C	67.5	0.07425	13.46801
D	67.3	0.07403	13.50804
E	58.9	0.06479	15.43448
F	57.7	0.06347	15.75548
G	57.0	0.0627	15.94896
H	54.2	0.05962	16.7729
I	53.3	0.05863	17.05611
J	51.4	0.05654	17.68659

Table 3: Average Current-Voltage Obtained At 400⁰c Roselle-Dye Sensitized Solar Cell For Various Surfactant Of TiO₂Films.

Surfactant	V _{sun} (V)	V _{illum} (V)	I _{sun} (μA)	I _{illum} (μA)
Dilute nitric acid	0.1	0.05	30.00	10.07
Vinegar	0.13	0.09	44.80	16.30
Dilute nitric acid + morning fresh	0.18	0.07	50.21	21.70
Vinegar + morning fresh	0.17	0.04	35.10	09.60
Dilute nitric acid + swanglue	0.24	0.05	0	0
Vinegar + swanglue	0.27	0.06	0	0
Dilute nitric acid + gum acacia	0.30	0.10	65.05	21.12
Vinegar + gum acacia	0.41	0.18	80.06	22.87

4.4 RESULT OF THICKNESS OF THE FILM DEPOSITED ON ITO GLASS SLIDES

From Table 5, when referring to the TiO₂ layer thickness, the short circuit current density, open circuit voltage decreases with increase in the thickness of the layer.

Table 4: Average Current-Voltage Obtained For The Effect Of Silver Paste TiO₂-Roselle Dye Sensitized Solar Cell.

sample	V _{sun} (V)	V _{illum} (V)	I _{sun} (μA)	I _{illum} (μA)
DSSC without silver paste	0.40	0.19	78.00	23.07
DSSC with silver paste	0.43	0.25	86.80	30.50

Table 5: Current-Voltage Obtained At 400⁰C TiO₂-Roselle Dye Sensitized Solar Cell For Various Thickness Of TiO₂ Films.

Sellotape layer	Thickness (mm)	Average V _{oc} (V)	Average I _{sc} (μA)
1	0.035	0.27	95.50
2	0.07	0.18	75.6
3	0.105	0.14	40.02
4	0.14	0.01	24.00

4.5 RESULT OF J-V CHARACTERISTICS ON TiO₂-ROSELLE DSSC

4.5.1 Effect of Degradation of Electrolyte on J-V Performance of TiO₂-Roselle DSSC

The J-V curves of the DSSCs fabricated at various temperature were recorded over a period of 3 weeks. The photocurrent density-voltage (J-V) curves obtained at a light intensity of 100 mWcm⁻² under a standard global Air Mass (AM) 1.5 irradiance are shown in Figure 3-17. In this work, the DSSCs Fabricated at 400°c shows the optimum energy conversion efficiency as shown in Figure 12, this can be explain by considering the charge transport and charge recombination effects of DSSC. The cell efficiency was measured every seven days after well storage in the dark at room temperature. The normalized efficiency of the DSSCs annealed at 250-300°c decreased gradually and retained ≈96% of its initial value after 3 weeks, whereas, the DSSCs based on 350-400°c retained ≈98% of its initial value. In the third week there exist no open circuit voltages for all the five samples as shown in Figure 5, 8,14 and 17. This is due to the electrolyte uptake, less retain capacity or gradual evaporation/leakage of the electrolyte etc. Thus, the durability of the DSSC is decreasing with time.

It's obviously seen that the electrical properties of TiO_2 -Roselle Dye Sensitized solar Cells tested under various temperature conditions degrade with time, in which the electrical properties of TiO_2 -Roselle Dye Sensitized solar Cells tested for the first week provide the optimum J-V characteristics. The same samples was tested in the second and third week, it shows a very low performance and shows no experimental open circuit voltage. This is because the electrolyte is drying with time and the cell can no longer work without the electrolyte.

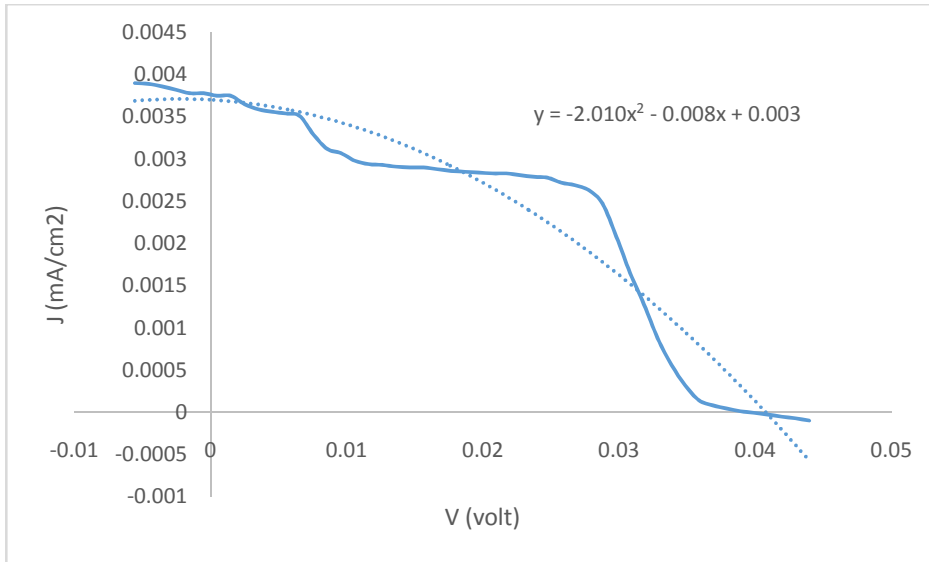


Figure 3: J-V curves of TiO₂-Roselle DSSC annealed at 250⁰C for the 1st week

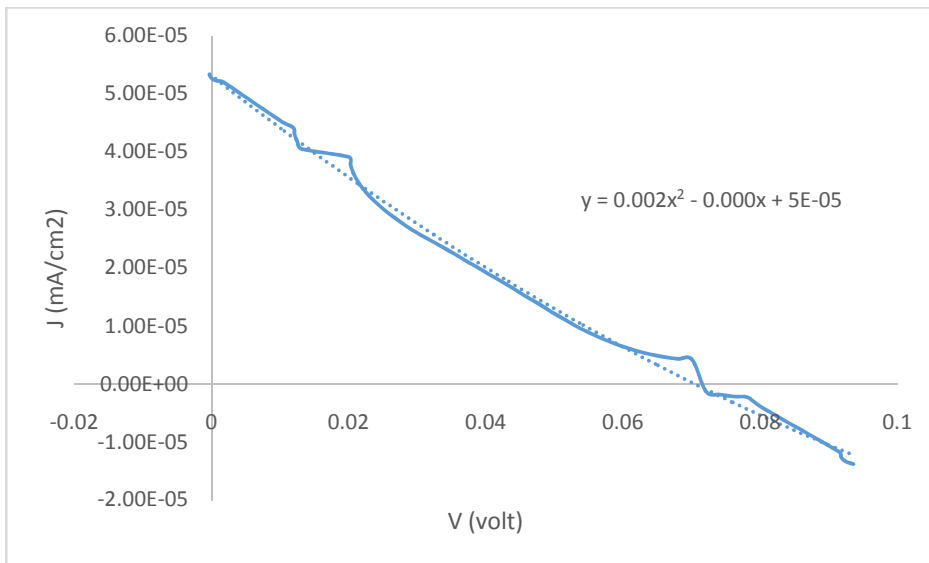


Figure 4: J-V curves of TiO₂-Roselle DSSC annealed at 250⁰C for the 2nd week

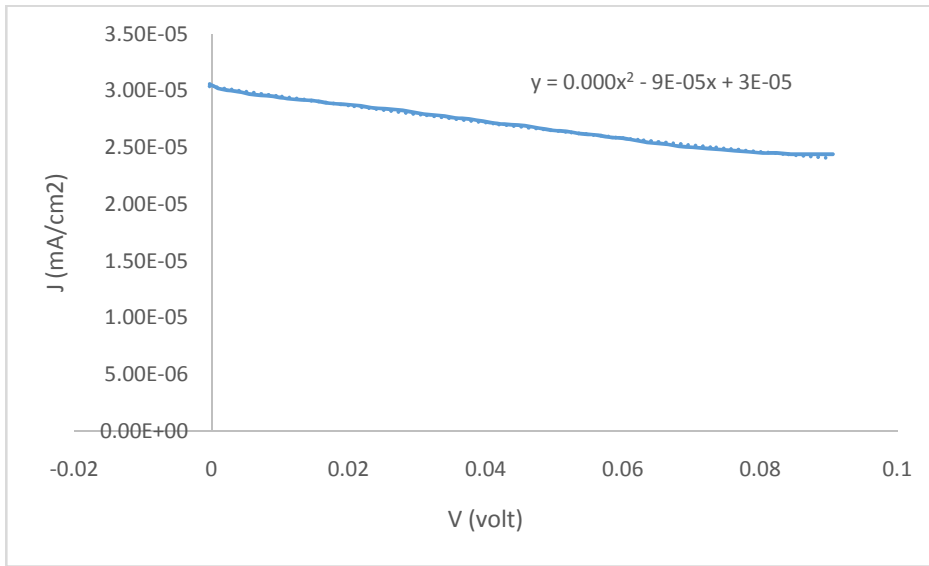


Figure 5: J-V curves of TiO₂-Roselle DSSC annealed at 250⁰C for 3rd week

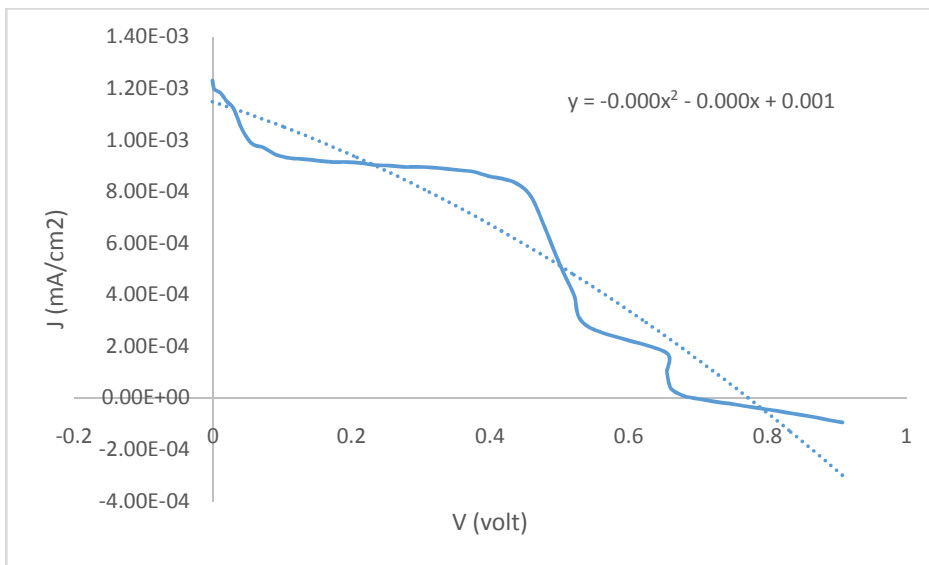


Figure 6: J-V curves of TiO₂-Roselle DSSC annealed at 300⁰C for 1st week

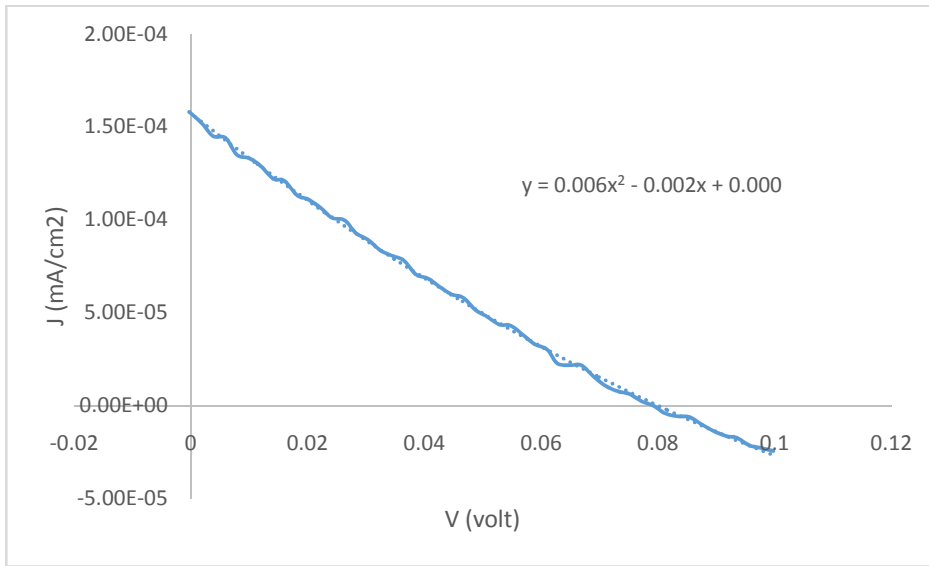


Figure 7: J-V curve of TiO₂-Roselle DSSC annealed at 300°C for 2nd week

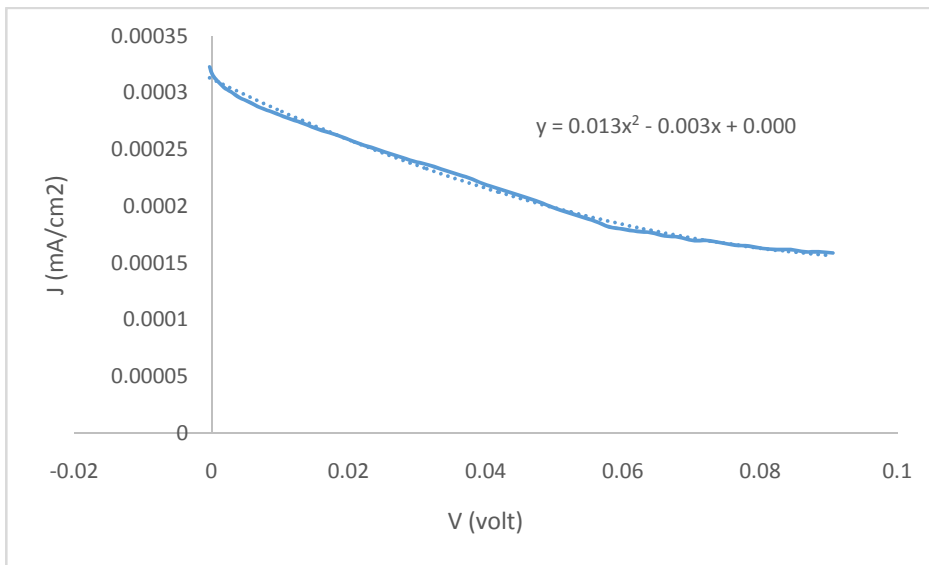


Figure 8: J-V curve of TiO₂-Roselle DSSC annealed at 300°C for 3rd week

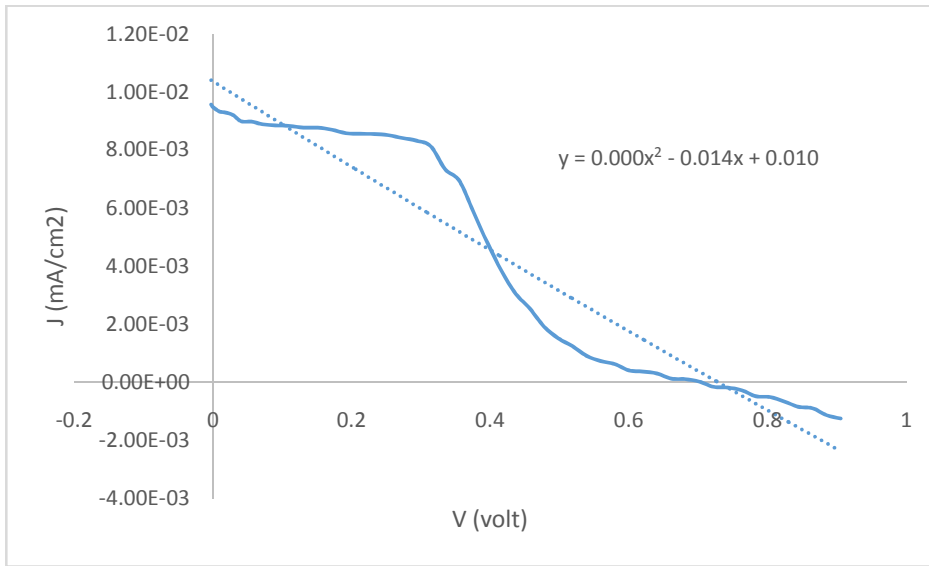


Figure 9: J-V curve of TiO₂-Roselle DSSC annealed at 350⁰c for 1st week

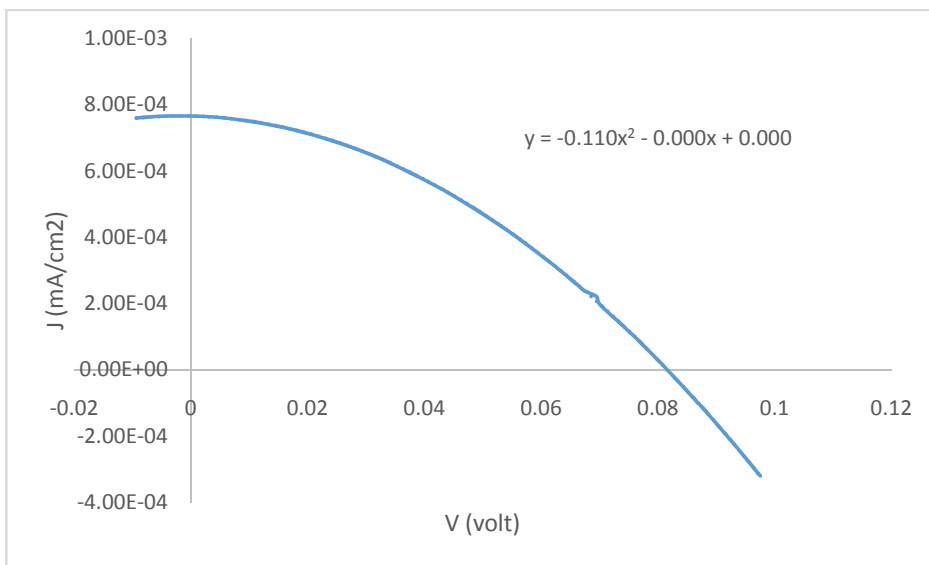


Figure 10: J-V curve of TiO₂-Roselle DSSC annealed at 350⁰C for 2nd week

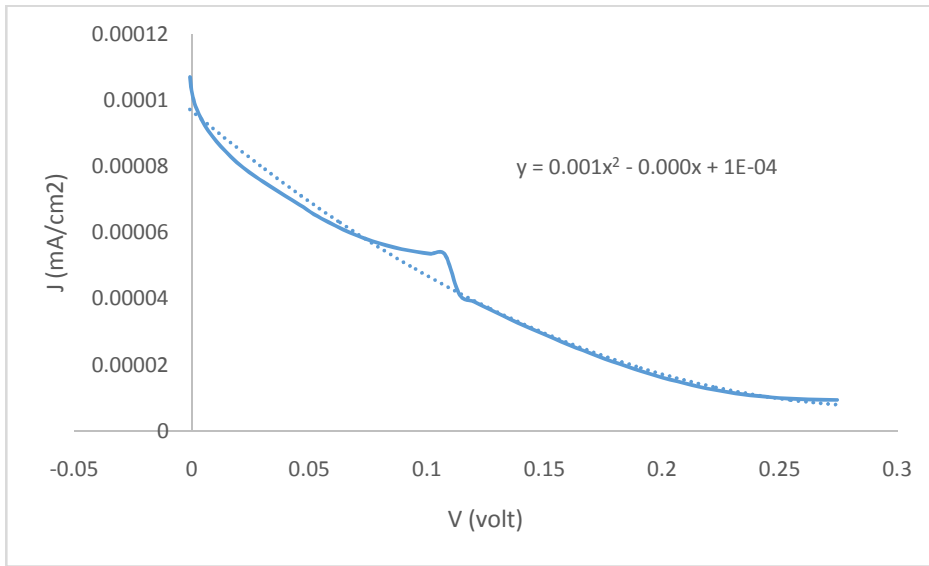


Figure 11: J-V curve of TiO₂-Roselle DSSC annealed at 300⁰C for 3rd week

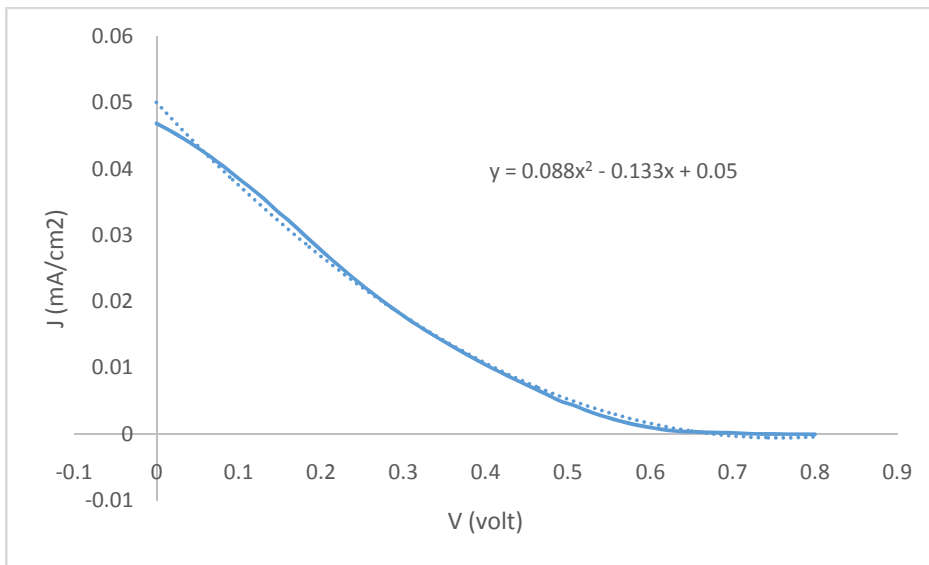


Figure 12: J-V curve of TiO₂-Roselle DSSC annealed at 400⁰C for 1st week

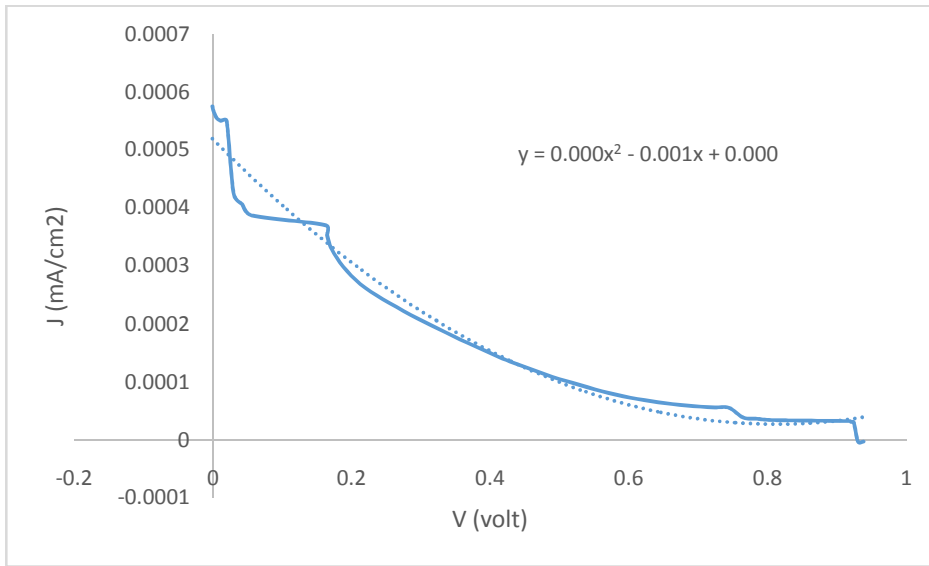


Figure 13: J-V curve of TiO₂-Roselle DSSC annealed at 400°C for 2nd week

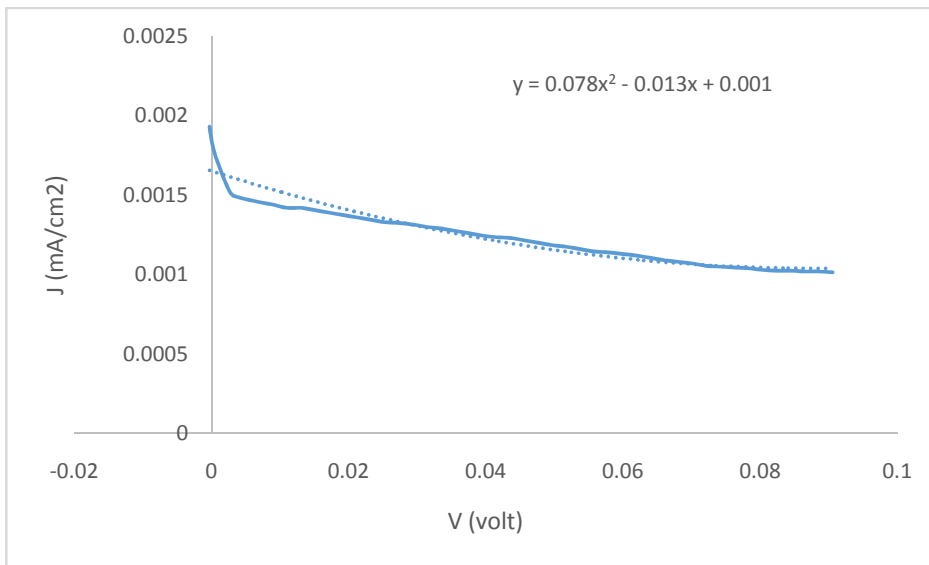


Figure 14: J-V curve of TiO₂-Roselle DSSC annealed at 400°C for 3rd week

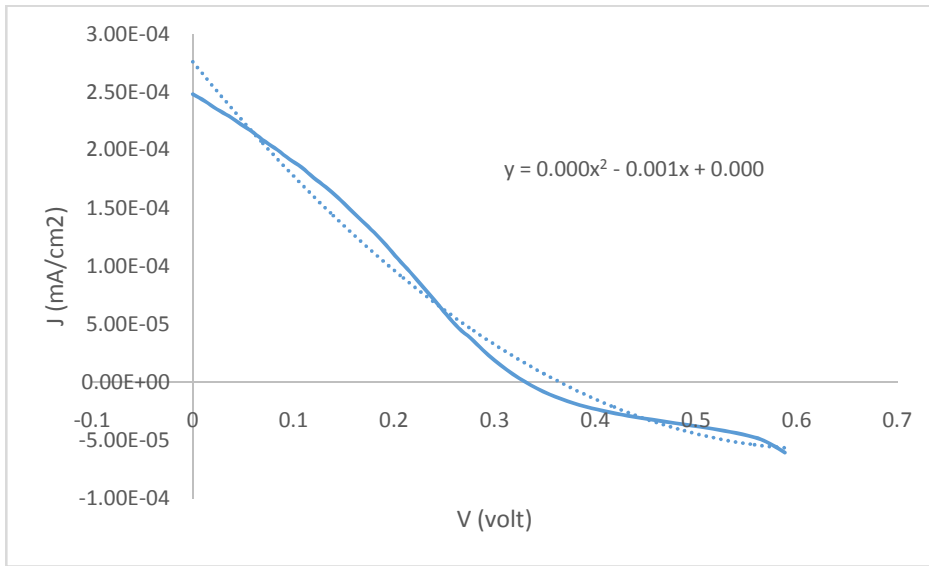


Figure 15: J-V curve of TiO₂-Roselle DSSC annealed at 450°C for 1st week

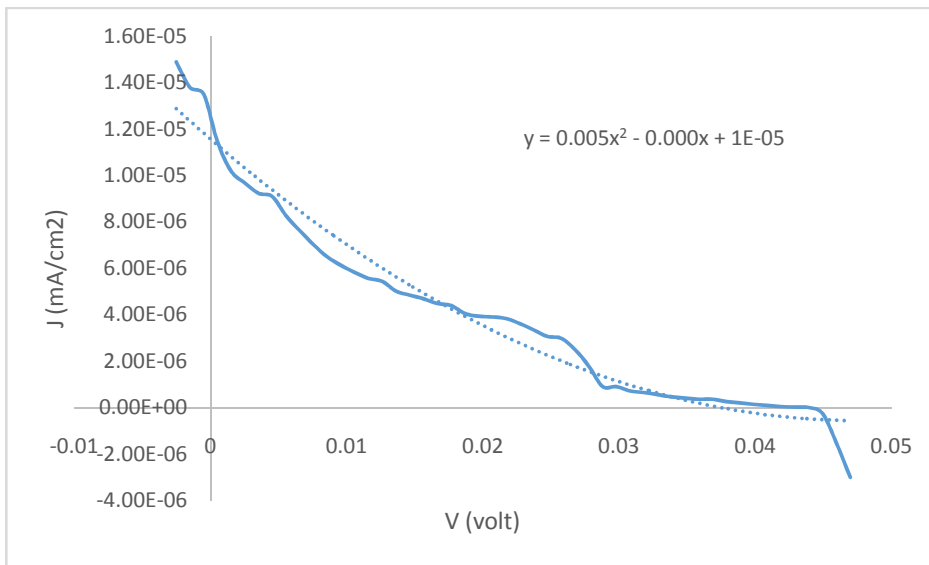


Figure 16: J-V curve of TiO₂-Roselle DSSC annealed at 450°C for 2nd week

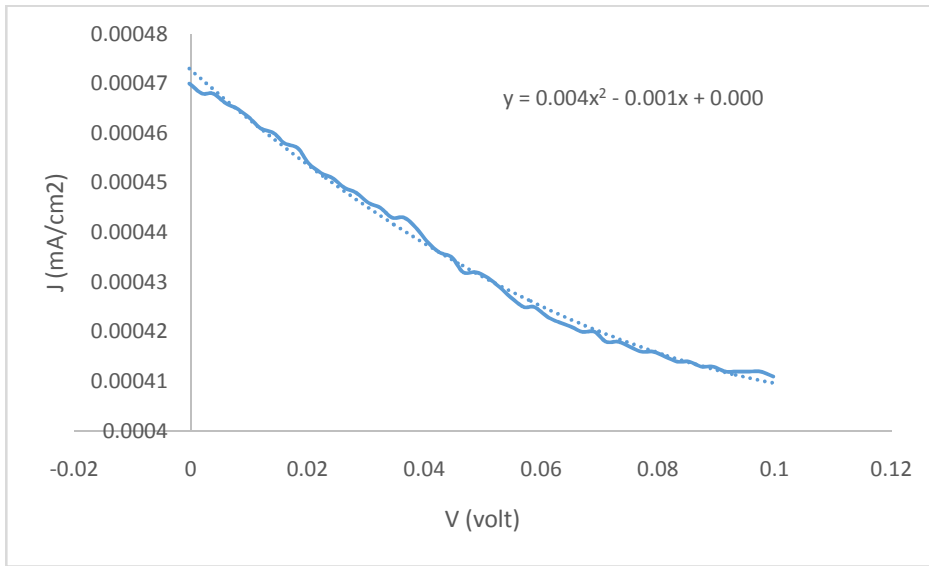


Figure 17: J-V curve of TiO₂-Roselle DSSC annealed at 300⁰C for 3rd week

4.5.2 J-V Output Parameters On TiO₂-Roselle DSSC

From Table 6, 7 and 8 it was observed that sample which annealed at 400°C for 30 minutes gives the optimum value of J-V compared to other samples. In this case, fill factor content after annealing at 250-300°C generated maximum value of 0.45, this is because the gum acacia reaches its melting point at 250°C. Since the fill factor (FF) is inversely proportional to the product between short circuit current density and open circuit voltage this parameters remain almost constant for the whole series (Ricardo et al., 2011). On the other hand, Rangga et al. (2011), With Ruthenium Complex (dye solution) had fill factor of 0.69 at 200°C. Again, Baba et al. (2012), used flame of the forest dye, had fill factor of 0.65 (this was achieved using screen printing method) and (Alu et al., 2014) used Ruthenium 620-1H3TBA (solaronix) had fill factor of 0.47. While in this work the TiO₂-Roselle Dye Sensitized solar Cell annealed at 250-300°C has a 0.45 fill factor which is closed to the recent work. Also Adenike, et al., (2013) investigate the performance of Hibiscuss sabdariffa (Roselle) and Azardirachta Indica (Nimtree) TiO₂ DSSC with fill factor, 0.739 and 0.4, respectively.

However, In this research work the optimum energy conversion efficiency after annealing at 400°C generated its maximum value of, 0.005% (Table

6), which is reasonably good when compared with work of Adenike, et al.,(2013) investigate the performance of Hibiscuss sabdariffa (Roselle/Zobo) and Azardirachta Indica (Nimtree) TiO₂ DSSC with solar energy conversion efficiency; 0.002 % and 0.00017 %.

Table 6: Summarized Results Titanium Dioxide-Roselle (Zobo) Dye

Sensitized Solar Cells Output Parameters For The First Week

Samples Temp.(°c)	Exp. V_{oc} (v)	Theo. V_{oc} (v)	Exp. J_{sc} ($\mu A/cm^2$)	Theo. J_{sc} ($\mu A/cm^2$)	Exp. P_{max} ($\mu W/cm^2$)	Theo. P_{max} ($\mu W/cm^2$)	Exp. FF	Theo. FF	Exp. η (%)	Theo. η (%)
250	0.039	0.041	3.75	3.70	0.073	0.056	0.45	0.37	0.000073	0.000056
300	0.68	0.74	1.20	1.1	0.364	0.245	0.45	0.30	0.00036	0.00025
350	0.70	0.73	9.41	10.4	2.55	1.838	0.39	0.24	0.0026	0.0018
400	0.78	0.83	45.8	50	5.643	5.529	0.16	0.13	0.0056	0.0055
450	0.32	0.41	0.242	0.3	0.00233	0.024	0.03	0.09	0.0000023	0.000024

Table 7: Summarized Results of Titanium Dioxide-Roselle (Zobo) Dye

Sensitized Solar Cell For The Second Week

Samples Temp.(°c)	Exp. V_{oc} (v)	Theo. V_{oc} (v)	Exp. J_{sc} ($\mu A/cm^2$)	Theo. J_{sc} ($\mu A/cm^2$)	Exp. P_{max} ($\mu W/cm^2$)	Theo. P_{max} ($\mu W/cm^2$)	Exp. FF	Theo. FF	Exp. η (%)	Theo. η (%)
250	0.07	0.07	0.0524	0.05	0.000742	0.000757	0.22	0.22	0.00000079	0.00000076
300	0.077	0.11	0.1524	0.2	0.00285	0.004503	0.24	0.21	0.0000029	0.0000045
350	0.082	0.083	0.765	0.8	0.02237	0.0253	0.38	0.38	0.000024	0.000025
400	0.923	0.71	0.565	0.5	0.0622	0.0613	0.11	0.17	0.000062	0.000061
450	0.044	0.065	0.0115	0.01	0.0000833	0.0000572	0.17	0.20	0.00000083	0.00000057

Table 8: Summarized Results of Titanium Dioxide-Roselle (Zobo) Dye Sensitized Solar Cell Output Performance For The Third Week

Sample s	Temp.(°c)	Exp. V_{oc} (v)	Theo. V_{oc} (v)	Exp. J_{sc} ($\mu A/cm^2$)	Theo. J_{sc} ($\mu A/cm^2$)	Exp. P_{max} ($\mu W/cm^2$)	Theo. P_{max} ($\mu W/cm^2$)	Exp. FF	Theo. FF	Exp. η (%)	Theo. η (%)
250	Not exist	0.225	0.0304	0.03	0.00221	0.00213	0.0027	Not exist	0.31	0.000022	0.0000021
300	Not exist	0.109	0.314	0.3	0.0144	0.0127	0.0129	Not exist	0.39	0.000014	0.000013
350	Not exist	0.125	0.468	0.5	0.04103	0.0439	0.0439	Not exist	0.70	0.000041	0.000044
400	Not exist	0.088	1.78	1.7	0.0919	0.0987	0.0987	Not exist	0.66	0.000091	0.000099
450	Not exist	0.583	0.0992	0.1	0.00574	0.00038	0.00038	Not exist	0.0065	0.0000057	0.00000038

4.5.3 Effect Of Annealing Temperature On Output parameters Of TiO₂-Roselle DSSC

It was observed that, the higher energy conversion efficiency and maximum power content generated increased with increased in annealing temperature from 250°C-400°C, and fall at 450°C as shown in Figure 18-29 (experimental and theoretical legends represented by series1 and series2). The measurement from each sample sometimes gives a very wide deviation value. This can happen because the surface of the TiO₂ is not homogeneous and at any temperature higher than 400°C the TiO₂ slowly turns from white brown to dark brown and it turns black at 500°C above, it happen due to the presence of Gum acacia in the TiO₂ paste.

The TiO₂-Roselle Dye Sensitized solar Cell electrical properties such as J_{sc} and V_{oc} are very important parameters. Figure 18-29 showing the variation of J_{sc} , V_{oc} , P_{max} , Fill factor and energy conversion efficiency plotted against the annealing Temperature of both the Experimental and Theoretical values, it can be seen that each graph has similar trend. Each graph increased and reach its maximum value at 400°C. It is seen that the annealing temperature will affect the electrical properties of TiO₂-Roselle Dye Sensitized solar Cell.

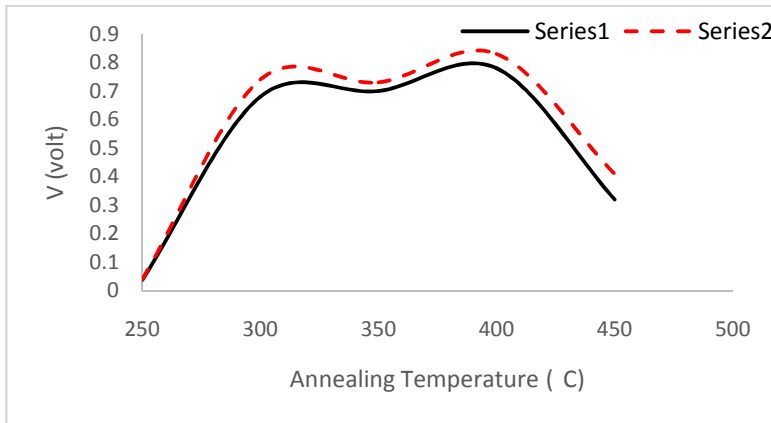


Figure 18: Variation of Output Voltage vs Annealing Temperature for 1st week

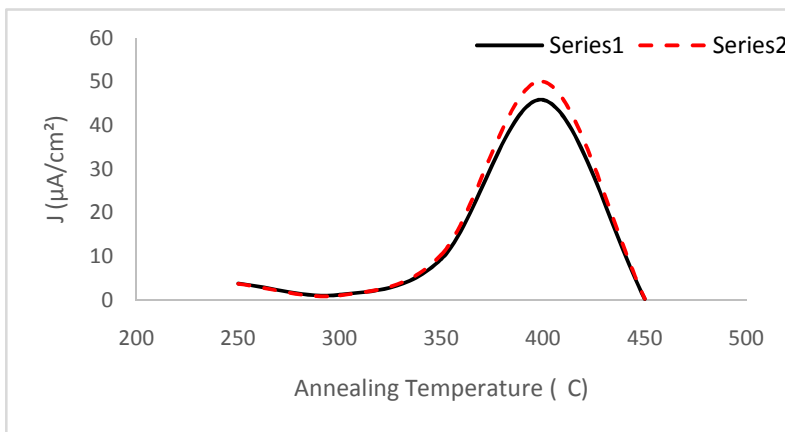


Figure 19: Variation of Output Current Density vs Annealing Temp for 1st week

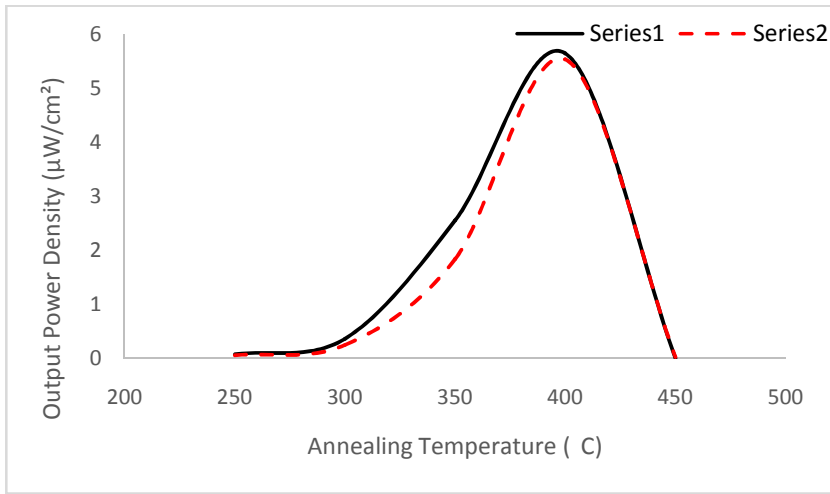


Figure 20: Variation of Output Power Density vs Annealing Temperature for 1st week

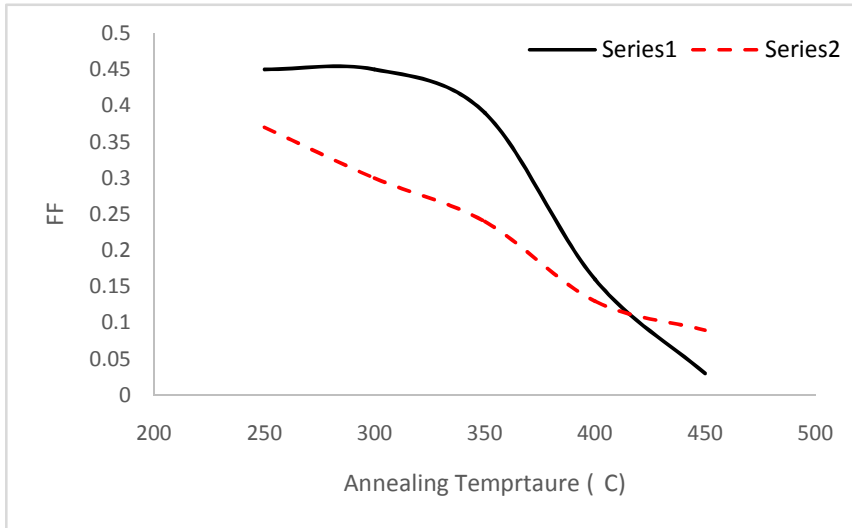


Figure 21: Variation of Fill Factor vs Annealing Temperature for the 1st week

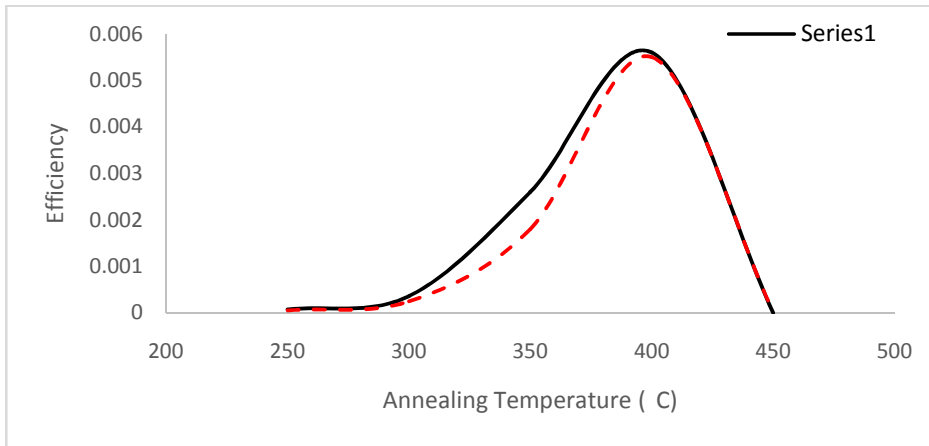


Figure 22: Variation of Energy Conversion Efficiency vs Annealing Temp for 1st week

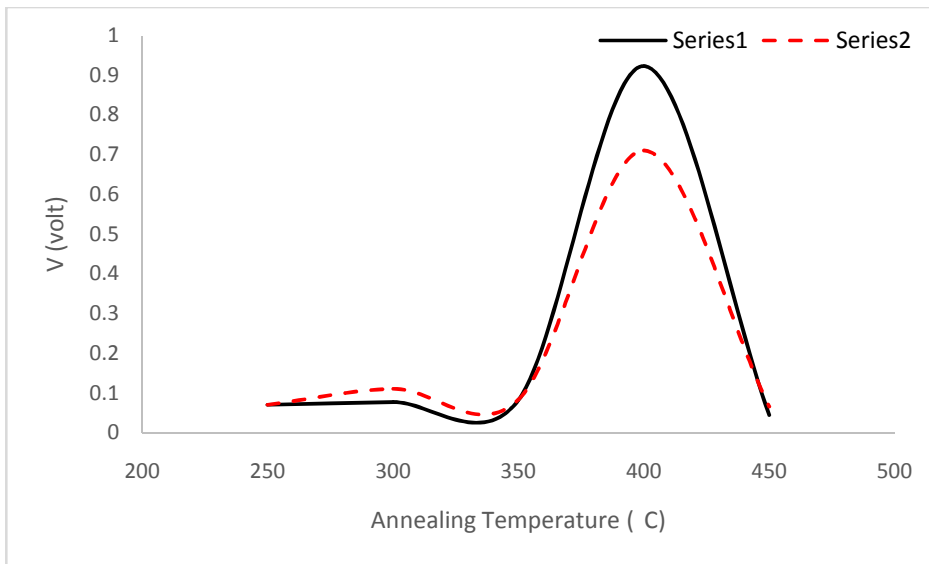


Figure 23: Variation of Output Voltage vs Annealing Temperature for 2nd week

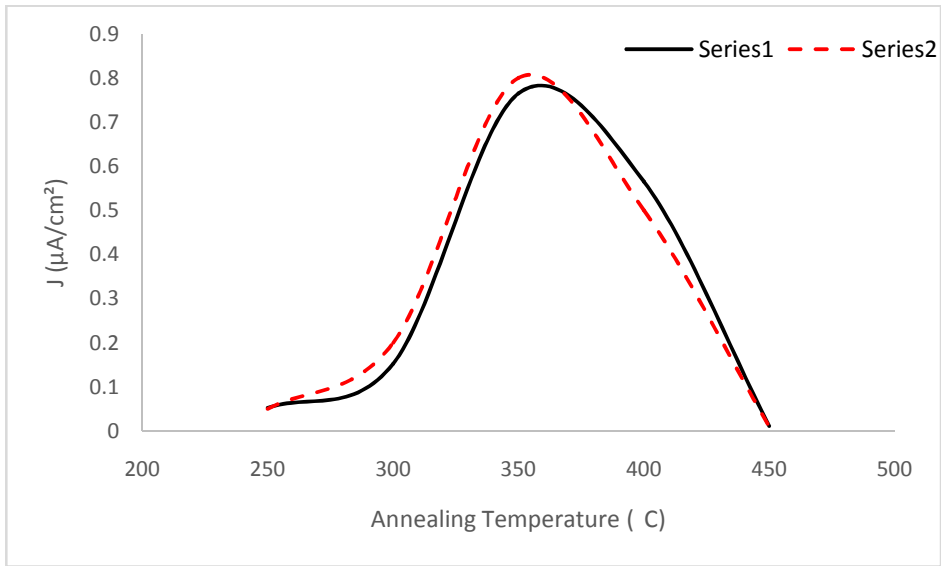


Figure 24: Variation of Output Current Density vs Annealing Temperature for 2nd week

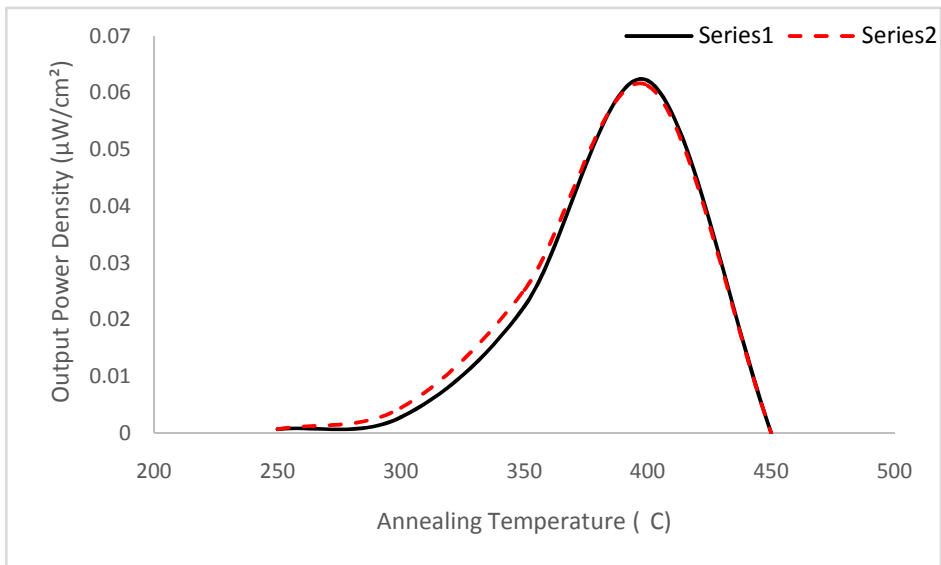


Figure 25: Variation of Output Power Density vs Annealing Temperature for 2nd week

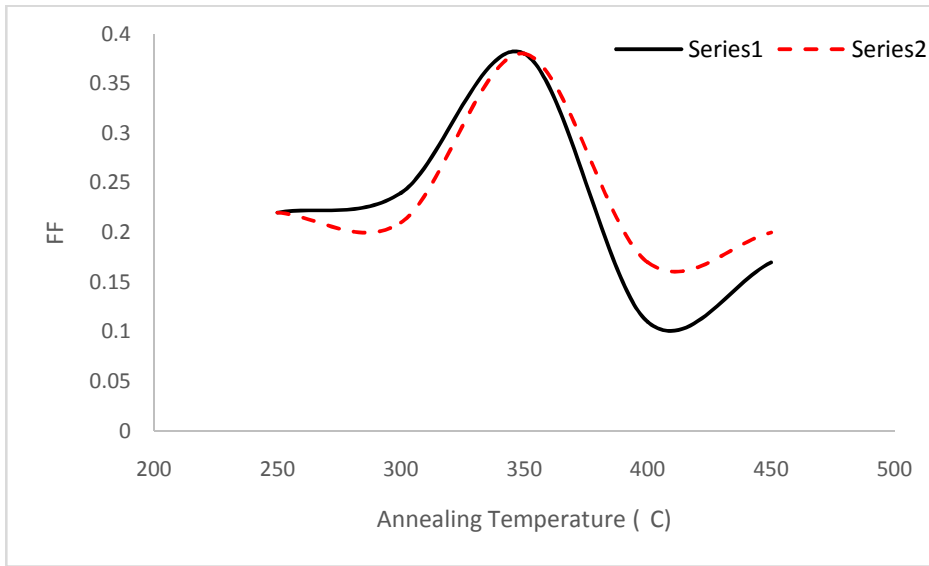


Figure 26: Variation of Fill Factor vs Annealing Temperature for 2nd week

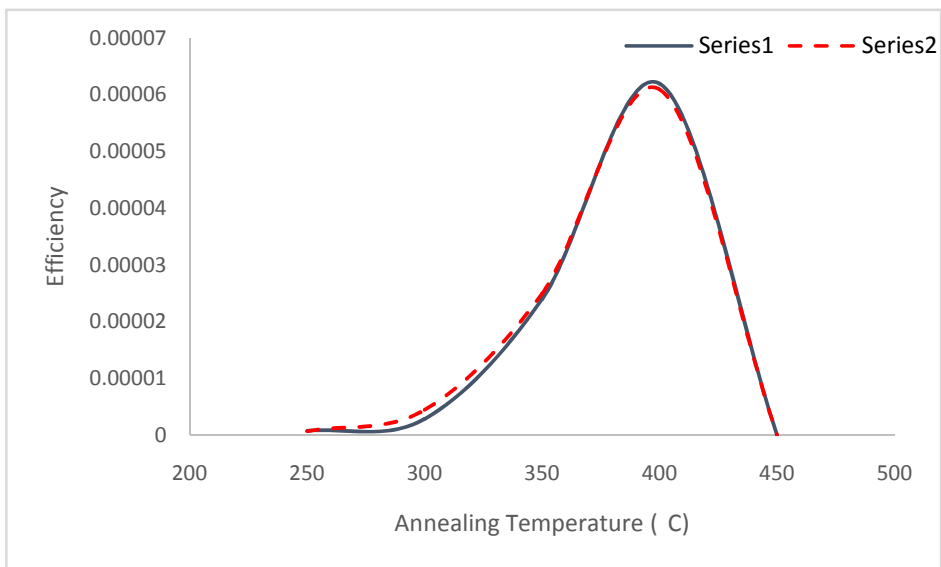


Figure 27: Variation of Energy Conversion Efficiency vs Annealing Temp. for 2nd week

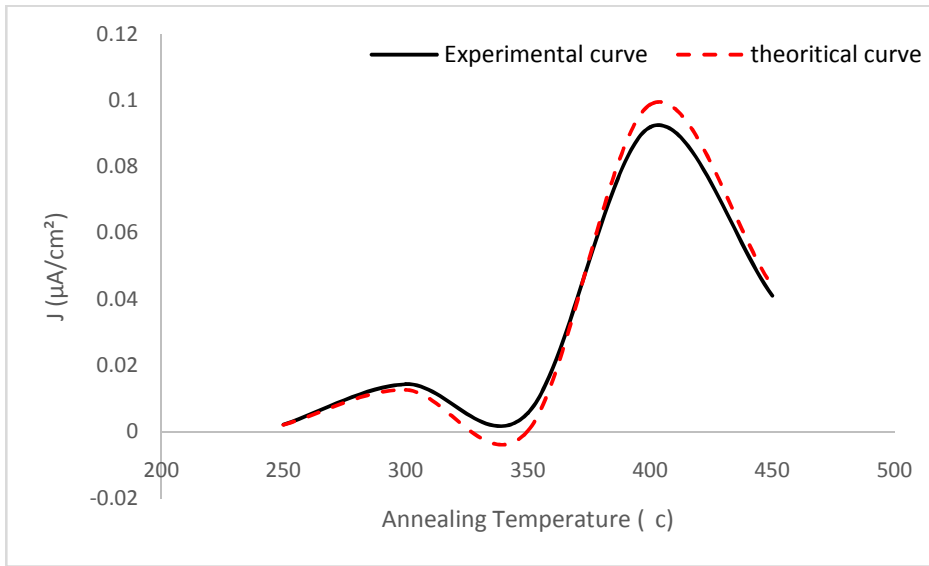


Figure 28: Variation of Output Current Density vs Annealing Temperature for 3rd week

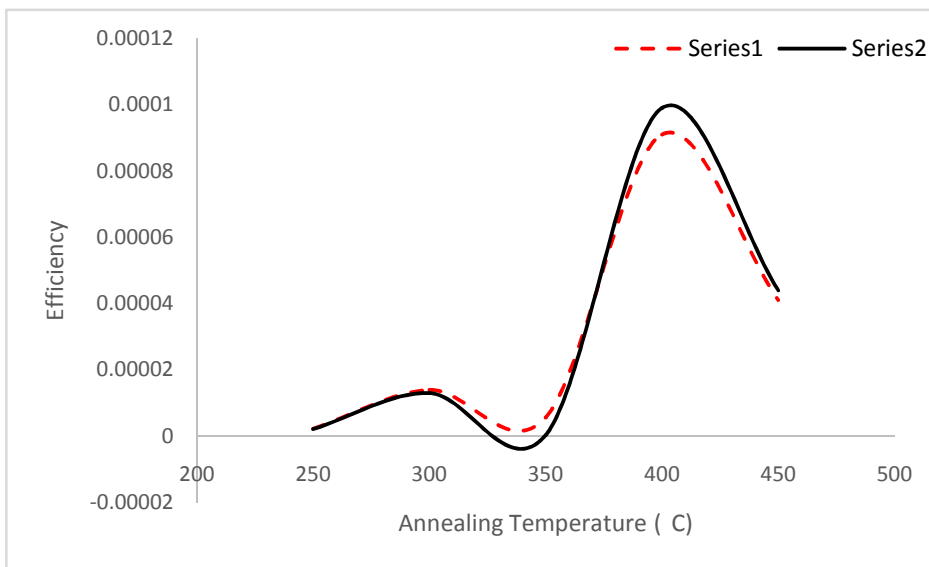


Figure 29: Variation of Energy Conversion Efficiency vs Annealing Temp. for 3rd week

CHAPTER FIVE SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.0 INTRODUCTION

This chapter presents a summary of the research work as well as the conclusion from the results obtained.

5.1 SUMMARY

Dye sensitized solar cell consists of two conductive glasses and sandwiched between; nanoscale titanium dioxide, dye and electrolyte. Dye is adsorbed on the titanium dioxide when it absorbs sunlight its electron will transit from ground state to the excited state then injected into the conductive layer of the titanium dioxide and the loop finally form current. The electrolyte is mainly to carry out the redox reaction. The working principle of dye sensitized solar cell is to convert solar energy into electricity.

Even though standard dye sensitized solar cells have a reasonably simple structure, their ability to convert solar energy into electrical currents is governed by a number of complex interface reactions. Although DSSCs have demonstrated their potential for solid-state p-n junction devices with power conversion efficiencies over 11% they are still far from other technologies such as multi-junction collectors where efficiencies over 41%

have been registered. These efficiencies differences are vast, so that the main advantage for the technological application of DSSCs should be based on the simplicity of the fabrication and the promise of a low cost technology (Ricardo et al., 2011). The reaction with the lowest overall efficiency effectively determines the overall device efficiency. To achieve general acceptance as a viable alternative to silicon solar cells, DSSCs must achieve higher performance.

The semiconductor layer in a DSSC is typically comprised of a nano-structured metal oxide, most often TiO_2 . Properties of a TiO_2 layer, including the particle sizes, porosity, electrical and optical are among the most significant determiners of device performance. These properties affect the amount of photosensitive dye that can be loaded onto the layer and also the conductivity of the layer. Of the many methods to deposit TiO_2 films, Blade-method offers potential gain because it require less and cheap materials over the deposition process and of the resulting characteristics of deposited TiO_2 films.

Based on the I-V characterized properties of the TiO_2 -Roselle dye sensitized solar cell and the corresponding effects on its performance, an increase in surface area overlap between two conductive was associated with a positive increase in performance of the fabricated TiO_2 -Roselle dye

sensitized solar cell also an increase in the annealing temperature is associated with increase in the performance of the device. Increasing the thickness of TiO₂ paste layers deposited on the ITO glass slides correlated with decrease in the performance of the device.

5.3 CONCLUSION AND RECOMMENDATIONS

Titanium Dioxide-Roselle (Zobo) Dye sensitized Solar Cells was successfully fabricated the difference in annealing temperature can result that the DSSC fabricated at 400⁰ is better than those fabricated at 250⁰C, 300⁰C, 350⁰C and 450⁰c over the period of three weeks, experimental investigation for different annealing temperatures produced an open circuit voltage, V_{oc} of 0.78V, 0.039V, 0.68, 0.70 and 0.32 respectively, their short circuit current density, J_{sc} of 45.8μAcm⁻², 3.75μAcm⁻², 1.20μAcm⁻², 9.41μAcm⁻² and 0.242μAcm⁻² respectively, fill factor, FF of 0.16,0.45,0.45, 0.39 and 0.03 respectively and energy conversion efficiency, η of 0.0055, 0.000056, 0.00025, 0.0018 and 0.000024 respectively. From these results it shows that the Titanium dioxide-Roselle (Zobo) Dye Sensitized Solar Cell (DSSC) fabricated at 400⁰c perform better compared to the samples fabricated at 250⁰c, 300⁰c, 350⁰c and 450⁰c. Based on the available experimental data, it can be seen that annealing temperature has important role on dye sensitized solar cell performance. The value of electrical

properties increases as the value of annealing temperature increase. The annealing temperatures higher than 400°C caused the value of electrical properties decrease. These occurred because of TiO₂ thin layer completely distorted, since it undergoes thermal degradation on the samples. This condition can cause poor adhesion of TiO₂ deposition, which resulting low dye absorption and reducing electrical-network between the particles. The normalized efficiency of the DSSCs annealed at 250-300°C decreased gradually and retained ≈96% of its initial value after the period of three weeks, whereas, the DSSCs based on 350-400°C retained ≈98% of its initial value. In the third week there exist no open circuit voltages. This is due to the electrolyte uptake, less retain capacity or gradual evaporation/leakage of the electrolyte etc. Thus, the durability of the DSSC is decreasing with time.

In this research, the optimum efficiency of 0.0055% was achieved. However, this efficiency may appear to be low for any practical application, the cell performance is comparable to similar low-cost DSSC technology available today. It was suggested good efficiency could be achieved by using different methods like screen printing, inkjet printing methods. Perhaps vinegar happened to be the best surfactant throughout this experiment. Recent proposition for DSSC that incorporates a barrier

such as ZnO, MgO as shell between the dye and the TiO₂ layer may greatly increase the efficiency of the cell as the core-shell technology reduces recombination of electron and oxidized dye molecule.

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