

Comparison of titania and europium tellurium oxide semiconductors in the use of dye- sensitised solar cells

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ABSTRACT

Energy demand is increasing rapidly every year due to the technological growth occurring across the globe. Photovoltaics are among the preferred methods to answer this ever increasing energy demand. Although photovoltaics are so highly preferred, there are still numerous drawbacks needed to be solved before it can be accepted as the main solution for energy production. Even if photovoltaics is not directly contributing to pollution by only harvesting solar energy, it still is a costly production process, encompassing expensive construction materials, and low efficiencies as well as costly energy storage methods.

Dye-sensitised solar cells are one of the photovoltaic technologies studied due to their cheap production process in comparison to its silicon solar cell counterpart. In this paper, characteristics of TiO_2 dye-sensitised solar cells are studied and compared to europium tellurium oxide dye-sensitised solar cells (DSSCs). The reason for this comparison is to mainly compare dark current production between the two types of dye-sensitised solar cells. Promising results have been seen when using Eu(II)TeO_6 as the semiconductor.

TiO_2 DSSCs have demonstrated a loss of max power output (P_m) of 99.6 % when illumination was halted, whereas Eu(II)TeO_6 DSSCs held the P_m above 80 % and even demonstrating a P_m while utilising pure dark current that is 35 % higher than the P_m obtained during illumination. While Eu(II)TeO_6 has exhibited this reoccurring increase in performance without illumination, it was also seen that when decreasing the particle size of Eu(II)TeO_6 , resulted in an increase of current produced. It has been seen that the smaller particle size Eu(II)TeO_6 obtained an increase in dark current as much as double the dark current produced before being illuminated. Eu(II)TeO_6 DSSCs with a particle size of 9.06 μm has been seen to be heavily affected by an increase in voltage whilst the Eu(II)TeO_6 DSSCs with a particle size of 30.07 μm were less affected by the increase in bias. When continuously illuminating the TiO_2 DSSCs for 5 minutes, it was seen that no P_m or efficiency could be calculated after illumination, because there was no current present the moment the voltage increased ($V_{oc} < 0.001 \text{ V}$) however, the Eu(II)TeO_6 DSSCs were able to produce a P_m as well as exhibit cell efficiency without being illuminated. All three types of DSSCs (TiO_2 , Eu(II)TeO_6 and Eu(III)TeO_6) were constructed by using identical components such as; N719 as the sensitizer, 0.5 lithium iodide and 0.05 M iodine solution in acetonitrile as the electrolyte and scotch tape used as the spacer (60 μm thick).

Even though Eu(II)TeO_6 exhibited a unique characteristic that is not present in TiO_2 , it still only produces a small fraction of current density when compared to the standard TiO_2 generally used in dye-sensitised solar cells.

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NOMENCLATURE

Table 1. Table of symbols.

Symbol	Description	Units
Symbols		
V_{oc}	Open circuit voltage	V
P_m	Max power produced	mW/cm ²
J_{sc}	Short circuit current density	mA/cm ²
FF	Fill factor	
Greek symbols		
λ_{max}	Maximum absorbance wavelength	nm
η	Overall cell efficiency	%
Abbreviations		
DSSC	Dye-sensitised solar cell	
DSSCs	Dye-sensitised solar cells	
TCO	Transparent conducting oxide	
FTO	Fluoride-doped tin oxide	
ITO	Indium-doped tin oxide	
ATO	Antimony-doped tin oxide	
ITiO	Titanium-doped indium oxide	
NIR	Near Infrared	
IPCE	Incident photon to current efficiency	
SEM	Scanning electron microscope	
PSD	Particle size distribution	
ssDSSC	Solid state dye-sensitised solar cell	
TBP	4-Tert-butylpyridine	
MPN	3-methoxypropionitrile	
MAN	Methoxyacetonitrile	
NMO	N-methyloxazolidinone	
GBL	γ -Butyrolactone	
MHIImI	methyl-hexyl-imidazolium iodide	

EMImSeCN	1-ethyl-3-methylimidazolium selenocyanate
Eu(II)	Europium(II) tellurium oxide
Eu(III)	Europium(III) tellurium oxide

1. INTRODUCTION

1.1 BACKGROUND & MOTIVATION

The global growth in technological advancement and automated systems, results in an exponential increase in energy demand [1]. Fossil fuels are currently the main source of energy generation, but it will not be able to satisfy energy demand indefinitely. It is projected that global fossil fuel reserves will only last for another 200 years for coal, 60 years for natural gas and 40 years for oil [2].

Not only are fossil fuels non-renewable, these sources are also the main contributor to air pollution due to the emission of carbon dioxide (CO₂) that accompanies the energy conversion process [1]. By increasing the carbon dioxide present in the atmosphere, the effects of global warming will increase drastically [3]. To maintain the ever-growing demand in energy, while mitigating the associated environmental damage, an alternative energy source has to be obtained, preferably a renewable energy source.

Renewable energy is of a natural origin, it is abundant and inexhaustible, and include tidal, wind and solar energy [1]. Solar energy is the most commonly used renewable energy source due to its accessibility in all regions [4]. It is an abundant, clean, cheap and safe energy source [5]. It has been shown that 120×10^{15} watts of solar energy falls onto the surface of the earth daily, and if this total amount could be captured, converted and stored, it would provide for roughly 20 years of global energy demand [6].

As the world faces increasing environmental problems that include natural resource depletion, waste disposal, global warming, pollution, climate change, acid rain and ozone layer depletion, renewable energy technologies are becoming more attractive as time progresses [7]. Solar energy can be harvested and converted into electrical energy by employing photovoltaic cells. Photovoltaic cells mostly comprise of silicon (Si), copper indium selenide (CIS), cadmium telluride (CdTe), perovskite solar cells as well as dye-sensitised solar cells (DSSCs) [8]. However, currently no suitable technology exists to store excess energy generated by the sun.

In the late 1960's, it was discovered that electricity can be generated by employing illuminated organic dyes in an electrochemical cell [9]. The first chlorophyll-sensitised zinc oxide (ZnO) electrode was synthesised in 1972, at the University of California at Berkeley, with the chlorophyll having been extracted from spinach [10]. The majority of the research conducted at the early stages comprised mostly of employing ZnO as the electrode, however the efficiency of the DSSCs were tremendously low and the dye molecules could only absorb 1 % of the incident light. The efficiency of the DSSCs were improved by optimising the porous structure of the electrode, which comprised of an oxide powder [9].

As research progressed, nanoporous titanium dioxide (TiO_2) was employed for a new DSSC electrode, having a 7 % efficiency [11]. DSSCs were originally invented by Michael Grätzel and Brian O'Regan at UC Berkeley in 1988, with these cells also being known as Grätzel cells. Grätzel and O'Regan subsequently grew DSSC research at Ecole Polytechnique Fédérale de Lausanne until the year 1991 [9]. It was Grätzel and O'Regan that built the very first dye-sensitised nanocrystalline solar cell that achieved a photoelectric energy conversion efficiency of 7 %, as mentioned above [12].

By optimising the simple structure of the DSSC, while still being able to use low cost technology to manufacture the cell, an energy efficiency of 10 % was subsequently obtained, which placed DSSCs in the competitive commercial market [12]. The predicted theoretical power conversion efficiency of DSSCs was stated to be around 20 % [13]. Extensive research has subsequently been conducted to improve the efficiency and to give DSSCs a strong foothold in the renewable energy market.

The overall structure of a DSSC consists of 4 main components [8]:

- 1) A photoanode that is comprised of a conducting glass substrate that is coated with a nanocrystalline semiconductor thin film such as TiO_2 , also referred to as the metal oxide semiconductor (MOS),
- 2) a layer of a sensitizer that is adsorbed onto the photoanode's surface,
- 3) an electrolyte that contains a redox couple such as I^-/I_3^- , and
- 4) a cathode, such as carbon or platinum, that is deposited onto the surface of a conducting glass substrate.

A schematic representation of a DSSC can be seen in Figure 1 [14]. These components are key to the effective operation of the solar cell [9].

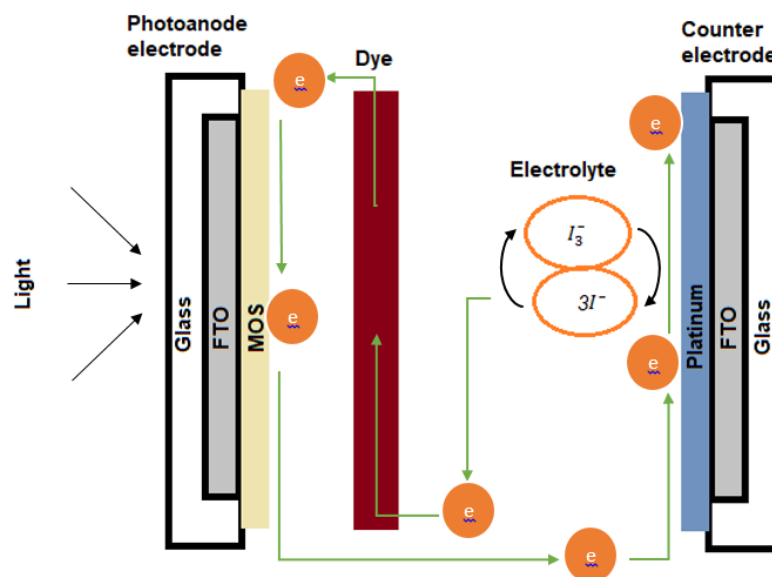


Figure 1 - Schematic representation of a DSSC redrawn from [9] [14]

1.1.1 PHOTOANODE

Semiconductors such as SnO_2 , ZnO , TiO_2 , and chalcogenides, have been thoroughly investigated as potential photoanodes due to their usage in environmental remediation and energy storage [12]. The most common semiconductor used in DSSCs are titanium dioxide (TiO_2) nanoparticles, that exhibits a wide bandgap, which makes it suitable for solar induced voltage generation [8].

Titanium dioxide exists in three forms, namely: brookite, rutile and anatase. Even though rutile is much more stable than the other two forms, crystalline anatase is more favoured in DSSCs due to it being more chemically active [8], but it is important to note that anatase is metastable and converts to rutile when heated [12]. TiO_2 is cheap, is readily available, is thermally stable, biocompatible, non-toxic, chemically inert and consists of a wide band gap of 3.2 electron volts (eV) [15].

1.1.2 SENSITISER

Dye-sensitisers are used to ensure efficient light harvesting in DSSCs [2]. A dye-sensitiser is judged on its ability to absorb all incident light ranging from the visible spectrum to the near-infrared section of the entire solar spectrum. An ideal sensitiser should be able to absorb all incident light up to a wavelength of 920 nm [16]. The dye is covalently bonded to the porous oxide layer which will enhance the light absorption of the cell. In other words, the dye acts as a molecular electron pump through the generation of excited electrons resulting from the absorption of light, and creates a movement of electrons from the dye to the semiconductor [17].

The sensitisers can be divided into inorganic and organic groups. As stated by Birel [18], the usage of a transition metal in the inorganic dye structure increases the activity of the dye, with complexes that consists of polypyridyl and ruthenium(II), having been regarded as the most efficient sensitisers [16]. To this regard, an electric power conversion efficiency of 11 % has been obtained by employing ruthenium-polypyridyl complexes as a dye [8].

1.1.3 ELECTROLYTE

The electrolyte's purpose is to regenerate the sensitiser subsequent to the sensitiser having injected electrons into the semiconductor's conduction band [16]. The electrolyte is solely responsible for the stability and lifespan of the DSSC, and has to consist of the following properties, i.e. it must [19]:

- 1) not absorb light in the visible region,
- 2) have good interfacial contact with the cathode and anode,
- 3) have low viscosity to ensure faster diffusion of electrons,

- 4) have excellent electrical conductivity, and
- 5) it must not cause degradation of the dye.

1.1.4 CATHODE

The cathode, also known as the counter electrode, consists of a glass plate substrate with a metal, such as platinum, deposited onto the surface. The function of the cathode is to obviously close the electrical circuit of the solar cell, but to also supply electrons to the electrolyte and thereby regenerating the electrolyte [16], subsequent to the electrolyte having regenerated the sensitiser. Graphene, in turn, consists of a high electro-catalytic activity, excellent conductivity properties, and is cost effective when compared to platinum, which makes it a satisfactory replacement for platinum [20]. By optimising all four components of the DSSC, a satisfactory efficiency can be obtained.

1.2 PROBLEM STATEMENT, AIM & OBJECTIVES

Solar cells exhibit remarkable potential within the renewable energy sector as a solar to electrical energy conversion technology however, it is restricted by economic factors that result from expensive materials and ineffective and costly electrical energy storage methods.

The aim of this research project is to investigate the development of a DSSC that not only converts solar energy into electrical energy, but that (i) also converts a portion of the incident solar radiation into chemical energy and stores it on-board, i.e. within the DSSC itself, and (ii) returns the stored energy as electrical energy during periods of no incident radiation, e.g. during the night. For this project, europium(III) tellurium oxide (Eu_2TeO_6) and europium(II) tellurium oxide (Eu_3TeO_6) will be employed as a semiconductor as it has exhibited capacity for both photocharging (during irradiation) and the release of stored charge (subsequent to the termination of irradiation) [21].

The following objectives have been formulated to work towards achieving the set project aim:

1.2.1 TIME VARIABLE OBJECTIVES:

The following objectives are based on determining the influence of time on the total efficiency of the solar cell:

- 1) Determine the effect of the sensitising time on the efficiency of the DSSC.
- 2) Determine the effect of extended contact time of incident light on the DSSC.

1.2.2 PROCESS VARIABLE OBJECTIVES:

The following objectives are based on determining how different material preparation processes influence the total efficiency of the solar cell:

- 1) Determine the effect of electrolyte preparation on the efficiency of the DSSC.
- 2) Determine the effect of photoanode preparation on the efficiency of the DSSC.

1.2.3 COMPONENT VARIABLE OBJECTIVES:

The following objectives are based on determining how a change in a specific component influences the total efficiency of the solar cell:

- 1) Determine the effect of spacer size on the efficiency of the DSSC.
- 2) Determine the effect of different dyes on the efficiency of the DSSC

1.2.4 OPERATING CONDITION OBJECTIVES:

The following objectives are based on determining how a change in operating conditions can influence the total efficiency of the solar cell:

- 1) Determine the effect of light intensity on the current production of the DSSC.

1.3 SCOPE OF INVESTIGATION

This study compares the effects of TiO_2 as well as europium(II) and (III) tellurium oxide used as semiconductors. Factors such as overall efficiency, incident photon to current conversion efficiency (IPCE), dark current produced as well as the max power output obtained will be monitored. Conventional TiO_2 DSSCs will be constructed with parameters that are beneficial to the standard TiO_2 DSSC. Europium(II) and (III) tellurium oxide will only be tested employing the same parameters used for the conventional TiO_2 DSSC. Parameters that will be kept constant are sonication temperatures, sonication intensity, annealing time and temperature during photoanode preparation as well as the standard doctor blade technique used to distribute the semiconductor across the glass substrate [22]. Only fluoride-doped tin oxide (FTO) will be used for the glass substrate during DSSC construction.

2. LITERATURE REVIEW

2.1 HISTORY OF PHOTOVOLTAIC CELLS

The conversion of light to electricity (known as the photovoltaic effect) was first discovered by a French experimental physicist named Edmund Becquerel in 1839 [1]. In 1873, Willoughby Smith discovered the photovoltaic effect in selenium [23]. It was the year 1883 when Charles Fritts, an American inventor, outlined the very first solar cells that was made from selenium wafers [24]. In 1904, Albert Einstein discussed the theoretical potential of the photovoltaic effect and received a Nobel Prize for his work done in 1923 [24].

Polish scientist Czochralski derived a method to produce silicon with a single-crystalline structure in 1918 [25]. In the 1950's, the commercialisation of photovoltaic cells were starting to take place by using the Czochralski process to produce pure crystalline silicon. In the year 1954, Bell Laboratories scientists used the Czochralski process to produce a photovoltaic cell with a recorded efficiency of 6 % [26]. In 1957, Hoffman Electronics constructed a solar cell that obtained an efficiency of 8 % [26]. Two years progressed with Hoffman Electronics constructing an improved solar cell with a reported efficiency of 10 % [27]. In 1960, Hoffman Electronics implemented a grid contact to reduce series resistance which led to an increase in efficiency to 14 % [27].

The year 1970, Zohres Alferov with his team in the USSR developed the first highly effective gallium arsenide heterostructure solar cell [28]. Numerous important events in the field of photovoltaic cells took place in the 1980's, with 20 % efficient solar cells being created by the Centre of photovoltaic engineering at the University of New South Wales [27].

From the year 2000 and onwards, photovoltaic cells began to be internationally deployed [27]. This time period begun with the implementation of the German Renewable Energy Sources Act which created a Solar Feed-In-Tariff that opened up a solar energy market in Europe [29]. In the year 2001, Suntech Power was formed in China hence beginning the period of commitment to the construction of solar cells with government subsidies and low cost labour [30]. The total solar photovoltaic installed capacity globally would grow from 1 gigawatts in 2002 to 134 gigawatts at the start of 2014 [31]. As of today, the silicon photovoltaic cell is still the dominant cell in the market.

2.2 CLASSIFICATION OF SOLAR CELLS

2.2.1 ORGANIC SOLAR CELLS

Organic solar cells (OSCs) are one of the leading technologies in the low cost energy production field with advantages such as being semi-transparent, flexible as well as solution

processable [32]. OSCs consist of organic semiconductors that are often made out of polymer which can be chemically tuned to adjust the properties of the solar cell [33]. Physical properties such as charge transport, solubility, band gap, morphological properties as well as conduction energies are usually altered [33].

Organic solar cells have achieved efficiencies of up to 10 % [34], and are based on a charge transfer process where two distinct materials are used, one being a donor and the other an acceptor [35]. To allow charge transfer, the difference between the lowest unoccupied molecular orbital (LUMO) levels of the two materials must be larger than the binding energy of the exciton [34].

In the early development stages of organic solar cells, the organic semiconductor was deposited as a single layer between electrodes that are made up of different metals [36]. These solar cells achieved efficiencies as low as 0.01 %, but in 1986, Tang *et al.*, introduced an organic solar cell that comprised out of a donor-acceptor (DA) heterojunction, thus improving the efficiency to 0.95 % [37].

The most used donor materials are polyacenes such as tetracene, pentacene and phthalocyanines such as CuPc and ZnPc [38]. Perylene compounds such as perylenetetracarboxylic bis-benzimidazole (PTCBI) is usually used as an acceptor in organic solar cells [39]. Another combination often used in organic solar cells is [6, 6]-phenyl C₆₁-butyric acid methylester (PCBM) blended with poly (3-hexylthiophene) (P3HT). The fullerene derivative-based compound mentioned above still uses the donor-acceptor approach and has recorded efficiencies up to 6 % [40].

2.2.2 INORGANIC SOLAR CELLS

The most used inorganic solar cell (ISC) to this day is comprised out of silicon. Silicon solar cells were first applied in the 1950's to power satellites [41]. Two types of silicon solar cells were available at that point of time namely, the p-type cell that uses boron which has one less electron than silicon, hence making the cell positively charged, and the n-type solar cell which includes phosphorus that has one more electron than silicon, thus making the solar cell negatively charged [41]. The p-type cells were chosen over their n-type counterparts due to difference in space-radiation hardness [42].

In present times, most solar cells are constructed out of boron-doped p-type crystalline silicon wafers with sizes of 156 × 156 mm² for multicrystalline silicon and 125 × 125 mm² for monocrystalline silicon [41]. Multicrystalline wafers are cut from cast silicon blocks whereas monocrystalline silicon wafers are obtained from silicon ingots via wire-cutting [43].

In present times, diamond-coated wires had an increase in usage due to its exceptional cutting speeds that are six to eight times faster than any other cutting process [44]. The usual

thickness of the silicon wafers were reported to be 180 μm , but during the last 15 years, options of reducing the wafer thickness have begun to surface [45, 46].

2.2.3 PEROVSKITE SOLAR CELLS

Perovskite solar cells (PSCs) are gaining immense attraction due to its exceptional photovoltaic performance, simple processing conditions as well as it being constructed out of cheap raw materials [47]. These PSCs can be synthesised by using wet chemistry paired with low-cost techniques, such as screen printing, spin coating, dual source evaporation techniques as well as dip coating [48]. However, PSCs also have drawbacks such as having an overall short lifetime as well as poor device stability [48].

The untapped potential of PSCs can be clearly seen by the exponential increase in the power conversion efficiency (PCE) from 3 % to 25.2 % in only a time duration of 10 years [49]. While PSCs have seen such an aggressive increase, other technologies took roughly 30 years to achieve the same milestone [48]. Perovskite materials can serve as an efficient charge transport layer as well as an absorber layer [50].

These perovskite materials are one of the leading benefactors for the new generation of photovoltaic technology because of their unique properties as listed below:

1. The material's high electron mobility ($800 \text{ cm}^2/\text{Vs}$) [51],
2. ambipolar charge transport behaviour [52],
3. low exciton binding energy (less than 10 meV) [53],
4. high carrier diffusion length (more than 1 μm) [53, 54], and
5. optimal bandgap that is also tuneable [48].

2.2.3.1 *History of perovskite solar cells*

Perovskite is simply calcium titanium dioxide (CaTiO_3) and was found by Gustav Rose in Russia's Ural Mountains *circa* 1939 [48]. Count Lev Alekseevich Perovski who was born in 1772 and passed away in 1856, was a Russian mineralogist that further researched calcium titanium dioxide, thus the material was named after him as "Perovskite" [53]. Mitzi and fellow researchers further investigated the optoelectronic properties of the organic-inorganic perovskites and reported strong exciton features, and shortly after suggested that it could be implemented in the field of solar cells, LEDs as well as transistors [55].

In 2009, perovskite materials were used as a liquid sensitiser in DSSCs. However these solar cells were highly unstable and had a short lifespan due to it containing a liquid electrolyte in the cell configuration [49]. By using quantum dots of crystalline materials and utilising similar DSSC concepts, the cell efficiency was increased from 3.8 % to 6.54 % [48]. However, the device only had a lifespan of 10 minutes due to the dissolution of the perovskite material quantum dots into the electrolyte solution [56].

In 2012, the constant problem arising due to the inclusion of a liquid electrolyte has been overcome by constructing a PSC with only solid-state materials [57]. A prominent change in the history of PSCs have been made due to this solid-state cell, for it did not only increase the overall efficiency of the cell, but also made an astounding enhancement in the cell's lifetime by withstanding a long term stability test for 500 hours without encapsulation [57].

In 2013, PSCs efficiency were increased to 15 % by utilising a 2-step sequential deposition technique as well as fabricating the cells in planar architecture [58]. This cell gave a high short circuit current density (J_{sc}) of 20 mA/cm² due to the newly dense developed perovskite layer [58]. Two years later in 2015, a new technique was implemented to deposit a FAPbI₃ film (perovskite material) with a (1 1 1) crystallographic orientation paired with large as well as dense microstructures [48]. The usual perovskite material, MAPbI₃, was exchanged with FAPbI₃ resulting in an increased PCE of 20.2 % [59].

In 2016, a perovskite film with crystalline and uniform morphology was constructed by implementing the vacuum flash solution processing method (VASP) [60]. With this method a PCE of 20.5 % was obtained [60]. At the end of 2016, a new perovskite film fabrication process was introduced involving the use of a polymer. By using the polymer, poly methyl methacrylate (PMMA), the electronic property as well as the nucleation process of the perovskite film was enhanced and a PCE of 21.6 % was obtained [61]. As of now, the highest PCE a single-junction PSC has achieved, was developed by KRICT (South Korea), with an efficiency of 25.2 % [48].

2.3 DYE-SENSITISED SOLAR CELLS

Dye-sensitised solar cells (DSSCs) fall under the thin film photovoltaics category and is a promising, cost-effective route toward sunlight harvesting [16]. Due to its simple manufacturing process and general low cost of production, dye-sensitised solar cells have made a large impact on the photovoltaics market [62].

A DSSC consists of a photoanode, electrolyte, counter electrode, and a monolayer of sensitizer, also known as a dye that is adsorbed onto a metal oxide semiconductor (MOS), which is usually titanium dioxide [16]. Contrasting the usual solar cell system, where the semiconductor is responsible for light absorption as well as being the charge carrier, the DSSC's sensitizer is responsible for light absorption and the charge separation occurs through electron injection from the sensitizer into the conduction band of the semiconductor used [63]. The success rate of injecting an excited electron from the sensitizer to the semiconductor is dependant on the energy difference between the LUMO of the sensitizer and the conduction band of the semiconductor [64]. Electron injection efficiency further improves the excited

electron availability within the semiconductor. Electron injection efficiency can be defined as [64]:

$$\phi_{inj} = \frac{N_{ox}}{N_p^A} = \frac{N_{electron}}{N_p^A} \quad \text{E2.1}$$

For clarification, N_{ox} refers to the number of oxidised dye molecules, while $N_{electron}$ and N_p^A refer to the number of electrons transported to the semiconductor and the number of absorbed photons, respectively [64]. It can be deduced from equation 2.1 that a higher injection efficiency can be obtained if the electron injection occurs more rapidly than the relaxation of the electrons from the excited state.

2.4 COMPONENTS OF A DYE-SENSITISED SOLAR CELL

2.4.1 SUBSTRATE

A standard DSSC is usually assembled between two glass substrates which are covered with a certain conductive layer. These substrates act out as a support structure to the cell as well as a sealant to a certain extent by protecting the cell from potential air bubbles or even other weather anomalies. The two main materials used as a transparent conducting oxide (TCO) include indium-doped tin oxide (ITO) as well as fluoride-doped tin oxide (FTO) [65].

Both TCO's are frequently used in the DSSC industry, however there are differences between the two materials, thus making the choice of an appropriate TCO quite challenging. Many studies such as Zumeta *et al.*, [66] proclaimed that FTO is far more efficient when compared to its ITO competitor. However, it has been stated by Yoo *et al.*, [38] that an ITO/ATO (antimony-doped tin oxide) hybrid TCO exhibits a more promising photovoltaic performance than the frequently used FTO.

It must be noted that both films have limitations when it comes to infrared (IR) radiation [67]. ITO also has low thermal stability whereas FTO is quite resistant to changes in temperature [65], hence most researchers prefer FTO as the material of choice when constructing a DSSC [68].

However it is worth noting that there are promising ITO hybrids being researched, such as titanium-doped indium oxide (ITiO) which has shown to have high electron mobility, low sheet resistance as well as near-IR transmittance [69]. ITiO's near-IR transmittance is the highest for wavelengths over 1000 nm, leading to a potential increase in dye sensitisation in DSSCs [67]. This new hybrid form also shows heat resistance identical to FTO. When both TCO's are heated to 500 °C, their diffraction intensities only decrease slightly whereas the ITO cannot withstand such high temperatures [67].

Flexible plastic substrates have also been considered to replace the conventional glass plates used in DSSCs. The reason behind this option is due to the fact that it is vastly cheaper and easier to handle than the glass substrates [70] however, these plastic polymer substrates have drawbacks when being used. Examples of these issues is the permeability of the substrate when in contact with water vapour and oxygen as well as the instability of the substrate when in the presence of an electrolyte [71].

2.4.2 METAL OXIDE SEMICONDUCTOR

The ideal semiconductor should be environmental friendly, stable, have a low cost, should be simple to prepare [72], and have a high surface area with good transparency [63]. Metal oxides such as niobium oxide (Nb_2O_5), titanium dioxide (TiO_2), zinc oxide (ZnO) and tin oxide (SnO_2) have been tested as semiconductors for DSSCs, with TiO_2 and ZnO delivering the highest efficiencies [73]. TiO_2 is the most used semiconductor due to its low-cost, biocompatibility, nontoxicity as well as its high availability [74].

2.4.3 SENSITISER

The sensitiser is responsible for light harvesting effects within the DSSC [16]. The properties of the sensitiser will have a significant influence on the overall efficiency of the cell. An ideal sensitiser should be able to absorb all light up to a wavelength of 920 nm and must bind firmly to the semiconductor [75].

The sensitiser's redox potential should furthermore be high enough in order for it to be rapidly regenerated via electron donation from the electrolyte [74]. Lastly, a sensitiser must be stable enough to sustain 108 redox turnovers under illumination, which is the equivalent to 20 years of natural light exposure [16].

The sensitisers obtaining the most successful results in terms of stability and efficiency form part of the Ru-bipyridyl compounds [15]. These dyes consists of excellent stability, exceptional electron injection and high absorption in the visible range of the light spectrum [76]. Even though ruthenium based dyes are capable of achieving conversion efficiencies greater than 10 %, the preparation process is tedious and time consuming [77]. Ruthenium dyes consist of rare metals, which results in a high price as well as a toxic nature [15].

Nonetheless, ruthenium-free sensitisers that could potentially achieve high efficiencies are also studied and might result in a decrease in the total cell cost when implemented [78]. Metal-complex porphyrin dyes as well as metal-free organic dyes are intensively studied with the goal of replacing the expensive ruthenium based dyes [15].

Metal-free organic dyes are low cost, consists of diverse molecular structures and offer exceptional molar extinction coefficients [15]. Sensitisers such as dialkylaniline,

tetrahydroquinoline and carbazole-based dyes have achieved electrical conversion efficiencies of up to 9 % [32].

Porphyrin dyes have also been implemented in DSSCs due to their superior absorption in the visible region of the light spectrum [33]. These dyes are the potential successors of ruthenium based dyes due to their tuneable physicochemical properties and high extinction coefficients in the visible light spectrum [79].

2.4.3.1 Organic sensitisers

Organic dyes used in DSSCs usually bear a resemblance to dyes that can be found in natural materials such as leaves, flowers, fruits, roots, etc. [76, 80]. The natural dyes used in DSSCs are environmentally friendly, fully biodegradable, non-toxic as well as cost-effective [77].

Fruits, flowers, leaves and even bacteria that are naturally available illustrates various colours and contains numerous pigments that can be extracted and incorporated into a DSSC [81]. The advantages of using these natural occurring dyes as sensitisers in DSSCs are due to the large absorption coefficients they consist in the visible region, ease of preparation and a relative abundance [82, 83]. The most attractive feature of using a natural dye is the simplicity and cost-effectiveness of its synthesis route for it does not involve any noble metals such as Ru [84].

Plant pigments consist over an electronic structure that reacts when in contact with sunlight, this structure alters the wavelengths that are reflected or transmitted by the plant tissue [85]. This process results to the observation of plant pigmentation where each individual pigment is defined from the maximum absorbance wavelength (λ_{max}) as well as the colour that is perceived by humans [85].

The most common pigment types found in fruit and flower colours are illustrated in Table 2. Pigments for natural dyes include anthocyanin, flavonoid, chlorophyll and carotenoid which are all quite easy to extract from natural sources in comparison to their synthetic dye competitors [86]. Plant pigments are classically grouped into four types as can be seen in Figure 2.

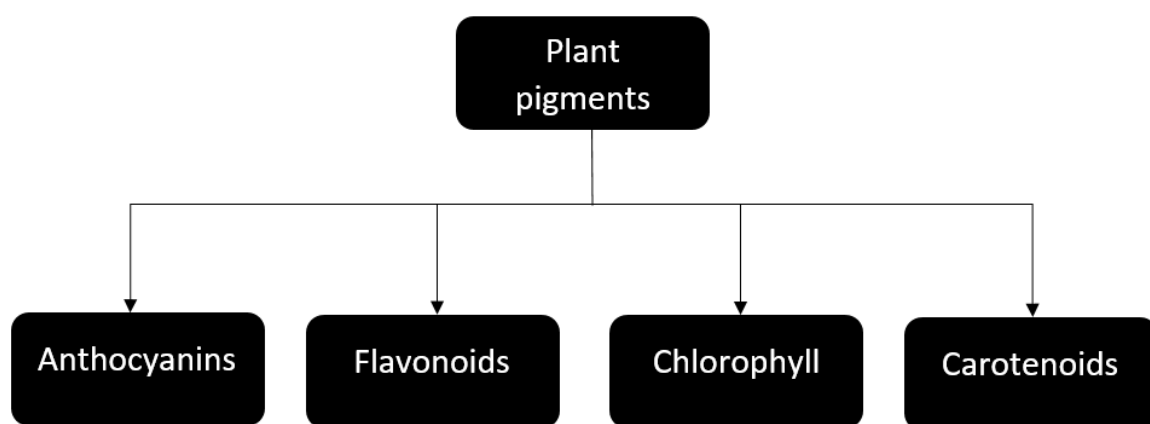


Figure 2 - Plant pigment classification redrawn from [85]

Table 2 Common pigment types found in fruit and flower colours adapted from [86]

Colour	Pigment type	Pigment group
Black	Delphinidin	Carotenoid and flavonoid mix
Cream	Flavones or flavonols	Flavonoid
Green		Chlorophyll
	Delphinidin	Flavonoid
	Cyanidin	Flavonoid
Orange		Carotenoid
	Pelargonidin	Flavonoid
	Aurone and anthocyanin mix	Flavonoid
	Chalcone and anthocyanin mix	Flavonoid
	Betacyanin	Betalain
Purple		Carotenoid
	Delphinidin and/or cyanidin	Flavonoid
	Delphinidin and/or cyanidin	Carotenoid and flavonoid mix
Red to pink		Carotenoid
	Cyanidin and/or pelargonidin	Flavonoid
	Carotenoid and anthocyanin mix	Flavonoid
	Betacyanin	Betalain
Yellow		Carotenoid
	Aurone	Flavonoid
	Chalcone	Flavonoid
	Flavonol	Flavonoid
	Betaxanthin	Betalain

2.4.3.1.1 CHLOROPHYLLS

Chlorophylls are part of the natural photosynthetic pigments group and is responsible for giving plants a green colour [87, 88]. Chlorophyll's primary function is to harvest light energy efficiently and then to transduce it for photosynthesis, this is achieved due to chlorophyll's spectral properties [85].

Chlorophylls consist of two main types, namely chlorophyll "a" and chlorophyll "b". Chlorophylls are used as sensitisers in DSSCs due to their light absorption of blue and red light [85]. The most efficient type is a variant of chlorophyll "a" (methyl trans-32-carboxy-pyropheo-phorbide) [89]. When comparing chlorophyll "b" with "a", it can be seen that chlorophyll "b" consists over a redshift and a blue tinge characteristic [85].

2.4.3.1.2 FLAVONOIDS

Flavonoids are the most physiologically active and widespread group of all the natural constituents that are necessary for the contribution of colour in flowers [85]. The term "Flavonoid" was initially applied by Hinreiner and Geissman to group up all compounds with a structure based on flavones, which means having a C₆-C₃-C₆ skeleton [90].

Despite having similar structures, only specific flavonoids have the light absorption ability in the visible region [89]. The flavonoid group also include flavanonols, flavanones and flavan-3, 4-diols [91]. There are also five compound classes included in the flavonoid group, such as dihydrochalcones, phynyl styryl ketones, 3-phenyl chromones, 4-phenyl coumarins and aurones [85]. The compounds in each class are defined by the orientation and number of methoxy and hydroxy groups in the two benzene rings [85].

When using flavonoids as a sensitiser, the charge transfer transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) require less energy, thus energising the pigment through the use of visible light, resulting in a broad absorption band in the visible region [92]. Specific flavonoids get quickly absorbed onto the TiO₂'s surface by displacing an OH⁻ counter ion from the titanium site which then combines with a proton that is donated by the flavonoid [84].

2.4.3.1.3 ANTHOCYANINS

Anthocyanins are the second most important pigment group that is visible to the human eye, with chlorophyll being the most important [85]. Anthocyanins are phenyl-2-benzopyrylium based substituted glycosides salts on a C₁₅ skeleton with a chromane ring which bears a second aromatic ring in position 2 (C₆-C₃-C₆) [93].

Anthocyanins are the reason for the existence of attractive colours, from scarlet to blue, in different flowers, leaves and plants [94]. Anthocyanins are also found in mosses and ferns.

This pigment group is also responsible for the change in quantity and quality of light that falls onto the chloroplasts of the subject [95]. When referring to flowers, anthocyanins can be mostly found in the epidermal cells or occasionally in the mesophyll of the flower [93].

Anthocyanin pigment molecules have hydroxyl and carboxyl groups bound on the surface of the TiO₂ semiconductor, which will then support the transfer and excitation of electrons from the anthocyanin pigment molecules to the conduction band of the porous TiO₂ film [84]. Table 3 shows a sample of hydroxyl groups substituted in various positions in the anthocyanin structure resulting in different colours produced.

Table 3 Anthocyanins paired with a characteristic hydroxyl group substitute adapted from [93]

Name	Substitute position	Colour produced
Apigeninidin	5,7,4'	Orange
Aurantidin	3,5,6,7,4'	Orange
Cyanidin	3,5,7,3',4'	Crimson and magenta
Delphinidin	3,5,7,3',4',5'	Blue, purple and mauve
6-Hydroxycyanidin	3,5,6,7,3',4'	Red
Luteolinidin	5,7,3',4'	Orange
Perlargonidin	3,5,7,4'	Salmon, orange
Triacetidin	5,7,3',4',5'	Red

2.4.3.1.4 CAROTENOIDS

Carotenoids are one of the largest natural dye groups with over 600 members which are mainly known as isoprenoids that provide yellow, orange and red colouring to flowers and fruits [85]. All carotenoids used in the following reactions can be considered as lycopene (C₄₀H₅₆) derivatives [96]: Hydrogenation, dehydrogenation, double bond migration, methyl migration, chain shortening, chain elongation, oxygen insertion, and cyclisation.

Carotenoids are also divided in primary and secondary groups. Primary carotenoids are a key component required in plants to carry out the photosynthesis process, whereas secondary carotenoids are mostly only found in fruits and flowers [85].

These primary carotenoids are located in the chloroplasts of green plants as a combination of α- and β-carotene, β-cryptoxanthin and lutein [97]. Most synthesised carotenoids are aliphatic, meaning the carbon atoms of the organic compound form open chains however, some carotenoids can still have aromatic rings in chloroflexaceae and chlorobiaceae [98]. Carotenoids have two main roles in the photosynthesis process, firstly acting as a photoprotector against oxidative damages and secondly as an accessory pigment in light

harvesting [85]. One of the most important characteristics of carotenoids is its light absorbing ability when paired with chlorophyll pigments [85]. This absorption process is accomplished by the photo-induced transformation of delocalised electrons of carotenoid molecules, which in turn transfers the absorbed energy from the carotenoid molecules to the chlorophyll molecules, resulting in a singlet chlorophyll state with increased energy [93].

Table 4 summarises the photoelectrochemical properties of DSSCs that used different natural dyes extracted from flower, fruits, leaves, etc. as sensitisers. Note that all the mentioned natural dyes were paired with TiO_2 as semiconductor and I^-/I_3^- as the redox electrolyte.

Table 4 Photoelectrochemical properties of DSSCs using natural dyes as sensitisers

Natural dye solution	Pigment	$\lambda_{\max}$ (nm)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	REF
Begonia	Anthocyanin	540	0.63	0.537	0.72	0.24	[99]
Black carrot	Anthocyanin	540	1.30	0.40	0.47	0.25	[100]
Dragonfruit	Anthocyanin	535	0.20	0.22	0.3	0.22	[101]
Henna	Anthocyanin	518	1.87	0.61	0.58	0.66	[102]
Hibiscus surattensis	Anthocyanin	545	5.45	0.39	0.54	1.14	[103]
Morinda lucida	Anthocyanin	440	1.15	0.35	0.63	0.25	[104]
Pomegranate	Anthocyanin	413	2.05	0.56	0.52	0.59	[81]
Red cabbage	Anthocyanin	537	0.5	0.37	0.54	0.13	[85]
Rosella	Anthocyanin	520	1.63	0.4	0.57	0.37	[85]
Madder	Anthraquinone	540	0.54	0.39	0.69	0.10	[105]
Ivy gourd fruit	B-Carotene	458	0.24	0.64	0.49	0.09	[106]
Cherries	Betacyanin	500	0.46	0.30	0.38	0.18	[107]
Raspberries	Betacyanin	540	0.26	0.42	0.65	1.50	[108]
Red Bougainvillea glabra	Betaxanthin, Betacyanin	483	2.34	0.26	0.74	0.45	[109]
Wild Sicilian prickly pear	Betalin	465	8.20	0.38	0.38	1.19	[110]
Gardenia yellow	Carotene	450	0.96	0.54	0.62	0.32	[111]
Achiote	Carotenoid	474	1.10	0.57	0.59	0.37	[112]
Anethum graveolens	Chlorophyll	666	0.96	0.57	0.40	0.22	[113]
Bitterleaf	Chlorophyll	400	0.07	0.34	0.81	0.69	[10]
Festuca ovina	Chlorophyll	421	1.18	0.54	0.69	0.46	[114]
Ficus retusa	Chlorophyll	670	7.85	0.52	0.29	1.18	[115]
Green algae	Chlorophyll	666	0.13	0.41	0.21	0.01	[113]
Shiso	Chlorophyll	441	3.56	0.55	0.51	1.01	[99]
Spinach	Chlorophyll	437	0.47	0.55	0.51	0.13	[116]
Botuje	Flavonoid	400	0.69	0.05	0.87	0.12	[117]
Cosmos sulphurous	Flavonoid	506	1.04	0.45	0.61	0.54	[118]
Tagetes erecta	Xanthophyll	465	2.89	0.48	0.61	0.80	[119]

2.4.3.2 Metal complex sensitisers

Among all the organometallic photosensitisers used in DSSCs, the Ru(II)polypyridyl complexes have been studied the most due to their unusual photophysical and redox properties [120, 121]. Ru(II)polypyridyl sensitisers also consist of excellent photovoltaic behaviour that is derived from having an ideally aligned excited and ground state, broad absorption spectrum and stability in the oxidised state [122].

The ruthenium's absorption properties are closely related to a metal to ligand charge transfer (MLCT) process and can be engineered through modification of the ligands to ensure wide visible spectrum coverage [123]. Ruthenium complexes paired with carboxylate ligands have been studied as potential sensitisers for semiconductors with wide bandgaps since as early as 1979 [124]. In 1991, the well-known O'Regan and Grätzel incorporated a synthesised ruthenium trinuclear complex with enhanced absorption characteristics in the first ever efficient DSSC [125]. In 1993, Nazeeruddin *et al.*, reported a crucial study on the electrochemical and optical properties of an entire series of Ru(II) complexes containing a general formula of cis-X₂bis(2,2'-bipyridyl-4,4'-dicarboxylate)-Ru(II) where X represents Br, I, SCN, CN as well as Cl [126]. The Ru(II) complex containing two groups of isocyanate ligands exhibited outstanding photovoltaics properties due to the usage of two thiocyanate groups instead of other ligands resulting in a red shift of the absorption spectrum up to 800 nm [123]. This Ru(II) sensitiser, also known as the N3 dye, has obtained a high J_{sc} of 18 mA/cm² with an overall efficiency of 10 % [123]. In Table 5, one can observe the progression of different ruthenium based sensitisers used throughout the years.

Table 5 Photovoltaic parameters of Ruthenium based sensitisers used in DSSCs

Dye code	λ_{max} (nm)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	REF
N3	534	18.20	0.720	0.730	10.00	[126]
N719	538	17.73	0.846	0.750	11.20	[127]
N749	610	20.53	0.720	0.704	10.40	[128]
Z907	525	14.20	0.764	0.676	7.80	[129]
Z910	543	17.20	0.777	0.764	10.20	[130]
K19	543	14.61	0.711	0.671	7.00	[131]
K51	-	16.60	0.738	0.679	8.10	[132]
K60	547	16.70	0.715	0.690	8.44	[133]
CYC-B1	553	23.92	0.650	0.540	8.54	[134]
CYC-B11	554	20.05	0.743	0.770	11.50	[135]
C101	547	10.50	0.747	0.760	11.70	[136]
C106	550	18.28	0.749	0.772	10.57	[137]
RC43	557	20.21	0.725	0.730	10.78	[138]
Z1	525	17.70	0.740	0.660	10.20	[139]
SCZ1	539	19.88	0.761	0.668	10.40	[140]
TFRS2	533	17.15	0.820	0.678	9.54	[141]
D-CF3	562	19.50	0.704	0.650	8.74	[142]
SA-246	585	14.55	0.845	0.747	9.40	[143]

The efficiency of photosensitisers depend on the degree of protonation, which influences two important electrical parameters, J_{sc} and V_{oc} . However, this influence occurs simultaneously as where after dye absorption, the TiO₂ surface is protonated and is thus positively charged [123]. By charging the surface, the dipole generated favours the adsorption of the ruthenium complex and thus assists electron injection from the excited state of the ruthenium sensitizer into the conduction band of the TiO₂ [123]. While the previous process takes place, the protonation of the TiO₂ also results in a positive shift of the conduction band edge, hence lowering the V_{oc} of the DSSC as well [123]. By balancing and optimising the two factors, the N719 dye has become one of the most promising ruthenium based sensitizers to this day [127].

With the aim of increasing absorption toward the near infrared (NIR) region, a new trithiocyanate-Ru(II) terpyridyl complex was investigated and reported in 1997 [144]. By further using thiocyanate groups in ruthenium complexes, sensitizers originated that covered the entire visible range and even extending into the NIR region up to 920 nm [123]. A derivation of the N3 dye, which is double de-protonated, is referred to as N749 dye and has been employed as an effective DSSC photosensitizer resulting in obtaining a high J_{sc} of 20.50 mA/cm² and an efficiency of 10.40 % [128].

In 2003, the Z907 dye was implemented in a DSSC which resulted in a relative good efficiency of 8 % however, the sensitiser showed remarkable long-term durability at a temperature of 55 °C under one sun illumination soaking [129]. Z907 has also been implemented in a quasi-solid state DSSC with a polymer gel electrolyte, resulting in an overall efficiency of 6 % and quite impressive stability [145]. The cell maintained 94 % of its initial performance after 1000 hours of irradiation at a temperature of 80 °C and maintained 95 % after 1000 hours under one sun light soaking at a temperature of 55 °C [145].

The use of hydrophobic tails with a π -conjugation extension has been intensively explored to replace the usual alkyl tails with the purpose of enhancing the molar absorption of the sensitiser, thus increasing the overall efficiency [130]. The Z910 dye made use of these hydrophobic tails where the bipyridyl ligand was functionalised with a methoxystyryl group [130]. When comparing Z907 with Z910, it can be seen that a red shift of 20 nm has been obtained with Z910, leading to a J_{sc} of 17.2 mA/cm² with an overall efficiency of 10.2 % [123]. Z910 was further evolved into K19 by replacing a hexyloxy tail with a methoxy group, thus resulting in an overall efficiency of 7 % with an exceptional high stability even while using a liquid electrolyte [131].

Ion coordinating tails were also introduced into sensitisers and was researched by Kuang *et al.*, [132, 133, 146]. The molecular structure of K51 in Table 5 includes a triethylene oxide methyl ether group which coordinates well with Li ions, resulting in the methyl ether group inhibiting these ions to connect to the TiO₂ surface which subsequently reduces the V_{oc} of the DSSC [123]. The overall efficiency of the DSSC while using K51 reached a maximum of 8.1 % by optimising the Li⁺ concentration in the electrolyte [132]. By extending the conjugation of the peripheral ligands, an increase in efficiency was recorded of 8.4 % [123]. This new variant, known as the K60 dye, consisted of exceptional long-term stability when under thermal stress of 80 °C or even at 60 °C under one sun illumination [133].

Ancillary ligands paired with thiophene groups have also been researched. Typical bipyridine ligands paired with a bithiophene moiety led to the creation of the CYC-B1 sensitiser, which achieved an overall efficiency of 8.54 % [134]. By replacing the alkyl chain in the CYC-B1 sensitiser with an electron rich thioalkyl group resulted in a more efficient sensitiser named CYC-B11, which achieved an overall efficiency of 11.5 % [135]. The exceptional performance of CYC-B11 was due to an improved molar extinction coefficient [123]. This resulted in increased absorptivity which allowed the TiO₂ layer to have reduced thickness, thus causing an increase in V_{oc} and a decrease in dark current leakage [123]. CYC-B11 was also implemented in a solid state DSSC (ssDSSC) with a TiO₂ layer of 2 μ m and achieved an overall efficiency of 4.7 % [135].

Other noteworthy Ru(II)-based sensitisers containing thiophene are C101 and C106 where the bipyridine ligand is functionalised by an individual thiophene ring [137, 147]. An interesting revelation was made when C101 was further studied as a sensitiser for DSSCs. It was shown that the temperature during the sensitisation process had an influence on the overall efficiency of the DSSC [137]. By carrying out the sensitisation process at a lower temperature, results in an increased structural order of the sensitiser layer which prevents electron back transfer from the TiO₂ layer to the electrolyte, thus reducing the dark current [123]. Ru(II)-based sensitisers have been the most promising candidates for DSSC usage however, a solution must still be found to answer for its scarcity, toxic nature and costly processes.

2.4.4 ELECTROLYTE

An electrolyte consists of five main components, namely: solvent, additives, ionic liquids, cations and a redox couple [9]. Iodide/tri-iodide (I^-/I_3^-) is deemed as an efficient electrolyte however, there are limitations to its application in DSSCs [147], as the I^-/I_3^- electrolyte is highly volatile and is also responsible for dye desorption and photodegradation [148]. Photodegradation is a major problem for semiconductor materials and causes polymer chain breaking while also affecting the chemical and mechanical properties of the material [149]

4-Tert-butylpyridine (TBP) can be used as an additive to shift titanium dioxide's conduction band higher, resulting in less injection force needed, an increase in open circuit voltage (V_{oc}) and a reduced short circuit current density (J_{sc}), which will lead to an overall increase in efficiency [9]. By adding TBP to TiO₂, recombination is reduced through back transfer to the electrolyte [9]. The biggest drawback of using a liquid ionic electrolyte is a possibility of leakage, and to that regard, solid-state electrolytes are developed to avoid this dilemma [150].

2.4.4.1 Liquid electrolyte

2.4.4.1.1 ORGANIC SOLVENTS

Organic solvents are one of the numerous components that a liquid electrolyte is comprised of. These solvents create an environment for the diffusion as well as dissolution of the ionic conductor [151].

The following requirements should be acquired for solvents used in DSSCs [152]: (i) Consist chemical stability under illumination as well as in the dark [153]; (ii) high dielectric constants so that the electrolyte salts can be soluble as well as be able to exist in a dissociated state [151]; (iii) the solvent must have a boiling point above 100 °C and a melting point lower than - 20 °C, this is necessary so that when these electrolytes are prepared with the solvents, it will not evaporate under operating conditions [152]; (iv) low viscosity to ensure that the redox mediators consist of high diffusion coefficients and the electrolytes have efficient conductivity [151]; (v) inertness regarding the sensitiser attached to the surface of the semiconductor [153];

(vi) insoluble in regards to the sealant materials; (vii) minor toxicity; (viii) little to no light absorption and cheap process cost [151]. Table 6 exhibits the parameters of organic solvents that are frequently used in DSSCs.

Table 6 Parameters of organic solvents used in DSSCs (All data at 760 mmHg and 25 °C unless specified otherwise) adapted from [122, 151-153]

Name of solvent	Formula	Boiling point (°C)	Melting point (°C)	Dielectric constant	Viscosity (cp)	Donor number
Acetonitrile	CH ₃ CN	82.00	-44.00	36.00	0.33 (30 °C)	14.10
Butyronitrile	CH ₃ (CH ₂) ₂ CN	118.00	-112.00	-	-	-
Diethyl carbonate	(CH ₃ CH ₂ O) ₂ CO	126.00	-74.30	2.81	0.75	-
Dimethyl carbonate	(CH ₃ O) ₂ CO	91.00	4.60	3.11	0.59 (20 °C)	-
Ethanol	CH ₃ CH ₂ OH	78.00	-114.00	25.00	1.08	29.00
Ethylene carbonate	C ₃ H ₄ O ₃	238.00	36.00	90.00	90.00	16.40
Glutaronitrile	NC(CH ₂) ₃ CN	287.00	-29.00	37.00	5.30	-
N-methyl-oxazolidinone	-	270.00	15.00	78.00	2.50	-
N-methylpyrrolidone	C ₅ H ₉ NO	203.00	-24.00	32.20	1.65	27.30
Propionitrile	CH ₃ CH ₂ CN	97.00	-93.00	27.00 (20 °C)	0.39 (30 °C)	16.10
Propylene carbonate	C ₄ H ₆ O ₃	241.00	-49.00	64.00	2.50	15.10
Valeronitrile	CH ₃ (CH ₂) ₃ CN	139.00	-96.00	21.00	0.78 (19 °C)	-
Water	H ₂ O	100	0	78.00	0.89	18.00
γ-Butyrolactone	C ₄ H ₆ O ₂	204.00	-44.00	42.00	1.70	18.00
3-Methoxy-propionitrile	CH ₃ O(CH ₂) ₂ CN	164.00	-63.00	36.00	2.50	16.10

It must be noted that no solvent can fulfil all the requirements mentioned previously. When one wants to construct an optimal DSSC, a mixture of solvents are usually used [151]. A popular example of a combination of solvents is a mixture of valeronitrile and acetonitrile in a ratio of 15:85 or 50:50 [154]. The purpose of the DSSC determines what type of solvent is needed [152]. Water is a common choice for a solvent and was used in liquid electrolytes at the initial research stages of DSSCs [151].

O'Regan *et al.*'s research indicated that when constructing a ruthenium-based DSSC, an addition of 20 % water in the nonaqueous electrolyte increased the overall efficiency from 5.5 % to 5.7 %, without decreasing the cell's long-term stability [70]. However, with a further increase in water addition, the efficiency of the cell greatly decreased.

An explanation for the long-term instability of DSSCs when it is combined with water as solvent is due to the oxidation reaction of iodide to iodate (IO₃⁻) instead of the sought after triiodide, which can't be reduced in the DSSC cycle at the counter electrode, leading to I₃⁻ depletion and an overall efficiency decrease [155]. Another explanation is that numerous organometallic

sensitisers are quite vulnerable toward hydrolysis, and some alcohols as well as water is lower in terms of chemical stability, thus making the two not optimal choices as solvents for an electrolyte [152].

Acetonitrile is known as one of the best electrolyte for fundamental research and studies due to its exceptional chemical stability, low viscosity and good solubility [156]. A supporting example for the previous mentioned statement, Hauch *et al.*, studied the change in diffusion constant for triiodide when included in different solvents and cations and discovered that the most promising diffusion constant was found when using acetonitrile with Li^+ [157]. It must be noted that acetonitrile consists over a low boiling point (as shown in Table 6) as well as toxicity, thus limiting its use in the industry [151]. Nonetheless, using acetonitrile as the main solvent for DSSCs has acquired high efficiencies of up to 13 % [158].

Other nitrile solvents involving methoxy groups with high boiling points and low toxicity is 3-methoxypropionitrile (MPN) and methoxyacetonitrile (MAN), which has been frequently used in DSSCs as electrolytes [122]. MPN consists over adequate chemical stability, which can bear long-term stability tests by retaining 98 % of its initial performance after being subjected to thermal stress at 80 °C in dark for 1000 hours however, the degradation was negligible after visible light soaking at a temperature of 60 °C for 1000 hours [159].

Lactones and esters compounds, such as propylene carbonate, N-methyloxazolidinone (NMO), ethylene carbonate and γ -Butyrolactone have been extensively used in DSSCs [151]. These compounds usually have high boiling – and melting points, such as NMO and ethylene carbonate, which have melting points of 15 and 36 °C respectively, thus it might be necessary to add solvents with lower melting points before using the compounds as electrolytes [122, 126]. The electrolyte implemented in the first efficient ruthenium-trimer dye based DSSC consisted of a mixture of ethylene carbonate and acetonitrile in an 80:20 volumetric ratio [11]. In the very first N3 dye based DSSC, an overall efficiency of 10 % was obtained while using an acetonitrile/NMO mixture (90 %:10 % volumetric) [126].

A popular solvent for outdoor DSSC use is γ -Butyrolactone (GBL), which has a low melting point and a high boiling point, thus making it favourable for outdoor conditions [151]. Kato *et al.*, studied DSSC stability for outdoor use by using GBL as the solvent electrolyte, the study resulted in continuous outdoor DSSC operation for 2.5 years [160].

The donor-acceptor interaction between the solvent and other components of the DSSC is a critical factor impacting the photovoltaic performance of the DSSC [151]. The Gutmann donor number of a solvent indicates the donating electron capacity of the solvent [161]. The donor number of a solvent mixture can be roughly calculated by taking the mole-fraction-weighted average of the donor numbers of all components [162]:

$$D_{mix} = (D_X \times X_{vol\%}) + (D_Y \times Y_{vol\%}) \quad \text{E2.2}$$

The higher the donor number of the solvent, the stronger basicity or donating electron capacity [151]. Kebede *et al.*, studied the donor-acceptor interaction between iodide species and nonaqueous solvents and found a relation between the transfer of iodide to triiodide ions and the donor number of the solvent used [163]. Fukui *et al.*, reported that an increase of the donor number of a solvent led to a decrease in J_{sc} and an increase in V_{oc} [164].

2.4.4.1.2 IONIC LIQUIDS

Ionic liquids, also known as molten salts, are defined as liquid electrolytes that are entirely comprised of ions [165]. Ionic liquids are quite often used for electrolytes in DSSCs due to their attractive characteristics such as great thermal and chemical stability, high ionic conductivity, nonflammability to a certain extent, very broad electrochemical potential window, tunable viscosity as well as consisting over an exceptionally low vapour pressure resulting in less leakage and evaporation [166, 167].

Ionic liquids serves two purposes when used in electrolytes for DSSC use. The first purpose is to function as an organic salt in quasi-solid-state electrolytes and the second purpose is to act as a solvent in a liquid electrolyte [151]. Table 7 exhibits examples of DSSCs that used ionic liquids as solvents in electrolytes [166]. All DSSCs mentioned in Table 7 were measured under solar light illumination of 100 mW/cm^2 (Xenon light source 100-1100 nm), AM (Air Mass) 1.5.

Table 7 Photovoltaic parameters of DSSCs using liquid electrolytes with ionic liquids as solvents adapted from [151]

Electrolyte composition	Dye	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	Ref
0.5 M I ₂ , 0.1 M CuI in HMIml	N3	13.60	0.54	0.62	4.54	[168]
0.1 M I ₂ , 0.1 M LiI, 0.1 M IILBOBs in PMII/EmimBOB (Vol ratio 3/1)	N719	13.91	0.54	0.65	5.38	[169]
0.12 M I ₂ , 0.5 M KI, 0.9 M BMIMl in GBL	N3	17.65	0.60	0.58	6.16	[170]
0.2 M I ₂ , 0.5 M NMBl in PMImI	K19	13.07	0.68	0.71	6.27	[171]
0.1 M I ₂ , 0.1 M LiI, 0.45 M NMBl in PMImI/EMImDCN (Vol ratio 13/7)	Z907	12.80	0.71	0.73	6.60	[172]
0.2 M I ₂ in PMImI/EMImTFSI/EMImTf (vol ratio 2/2/1)	D149	16.13	0.61	0.68	6.67	[173]
0.1 M I ₂ , 1 M PMII, 0.2 M LiTFSI, 0.5 M NBB in MPN	D205	15.30	0.66	0.67	6.8	[151]
0.2 M I ₂ , 0.5 M NMBl, 0.1 M GuanSCN in REImI/REImTFSI (Vol ratio 13/7)	K60	13.54	0.70	0.72	6.80	[151]
0.2 M I ₂ , 0.14 M GuanSCN, 0.5 M TBP in PMImI/EMImSCN (Vol ratio 13/7)	Z907	13.30	0.75	0.72	7.00	[174]
0.2 M I ₂ , 0.5 M NMBl, 0.1 M GuanSCN in PMImI/EMImB(CN) ₄ (Vol ratio 13/7)	Z907-Na	13.55	0.74	0.70	7.00	[175]
0.2 M I ₂ , 0.5 M NMBl, 0.12 M GuanSCN in PMImI/EMImSCN (Vol ratio 13/7)	K19	13.99	0.71	0.71	7.05	[176]
1 M PMII, 0.1 M 4-OH-TEMPO, 0.01 M NOBF ₄ , 0.2 M LiTFSI, 0.5 M NBB in MPN	D205	17.40	0.71	0.58	7.2	[177]
0.05 M [Co((Melm-Bpy)PF ₆) ₃] ²⁺ , 0.02 M NOBF ₄ , 0.14 M GuNCS, 0.5 M TBP in PMII/EMINCS (Vol ratio 13/7)	N719	15.10	0.71	0.69	7.37	[170]
0.2 M I ₂ , 0.5 M NMBl in PMImI/EMImTCM (Vol ratio 1/1)	Z907Na	12.80	0.75	0.76	7.40	[178]
0.8 M PMImI, 0.15 M I ₂ , 0.1 M GuanSCN, 0.5 M NMBl in MPN	K19	15.10	0.75	0.70	8.00	[179]
1 M PMII, 0.1 M [Melm-TEMPO][TFSI], 0.01 M NOBF ₄ , 0.2 M LiTFSI, 0.5 M NBB in MPN	D205	18.40	0.73	0.61	8.20	[177]
1 M DMIII, 0.15 M I ₂ , 0.5 M NBB, 0.1 M GNCS in MPN	C103	17.51	0.77	0.71	9.60	[151]
1 M DMII, 0.15 M I ₂ , 0.5 M NBB, 0.1 M GuNCS, 50 mM NaI in BN	C106	17.90	0.73	0.76	10.00	[180]

Ionic liquids are comprised of cations and anions [151]. Cations are usually phosphonium or ammonium salts that are generally bulky, with low charge densities, low symmetry and weak intermolecular interactions [181]. Anions found in ionic liquids can be divided into two groups: complex anions, such as triflate derivatives and various borates, and secondly the halide/pseudohalide anions [166, 181].

In 1996, Papageorgiou *et al.*, first demonstrated a DSSC with long-term stability while using an ionic liquid as a solvent in the electrolyte [182]. By pairing the ionic liquid with methyl-hexyl-imidazolium iodide (MHImI) as an involatile electrolyte, the DSSC exhibited exceptional stability with a sensitizer redox turnover of roughly 50 million [151]. Wang *et al.*, reported an

ionic liquid electrolyte-based $\text{SeCN}^-/(\text{SeCN})_3^-$ redox couple [174]. The conductivity and viscosity of the ionic liquid, 1-ethyl-3-methylimidazolium selenocyanate (EMImSeCN), was 14.1 mS/cm and 25 cP respectively [151, 174]. Due to the visible–light absorbance, low viscosity and high conductivity of the ionic liquid electrolyte, an overall efficiency of 7.5-8.3 % was obtained [174]. It must be noted that the DSSC had long-term stability issues, thus Z907Na had to be used as a sensitizer paired with a solvent-free ternary eutectic melt ionic liquid electrolyte to decrease the mass-transport limitation as well as the melting point, which solved the stability issues, resulting in an overall efficiency of over 8 % [183].

Imidazolium-based ionic liquids are the most efficient and widely used electrolytes in DSSC application [184]. Other solvent-free electrolytes with cations such as ammonium, pyridium, phosphonium, guanidinium or sulfonium has also been investigated for DSSC usage, but showed low photocurrents and efficiencies due to high mass-transport limitations and viscosity [151]. Xi *et al.*, indicated an increase in device efficiency by implementing a high-fluidity tetrahydrothiophenium melt, which demonstrated that nonimidazolium ionic liquids can actually be used for highly efficient DSSCs [185].

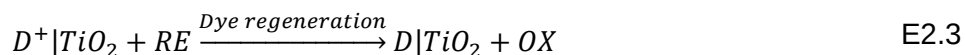
The nature of the cation and anion tremendously affects the photoelectrochemical properties of the ionic liquid [186]. When focusing on Lewis acid-base behaviour, the cations found in ionic liquids are weak Lewis acids, resulting in the coordination of electron-rich species in the ionic liquids [152]. Son *et al.*, used a series of substituted imidazolium iodides as electrolytes to show that small cation substitutes resulted in higher photocurrents due to higher diffusion coefficients of triiodide being created, whereas the larger substitutes only displayed an increase in photovoltage [187].

Most ionic liquids suffer from high mass-transport limitations, however ionic liquids can be diluted with an organic solvent such as acetonitrile to greatly reduce the mass-transport limitations [166]. It is important to note that a high concentration of imidazolium iodides cause a reduction of the dye molecules, which results in the reduced dye ineffectively injecting the electrons into the semiconductor [178]. An alternative solution to the high mass-transport limitation dilemma of pure ionic liquids is to mix imidazolium iodides with low-viscosity ionic liquids [151, 188]. Ionic liquids are a competitive replacement for organic solvents as the electrolyte solvent for DSSCs however, the drawbacks of low ion mobility and high viscosity must be overcome first [166].

2.4.4.1.3 IODIDE/TRIIODIDE REDOX COUPLES

When referring to the photoelectrochemical cycle of a DSSC, it should be noted that the reduced state of the redox couple (iodide) is responsible for the regeneration of the photo-oxidized dye (D^+), when this occurs, the oxidized state of the couple (triiodide) diffuses to the counter electrode of the DSSC, where it is reduced [151]. The redox couple plays a vital role

in the DSSC. In terms of reaction kinetics, the redox couple in the DSSC should exhibit an asymmetric behaviour, meaning that the electron donation step from the iodide to D^+ should occur quickly to ensure efficient dye regeneration, whilst this process takes place rapidly, the electron acceptance process from the TiO_2 layer to the triiodide should occur slowly to decrease the total electron recombination losses [152, 189]. The dye regeneration process can be defined as shown in equation 2.3 [151].



The reduction of the triiodide to form iodide at the counter electrode section of the DSSC should occur quickly to provide a substantial amount of couple sources to complete the electrochemical cycle in the DSSC [190]. When focusing on the increase of photovoltage in the DSSC, it is of utmost importance to include a redox electrolyte that has energy similar to the D^+/D energy level however, the electrolyte must also have sufficient driving force to ensure dye regeneration [191]. The iodide/triiodide couple provides fast dye regeneration, slow electron recombination rates and also consists over a suitable redox potential while also having long-term stability, good solubility characteristics, efficient conductivity, miniscule light absorption and a sought after penetration ability into the semiconductor film [191]. These unique features are the main reason as to why the iodide/triiodide couple has been used as the preferred redox couple since the initial development phases of DSSCs [151].

When focusing on the solution, the iodine binds with the iodide which results in the formation of triiodide in an equilibrium reaction [151].



When the iodine concentration is too high, the probability of polyiodide species formation such as I_5^- , I_7^- and I_9^- will be high as well [151]. It must be noted that only triiodide is sought after in DSSC electrolytes and any other variation would just lower the overall performance of the system. Even though iodide/triiodide redox couple is the most used redox couple in DSSCs, its recombination rate still suffers from temperature variations [192]. Additives such as 4-tert-butylpyridine and guanidium thiocyanate can reduce the recombination rate [193, 194]. Dyes that include hydrophobic chains can reduce the recombination as well with a blocking effect, an example of such a sensitizer is the Z907 dye [123]. Certain dyes that absorb onto the TiO_2 layer increase the recombination rate, which may result in an increased concentration of triiodide near the sensitizer [195].

For rapid dye regeneration, iodide should consist over a high diffusion rate and concentration [151]. When using a nonviscous solvent such as acetonitrile, an iodine concentration of 0.3 M would be sufficient for use in the electrolyte, however when using a viscous ionic liquid, a

higher iodine concentration might be necessary [178]. It is possible that the triiodide transportation to the counter electrode can be a rate-limiting step in a DSSC if the solvent used is viscous or if the triiodide concentration is low [182]. When the DSSC contains high triiodide concentration, the diffusion coefficient might increase by the Grotthus mechanism [151].

The combination of the cations and the I^-/I_3^- anions in the electrolyte have indirectly an influence on the photovoltaic performance of the DSSC as well as the properties of the liquid electrolyte used in the DSSC [151]. The influence consists over three aspects with regards to the DSSC. (i) The cations found in the electrolyte affects the electron transportation in the TiO_2 layer [196]. The electron diffusion found in the conduction band of the TiO_2 layer is known as an ambipolar diffusion mechanism, which means there is a strong correlation between the electron transportation and the ion diffusion, which ensures electron neutrality at the TiO_2 layer [151, 194]. (ii) The position of TiO_2 's conduction band edge is dependant on the concentration as well as type of cations within the electrolyte [122]. (iii) When focusing only on the TiO_2 layer, it can be noted that the negative influence of the cations results in an efficient combination with the triiodide, which results in recombination losses as well as an overall decrease in V_{oc} of the DSSC [13, 197].

It has been found that cations consisting over higher charge densities had a more prominent effect on the photovoltaic properties of DSSCs, which was caused due to recombination losses as well as energy band shifts [198]. An imidazole cation with a much larger ionic radius was implemented in the liquid electrolyte to create a Helmholtz layer on the outer surface of the TiO_2 layer [199]. This would block the direct contact of triiodide with ambipolar $Li^+ - e^-$, thus counteracting the combination of triiodide and ambipolar $Li^+ - 2e^-$, resulting in an increase in V_{oc} [197].

Even though I^-/I_3^- redox couple is performing remarkably in DSSCs, there are still numerous negative aspects that is limiting its usage in further applications: (i) Iodine is corrosive to most sealing materials, causing numerous assembling and sealing problems, resulting in poor long-term stability in DSSCs [200]; (ii) iodine has a high vapour pressure, resulting in difficulty for device encapsulation [151]; (iii) the triiodide ions as well as the other polyiodides slight absorb the visible light, thus lowering the overall efficiency of the DSSC [189]; (iv) a mismatch between the redox potential of the I^-/I_3^- redox couple and a typical sensitiser results in a loss in V_{oc} [189]. Only after these negative effects are solved, can the I^-/I_3^- redox couple be used as the leading couple in DSSCs.

2.4.4.2 Hole-transporting material

2.4.4.2.1 INORGANIC HOLE-TRANSPORTING MATERIAL

When referring to DSSC principles, the redox couple I^-/I_3^- and the TiO_2 layer can be classified as the hole-transporting layer and electron-transporting layer respectively, thus the redox couple can be replaced with a p-type semiconductor as an alternative hole-transporting material (HTM) [20]. HTM is generally defined as a semiconductor due to the charge carrier transportation is done by electrons or holes [201]. Charge carrier transport occurs through hole hopping between molecules located near each other, this is known as electronic transport [122]. In ssDSSCs, HTMs usually contain salts that promotes ionic conductivity, which is important for charge compensation [122].

A HTM used in ssDSSCs has several requirements to fulfil before being used. (i) The HTM must be transparent in the visible range and should not be able to dissolve the sensitizer during the deposit process [202]. (ii) The HTM's hole mobility should be high, as a low mobility would decrease overall device performance [203, 204]. (iii) The HTM must be able to be deposited within the TiO_2 layer while being in an amorphous state [205]. If the HTM were not in an amorphous state, it would lead to efficient pore filling of the TiO_2 layer, which would limit the device performance greatly [206]. (iv) The HTM must be capable of hole transportation from the sensitizer after electron injection into the TiO_2 layer [207]. It is important to ensure that the valence band of the p-type semiconductors are above the ground state of the sensitizer [207].

2.4.4.2.2 ORGANIC HOLE-TRANSPORTING MATERIAL

In comparison to its inorganic counterpart, organic hole-transporting materials display promising features such as, simple low cost preparation and being an abundant resource [151]. Most organic HTMs are soluble in organic solvents [208]. Methods such as photochemical polymerisation methods, spin coating or in situ electrochemical polymerisation can be used for ssDSSC fabrication with an organic HTM and TiO_2 mesoporous films [208].

Organic HTMs can be tailored by using different chemical methods to fulfil different purposes and is often used in organic light-emitting diodes [209], organic thin film transistors [210] and organic solar cells [211]. Organic HTMs can be divided into two groups, molecular HTMs and polymeric HTMs [208].

In 1997, Yanagida *et al.*, used polypyrrole (PPy) as an organic HTM in one of the very first ssDSSCs ever made [212]. To improve HTM and TiO_2 connectivity, in situ photoelectrochemical polymerisation was used to deposit PPy on the N3 dye-anchored TiO_2 layer and obtained an overall efficiency of 0.1 % [212]. Shortly after, the N3 dye was replaced

with *cis*-Ru(4,4'-dicarboxy-2,2'-bipyridine)₂(3-(pyrrole-1-ylmethyl)pyridine)₂, while the platinum counter electrode was replaced with a carbon-based counter electrode, these changes led to an increase in overall efficiency to 0.62 % [213, 214]. The reason for the cell's poor performance was due to the polypyrrole absorbing the visible light [212-214].

HTMs have great long-term stability however, the efficiencies of ssDSSC are much lower than their liquid DSSC counterparts due to ineffective interfacial contact [151]. It is still important to note that certain HTMs, such as 2,2',7,7'-tetrakis(N,N-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD) paired with organolead halide perovskite, resulted in an overall efficiency of nearly 20 % [215]. This shows that HTMs will still exhibit promising developments in the near future.

2.4.5 COUNTER ELECTRODE

Platinum is mostly used as the counter electrode for a DSSC, for it demonstrates high efficiencies however, a replacement is required as platinum is expensive and contributes substantially to the overall cost of a DSSC [9]. The counter electrode's role is to retrieve electrons situated in the external circuit and returning them to the redox electrolyte, hence closing the circuit loop [216]. The performance of the counter electrode depends highly on the method of platinum deposition onto the glass substrate's surface [217].

Other potential counter electrodes have been tested such as, carbonylsulfide (CoS), carbon, graphene and gold [218]. Even though the aforementioned carbon counter electrodes are cost effective, the electrodes are fragile and suffer from mechanical instability [216]. Conducting polymers can also be used as potential counter electrodes, but require a complex electrolytic polymerisation process to be constructed [216].

2.5 I-V CHARACTERISTICS OF A DYE-SENSITISED SOLAR CELL

Södergren *et al.*, stated that the current-voltage characteristics of a solar cell is recorded by measuring the current produced while varying the external voltage opposite the photovoltage [219]. Another method to measure the I-V characteristics is to vary the external resistance. If the semiconductor is forward-biased, the Fermi-level at the semiconductor interface will subsequently increase, which will also result in an increase in electron concentration [219]. The change in potential regarding the semiconductor interface is then written as:

$$V_{sc} = \frac{kT}{q} \ln \frac{n}{n_0} \quad \text{E2.5}$$

Focusing on equation 2.5, n_0 and n is the electron concentration before and after implementing a forward bias while T is the absolute temperature and k is the Boltzmann's constant [219]. The photopotential measured, V , must also account for potential drops regarding the

semiconductor interface as well as in the electrolyte. The potential drops will cause changes in the measured photopotential, thus it must be corrected by using an ideality factor, m [219]:

$$V_{sc} = \frac{V}{m} \quad \text{E2.6}$$

With regards to photocurrent as a function of voltage, expressions can be derived by applying appropriate boundary equations [219]. The first boundary equation is when focusing on substrate-electrode (SE) illumination. The initial electron concentration is now equal to the increased electron concentration due to the increase in voltage:

$$n(0) = n \quad \text{E2.7}$$

The secondary boundary equation indicates the outer electrons in the semiconductor film, $x = d$, that will reflect on the outer layer and diffuse into the inner layers of the semiconductor [219]:

$$\frac{dn(x)}{dx} |_{x=d} = 0 \quad \text{E2.8}$$

By using the two boundary equations to solve the diffusion equation given as:

$$Dn''(x) - (n(x) - n_0)/\tau + \phi\alpha e^{-\alpha x} = 0 \quad \text{E2.9}$$

Where D is the diffusion constant of the electrons, $n(x)$ is the electron density that is in excess, τ is the mean charge carrier lifetime, ϕ is the light intensity, α is the reciprocal absorption length and n_0 is described at equation 2.5 [219]. The photocurrent can then be expressed as:

$$J_{SE} = J_{SE}^0 - \frac{qDn_0 \sinh\left(\frac{d}{L}\right)}{L \cosh\left(\frac{d}{L}\right)} (e^{\frac{qV}{kTm}} - 1) \quad \text{E2.10}$$

Where d is the diffusion length, L is the film thickness and q is the electronic charge.

However, when referring to titanium dioxide used in dye-sensitised solar cells, the semiconductor only experiences excitation when being illuminated with UV light [220]. Titanium dioxide consists over a wide band gap of 3.2 eV, but still requires a sensitiser to excite an electron within its structure, resulting in a flow of excited electrons from the sensitiser to the semiconductor.

To complete this process of electron transport, the energy level of the lowest unoccupied molecular orbital (LUMO) of the sensitiser must be higher than the conduction band energy of the semiconductor, otherwise no electron flow will occur within the system [220]. Figure 3 indicates the difference between the energy levels of the ruthenium dyes N719 and N749 as well as the conduction band of titanium dioxide used in dye-sensitised solar cells:

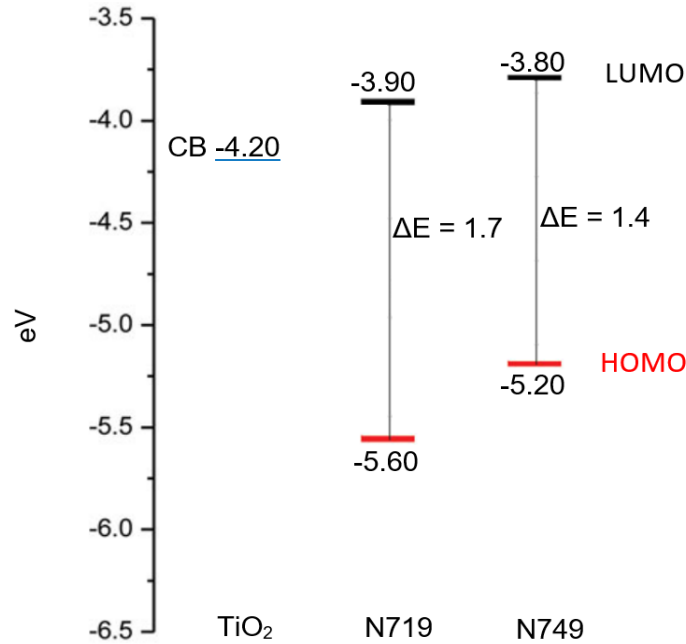


Figure 3 - Energy diagram indicating the energy levels of N719 and N749 with regards to the conduction band of titanium dioxide. Adapted from [220].

There is an abundance in information regarding the physical and chemical properties of TiO₂ however, not much is known about the europium tellurium oxide compound. Europium tellurium oxide consists over a bandgap of 4.31 eV, which is a much larger in comparison to TiO₂'s bandgap [21]. It is also worth noting that europium tellurium oxide consists over a well-defined crystalline structure when calcinated at 900 °C [21].

2.5.1 DARK I-V CHARACTERISTICS OF A DYE-SENSITISED SOLAR CELL

Electrical properties of solar cells while being under dark conditions can allow the user to predict the performance of the solar cell prior to being deployed [221]. The dark I-V curves can be fitted into a model which can then be used to extract the electrical properties of the solar cell [222].

The current-voltage characteristics of a p-n junction solar cell at forward bias with parasitic resistances while under dark conditions can be given as:

$$I = I_0 \cdot \left(\exp \left\{ \frac{q}{nkT} (V - IR_s) \right\} - 1 \right) + \left(\frac{V - IR_s}{R_{sh}} \right) \quad \text{E2.11}$$

Where R_{sh} is the shunt resistance which represents the current leakages across the p-n junction, R_s is the series resistance which takes ohmic losses into consideration and n , the ideality factor, that is responsible to provide information on the quality of the junction [223]. The saturation current (I_0) is related to the semiconductor properties that can be expressed as:

$$I_0 = qAn_i^2 \left\{ \frac{D_n \cdot F_p}{L_n \cdot N_A} + \frac{D_p \cdot F_n}{L_p \cdot N_D} \right\} \quad \text{E2.12}$$

N_A and N_D represent the densities of the acceptors and donors respectively, q is the electron charge, D_n and D_p represent the diffusion coefficients of electrons and holes respectively, A is the active area of the cell and n_i is the intrinsic carrier concentration [221]. F_n and F_p represent the finite recombination velocity of the electrons and holes. The recombination velocity at both surface sides are dependant on the chemical and physical state of the surfaces [221]. L_n and L_p represent the diffusion lengths that affect the saturation current of the junction. The diffusion lengths must be long enough to ensure that the electron carriers reach the contact areas of the cell before recombination [224].

Wolf *et al.*, investigated the influence of defects on the I-V characteristics of solar cells by implementing proton radiation (20 – 80 MeV) at fluences of $10^{12} - 10^{15} \text{ cm}^{-2}$ to inhibit recombination centres in the space-charge region [225]. It was reported that as the trap density increased in the space-charge region, the recombination of these traps affected and dominated the I-V characteristics of the cell [221]. The proton radiation resulted in a saturation current which consisted over an activation energy of half the bandgap, this occurrence affected the recombination current which can be expressed as [226]:

$$I_{rec} = I_{sr} \left[\left(\exp \frac{qV}{n_R kT} \right) - 1 \right] \quad \text{E2.13}$$

The recombination saturation current (I_{sr}) is directly proportional to the depletion region width and is inversely proportional to the carrier lifetimes [221]. The ideality factor n_R is roughly equal to two. The dark I-V characteristics is a superposition of the diffusion and recombination process, thus solar cells can be modelled by using both processes. The final applied voltage to current relation can then be given as [225]:

$$I = I_0 \cdot \left(\exp \left\{ \frac{q}{n kT} (V - IR_s) \right\} - 1 \right) + I_{sr} \left[\left(\exp \frac{q(V - IR_s)}{n_R kT} \right) - 1 \right] + \frac{V - IR_s}{R_{sh}} \quad \text{E2.14}$$

3. EXPERIMENTAL PROCEDURE

3.1 DYE-SENSITISED SOLAR CELL CONSTRUCTION

3.1.1 SUBSTRATE

The substrate chosen to be used in the construction of the DSSC was fluoride-doped tin oxide glass substrates (FTO). The transmittance of the FTO glass substrate used is $\geq 83\%$. The thickness of the FTO glass substrate used is 1.6 mm and has a sheet resistance less than 15 ohm/sq (Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Item number: FTO-P003). When comparing FTO with its ITO rival, it has been observed that in general FTO results in higher overall efficiencies.

The glass substrate was cut with a diamond cutter into squares with dimensions of 20×20 mm. After cutting, the substrate was rinsed with ethanol to remove any unwanted particles from the surface area and then left to dry at room temperature. After drying, the coated side of the substrate was identified by using a digital multimeter. The coated section of the substrate was then placed facing upwards in preparation for semiconductor application. Scotch tape was used to secure the position of the substrate and also to create an open area of 10×20 mm where the semiconductor will be placed. Lastly, the open area of the substrate was gently wiped with ethanol again and left to dry at room temperature.

3.1.2 PHOTOANODE AND CATHODE

The semiconductor first used to create the photoanode is TiO_2 (Degussa P25, nano-powder). Four different concentrations were prepared for experimentation, namely: 0.17; 0.20; 0.23, 0.26 and 0.31 g/ml. The TiO_2 was weighed off into a glass container that consists of a sealer to ensure no evaporation of the ethanol occurs after a long time period. After the TiO_2 was weighed, ethanol (99.9 %) was used as the dispersant and samples of 10 ml were made. The samples were then sonicated at 25 °C for 15 minutes.

After sonication, 0.5 ml of titanium(IV) tetraisopropoxide was added to create a thicker suspension. The samples were sonicated for another 15 minutes at 25 °C. After sonication, 50 μl of the TiO_2 sample was pipetted using an electronic pipette and deposited onto the glass substrate. The TiO_2 sample was then spread slowly over the open area of the glass substrate by using the doctor blade technique (the technique of using a smooth knife to spread a slurry onto a carrier film) and using the scotch tape on the substrate to ensure a constant thickness was being implemented. The TiO_2 layer applied was left to dry at room temperature for one minute.

After drying, the scotch tape was removed and the photoanode was placed onto a heating plate for sintering. The heating plate was heated up to 280 °C while the photoanode was placed above it to ensure that the substrate won't crack while being in contact with the plate. When the plate reached a temperature of 280 °C, the substrate continued to be heat treated for 10 minutes.

After the sintering process, the heating plate was turned off, but the photoanode was left on the plate to ensure slow cooling, because changing the temperature of the glass substrate too quickly might result in cracking. After cooling down to room temperature the photoanode was fully immersed in the sensitizer. The europium semiconductor preparation process is identical to TiO₂'s process, except no titanium(IV) tetraisopropoxide was added, because the effects of pure europium tellurium oxide wants to be investigated. The cathode comprised out of a glass FTO substrate that was cut into squares of 20 × 20 mm. Platinum was deposited onto the substrate with a thickness of 100 nm by using the physical vapour deposition method employing a PVD Project 270 physical vapour deposition apparatus (PVD Products, USA).

3.1.3 ELECTROLYTE

Lithium iodide as well as sodium iodide was tested for the use as an iodide/triiodide redox couple electrolyte. Iodine was used for both iodides in the electrolyte preparation process. Four different concentrations of iodide and iodine were researched independantly. Samples of 5 ml using acetonitrile (99.9%) as solvent were created, with iodide concentrations of 0.4, 0.5, 0.6 and 0.7 M and iodine concentrations of 0.04, 0.05, 0.06 and 0.07 M.

The iodine concentration was first kept constant at 0.05 M while the iodide concentration was varied. After the best iodide concentration was obtained, the iodine concentration was then varied. The iodine and iodide was weighed off into a glass bottle that can be sealed to ensure no evaporation takes place. After both solids were weighed off, acetonitrile (99.9 %) was used as solvent to create samples of 5 ml each. The samples were then sonicated at 25 °C for 15 minutes. After the samples were sonicated, 0.5 M of 4-tert-butylpyridine (TBP) was added to ensure longer stability of the electrolyte. The sample was sonicated for another 15 minutes at 25 °C.

3.1.4 SENSITISER

Rhodamine blue, Rhodanile blue, N749 and N719 were all tested as viable sensitizers for DSSCs. Firstly, N749 was used as a benchmark to evaluate the other sensitizers. Dye concentrations of 0.25, 0.5, 0.75 and 1 mM were all individually tested in a DSSC . Each dye was weighed off into glass containers that could be sealed to ensure that the solvent can't evaporate. Ethanol was used as solvent and 5 ml samples were made up for all dyes. After

the dry dye powders were weighed off, the 5 ml ethanol was added and the samples were sonicated for 15 minutes at 25 °C.

After sonication, the photoanode was then submerged into the dye to begin the sensitising process. The sensitising time was varied for 10 minutes, 6, 18 and 30 hours. The reason behind these obscure time variations was due to COVID-19 regulations, at the time, prohibiting lab entrance at certain times of the day. After sensitising, the photoanode was taken out of the solution and rinsed with ethanol to remove any excess dye. The photoanode was then left to dry for 30 seconds at 100 °C. After drying, a spacer constructed out of scotch tape is attached onto the open area of the semiconductor. A hole was cut into the spacer with dimension of 5 × 5 mm, thus the active area of the DSSC is 0.25 cm².

After the spacer was secured into place by adding pressure onto the tape, 20 µl of the electrolyte solution was then pipetted onto the active area. The platinum cathode was then placed on top of the electrolyte and secured with two clips to ensure a connection between the anode and cathode as well as to clear any air bubbles located in the active area.

3.2 DYE-SENSITISED SOLAR CELL CHARACTERISATION

3.2.1 CURRENT-TO-VOLTAGE CHARACTERISTICS

DSSCs are evaluated by power conversion efficiency (PCE). To calculate PCE, a current density – voltage graph is required. By illuminating the solar cell by using a Toption-X300 (Xenon light source 100-1100 nm) solar simulator, while alternating the voltage and measuring the current with a potentiometer (Scan rate of 50 mV/s), a current-voltage graph can be plotted. The photocurrent obtained at zero voltage is known as the short circuit current density (J_{sc}) and the photovoltage obtained at zero current density is known as the open circuit voltage (V_{oc}).

PCE can be defined as the ratio of maximum solar cell power (P_m) to the light intensity illuminating the cell. Power is defined as the product of current and voltage, P_m is the maximum power that can be obtained while voltage is varied. When working under standard 1.5 AM conditions, 100 mW/cm² of incoming light is being distributed over the solar cell. P_{in} changes as light intensity changes, but for this discussion P_{in} will be used as 100 mW/cm². The formula used for PCE is defined as:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{P_{max} [\frac{mW}{cm^2}]}{100 [\frac{mW}{cm^2}]} \quad E3.1$$

Another important factor calculated using J/V graphs is the fill factor (FF), which can be defined as the ratio of P_m in relation to the product of V_{oc} and J_{sc} . The optimal fill factor would be equal to one which results in a perfect DSSC where no current is lost as voltage is increased. This means that the product of V_{oc} and J_{sc} would be equal to P_m . The formula for FF is:

$$FF = \frac{P_{max}}{J_{sc} \times V_{oc}} \quad E3.2$$

By substituting equation 3.1 into equation 3.2, the following can be deduced:

$$FF = \frac{\eta \times P_{in}}{J_{sc} \times V_{oc}} \quad E3.3$$

When writing in respect of the PCE:

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}} \quad E3.4$$

Thus simplifying again to obtain:

$$\eta = \frac{P_{max}}{P_{in}} \quad E3.5$$

3.2.2 INCIDENT PHOTON TO CURRENT EFFICIENCY

Incident photon to current efficiency (IPCE) is the response given off by a solar cell when illuminated with light in terms of current. The wavelength of the incoming light is incrementally altered whilst the current of the solar cell is being measured at each increment. Optical filter lenses were used to disrupt the incoming light which only allowed specific wavelengths to reach the solar cell. The DSSC IPCE can be calculated by:

$$IPCE = \frac{\text{Collected electron rate number}}{\text{Incident photon rate number}} = \frac{J_{measured}/e [mA.cm^{-2}.C^{-1}]}{\frac{P_{in}(\lambda)}{hc/\lambda} [\frac{mW.cm^{-2}}{eV}]} \quad E3.5$$

The equation can be simplified further:

$$IPCE = 1240 \times \frac{J_{measured}}{P_{in}(\lambda). \lambda} \quad E3.6$$

The intensity of light usually used is 100 mW/cm², when all specific wavelengths have been tested, a graph can be created that defines the device's efficiency concerning the different sections of the spectrum of light.

3.2.3 CHRONOAMPEROMETRY

Chronoamperometry (CA) is defined as the change in current with a fixed voltage as time progresses. The effect of voltage is also tested by setting the fixed voltage higher/lower, resulting in a change in bias hence affecting the current being produced. The most important factor for using CA is to observe the lifetime and durability of the cell constructed. As time progresses, cell degradation will occur, resulting in the current decreasing. No additional calculations are needed, except converting the current reading into current density which is defined as:

$$\text{Current density [mA/cm}^2\text{]} = \frac{\text{Current [mA]}}{\text{Active area of DSSC [cm}^2\text{]}} \quad \text{E3.7}$$

3.3 PHYSICAL CHARACTERISATION OF CHEMICAL COMPOUNDS

3.3.1 SCANNING ELECTRON MICROSCOPE

Scanning electron microscope (SEM) was used to determine the thickness of the semiconductor layer constructed by using the doctor blade technique. As stated by Shirkavand *et al.*, the optimal thickness for the semiconductor layer ranges from 12 to 16 µm [227]. The purpose of the SEM analysis was to not only determine the semiconductor thickness, but also to ensure that a consistent thickness resided on the glass substrate.

SEM analysis was done on the TiO₂ layer and a thickness range of 20 – 30 µm was observed. The SEM scan of TiO₂ can be seen in Figure 4. It was observed that the upper side of the semiconductor layer was consistent, hence concluding that the doctor blade technique was effective, however the bottom side of the layer indicated small inconsistencies on the surface area of the glass substrate, thus resulting in a varied thickness between 20-30 µm.

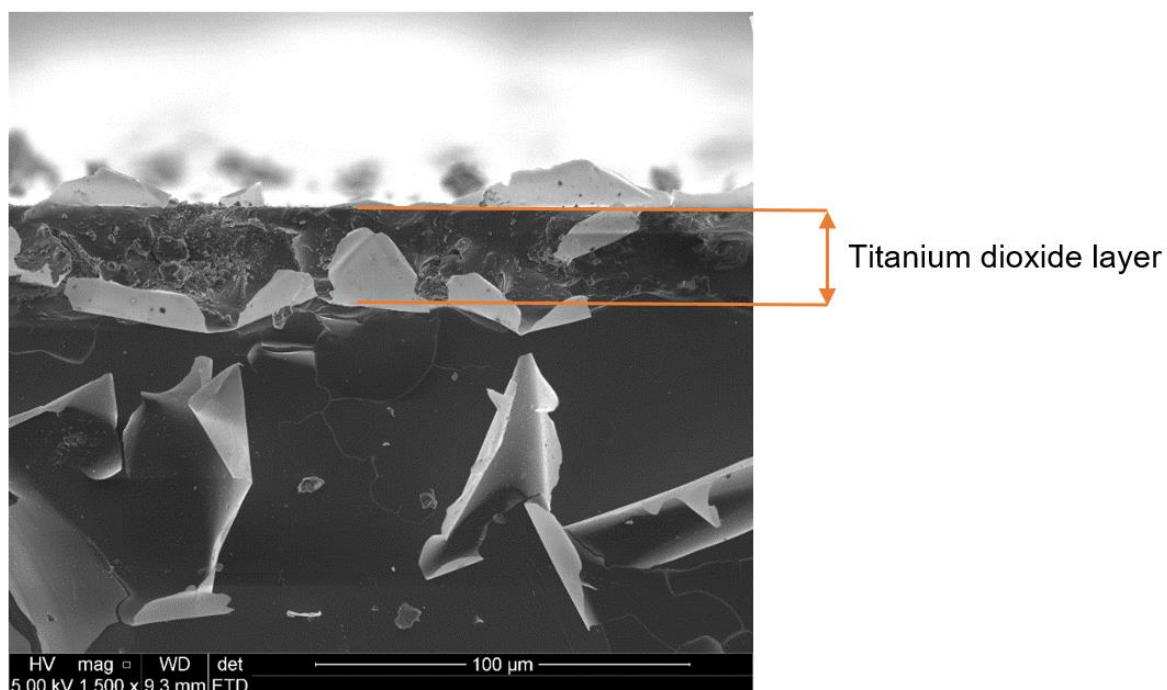


Figure 4 - 100 μm SEM of TiO_2 without sensitizer

For europium(II) tellurium oxide (Eu(II)), two samples were prepared with different particle sizes to indicate if it would make a difference to the layer formed. A layer thickness of $27.1\ \mu\text{m}$ was observed while using the Eu(II) sample with a particle size of $30.70\ \mu\text{m}$. After pestle and mortar treatment, the finer Eu(II) used to create a layer of semiconductor resulted in a layer thickness of roughly $400 - 500\ \text{nm}$. The SEM scans of the Eu(II) semiconductor layers can be seen in Figure 5 and Figure 6.

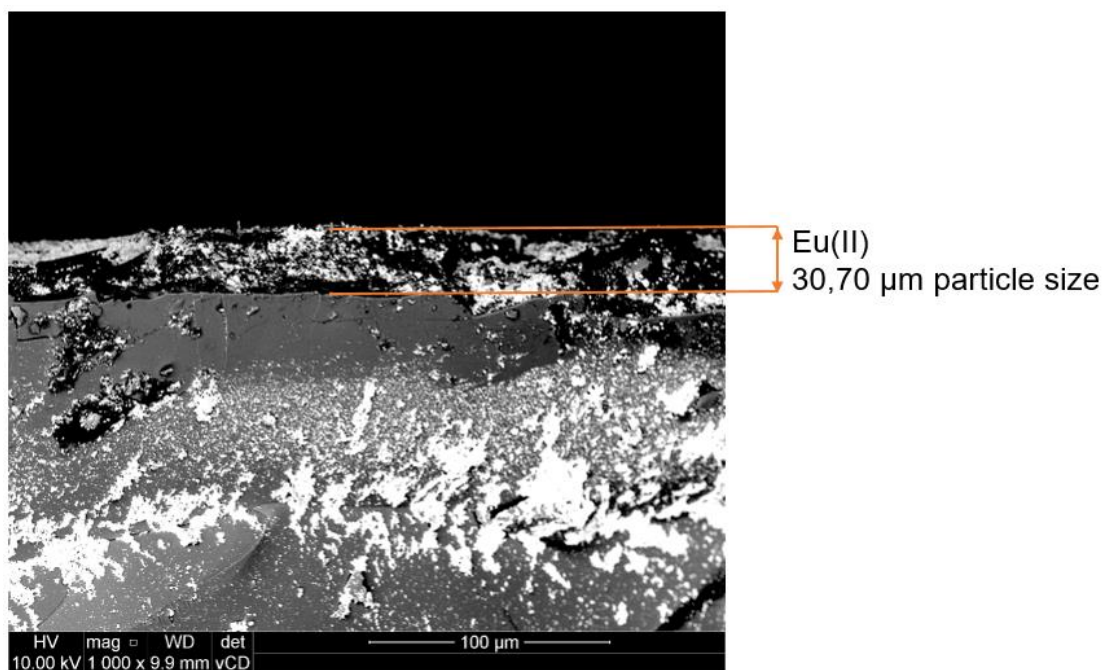


Figure 5 - SEM scan for Eu(II) with a particle size of $30.70\ \mu\text{m}$

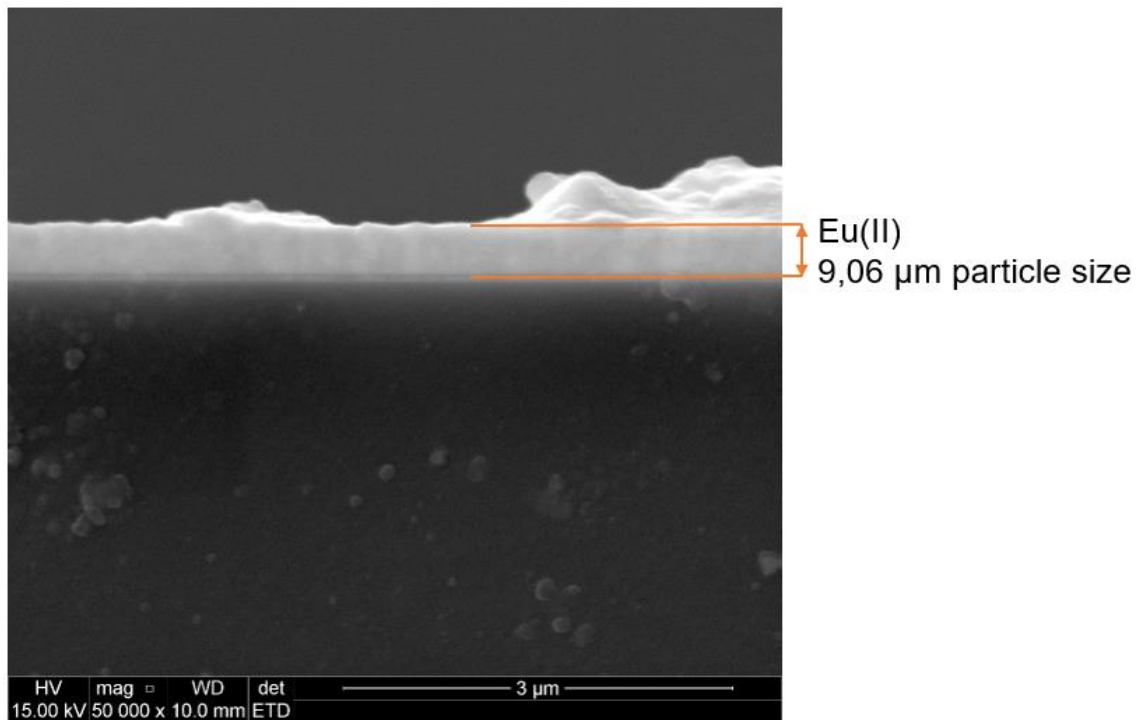


Figure 6 - SEM scan for Eu(II) with a particle size of 9.06 μm

SEM scans were also done on the two spacer options. It was seen that the parafilm consisted over a thickness of 126 μm , while the scotch tape consisted over a thickness of 60 μm . The SEM scans of the parafilm and scotch tape can be seen in Figure 7 and Figure 8 respectively.

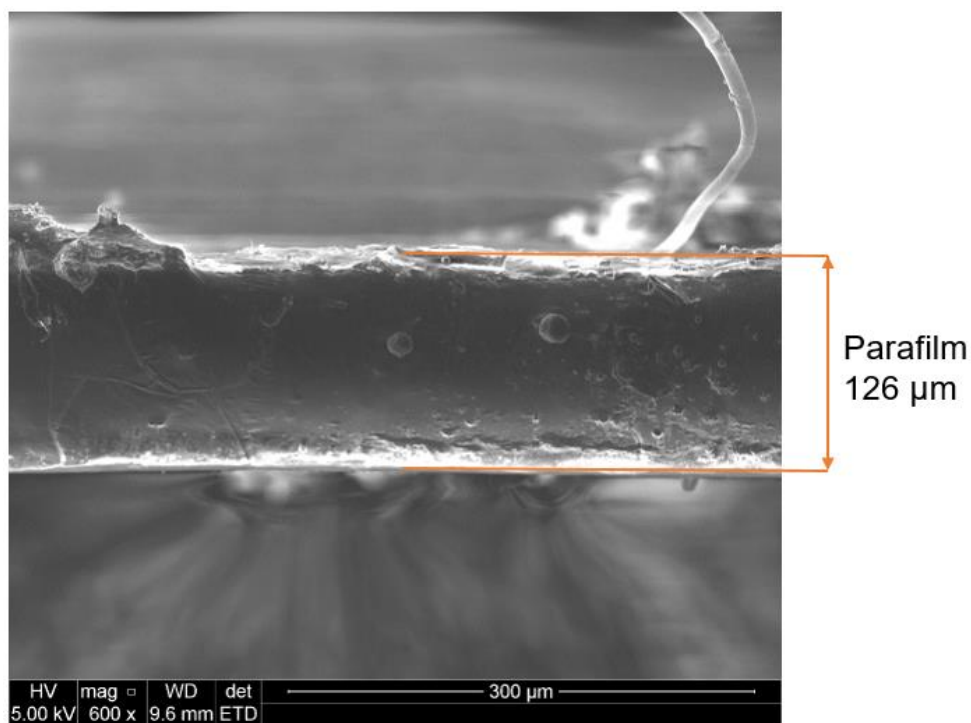


Figure 7 - SEM scan of parafilm spacer

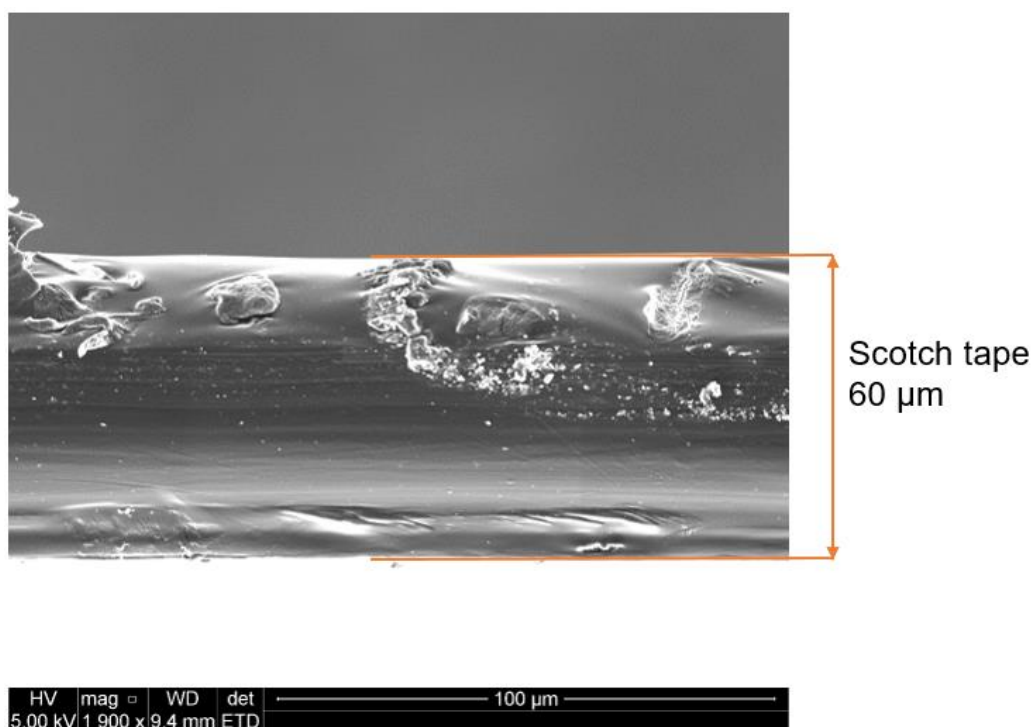


Figure 8 - SEM scan of scotch tape spacer

3.3.2 PARTICLE SIZE DISTRIBUTION

Particle size distribution (PSD) analysis was done on the titanium dioxide as well as Eu(II) to indicate if there is a difference in particle size regarding the two semiconductors. These tests were carried out at the North West University's Engineering campus on the Malvern particle size distributor (MasterSizer 3000). Ethanol was used as a dispersant for all the samples. The Malvern was rinsed with deionized water three times before rinsing it with ethanol prior to the sample run. The samples were suspended in 500 ml of ethanol and then sonicated for five minutes before being sent through the Malvern for particle size testing.

For the TiO_2 test, the particle name on the database was chosen to be Titanium Dioxide TiO_2 (Anatase) with a refractive index of 2.510 and an absorption index of 0.01. After sonication, the sample was then pumped throughout the instrument which flows between two glass plates where a laser is shined through while being obscured by the particles flowing between the aforementioned plates. The analysis indicated that 10 % of the TiO_2 particles were $1.15\ \mu\text{m}$, 50 % of the particles were smaller than $3.60\ \mu\text{m}$ and lastly, 90 % of the particles were $11.3\ \mu\text{m}$ and smaller. The PSD analysis was carried out three times and an average plot was constructed between the three readings, the plot can be observed in Figure 9.

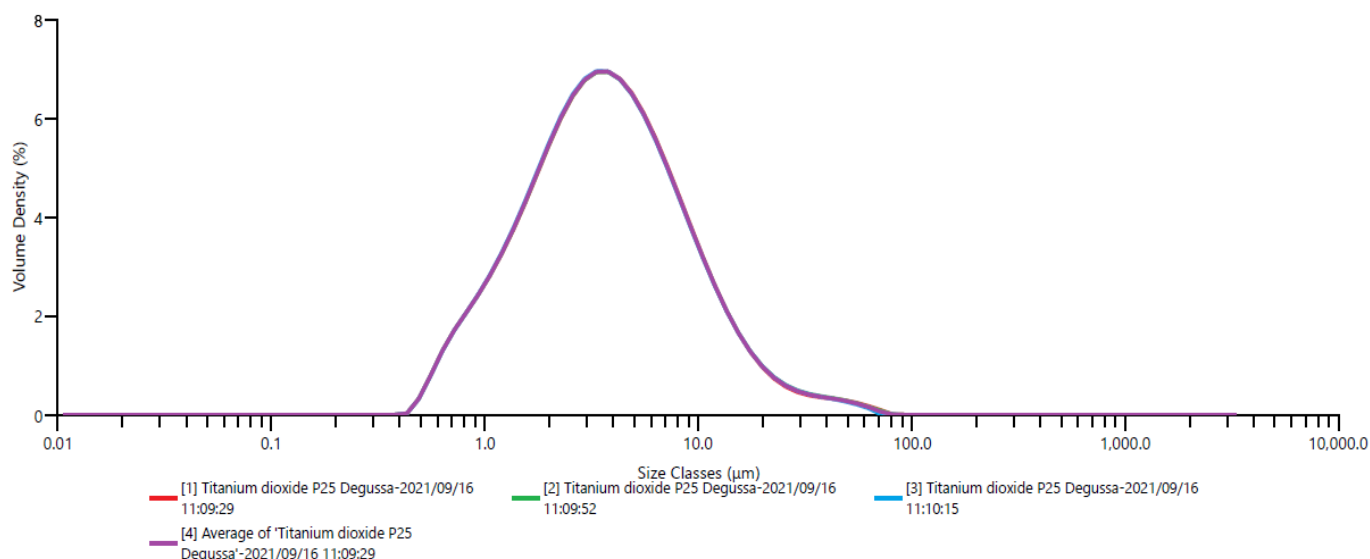


Figure 9 - PSD of TiO_2 Degussa nanopowder

The Malvern database did not have Eu(II) in its data list, thus a particle name was chosen to represent Eu(II). Titanium dioxide (Anatase) was chosen to represent Eu(II). The analysis resulted in a particle spread which indicated 10 % of particles that were smaller than 1.31 μm , 50 % of particles that were smaller than 9.28 μm and lastly, 90 % of particles smaller than 30.7 μm . The PSD for Eu(II) was tested three times with an average plot also being calculated out of the data set. The PSD graph can be seen in Figure 10.

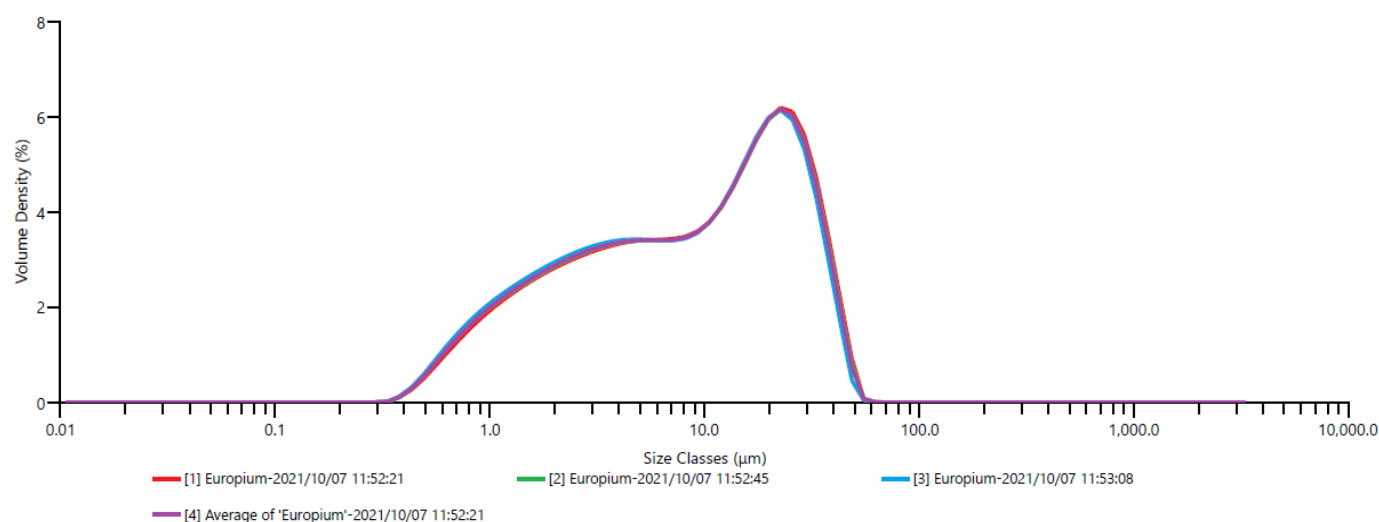


Figure 10 - PSD of europium(II) tellurium oxide prior to pestle and mortar handling

With the prior tests, it was observed that Eu(II) had a much larger particle size than TiO_2 . To conduct a study to observe if the particle size has an effect on DSSC efficiency, the Eu(II) underwent a pestle and mortar process for 30 minutes where ethanol was gradually added with the goal to decrease the particle size. After 30 minutes of pestle and mortar, the sample was heated to 110 $^{\circ}\text{C}$ so that remaining ethanol can be evaporated. After the pestle and mortar treatment, a PSD analysis was done on the new Eu(II) sample. The pestle and mortar process

resulted in a dramatic decrease of Eu(II) particle size where, 10 % of the particles were smaller than 0.67 μm , 50 % of the particles were smaller than 2.50 μm and lastly, 90 % of the particles were smaller than 9.06 μm . It can be noted that the pestle and mortar process is a successful method to decrease semiconductor particle size. The PSD graph for the pestle and mortar Eu(II) sample can be seen in Figure 11.

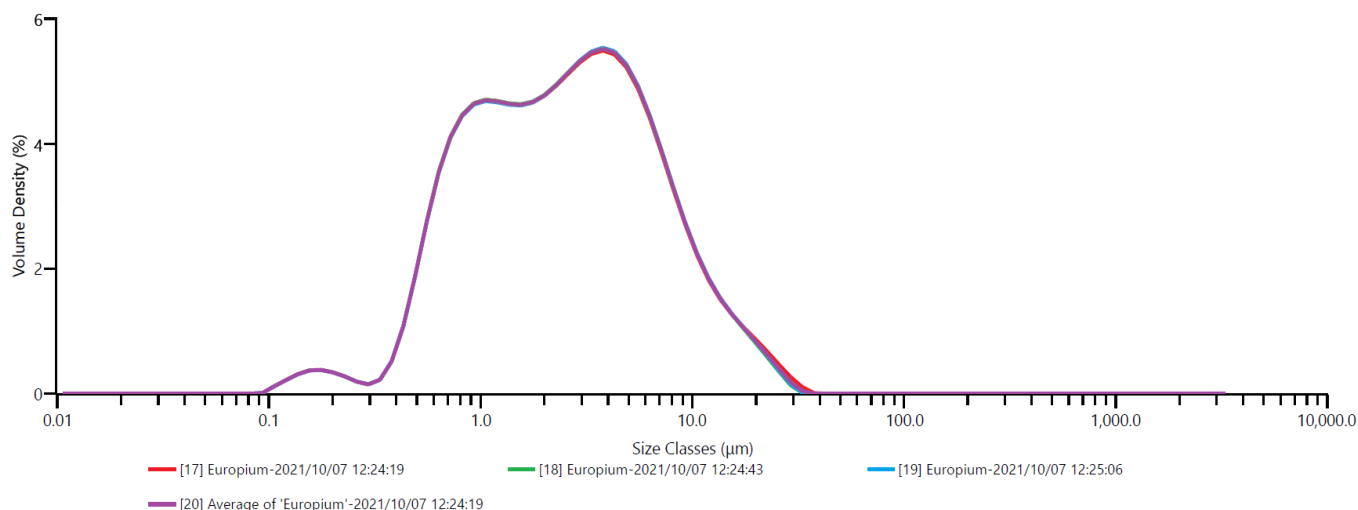


Figure 11 - PSD of europium(II) tellurium oxide after pestle and mortar handling

3.4 EXPERIMENTAL AND RESULTS LAYOUT

Chapter 4 (Results & discussion) consists over a vast amount of graphs and tables which can become overwhelming. A break down structure of all experiments are given in this section. Please note that Chapter 4.5 and 4.7 is not part of the break down because it is a repetition of the experiments done in the other chapters, with only a difference in light intensity (100 mW/cm^2 (100-1100 nm) was used).

Chapter 4.1 is done to test all parameters regarding a DSSC's components. As stated in Chapter 1.3, the parameters will be fixed through experimentation while using TiO_2 as the semiconductor. When the parameters have been tested and fixed as a constant, it will be employed in Eu(II) and Eu(III) DSSCs, as stated in the scope of investigation.

After the parameters have been set, illumination tests will be done in Chapter 4.2 on all three types of DSSCs (TiO_2 , Eu(II), Eu(III)). Chapter 4.3 and 4.4 discuss the results obtained by doing chronoamperometry and IPCE tests, respectively. After these experiments, it was noted that the Eu(II) DSSC exhibited higher dark current than the Eu(III) DSSC. Chapter 4.6 focuses on Eu(II) and the potential effects of particle size reduction on the total dark current produced as well as extended illumination times, while comparing it to the conventional TiO_2 DSSC. The following pages present the complete break down of all experiments done in this dissertation.

Semiconductor paste concentration:

- TiO₂ paste concentration is varied
- N749 dye is used
- Semiconductor is sensitised for 10 minutes
- Parafilm is used as the spacer
- 0.5 M Li iodide / 0.05 M iodine electrolyte solution is used
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 1 minute



Spacer thickness and active area:

- Parafilm and scotch tape is tested as spacers
- N749 dye is used
- Semiconductor is sensitised for 10 minutes
- TiO₂ paste concentration is kept constant from previous test
- 0.5 M Li iodide / 0.05 M iodine electrolyte solution is used
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 1 minute



Sensitising time:

- Dye sensitising time is varied
- N749 dye is used
- Scotch tape is used as the spacer
- TiO₂ paste concentration is kept constant from first parameter test
- 0.5 M Li iodide / 0.05 M iodine electrolyte solution is used
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 1 minute



Electrolyte comparison:

- 0.5 M Li iodide and 0.5 M Na iodide is compared
- 0.05 M iodine concentration is kept constant for both tests
- Semiconductor is sensitised for 18 hours
- Scotch tape is used as the spacer
- N719 dye is used
- TiO₂ paste concentration is kept constant from first parameter test
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 1 minute



Sensitiser concentration:

- N719 dye concentration is varied
- Semiconductor is sensitised for 18 hours
- Scotch tape is used as the spacer
- TiO₂ paste concentration is kept constant from first parameter test
- 0.5 M Li iodide / 0.05 M iodine electrolyte solution is used
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 1 minute



Sensitiser comparison:

- Different sensitisers are tested
- Semiconductor is sensitised for 18 hours
- Scotch tape is used as the spacer
- TiO₂ paste concentration is kept constant from first parameter test
- 0.5 M Li iodide / 0.05 M iodine electrolyte solution is used
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 1 minute



Iodide concentration:

- Li iodide concentration is varied
- 0.05 M iodine concentration is used
- Semiconductor is sensitised for 18 hours
- Scotch tape is used as the spacer
- TiO₂ paste concentration is kept constant from first parameter test
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 1 minute



Iodine concentration:

- Iodine concentration is varied
- 0.05 M Li iodide concentration is used
- Semiconductor is sensitised for 18 hours
- Scotch tape is used as the spacer
- TiO₂ paste concentration is kept constant from first parameter test
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 1 minute



4-Tert-Butylpyridine addition:

- Addition of TBP tested
- Semiconductor is sensitised for 18 hours
- Scotch tape is used as the spacer
- TiO₂ paste concentration is kept constant from first parameter test
- 0.5 M Li iodide / 0.05 M iodine electrolyte solution is used
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 1 minute

Chapter 4.2:

5 Minute alternating illumination:

- Test is carried out for TiO₂, Eu(III) and Eu(II) DSSCs
- Parameters are kept constant from chapter 4.1
- 140 mW/cm² (100-1100 nm) light source is used
- DSSC is illuminated in 1 minute intervals for a total of 5 minutes



Dark current measurements:

- Test is carried out for TiO₂, Eu(III) and Eu(II) DSSCs
- Parameters are kept constant from chapter 4.1
- After 1 minute of illumination, the light source is switched off
- There is wait period of 15 seconds to ensure complete shutdown of the light source
- Dark current of the DSSC is measured
- The light source is switched on again and the DSSC is illuminated for another minute
- Steps are repeated for a total of 5 measurements



UV range tests:

- Test is carried out for TiO₂, Eu(III) and Eu(II) DSSCs
- New DSSCs are built and not reused from previous experiments
- Parameters are kept constant from chapter 4.1
- Light source intensity is still used at 140 mW/cm²
- An optical UV filter is attached to the light source (280-315 nm)
- The DSSC is illuminated for 1 minute before the current measurement is taken

Chapter 4.3:

Dark current chronoamperometry:

- Test is carried out for TiO₂, Eu(III) and Eu(II) DSSCs
- Parameters are kept constant from chapter 4.1
- 140 mW/cm² (100-1100 nm) light source is used
- 4 DSSCs are illuminated for 1 minute
- Light source is switched off and 15 seconds is waited for complete shutdown
- The 4 separate DSSCs undergo dark current measurement with each being subjected to a different total voltage (0 V, 0.01 V, 0.02 V and 0.03 V)
- Another DSSC is constructed and used as the baseline measurement
- The baseline DSSC does not undergo illumination and is rather just instantly measured for potential dark current



Chronoamperometry long exposure to light:

- Test is carried out for TiO₂, Eu(III) and Eu(II) DSSCs
- Parameters are kept constant from chapter 4.1
- New DSSCs are built and not reused from previous experiments
- 140 mW/cm² (100-1100 nm) light source used
- DSSC is illuminated for 18 minutes
- Current is measured as a function of time for 18 minutes



Dark current chronoamperometry measurement:

- Test is carried out for TiO₂, Eu(III) and Eu(II) DSSCs
- Parameters are kept constant from chapter 4.1
- After 18 minutes of illumination, the light source is switched off
- There is wait period of 15 seconds to ensure complete shutdown of the light source
- The dark current is then measured directly after the 15 second waiting period
- The second dark current measurement is taken after 10 minutes without illumination.
- This is done to observe any decrease in dark current
- After the second measurement, another 10 minutes are waited (overall total of 20 minutes waited), before taking the final dark current measure
- This test can indicate a slow decrease of dark current as time without illumination is increased
- Another DSSC is constructed and used as the baseline measurement

Chapter 4.4:

Incident photon-to-current conversion efficiency:

- Test is carried out for TiO₂, Eu(III) and Eu(II) DSSCs
- Parameters are kept constant from chapter 4.1
- 140 mW/cm² (100-1100 nm) light source is used
- Optical filters are attached to the light source to ensure that only specific wavelengths of light reach the DSSC
- Following optical filters were used with maximum peaks at the following wavelengths:
 - Filter 1: 254 nm
 - Filter 2: 365 nm
 - Filter 3: 380 nm
 - Filter 4: 420 nm
 - Filter 5: 475 nm
 - Filter 6: 550 nm

Chapter 4.6:

5 Minute alternating illumination:

- Test is carried out for finer (9.06 μm) Eu(II) DSSCs
- (30.70 μm) Eu(II) and TiO₂ DSSCs were already tested in Chapter 4.2
- Parameters are kept constant from chapter 4.1
- 140 mW/cm² (100-1100 nm) light source is used
- A current measurement is done prior to illumination to obtain a baseline reference for dark current
- DSSC is illuminated in 1 minute intervals for a total of 5 minutes

Dark current measurements:

- Test is carried out for finer (9.06 μm) Eu(II) DSSCs
- Parameters are kept constant from chapter 4.1
- After 1 minute of illumination, the light source is switched off
- There is wait period of 15 seconds to ensure complete shutdown of the light source
- Dark current of the DSSC is measured
- The light source is switched on again and the DSSC is illuminated for another minute
- Steps are repeated for a total of 5 measurements



Dark current measurements:

- Test is carried out for TiO₂, 9.06 μm Eu(II) and 30.70 μm Eu(II) DSSCs
- Parameters are kept constant from chapter 4.1
- After 3 minutes of illumination, the light source is switched off
- There is wait period of 15 seconds to ensure complete shutdown of the light source
- Dark current of the DSSC is measured
- After the initial dark current measurement, another measurement is taken every minute for 5 minutes
- No illumination occurs during these 5 measurements
- This test can indicate a slow decrease of dark current as time without illumination is increased



3 Minute prolonged illumination:

- Test is carried out for TiO₂, 9.06 μm Eu(II) and 30.70 μm Eu(II) DSSCs
- New DSSCs are built and not reused from previous experiments
- Parameters are kept constant from chapter 4.1
- 140 mW/cm² (100-1100 nm) light source is used
- A current measurement is done prior to illumination to obtain a baseline reference for dark current
- DSSC is illuminated for 3 minutes



Dark current measurements:

- Test is carried out for TiO₂, 9.06 μm Eu(II) and 30.70 μm Eu(II) DSSCs
- Parameters are kept constant from chapter 4.1
- After 5 minutes of illumination, the light source is switched off
- There is wait period of 15 seconds to ensure complete shutdown of the light source
- Dark current of the DSSC is measured
- After the initial dark current measurement, another measurement is taken every minute for 5 minutes
- No illumination occurs during these 5 measurements
- This test can indicate a slow decrease of dark current as time without illumination is increased



5 Minute prolonged illumination:

- Test is carried out for TiO₂, 9.06 μm Eu(II) and 30.70 μm Eu(II) DSSCs
- New DSSCs are built and not reused from previous experiments
- Parameters are kept constant from chapter 4.1
- 140 mW/cm² (100-1100 nm) light source is used
- A current measurement is done prior to illumination to obtain a baseline reference for dark current
- DSSC is illuminated for 5 minutes

4. RESULTS & DISCUSSION

4.1 J/V CURVES – PARAMETERS

4.1.1 SEMICONDUCTOR PASTE CONCENTRATION

Figure 12 (a) and Table 8 indicates the change in DSSC characteristics as the TiO_2 paste concentration is varied before being implemented into the DSSC. Figure 12 (b) indicates the current density produced while being subjected to 0.15 V and is used to emphasise on the performance difference between the DSSCs. By using Takechi *et al.*, [228] as reference point, five concentrations were chosen to be investigated. It can be seen in Figure 12 (a) and (b) that a 2.88 molar concentration yielded the highest results with an overall efficiency (η) of 0.4215 % and a max power output (P_m) of 0.59 mW/cm^2 as can be seen in Table 8. It was noted when creating the 3.88 molar sample, the ethanol being used as dispersant became saturated due to an overexcess amount of TiO_2 , resulting in a low η of 0.0171 % and a P_m of 0.024 mW/cm^2 , which is only 4 % of what the DSSC with a concentration of 2.88 M produced. The lower TiO_2 concentrations, 2.13 M and 2.50 M, did not perform as poorly as the 3.88 M sample and obtained efficiencies of 0.22 % and 0.25 % respectively however, only acquired 50 - 55 % of the efficiency that the 2.88 M sample achieved.

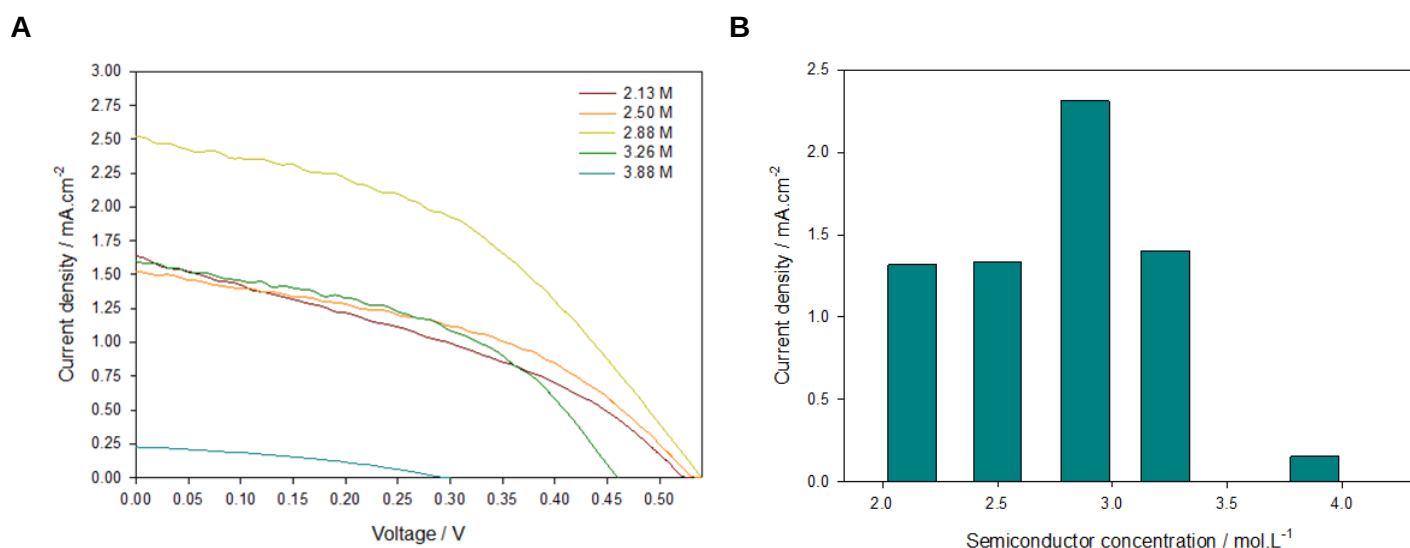


Figure 12 – (a) J/V curves to indicate effect of TiO_2 paste concentration on DSSC efficiency while using N749 dye, parafilm as the spacer and 0.5 M Li iodide and 0.05 M iodine electrolyte solution, and (b) the effect of TiO_2 paste concentration on current density produced at 0.15 V.

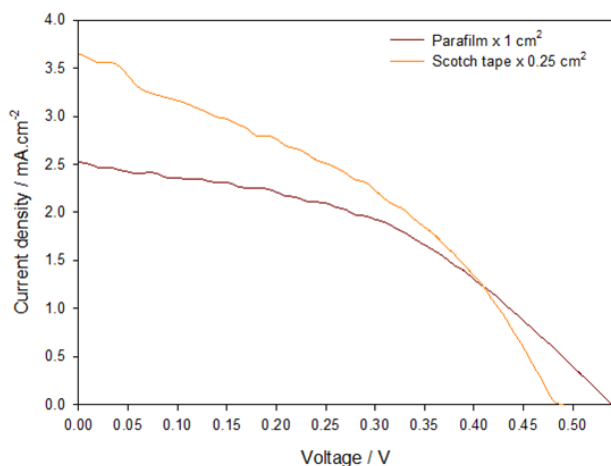
Table 8 - DSSC characteristics regarding change in TiO_2 paste concentration while using N749 dye, parafilm as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Semiconductor concentration (M)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
2.13	1.637	0.52	0.941	0.32	0.3011	0.35	0.2151
2.50	1.526	0.53	1.041	0.34	0.3539	0.44	0.2528
2.88	2.523	0.54	1.788	0.33	0.5900	0.43	0.4215
3.26	1.600	0.46	1.062	0.31	0.3292	0.45	0.2352
3.88	0.141	0.30	0.141	0.17	0.0240	0.58	0.0171

4.1.2 SPACER THICKNESS AND ACTIVE AREA

Figure 13 (a) and Table 9 demonstrates the effect of spacer thickness and active area of the semiconductor on the performance of the DSSC. Figure 13 (b) indicates the current density produced while being subjected to 0.15 V. By comparing scotch tape and parafilm as spacers, a distinct change in short circuit current density can be witnessed as the J_{sc} can be seen to increase by 45 % when using scotch tape as a spacer. El-Shater *et al.*, [229] states that the thickness of a spacer has a significant influence on the performance of a DSSC and that a spacer size thickness larger than 40 μm will start to negatively impact the DSSC hence, the scotch tape outperformed the parafilm in terms of P_m and efficiency. The reason why spacer thickness has such an influence on the DSSC's performance is due to the fact that the amount of electrolyte captured between the two substrate plates is dependant on the spacer thickness. If the spacer thickness is too small, an inadequate amount of electrolyte will be present in the DSSC resulting in having too little free electrons generated to compensate for the used electrons in the sensitizer. If the spacer thickness is too large, the amount of electrolyte would be adequate however, the path length between the substrates would be increased, resulting in the increase of recombination loss probability.

A



B

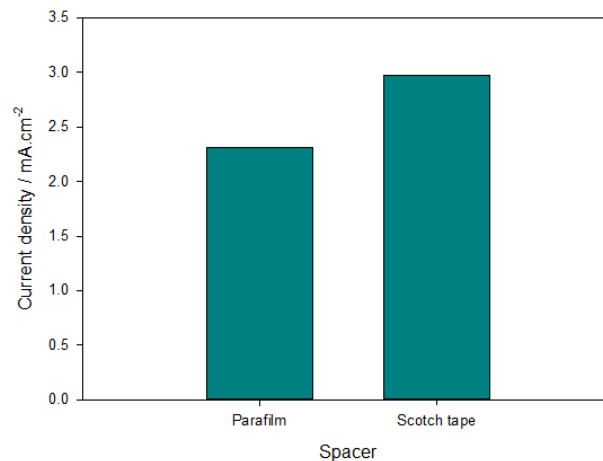


Figure 13 – (a) J/V curves to indicate effect of spacer size and active area on DSSC efficiency while using TiO_2 paste as the semiconductor, N749 dye and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution, and (b) the effect of spacer size and active area on current density produced at 0.15 V.

Table 9 - DSSC characteristics regarding change in spacer size and active area while using TiO_2 paste as the semiconductor, N749 dye and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Spacer thickness (μm)/ Active area (cm^2)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_{M} (mA/cm^2)	V_{M} (V)	P_{M} (mW/cm^2)	FF	η (%)
Parafilm (126 μm) Active area 1 cm^2	2.523	0.54	1.788	0.33	0.5900	0.43	0.4215
Scotch tape (60 μm) Active area 0.25 cm^2	3.652	0.48	2.316	0.29	0.6716	0.38	0.4797

4.1.3 SENSITISING TIME

Figure 14 (a) and Table 10 indicates the effect of increasing the sensitising time of the semiconductor in the dye after the annealing process. Figure 14 (b) indicates the current density produced while being subjected to 0.15 V. It can be seen that a sensitising time of 18 hours yielded the highest results with a η of 1.01 % and a P_{m} of 1.42 mW/cm^2 as can be seen in Table 10. Takechi *et al.*'s [228] sensitising time of ten minutes resulted in the lowest η of 0.48 % and a P_{m} of 0.67 mW/cm^2 , where both characteristics of the DSSC are only 47.37 % of the efficiency and max power obtained by sensitising for 18 hours. This could be due to the fact the the long molecular chain of N749 dye requires a prolonged contact time with the semiconductor to fully bind within its porous structure. It can also be seen in Figure 14 (a) that a sensitising time of 30 hours yielded the same results as the 10 minute sensitising time. This could be due to the long molecular ruthenium complex chains starting to blind the pores of the TiO_2 semiconductor, resulting in a hindered pathway for the electrons to flow and complete the DSSC cycle.

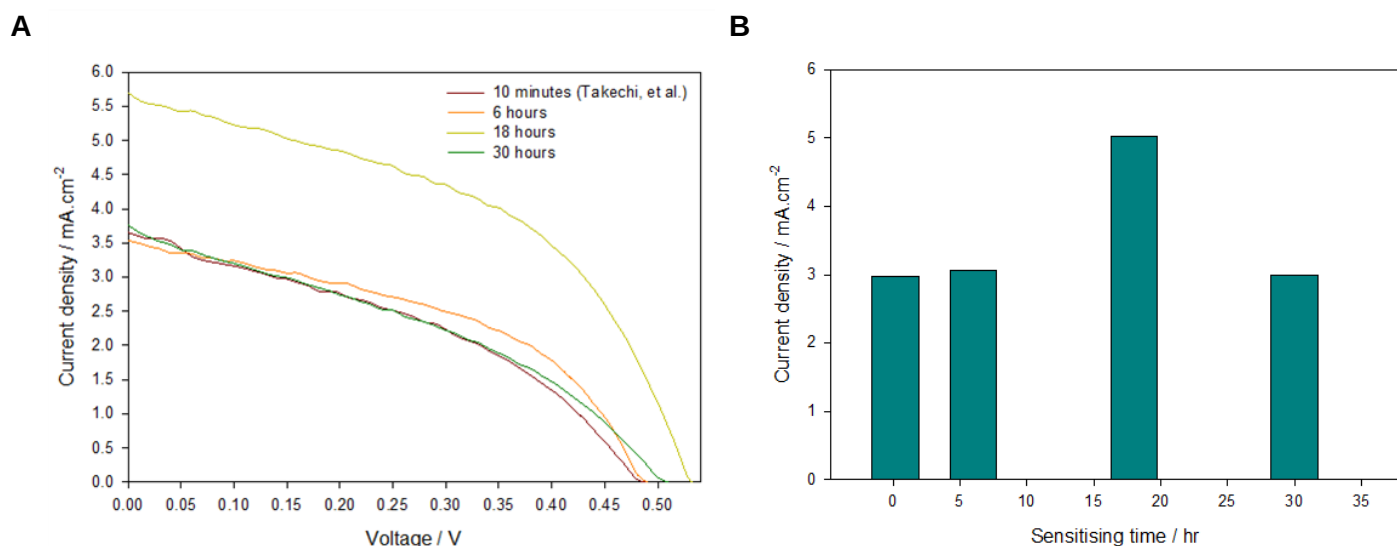


Figure 14 – (a) J/V curves to indicate the effect of N749 dye sensitising time on DSSC efficiency while using TiO_2 paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution, and (b) the effect of sensitising time on current density produced at 0.15 V.

Table 10 - DSSC characteristics regarding change in N749 dye sensitising time, while using TiO_2 paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Sensitising time (hrs)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
0.17	3.652	0.48	2.316	0.29	0.6716	0.38	0.4797
6	3.532	0.48	2.360	0.33	0.7788	0.46	0.5563
18	5.700	0.53	3.832	0.37	1.4178	0.47	1.0127
30	3.768	0.501	2.044	0.33	0.6745	0.36	0.4818

4.1.4 SENSITISER COMPARISON

4.1.4.1 Titanium dioxide

Figure 15 (a) and Table 11 illustrates the effect of N719, N749, rhodanile blue (RLB) and rhodamine blue (RMB) at a concentration of 1mM on the performance of a TiO_2 DSSC. Figure 15 (b) indicates the current density produced while being subjected to 0.15 V. First off, as expected the ruthenium complex dyes outperformed the RLB and RMB dye. Both ruthenium dyes achieved efficiencies of over 1 %, whereas RLB and RMB obtained efficiencies of 0.019 % and 0.037 % respectively. The reason behind the poor performance of RLB and RMB is a result of the HOMO and LUMO levels of the dyes that are not compatible regarding TiO_2 's conduction band, thus the electrons will be hindered to traverse between the sensitiser and the semiconductor. The ruthenium dyes are well known for their light trapping characteristics as well as their high HOMO and LUMO levels, hence resulting in a more efficient DSSC.

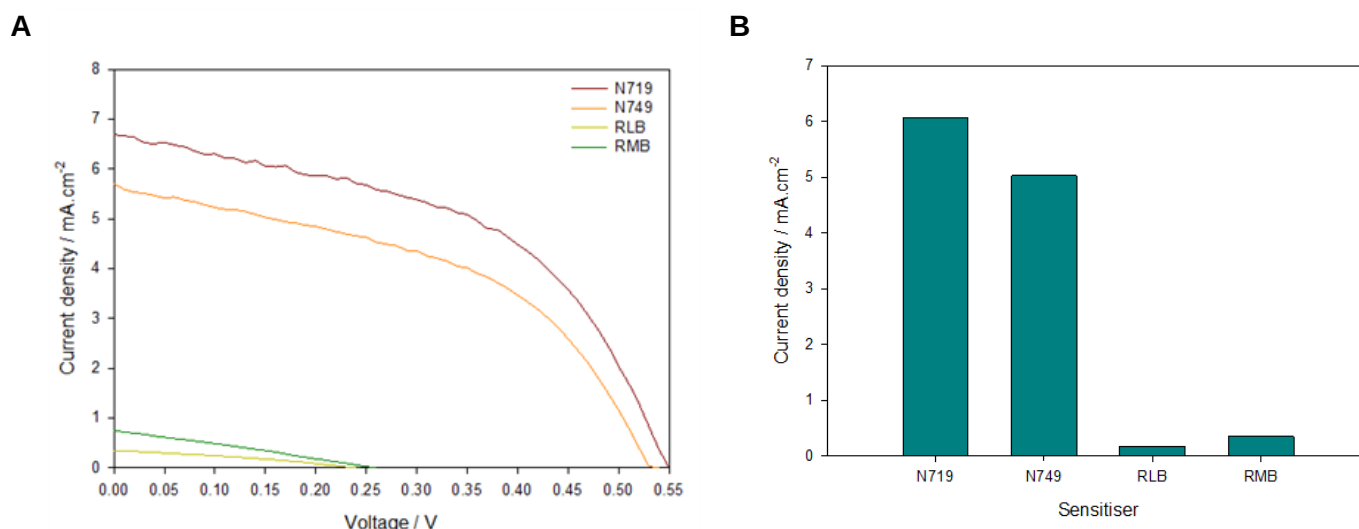


Figure 15 – (a) J/V curves to indicate the effect of different sensitisers on DSSC efficiency, while using TiO_2 paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution, and (b) the effect of different sensitisers on current density produced at 0.15 V.

Table 11 - DSSC characteristics regarding different sensitisers while using TiO_2 paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Sensitiser	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
N719	6.692	0.55	4.788	0.38	1.8194	0.50	1.2996
N749	5.700	0.53	3.832	0.37	1.4178	0.47	1.0127
RMB	0.753	0.26	0.373	0.14	0.0523	0.27	0.0373
RLB	0.345	0.24	0.205	0.13	0.0267	0.32	0.0190

4.1.4.2 Europium(III) tellurium oxide

Figure 16 (a) and Table 12 illustrates the effect of N719, N749, RLB and RMB at a concentration of 1mM on the performance of a DSSC using europium(III) tellurium oxide as semiconductor. Figure 16 (b) indicates the current density produced while being subjected to 0.15 V. It can be seen that all sensitisers exhibited lower performance than what was observed for the TiO_2 DSSC as in Figure 15 (a). When comparing the sensitisers, it can be noted that the N719 dye still performed the best regarding overall efficiency and max power output. It is interesting to note that when used with N749, the DSSC couldn't generate a noteworthy amount of current, resulting in a fill factor of zero. It can even be seen in Figure 16(b) that only N719 and RLB was able to produce current density while being exposed to 0.15 V. The DSSC is also much more susceptible to bias influence and degradation, which means it is more prone to layer breaking, as can be seen from the N719 dye DSSC graph in Figure 16(a). The low J_{sc} 's indicates a struggle to inject excited electrons into the semiconductor which afterwards enters the DSSC cycle, by increasing the voltage, the current flowing will be obstructed to

such an extent that barely any electrons will be able to get excited, hence the sudden drop in current density is witnessed.

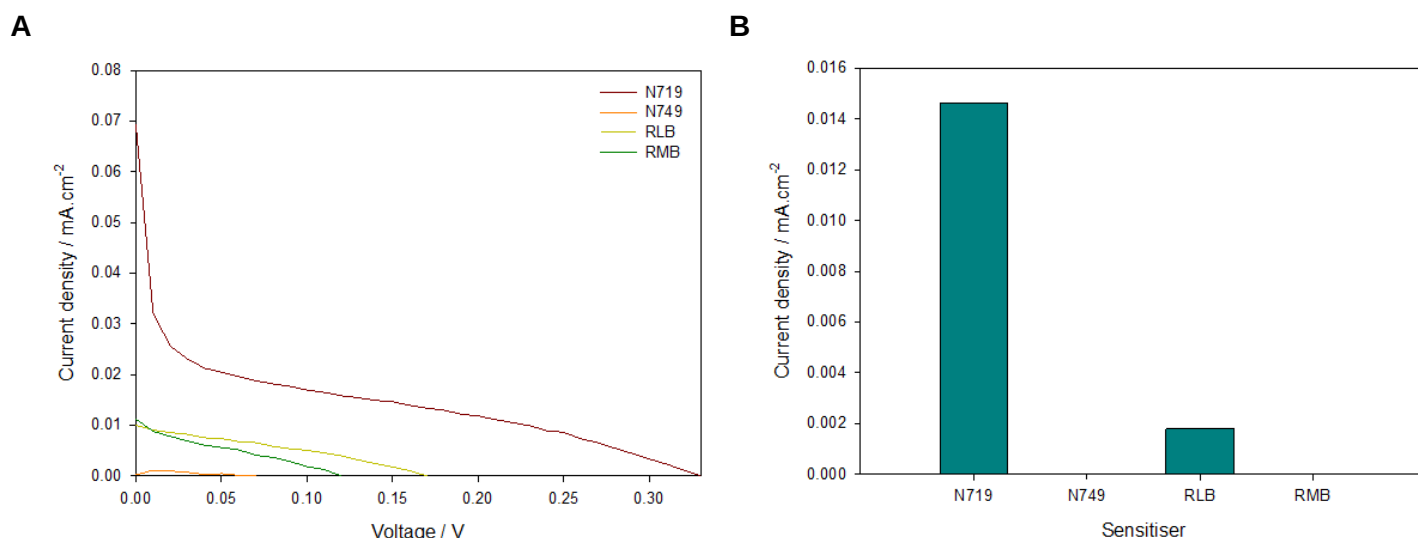


Figure 16 – (a) J/V curves to indicate the effect of different sensitisers on DSSC efficiency while using Eu_2TeO_6 paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution, and (b) the effect of different sensitisers on current density produced at 0.15 V.

Table 12 - DSSC characteristics regarding different sensitisers while using Eu_2TeO_6 paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Sensitiser	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
N719	0.069	0.33	0.012	0.20	0.0024	0.10	0.0017
N749	-	0.06	-	0.05	-	-	-
RMB	0.011	0.12	0.005	0.06	0.0003	0.23	0.0002
RLB	0.010	0.17	0.005	0.10	0.0005	0.30	0.0004

4.1.4.3 Europium(II) tellurium oxide

Figure 17(a) and Table 13 illustrates the effect of N719, N749, RLB and RMB at a concentration of 1mM on the performance of a DSSC using europium(II) tellurium oxide as semiconductor. Figure 17 (b) indicates the current density produced while being subjected to 0.15 V. It can be seen in Figure 17 (b) that only N719 was able to produce current while being subjected to 0.15 V. When comparing Figure 17 (a) and Figure 16 (a), it can be seen that when using Eu(II) (Eu_2TeO_6) as the semiconductor, resulted in a decrease in DSSC performance if one compares it to Eu(III)'s DSSC performance. When comparing all three semiconductor J/V graphs, it can be deduced that the N719 dye is still overall the best dye for DSSC use under these specific conditions and will thus be taken as the primary sensitiser for future DSSC construction. When comparing the N749 J/V curve of Eu(III) and Eu(II), it can be seen that when using Eu(II) as the semiconductor, a current could be generated as well as

an open circuit voltage (V_{oc}) of 0.13 V could be achieved, whereas the Eu(III) counterpart instantly lost all current when the voltage increased to 0.06 V. This could be due to the difference in chemical composition of the semiconductors, where Eu(III) is Eu_2TeO_6 and Eu(II) is Eu_3TeO_6 .

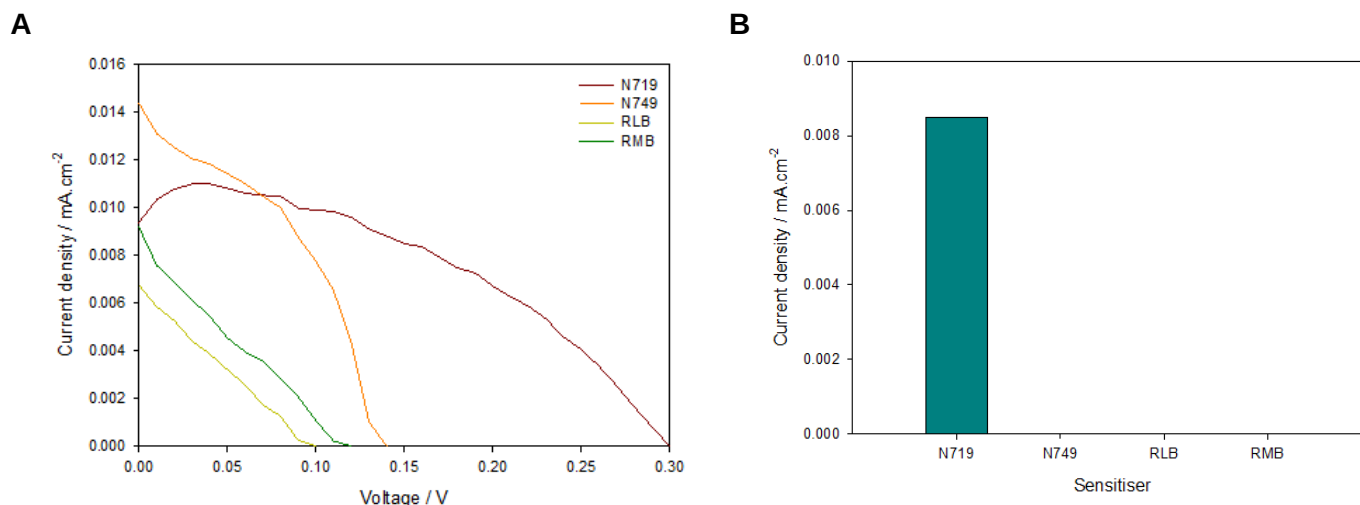


Figure 17 - (a) J/V curves to indicate the effect of different sensitisers on DSSC efficiency while using Eu_3TeO_6 paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution, and (b) the effect of different sensitisers on current density produced at 0.15 V.

Table 13 - DSSC characteristics regarding different sensitisers while using Eu_3TeO_6 paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Sensitiser	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
N719	0.009	0.30	0.007	0.19	0.0014	0.49	0.0010
N749	0.014	0.13	0.010	0.08	0.0008	0.43	0.0006
RMB	0.009	0.12	0.004	0.07	0.0003	0.23	0.0002
RLB	0.007	0.10	0.003	0.05	0.0002	0.24	0.0001

4.1.5 SENSITISER CONCENTRATION

Figure 18 (a) and Table 14 illustrates the effect of the N719 dye concentration on the performance of the DSSC. Figure 18 (b) indicates the current density produced while being subjected to 0.15 V. It can be seen that a concentration of 1mM yielded the best results, with a J_{sc} of 6.69 mA/cm^2 , V_{oc} of 0.55 V, P_m of 1.82 mW/cm^2 and a η of 1.30 %. It can be seen as the dye concentration increased from 0.25 mM to 0.5 mM, so did the overall performance of the DSSC. The efficiency of the 0.5 mM DSSC increased with 8.57 % when compared to the 0.25 mM DSSC's efficiency. However, a decrease in performance can be noted when a concentration of 0.75 mM was used as the J_{sc} lowered to 3.16 mA/cm^2 and the V_{oc} increased to 0.58 V, but still consequently resulted in a lowered efficiency equal to 0.41 %. When

observing Figure 18 (a), it can be seen that when using a concentration of 0.75 mM, the current produced linearly decreased as voltage increased, whereas in the DSSC of the 1 mM concentration, the current held a plateau, until reaching a voltage of 0.38 V (V_m), where it started to decrease significantly. The decrease in performance when using the 0.75 mM concentration might be due to placement of the DSSC during the sensitising process.

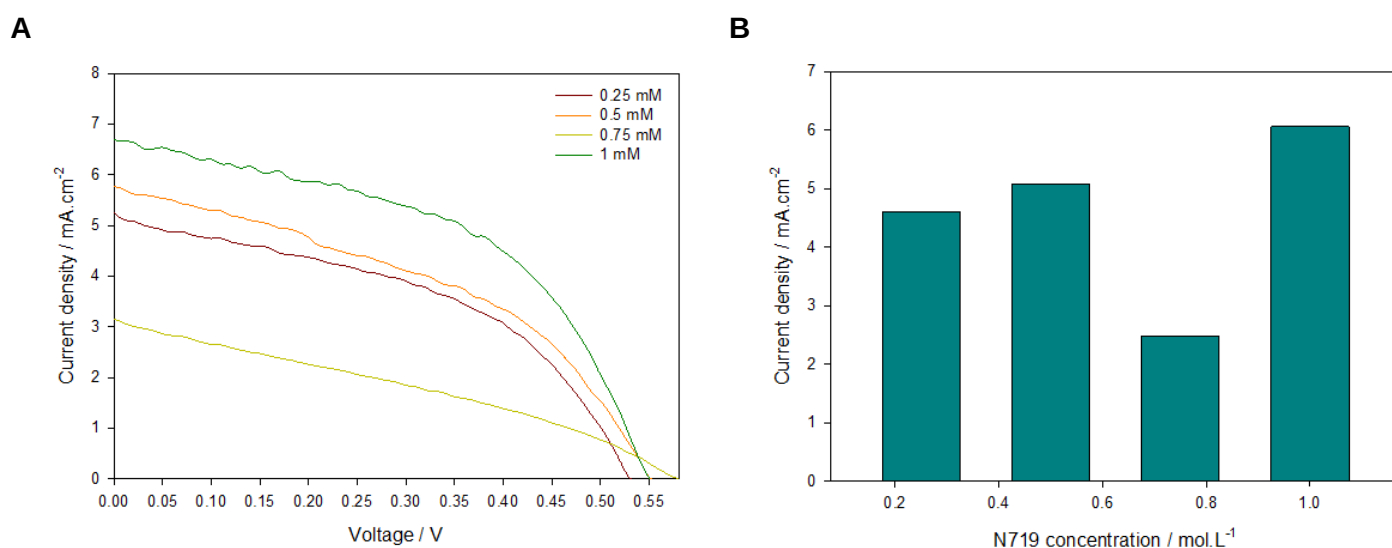


Figure 18 – (a) J/V curves to indicate the effect of N719 concentration on DSSC efficiency while using TiO₂ paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution, and (b) the effect of N719 concentration on current density produced at 0.15 V.

Table 14 - DSSC characteristics regarding change in N719 concentration while using TiO₂ paste as the semiconductor, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

N719 Concentration (mM)	J _{sc} (mA/cm ²)	V _{oc} (V)	J _m (mA/cm ²)	V _m (V)	P _m (mW/cm ²)	FF	η (%)
0.25	5.252	0.53	3.548	0.35	1.2418	0.45	0.8870
0.50	5.776	0.55	3.548	0.38	1.3482	0.42	0.9630
0.75	3.160	0.58	1.692	0.34	0.5753	0.32	0.4109
1.00	6.692	0.55	4.788	0.38	1.8194	0.50	1.2996

4.1.6 ELECTROLYTE COMPARISON

Figure 19 (a) and Table 15 illustrates the difference of using sodium iodide in comparison to lithium iodide and the effect the redox couple consists over the performance of the DSSC. Figure 19 (b) indicates the current density produced while being subjected to 0.15 V. It can be seen in Table 15 that the J_{sc} of both DSSCs are almost similar with only a 0.132 mA/cm² difference however, a significant difference can be witnessed when comparing the V_{oc} of the sodium iodide redox couple DSSC, which is 84 % of what the V_{oc} of the lithium iodide redox couple DSSC is. When comparing the overall efficiencies of the two DSSCs, it can be seen

that the lithium iodide redox couple DSSC obtained a η of 1.65 % and the sodium iodide redox couple DSSC obtained a η of 1.37 %. Lithium ions are usually of small size and consists over a high charge density due to its size. It must be noted that due to the size of the lithium cations, it is possible for the lithium ions to intercalate into the semiconductor of the DSSC, thus positively affecting the electron depositing process between the dye and the semiconductor [230].

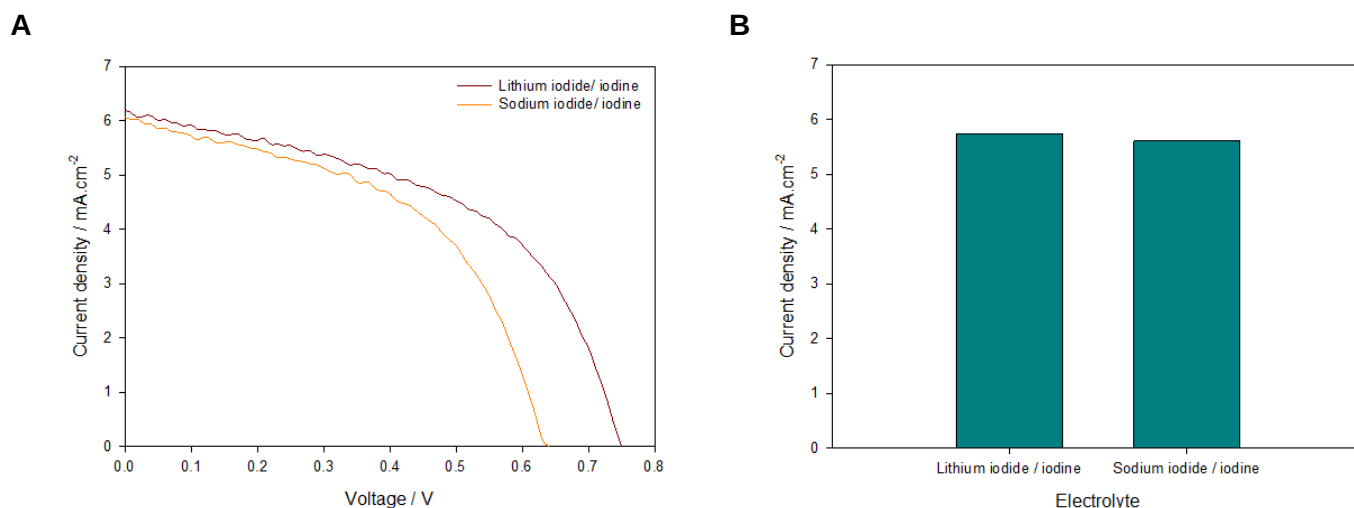


Figure 19 – (a) J/V curves to indicate the efficiency comparison between lithium- and sodium iodide/iodine (0.5 M/ 0.05 M) redox couples while using TiO_2 paste as the semiconductor, scotch tape as the spacer and N719 as the dye, and (b) the effect of a different iodide on current density produced at 0.15 V.

Table 15 - DSSC characteristics comparison between lithium- and sodium iodide/iodine (0.5 M/ 0.05 M) redox couples while using TiO_2 paste as the semiconductor, scotch tape as the spacer and N719 as the dye.

Electrolyte pair	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
Lithium iodide/iodine	6.200	0.75	4.20	0.55	2.31	0.50	1.6500
Sodium iodide/iodine	6.068	0.63	4.252	0.45	1.9134	0.50	1.3667

4.1.7 IODIDE CONCENTRATION

Figure 20 (a) and Table 16 illustrates the effect of lithium iodide concentration on the overall performance of a DSSC. Figure 20 (b) indicates the current density produced while being subjected to 0.15 V. For this data set, the iodine concentration was kept at a constant concentration of 0.05 M. When comparing the concentrations in Table 16, it can be seen that as the iodide concentration increased from 0.4 M to 0.5 M, the η increased from 0.07 % to 1.46 % and the P_m increased from 0.1 mW/cm² to 2.04 mW/cm². This phenomena can be explained by the equation: [230]



The D^+ in equation 4.3 refers to the oxidative dye molecules, so as the lithium iodide concentration increases, the total I_3^- will increase as well which will in return support electron recombination of the dye by increasing the charge transfer quantity from the electrolyte into the dye [231]. However, it can be seen when increasing the iodide concentration from 0.5 M to 0.6 M and 0.7 M, the J_{sc} started to stagnate or slightly decrease. This is due to the fact that the electron recombination and dye reduction is starting to become saturated, which results in a slowed down electron cycle in the DSSC [230].

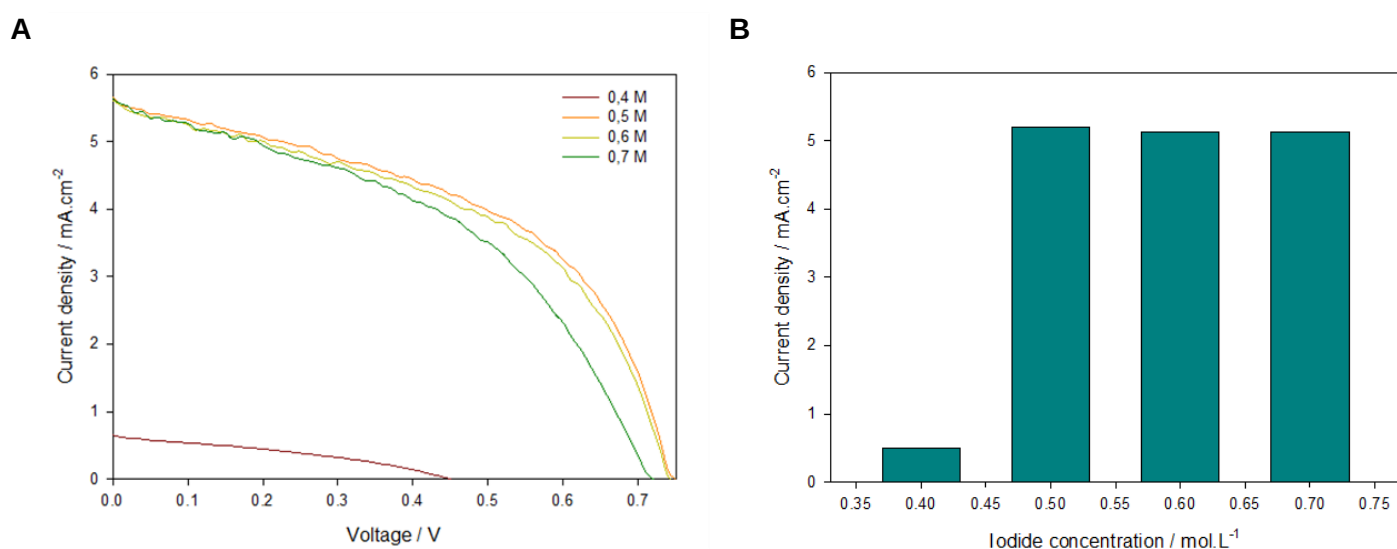


Figure 20 – (a) J/V curves to indicate the effect of iodide concentration on DSSC efficiency while using TiO_2 paste as the semiconductor, scotch tape as the spacer, N719 as the dye and a constant iodine concentration of 0.05 M, and (b) the effect of iodide concentration on current density produced at 0.15 V.

Table 16 - DSSC characteristics regarding change in iodide concentration while using TiO_2 paste as the semiconductor, scotch tape as the spacer, N719 as the dye and a constant iodine concentration of 0.05 M.

Iodide concentration (M)	J_{sc} (mA/cm²)	V_{oc} (V)	J_M (mA/cm²)	V_M (V)	P_M (mW/cm²)	FF	η (%)
0.4	0.652	0.45	0.360	0.27	0.0972	0.33	0.0694
0.5	5.664	0.74	3.648	0.56	2.0429	0.49	1.4592
0.6	5.616	0.74	3.804	0.52	1.9781	0.48	1.4129
0.7	5.648	0.72	3.828	0.46	1.7609	0.44	1.2578

4.1.8 IODINE CONCENTRATION

Figure 21 (a) and Table 17 illustrates the effect of iodine concentration on the overall performance of the DSSC. Figure 21 (b) indicates the current density produced while being subjected to 0.15 V. In this data set, the lithium iodide concentration was fixed at 0.5 M. In Table 17 it can be seen that the maximum J_{sc} obtained was 5.73 mA/cm² and maximum η and P_m obtained was 1.46 % and 2.04 mW/cm² respectively. The iodine concentration of 0.04 M obtained the highest J_{sc} , but the 0.05 M concentration achieved the best overall performance. It can be seen that when increasing the iodine concentration to 0.07 M resulted in a decrease of J_{sc} to 3.92 mA/cm². Kalaigian *et al.*, [231] has demonstrated that iodine concentration is proportional to I_3^- , which means that as the iodine concentration increases, so does I_3^- . By increasing the concentration of I_3^- , the viscosity of the electrolyte will also increase [232]. When increasing the viscosity of the electrolyte, the interactions of I_3^- becomes strengthened, which will then alter the focus point of the charge transfer carrier which will then lessen the focus on the recombination of the oxidated dye, leading to a poorer performance inside the DSSC [233].

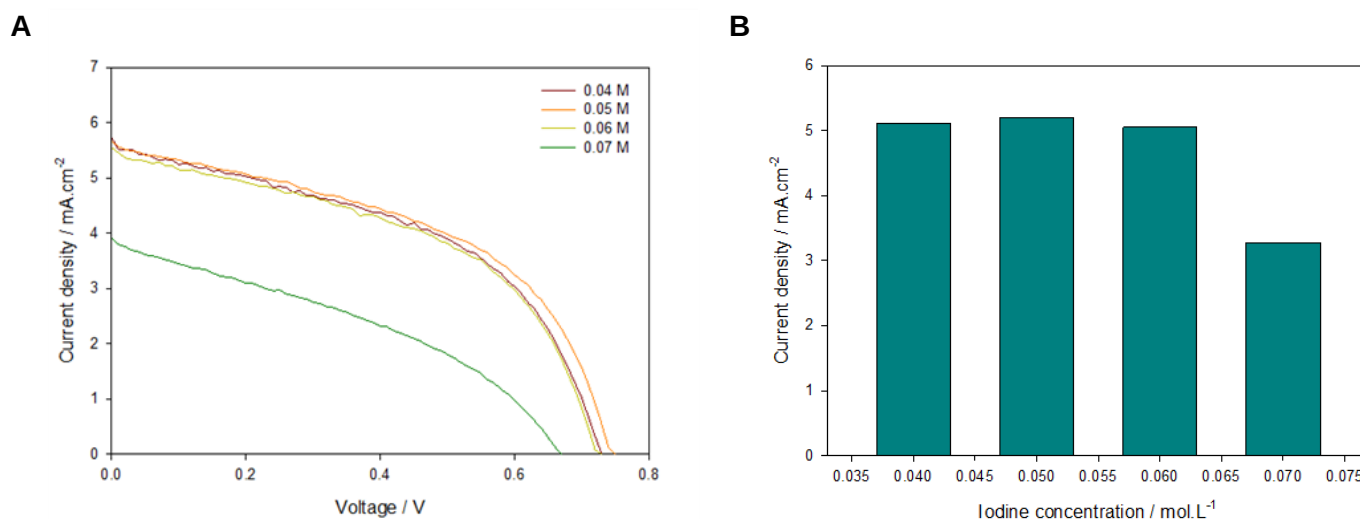


Figure 21 - (a) J/V curves to indicate the effect of iodine concentration on DSSC efficiency while using TiO₂ paste as the semiconductor, scotch tape as the spacer, N719 as the dye and a constant Li iodide concentration of 0.5 M, and (b) the effect of iodine concentration on current density produced at 0.15 V.

Table 17 - DSSC characteristics regarding change in iodine concentration while using TiO₂ paste as the semiconductor, scotch tape as the spacer, N719 as the dye and a constant Li iodide concentration of 0.5 M.

Iodine concentration (M)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
0.04	5.731	0.73	3.647	0.54	1.9675	0.47	1.4068
0.05	5.664	0.74	3.648	0.56	2.0429	0.49	1.4592
0.06	5.544	0.72	3.520	0.55	1.9360	0.48	1.3829
0.07	3.920	0.67	2.304	0.41	0.9446	0.36	0.6747

4.1.9 4-TERT-BUTYLPYRIDINE ADDITION

Figure 22 (a) and Table 18 illustrates the effect of including 4-tert-butylpyridine to the electrolyte solution before using it in a DSSC. Figure 22 (b) indicates the current density produced while being subjected to 0.15 V. 4-Tert-butylpyridine is known for enhancing the V_{oc} of a DSSC while also lowering the J_{sc} of the cell. As seen in Table 18, the V_{oc} has been increased by 34.5 % whereas the J_{sc} only decreased with 15.4 %, which still results in a positive increase of η from 1.30 % to 1.46 %. When only observing Figure 22 (b), it can be misunderstood that TBP might have a negative impact on the DSSC performance. The reason behind this change is due to the TBP shifting the quasi-fermi level of the semiconductor to a higher potential however, the addition of TBP reduces the difference between the conduction band of the semiconductor and the HOMO and LUMO levels of the dye, resulting in a lower injection rate of the electron at the TiO_2 's surface and thus a lowered J_{sc} [234].

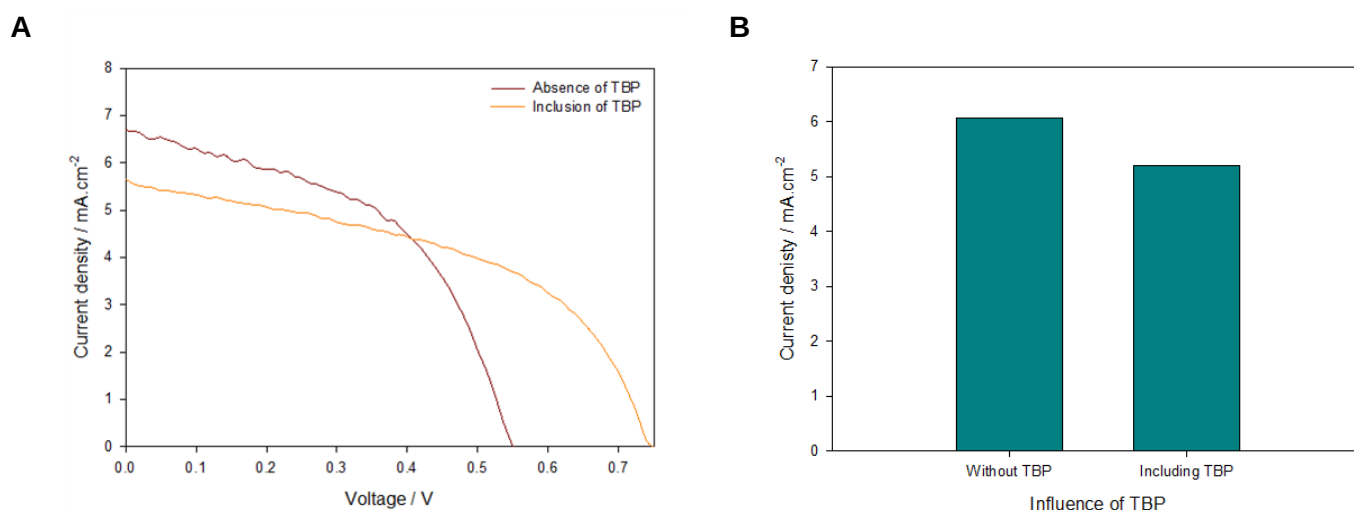


Figure 22 - (a) J/V curves to indicate the effect of TBP inclusion on DSSC efficiency while using TiO_2 paste as the semiconductor, scotch tape as the spacer, N719 as the dye and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution, and (b) the effect of TBP inclusion on current density produced at 0.15 V.

Table 18 - DSSC characteristics comparison between DSSCs with and without TBP while using TiO_2 paste as the semiconductor, scotch tape as the spacer, N719 as the dye and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

TBP inclusion	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
Absence of TBP	6.692	0.55	4.788	0.38	1.8194	0.50	1.2996
Inclusion of TBP	5.664	0.74	3.648	0.56	2.0429	0.49	1.4592

4.2 J/V CURVES – 140 MW/CM²

With regards to repeatability, the following experiments were carried out more than once and the current measurements done with the potentiometer was also measured more than once

to identify if the DSSC was producing stable current. The uncertainty analysis tables for the alternating illumination time experiments can be found in Appendix A: Uncertainty analysis for Chapter 4.2.

4.2.1 TITANIUM DIOXIDE J/V CURVE

Figure 23 and Table 19 illustrates the effect of one minute alternating illumination at 140 mW/cm^2 (100-1100 nm) on the performance of the DSSC using TiO_2 as the semiconductor. The DSSC was illuminated for 5 minutes while testing the dark current at every one minute by switching off the light source and waiting for 15 seconds before measuring the current. It can be seen in Figure 23 that the DSSC using TiO_2 is producing stable results while being exposed to light. Table 19 indicates the cell achieved a maximum of 1.65 % efficiency with a J_{sc} of 6.20 mA/cm^2 and a V_{oc} of 0.75 V. The V_{oc} is quite high due to the addition of the TBP additive. As illumination time increases, the efficiency is decreasing due to the degradation done by the extended contact time with the electrolyte however, TiO_2 is a stable semiconductor and the scotch tape used as a spacer prevented electrolyte leakage, hence no major deterioration was observed.

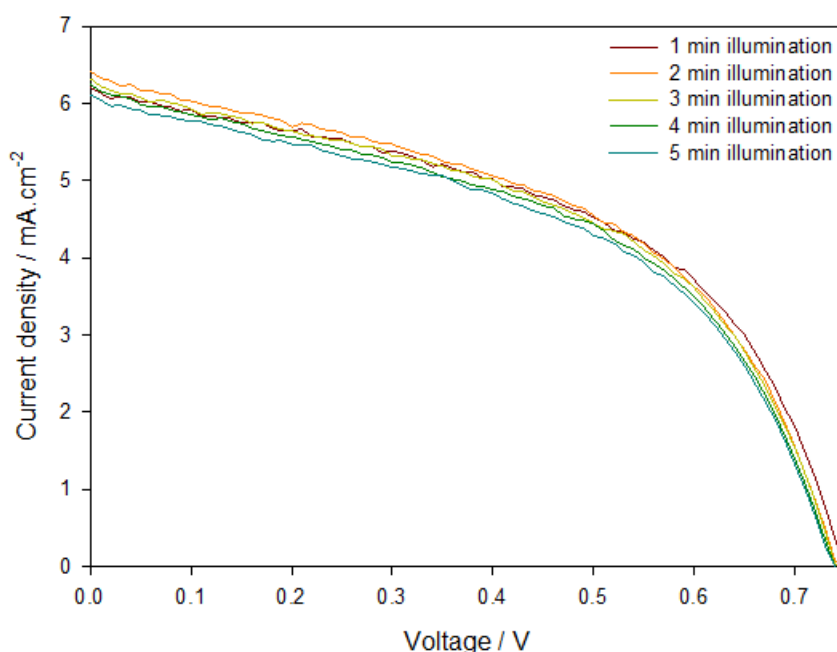


Figure 23 - J/V curve of TiO_2 during alternating illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 19 - J/V characteristics of TiO_2 during alternating illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
1	6.20	0.75	4.20	0.55	2.31	0.50	1.65
2	6.42	0.75	4.28	0.54	2.31	0.48	1.65
3	6.33	0.75	4.31	0.53	2.29	0.48	1.63
4	6.24	0.74	4.12	0.54	2.22	0.48	1.59
5	6.11	0.74	4.20	0.52	2.18	0.48	1.56

Figure 24 and Table 20 illustrates the dark current produced after every minute of illumination for a total of 5 minutes while using TiO_2 as the semiconductor. It can be noted that even though an additive such as TBP is present in the electrolyte, the V_{oc} decreased to 32 % of the initial V_{oc} during illumination. While time progresses without any illumination, the dark current density slowly decreases as well, exhibiting that the electron cycle in the DSSC is still slowly decreasing. However, when comparing the dark current with the current during illumination, only 0.23 % of the current still remains after one minute with no illumination.

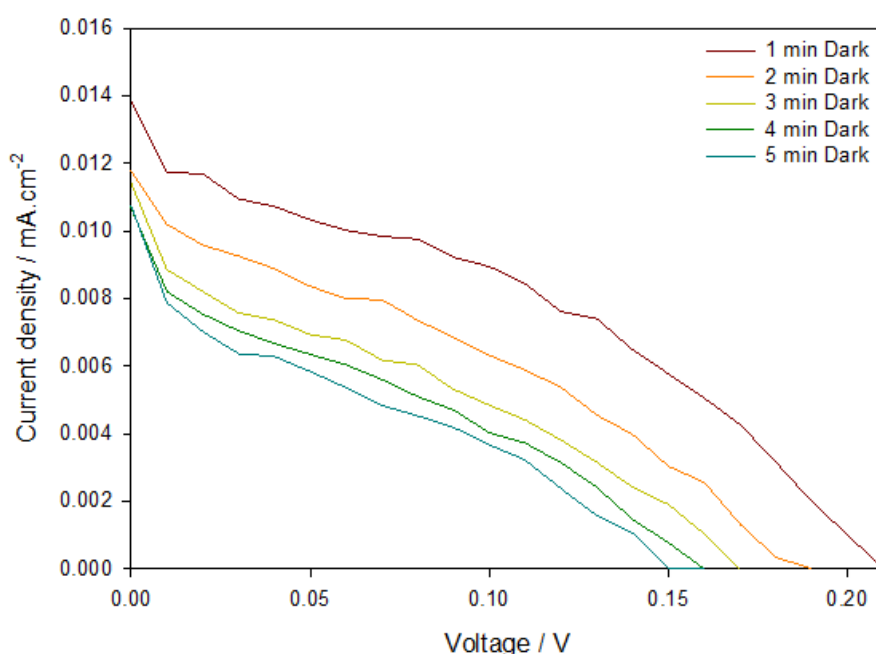


Figure 24 - J/V curve of TiO_2 dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 20 - J/V characteristics of TiO₂ without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J _{sc} (mA/cm ²)	V _{oc} (V)	J _M (mA/cm ²)	V _M (V)	P _M (mW/cm ²)	FF	η (%)
1	0.014	0.21	0.007	0.13	0.0010	0.33	0.0007
2	0.012	0.19	0.006	0.11	0.0007	0.29	0.0005
3	0.011	0.17	0.004	0.11	0.0005	0.25	0.0003
4	0.011	0.16	0.005	0.09	0.0004	0.25	0.0003
5	0.011	0.16	0.004	0.09	0.0004	0.22	0.0003

4.2.2 EUROPIUM(III) TELLURIUM OXIDE J/V CURVE

Figure 25 and Table 21 illustrates the effect of one minute alternating illumination at 140 mW/cm² on the performance of the DSSC using Eu(III) as the semiconductor. First important difference between the TiO₂ and Eu(III) DSSC is that the second mentioned DSSC is heavily affected by the changing voltage which can be seen in Figure 25. This drastic decrease in current density indicates that the excited electrons can't move into the conduction band of the semiconductor and into the circuit. The excited electrons will rather return to a steady state within the sensitizer. One way to overcome this dilemma is to increase the difference between the conduction band of Eu(III) and the LUMO level of the dye, this will reduce the amount of excited electrons falling back into steady state. Eu(III) also produced low current densities of 0.6 – 0.7 mA/cm² which indicates that a higher electron injection force from the sensitizer to semiconductor is needed. During illumination an overall efficiency of 0.0017 % was obtained after one minute of illumination which slowly decreased as time progressed. It must be noted that when observing changes in V_{oc}'s, Eu(III) only lost 12 % of its initial voltage after 5 minutes of illumination.

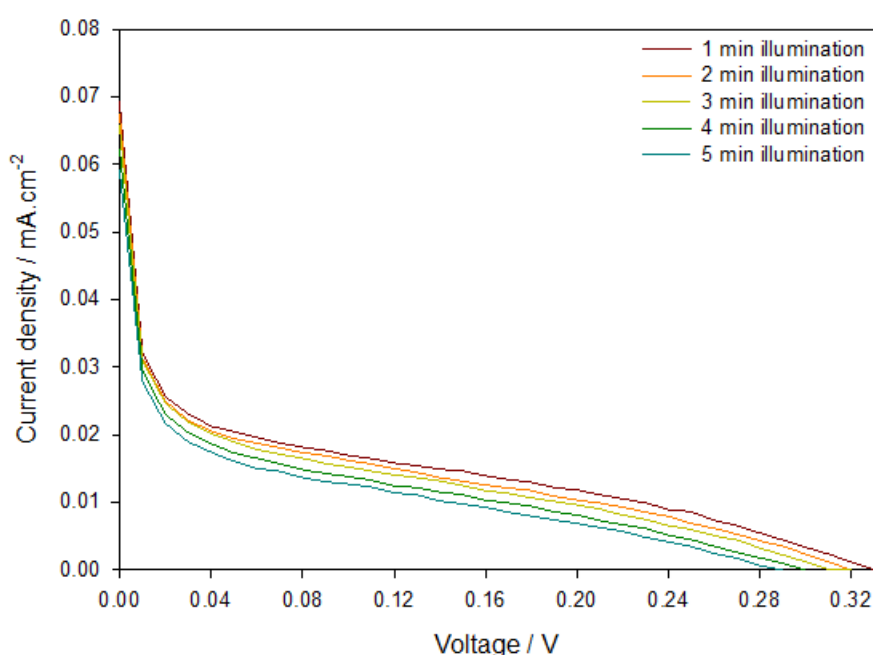


Figure 25 - J/V curve of Eu(III) during alternating illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 21 - J/V characteristics of Eu(III) during alternating illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
1	0.069	0.33	0.012	0.20	0.0024	0.10	0.0017
2	0.067	0.32	0.012	0.18	0.0021	0.10	0.0015
3	0.066	0.32	0.010	0.20	0.0019	0.09	0.0014
4	0.062	0.30	0.009	0.18	0.0017	0.09	0.0012
5	0.059	0.29	0.009	0.16	0.0015	0.09	0.0011

Figure 26 and Table 22 illustrates the dark current produced after every minute of illumination for a total of 5 minutes using Eu(III) as the semiconductor. In Table 22 it can be seen that the average of J_{sc} is 0.03 mA/cm^2 which is only 50 % of the J_{sc} obtained during illumination. When comparing the decrease of J_{sc} with no illumination present, Eu(III)'s J_{sc} decreased with 50 % while TiO_2 suffered losses greater than 99 % of its original J_{sc} . The max power output maintained during no illumination is only 30 % of what the Eu(III) produced while being illuminated. When observing TiO_2 's P_m loss after the first minute when no illumination is present, the P_m obtained without any illumination is only 0.04 % of the P_m obtained during illumination. This observation indicates that Eu(III) withholds the current and power produced within its porous structure more efficiently than the TiO_2 DSSC.

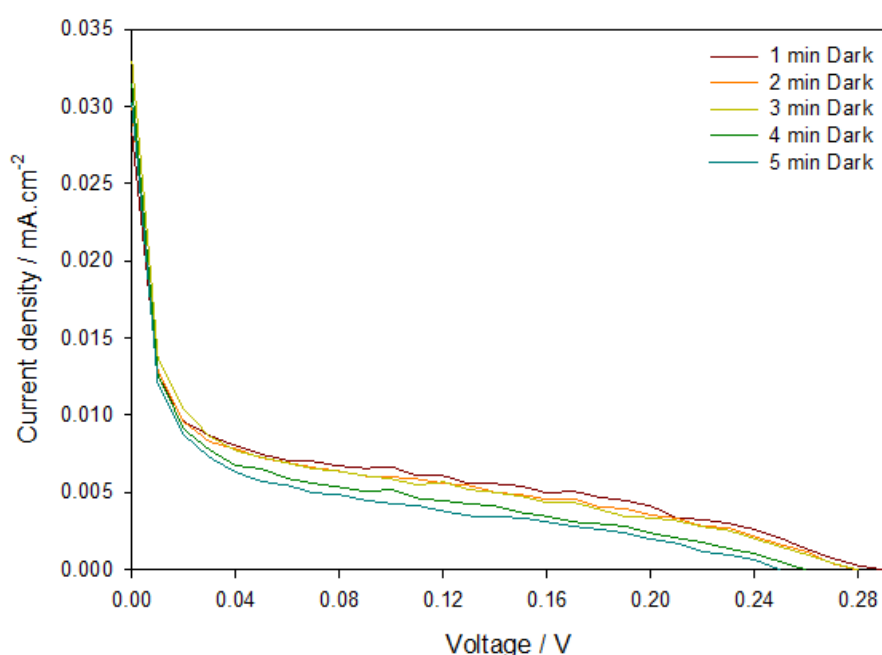


Figure 26 - J/V curve of Eu(III) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 22 - J/V characteristics of Eu(III) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
1	0.028	0.29	0.005	0.17	0.0009	0.11	0.0006
2	0.030	0.28	0.005	0.17	0.0008	0.09	0.0006
3	0.033	0.28	0.004	0.17	0.0007	0.08	0.0005
4	0.031	0.26	0.004	0.14	0.0006	0.07	0.0004
5	0.030	0.25	0.003	0.15	0.0005	0.07	0.0004

4.2.3 EUROPIUM(II) TELLURIUM OXIDE J/V CURVE

Figure 27 and Table 23 illustrates the effect of one minute alternating illumination at 140 mW/cm² on the performance of the DSSC using Eu(II) as the semiconductor. As seen in Figure 27, the overall J_{sc} and V_{oc} kept consistent through all 5 minutes of illumination however, the P_m of the cell does decrease as time progresses, leading to a decrease in fill factor as well as overall efficiency. The reason for the decrease in P_m can be due to how susceptible Eu(II) is to photodeterioration. Eu(II) might be more affected by the illumination period which results in layer cracking as well as alterations regarding its chemical properties. The J_{sc} obtained by Eu(II) is only 13 % of the J_{sc} obtained by Eu(III) when comparing Figure 25 and Figure 27. This

indicates that Eu(II) possibly consists a higher conduction band than Eu(III), meaning that a higher electron injection force is needed from the sensitiser to the semiconductor. It is important to note that the change in europium composition (Eu(II) vs Eu(III)) affects the photovoltaic properties greatly.

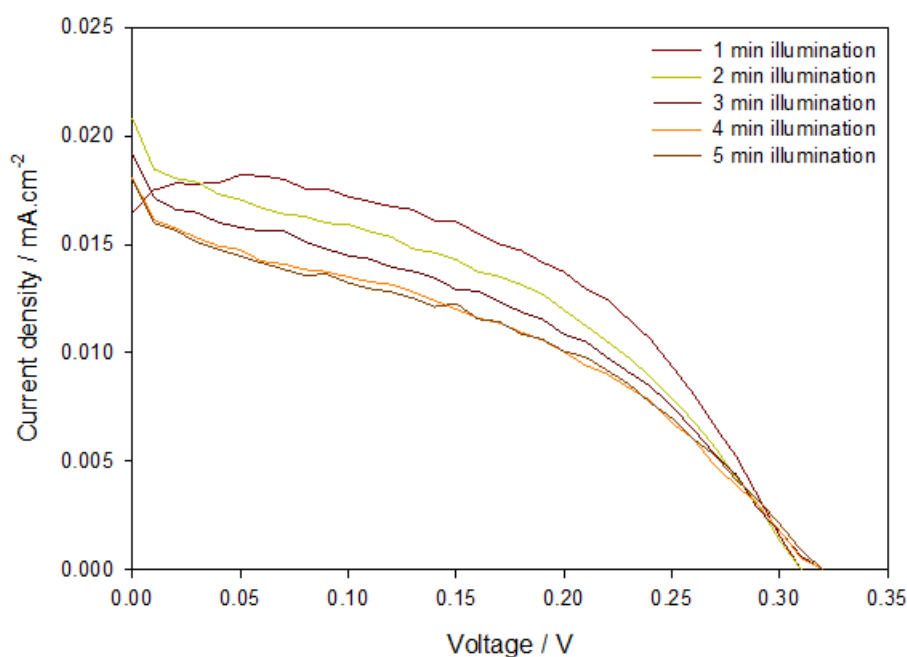


Figure 27 - J/V curve of Eu(II) during alternating illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 23 - J/V characteristics of Eu(II) during illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
1	0.016	0.31	0.014	0.20	0.0027	0.54	0.0020
2	0.021	0.31	0.013	0.19	0.0024	0.37	0.0017
3	0.019	0.32	0.011	0.21	0.0022	0.36	0.0016
4	0.018	0.32	0.011	0.19	0.0020	0.35	0.0014
5	0.018	0.32	0.010	0.21	0.0021	0.36	0.0015

Figure 28 and Table 24 illustrates the dark current produced after every minute of illumination for a total of 5 minutes using Eu(II) as the semiconductor. It is important to note that at the three minute mark, the P_m during no illumination is higher than during illumination. This phenomena can be observed again at the 5 minute period. This indicates that an extra intermediate step can be found here that produces an energy storing effect inside the semiconductor of the cell. Only the Eu(II) DSSC demonstrated an increase in P_m and η during

no illumination. An intriguing aspect to note is that the europium semiconductors maintained a V_{oc} of roughly 0.3 V, regardless of illumination or the absence of it, whereas the TiO_2 instantly suffered a decrease of 68 %.

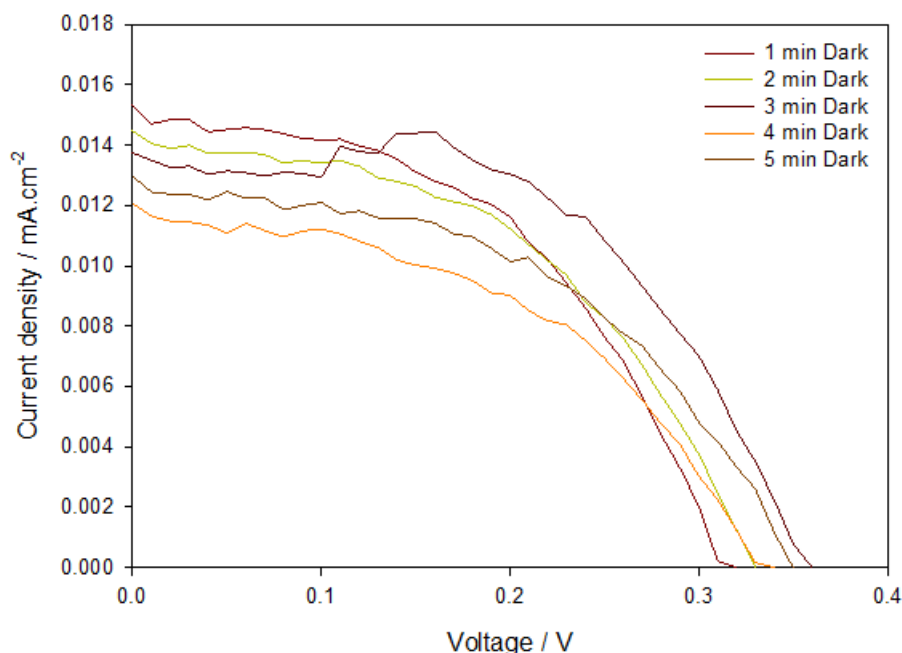


Figure 28 - J/V curve of Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 24 - J/V characteristics of Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
1	0.015	0.32	0.012	0.20	0.0023	0.47	0.0017
2	0.014	0.33	0.011	0.21	0.0022	0.47	0.0016
3	0.014	0.36	0.012	0.24	0.0028	0.56	0.0020
4	0.012	0.34	0.008	0.23	0.0018	0.45	0.0013
5	0.013	0.35	0.010	0.21	0.0022	0.48	0.0015

4.2.4 TITANIUM DIOXIDE J/V CURVE – UV RANGE

Figure 29 and Table 25 illustrates the effect of only illuminating the DSSC with an ultraviolet light (UVB 280-315 nm) at 140 mW/cm² while using TiO_2 as the semiconductor. The DSSC was illuminated for one minute before measuring the current density produced. When comparing the J_{sc} produced after one minute illumination with the Toption-X300 in Table 19 with the J_{sc} obtained in Table 25, it can be seen that when using only UV light a J_{sc} of 0.91

mA/cm^2 was obtained which is only 15 % of the J_{sc} obtained while being illuminated with the full spectrum of light. This indicates that TiO_2 is much more dependant on the visible spectrum of light (400-700 nm) than the UV range of light (100-400 nm). It must be noted that the absorption spectra of N719 is only effective in the visible spectrum of light (400-700 nm), thus when carrying out the UV illumination experiment, little to no excited electrons are produced by the N719 sensitiser.

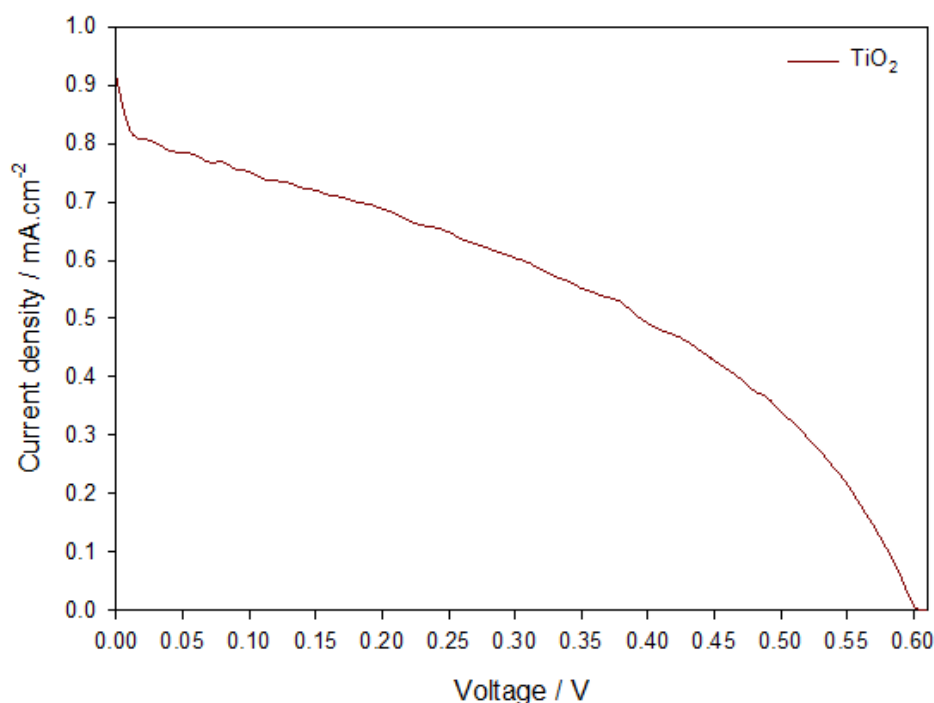


Figure 29 J/V curve of TiO_2 during UV irradiation ($140 \text{ mW}/\text{cm}^2$) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 25 - J/V characteristics of TiO_2 during UV irradiation ($140 \text{ mW}/\text{cm}^2$) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Semiconductor	J_{sc} (mA/cm^2)	V_{oc} (V)	J_{M} (mA/cm^2)	V_{M} (V)	P_{M} (mW/cm^2)	FF	η (%)
TiO_2	0.912	0.60	0.528	0.38	0.2006	0.37	0.1433

4.2.5 EUROPIUM(II)/EUROPIUM(III) TELLURIUM OXIDE J/V CURVE – UV RANGE

Figure 30 and Table 26 illustrates the effect of only illuminating the DSSC with an ultraviolet light (UVB 280-315 nm) at $140 \text{ mW}/\text{cm}^2$ while using Eu(III) or Eu(II) as the semiconductor. The DSSCs were illuminated for one minute before measuring the current density produced. When comparing the J_{sc} produced by using Eu(III) as semiconductor in Table 26, a current density of $0.004 \text{ mA}/\text{cm}^2$ was obtained which is only 5 % of the J_{sc} obtained in Table 21. This indicates

that Eu(III) is also quite dependant on the visible regions of the light spectrum. It is interesting to note that Eu(II) produced double the J_{sc} than what Eu(III) produced. Eu(II) produced a J_{sc} of 0.008 mA/cm^2 which is 38 % of the maximum J_{sc} obtained while being illuminated with the full spectrum of light in Table 23. When comparing all three semiconductors, it can be noted that Eu(II) is the most dependant on the UV range (100-400 nm) of the light spectrum in comparison to TiO_2 and Eu(III). As stated in Chapter 4.2.4, N719 only absorbs light in the visible spectrum, hence when illuminating the cell with a UV light, almost no electrons are excited within the sensitiser.

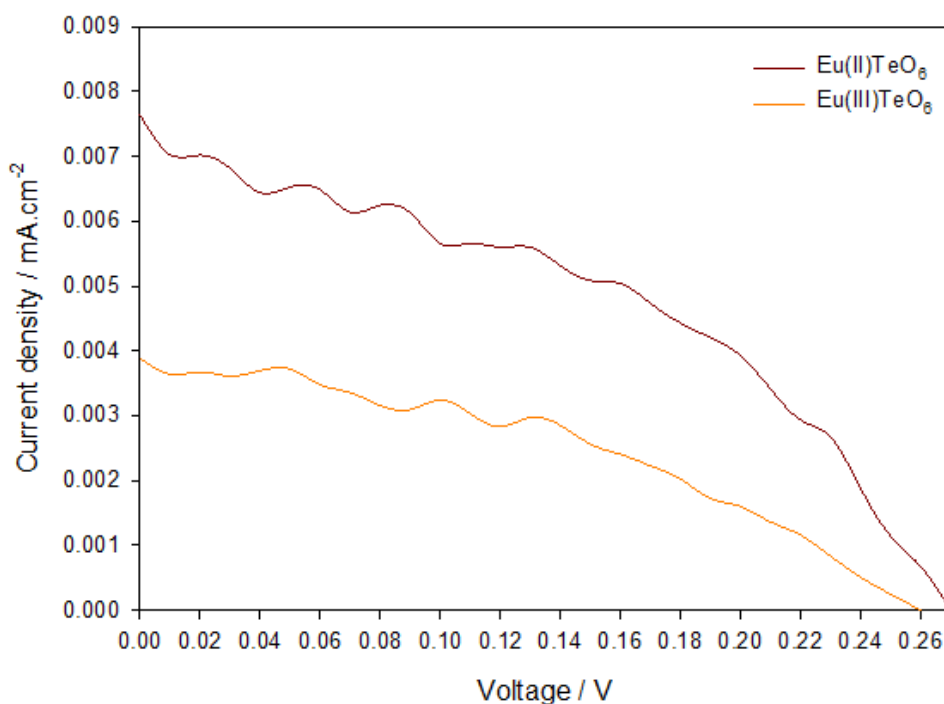


Figure 30 - J/V curve of Eu(III) and Eu(II) during UV irradiation (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 26 - J/V characteristics of Eu(III) and Eu(II) during UV irradiation (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Semiconductor	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
Eu(II)	0.008	0.27	0.005	0.16	0.0008	0.40	0.0006
Eu(III)	0.004	0.26	0.003	0.14	0.0004	0.41	0.0003

4.3 CHRONOAMPEROMETRY – 140 MW/CM²

4.3.1 TITANIUM DIOXIDE CHRONOAMPEROMETRY

Figure 31 illustrates the effect of voltage on the dark current produced by TiO₂ DSSCs. Each DSSC was illuminated for one minute at 140 mW/cm², then 15 seconds was given for the solar simulator to completely shut down before measuring the dark current produced while being affected by a bias (Voltage). It is known that as the voltage increase, the current produced will decrease because the bias will start to obstruct the current. This can be exactly seen in Figure 31 as the DSSC that was put under 0.03 V generated 0.009 – 0.01 mA/cm² for 60 seconds, while the DSSC that had no bias (0 V) generated a current of roughly 0.012 mA/cm². The same can be said for the DSSC that was affected by 0.01 V and 0.02 V, where the DSSCs produced a current of 0.0115 mA/cm² and 0.011 mA/cm² respectively. A baseline was also constructed by measuring the dark current of the DSSC before illuminating the cell for one minute. The baseline also had no bias that could constrict current flow. Figure 31 illustrates the effect of photodegradation of the solar cell as the baseline consisted over the highest current density even though it was not illuminated at all, hence supporting the notion that a DSSC degrades over time as it is being illuminated. Photodegradation occurs when a DSSC stays in contact with an electrolyte as well as when it is subjected to illumination, hence the baseline that wasn't illuminated suffered the least photodegradation.

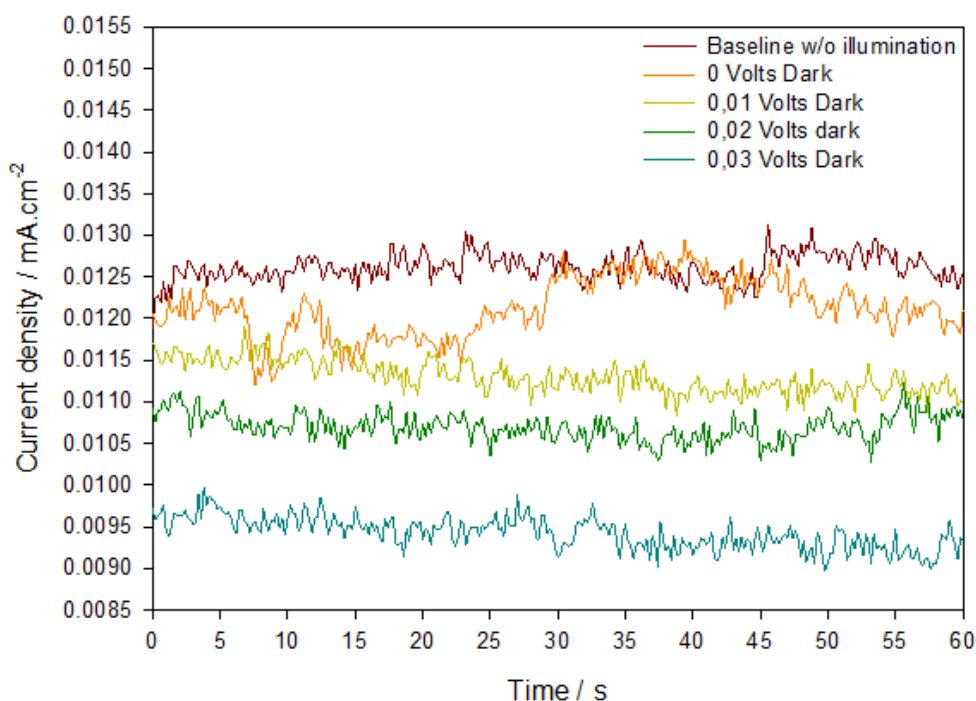


Figure 31 - Effect of voltage on dark current produced - (140 mW/cm²) while using TiO₂ paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

4.3.2 EUROPIUM(III) TELLURIUM OXIDE CHRONOAMPEROMETRY

Figure 32 illustrates the effect of voltage on the dark current produced by Eu(III) DSSCs. The chronoamperometry process for Eu(III) is done exactly as described by the TiO₂'s chronoamperometry. As seen in Figure 32, the increase in voltage results in a decrease in current density produced. Eu(III) is more affected by a voltage increase than TiO₂, as can be seen in Figure 32 where the DSSC that was put under 0.03 V produced no current at 53 seconds. It can also be seen that the baseline for the Eu(III) DSSC was much more inconsistent than the TiO₂ DSSC. This indicates resistance within the circuit of the Eu(III) DSSC. Not all of the excited electrons are able to overcome the internal resistances present in the porous structure of the Eu(III) semiconductor, hence resulting in the inconsistent current measurement.

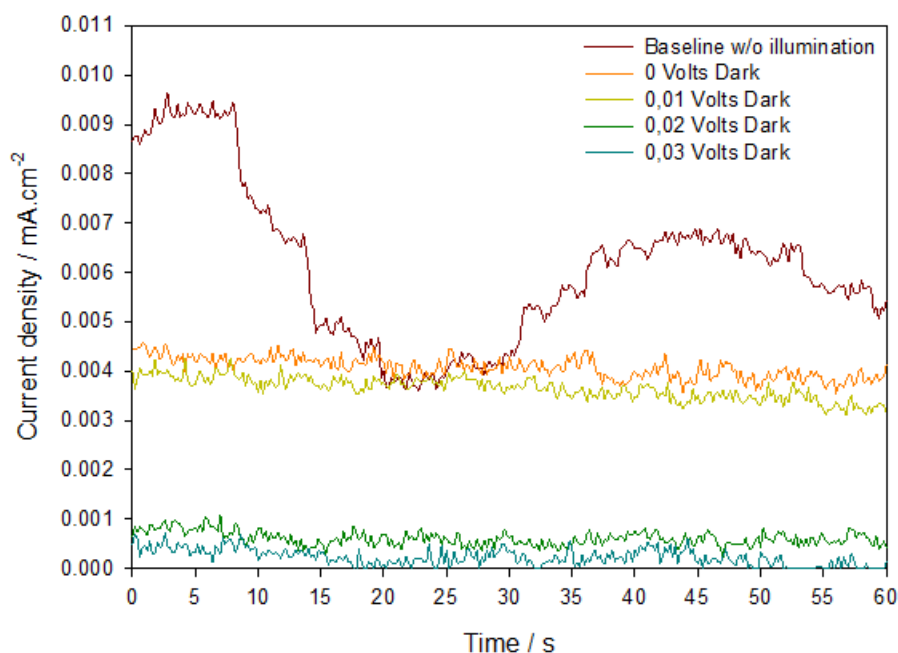


Figure 32 - Effect of voltage on dark current produced - (140 mW/cm^2) while using Eu(III) paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

4.3.3 EUROPIUM(II) TELLURIUM OXIDE CHRONOAMPEROMETRY

Figure 33 illustrates the effect of voltage on the dark current produced by Eu(II) DSSCs. The chronoamperometry process for Eu(II) is done exactly as described by the TiO₂ chronoamperometry. First off, just as seen in the previous two chronoamperometry's, the DSSCs that were tested under a higher voltage produced lower currents. When comparing Figure 33 and Figure 32 it can be seen that Eu(II) produced higher dark current than Eu(III). When comparing the DSSCs that were tested at 0.03 V, Eu(III) barely produced any current

while Eu(II) produced a constant current density of 0.005 mA/cm². All three types of DSSCs showed consistent dark current readings as time progressed, indicating that the electron cycle kept completing even though no illumination was present.

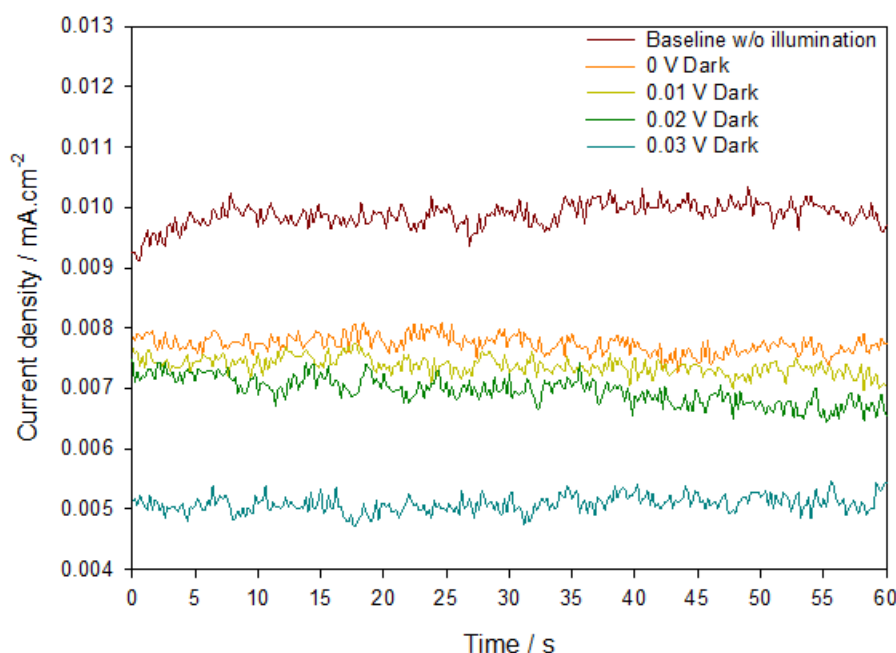


Figure 33 - Effect of voltage on dark current produced - Eu(II) (140 mW/cm²) while using Eu(II) paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

4.3.4 TITANIUM DIOXIDE CHRONOAMPEROMETRY – LONG EXPOSURE

Figure 34 illustrates the current density produced during illumination as time progresses. Kriek *et al.*, [21] illuminated their Eu₂TeO₆ photoelectrocatalyst for 150 minutes with a light source intensity of 16 mW/cm² (wavelength of 250-950 nm). For this test, a light source of 140 mW/cm² (Xenon light source 100-1100 nm) was used to test the semiconductors as being part of a DSSC. As the light intensity used is 8.75 times larger than the source used by Kriek *et al.*, [21] the time duration of illumination was also decreased with a factor of 8.75 just to keep the experiment within scale, resulting in an illumination time of 18 minutes. The DSSC was illuminated for 18 minutes before being switched off and the current being measured after 10 and 20 minutes in complete darkness. In Figure 34 it can be seen as time progress, the current density of the TiO₂ DSSC increases and reaches a maximum current density at 110 seconds before slowly decreasing. This increase of current density can be explained by inspecting the flow of electrons within the DSSC. There are no excited electrons present in the electrolyte or the semiconductor until the first instance of illumination. The exact moment the cell is being illuminated, excited electrons will start to move from the dye to the semiconductor. The amount of excited electrons increase as time progresses, this can be

declared as the growth phase where the amount of electrons being excited is increased. This phase occurs in the first few seconds of illumination. Where the maximum can be observed in Figure 34, is where the cycle has reached an optimal point where the electrons are being excited into the semiconductor while the dye recovers expended electrons from the electrolyte through electron recombination. The slow decrease of current density indicates the degradation of the DSSC which means that the excited dye molecules aren't retrieving expended electrons from the electrolyte quick enough, thus resulting in a loss of current. Another reason for the decrease in current flow is the extended illumination time, which results in photodegradation that alters the chemical properties of the semiconductor.

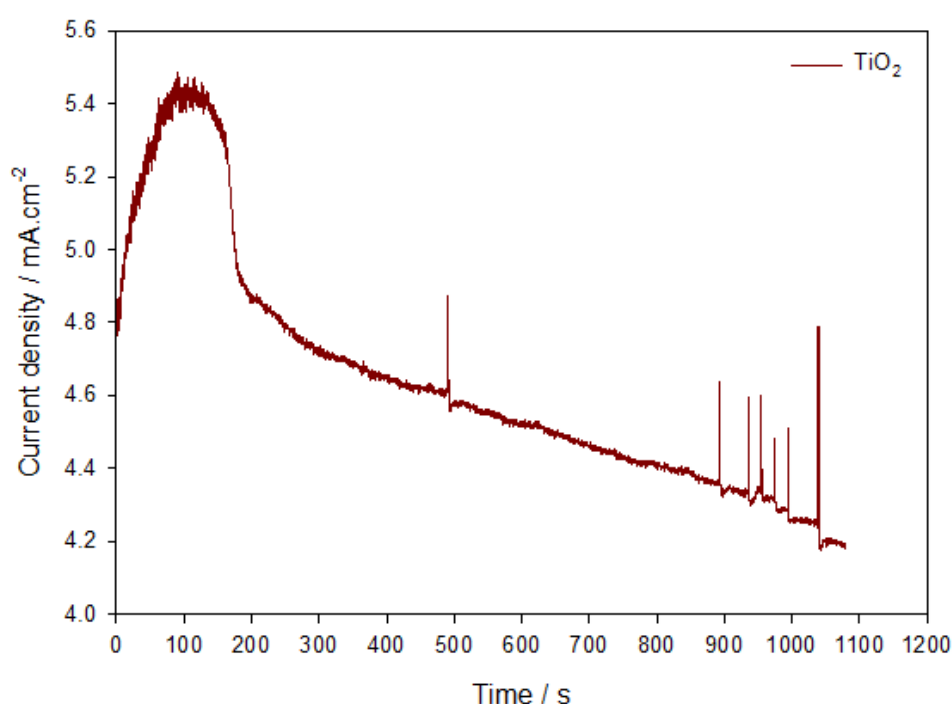


Figure 34 - Current density produced during illumination as a function of time- (140 mW/cm^2) while using TiO_2 paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Figure 35 illustrates the dark current produced after being illuminated for 18 minutes with a light intensity of 140 mW/cm^2 . The initial measurement was only taken 15 seconds after the solar simulator was switched off to ensure complete darkness. It can be seen that even though the cell was illuminated for 18 minutes the dark current produced after illumination is lower than the dark current prior to illumination. This indicated that the DSSC, more specifically the electrolyte and sensitizer's excited electrons, began to revert to steady state after such a long illumination time period rather than moving through the semiconductor's porous structure, resulting in a lower current being produced. Figure 34's decrease in current supports this notion as the DSSC started to perform poorer as time progressed. Even though the baseline

produced a higher current density, the difference between the baseline and current measurement directly after illumination has a 20 % decrease in current density. It can also be seen that after 10 minutes in complete darkness, the current density decreased to 0.003 mA/cm² and 0.0023 mA/cm² at 20 minutes. This indicates that even though the dark current was already initially low, the electron cycle still occurred and decreased in speed as time progressed without illumination.

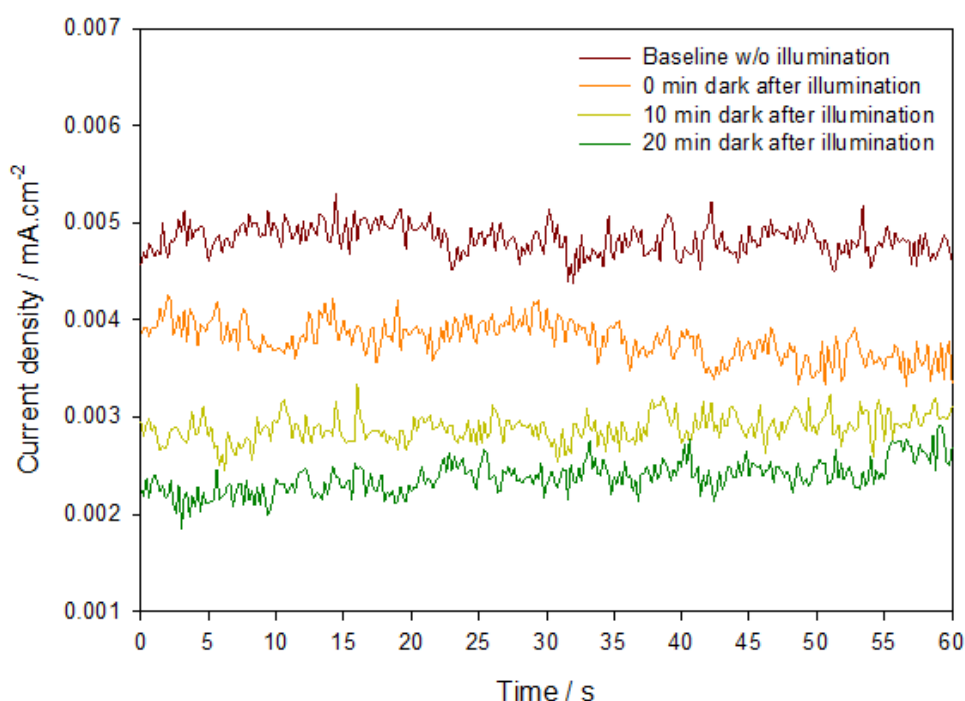


Figure 35 - Dark current produced after long exposure to light - (140 mW/cm²) while using TiO₂ paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

4.3.5 EUROPIUM(III)/EUROPIUM(II) TELLURIUM OXIDE CHRONOAMPEROMETRY – LONG EXPOSURE

Figure 36 illustrates the current density produced during illumination as time progresses while using Eu(III) and Eu(II) as semiconductors. The chronoamperometry process for Eu(III) is done exactly as described by the TiO₂'s chronoamperometry. First thing to notice between Eu(III)'s current density trend in comparison to TiO₂'s trend in Figure 34 is that there was no increase in Eu(III)'s current density as time progressed, but just a linear decrease and plateau. This indicates that even though the electron cycle successfully completed in the DSSC, there was no increase of electrons flowing from the semiconductor to the cathode and then returning to the dye. This indicates constant resistance to inject an electron into the semiconductor and

then to the electrolyte. When observing Eu(II)'s trend, a slight increase in current density can be seen up to 110 seconds where the current density starts to linearly decrease. Unlike Eu(III), Eu(II) followed the same trend that the TiO₂'s DSSC followed which shows that there was also a growth of electron excitation within the Eu(II)'s DSSC. It can be seen in Figure 36 and Figure 69 in Appendix C.5 that both Eu(II) and Eu(III) experienced a spike of current before stabilising. This reason behind this spike is due to the europium itself being used as the semiconductor, because this spike was not witnessed with the TiO₂ DSSCs. The reason behind this spike of current could possibly be due to the crystal structure of the europium semiconductor withholding and releasing electrons that were built up inside the porous structure of the europium.

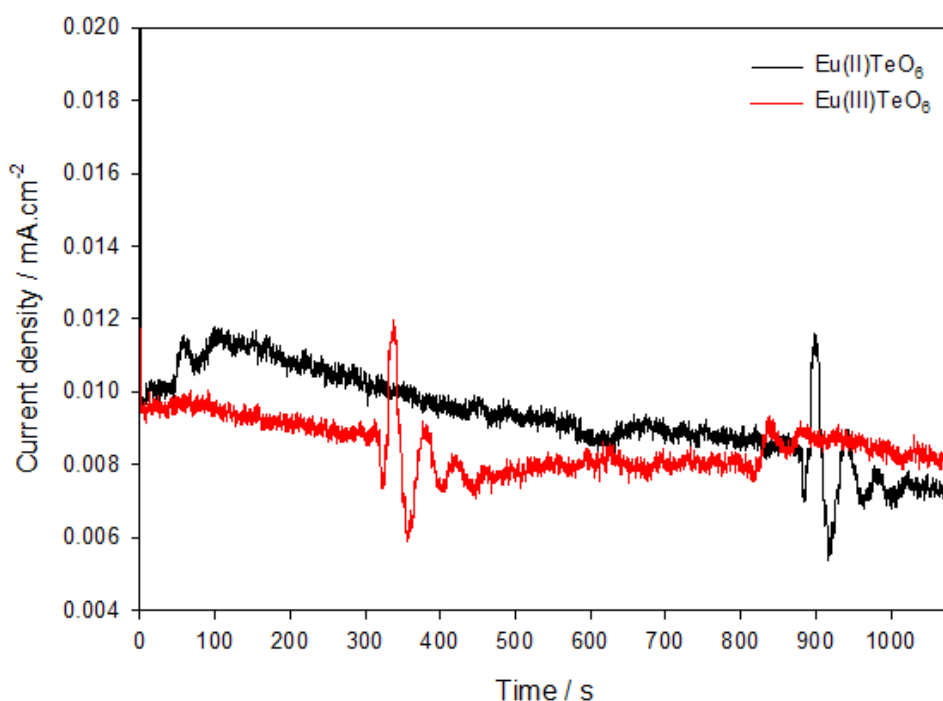


Figure 36 - Current density produced during illumination as a function of time - (140 mW/cm²) while using Eu(II) and Eu(III) paste as the semiconductor respectively, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Figure 37 illustrates the dark current produced by using Eu(III) as semiconductor after being illuminated for 18 minutes with a light intensity of 140 mW/cm². Even though 10 minute increments were made after illumination, there is no significant difference between the current readings after taking the current measurement directly after illumination and waiting 20 minutes after illumination. When comparing the dark current of Eu(III) with TiO₂'s dark current in Figure 35, it can be seen that Eu(III) consisted of a dark current density between 0.004 and 0.005 mA/cm², whereas TiO₂ had a much larger current density decline between time intervals and consisted over a dark current of 0.002 to 0.003 mA/cm² after 20 minutes of darkness.

Even though the TiO_2 had more electron flow through the DSSC cycle during illumination, it consisted over less dark current than the Eu(III) . We can see that Eu(III) barely gets an excited electron injected into the DSSC. This can be noted when comparing the current produced during illumination in Figure 36 with the baseline current produced by the DSSC without any illumination which is 0.0095 mA/cm^2 and 0.0077 mA/cm^2 respectively.

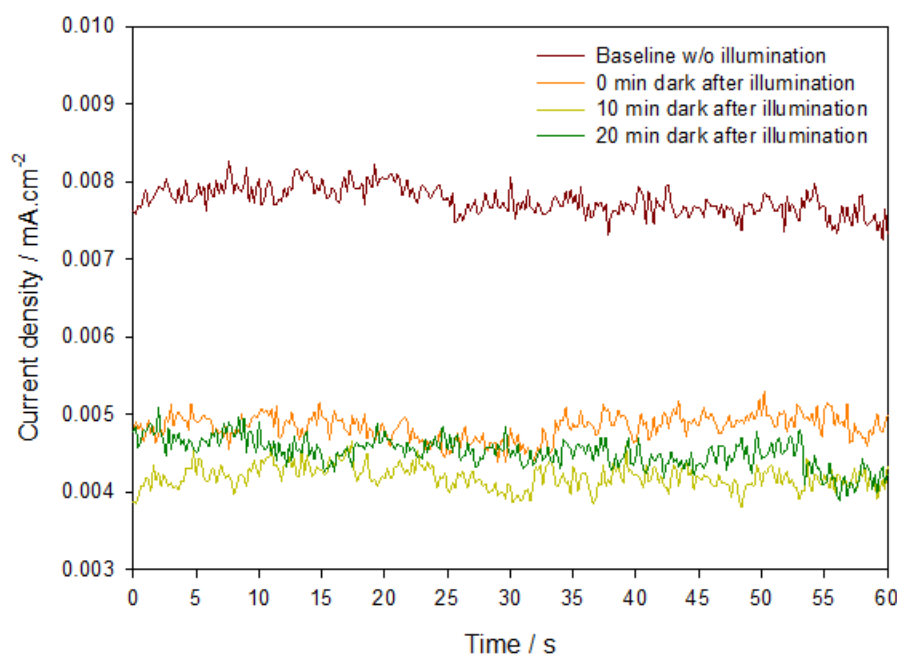


Figure 37 - Dark current produced after long exposure to light – (140 mW/cm^2) while using Eu(III) paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Figure 38 illustrates the dark current density produced after being illuminated for 18 minutes with a light intensity of 140 mW/cm^2 . Just as seen when comparing the current density produced between Eu(II) and TiO_2 in Figure 36 and Figure 34, a significant decrease in dark current density can be seen in the Eu(II) DSSC as the time is increased where the DSSC is left in complete darkness. From the Eu(II) DSSC initially having a current density of 0.0048 mA/cm^2 to producing a dark current density between 0.003 and 0.004 mA/cm^2 .

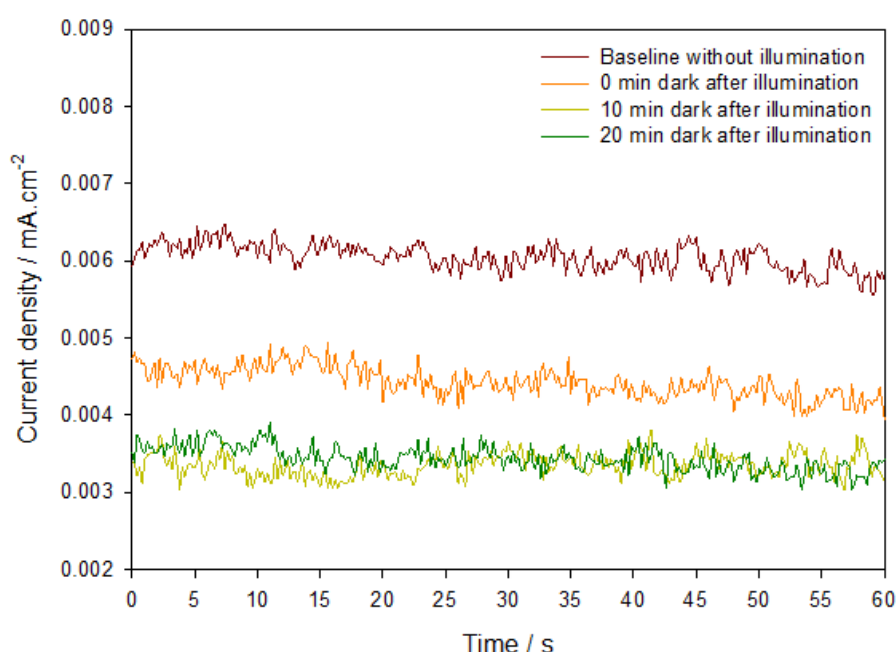


Figure 38 - Dark current produced after long exposure to light - (140 mW/cm^2) while using Eu(II) paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

4.4 INCIDENT PHOTON TO CURRENT CONVERSION EFFICIENCY – 140 MW/CM^2

4.4.1 TITANIUM DIOXIDE IPCE

Figure 39 illustrates the IPCE obtained by using a xenon light source ($100\text{-}1100 \text{ nm}$, 140 mW/cm^2) coupled with optical filters. Optical filters were attached to the solar simulator to only allow a specific wavelength to be shined onto the surface of the DSSC. A DSSC only came into contact with one specific wavelength at a time to ensure no excitation is carried over when testing a new wavelength, thus meaning there was one DSSC test per wavelength. The DSSC was illuminated for one minute before a measurement was taken. As seen in Figure 39, the TiO_2 absorbs more light from the visible light spectrum than the UV range ($100\text{-}400 \text{ nm}$). Light from a wavelength of 430 nm and higher resulted in an IPCE higher than 3% . TiO_2 has the lowest IPCE of 1.4% between 350 nm and 400 nm .

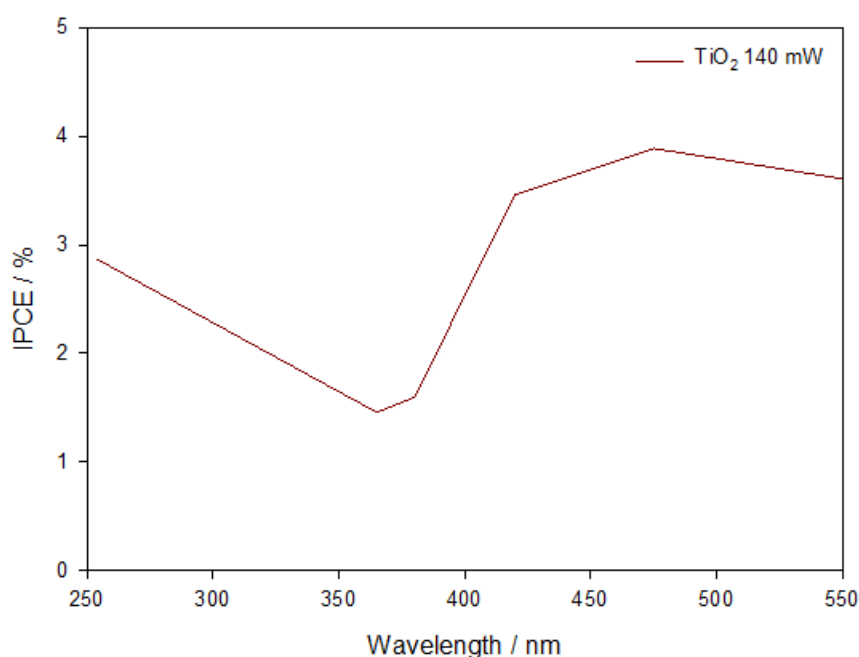


Figure 39 - IPCE at 0 Volts (140 mW/cm^2) while using TiO_2 paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

4.4.2 EUROPIUM(III) TELLURIUM OXIDE IPCE

Figure 40 illustrates the IPCE obtained by using a xenon light source coupled with optical filters. The IPCE of Eu(III) was tested by using the exact same process as described in the TiO_2 's IPCE paragraph. When comparing the IPCE of TiO_2 with Eu(III), it can be noted that Eu(III) obtained very low IPCE's, but it is important to note that the current produced by the Eu(III) DSSC is also minimal in comparison to TiO_2 . It can be seen in Figure 40 that the IPCE increased as the wavelength increased of the light source. This indicates that the Eu(III) DSSC is also dependant on the visible spectrum of light. The reason behind this is due to the sensitising of the semiconductor with N719 that only absorbs light within the range of 400-700 nm.

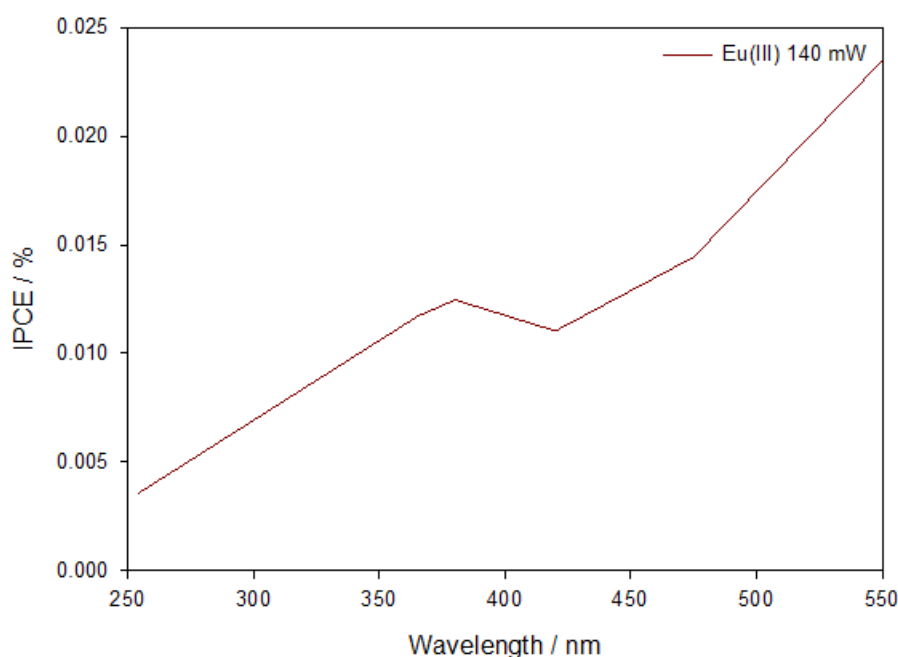


Figure 40 - IPCE of at 0 volts (140 mW/cm^2) while using Eu(III) paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

4.4.3 EUROPIUM(II) TELLURIUM OXIDE IPCE

Figure 41 illustrates the IPCE obtained by using a xenon light source coupled with optical filters. The IPCE of Eu(II) was tested by using the exact same process as described in the TiO_2 's IPCE paragraph. When comparing the three IPCE's of the different semiconductors, it can be seen that Eu(II) is the only semiconductor that favours the UV light region. Eu(II) obtained an IPCE of 0.25 % at a wavelength of 250 nm which steadily decreases until it drastically lowers to 0.006 % at a wavelength of 365 nm. This phenomena can be the reason behind the P_m and η increase in Figure 28 which illustrated the J/V curve of Eu(II) after illumination. It might be possible that the UV light excites electrons within the Eu(II) itself which only gets released after the sensitiser stagnates to induce excited electrons into the DSSC cycle.

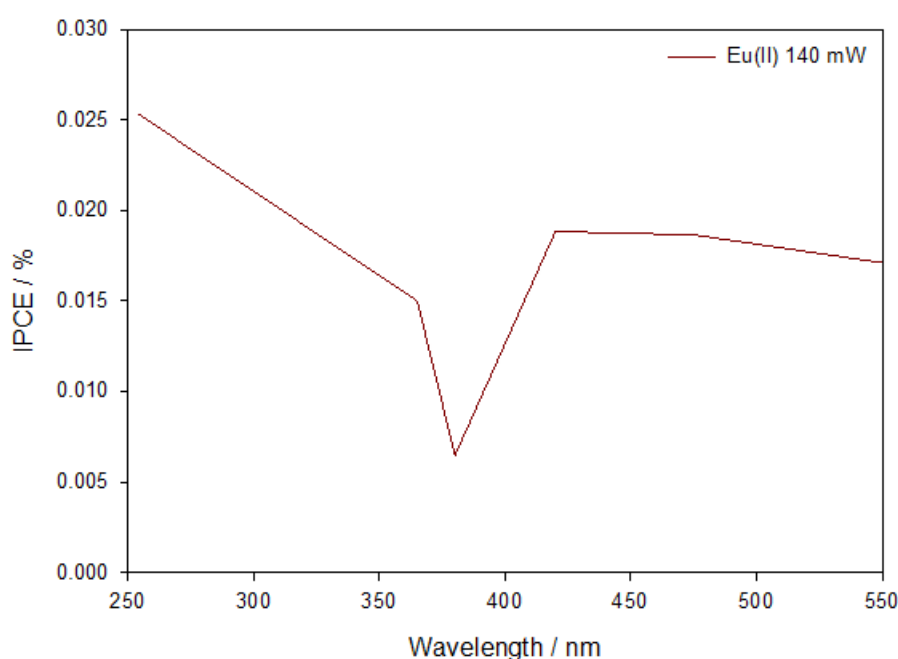


Figure 41 - IPCE of at 0 volts (140 mW/cm^2) while using Eu(II) paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

4.5 J/V CURVES – 100 MW/CM^2

Experiments done in chapter 4.2, 4.3 and 4.4 were repeated again while using a new light intensity of 100 mW/cm^2 . The experiments produced results that follow nearly identical trends to the data seen with the 140 mW/cm^2 tests, but the currents produced were lower due to the intensity of light being lower. The J/V curves done on the three semiconductors can be found in Appendix B: J/V curves – 100 mW/cm^2 .

The first distinctive change observed between using a light intensity of 100 mW/cm^2 rather than 140 mW/cm^2 is the J_{sc} produced. Figure 23 achieved an average J_{sc} of 6.20 mA/cm^2 while the J_{sc} obtained in Figure 56 in Appendix B1: Titanium dioxide J/V curve ranged between 1.15 mA/cm^2 and 2.74 mA/cm^2 , which even at its highest is only 44 % of the average J_{sc} produced while using a light intensity of 140 mW/cm^2 . This makes sense due to the fact that the amount of light available to be absorbed by the sensitizer decreased significantly, hence the frequency of electron injection into the DSSC cycle has decreased as well. It can also be seen in Figure 56 that the maximum J_{sc} , P_m and η was achieved at the 3 minute mark, which indicates that the DSSC required a longer time to create constant excited electrons to be injected into the DSSC. As for Figure 23, the light intensity was high enough from minute one to already create an efficient electron cycle within the DSSC.

Regarding Eu(III)'s performance as light intensity is decreased, it can be seen that the J/V curve trend was still nearly identical with just a decrease in J_{sc} . The J_{sc} obtained while using a

light intensity of 100 mW/cm^2 was 30 – 35 % of the J_{sc} obtained while using a light intensity of 140 mW/cm^2 . The decrease in performance was expected, because the Eu(III) DSSC already indicated signs of struggle to shift excited electrons from the dye to the semiconductor. By decreasing the light intensity, the probability of inducing an excited electron within the sensitiser is lowered as well. The Eu(II) DSSCs also exhibited a decrease in current density as light intensity was decreased, but interestingly indicated a slight resistance to the decrease in voltage, similar to TiO_2 's characteristics, which makes it a promising DSSC semiconductor.

The chronoamperometry results while using a light of intensity of 100 mW/cm^2 can be found in Appendix C: Chronoamperometry - 100 mW/cm^2 . The dark current density produced was seen to be larger when using a light intensity of 140 mW/cm^2 . The reason for this is that more electrons are simultaneously excited when using a light with a higher intensity, thus when stopping illumination, more electrons need to revert back to a steady state which results in a larger dark current being observed. This has been witnessed in all three types of DSSCs.

The IPCE experiments for all three semiconductors can be found in Appendix D: Incident Photon to Current conversion efficiency – 100 mW/cm^2 . The IPCE of all three DSSCs showed similar trends as the IPCE calculated while using a light intensity of 140 mW/cm^2 , but the IPCE values are higher when using a light intensity of 100 mW/cm^2 . This makes sense when observing equation 3.6 which indicates that the light intensity is a denominator, thus increasing the intensity will subsequently lower the IPCE. It is important to note that the current measured is part of the numerator of equation however, the denominator decreases with a value of 40 where as the numerator only decreased with a value of roughly 1-5, hence resulting in an overall increase in IPCE. All graphs done with a light intensity of 100 mW/cm^2 consist over detailed discussions that can be found in the respective appendix.

4.6 INFLUENCE OF EUROPIUM(II) TELLURIUM OXIDE PARTICLE SIZE

4.6.1 140 MW/CM^2 ILLUMINATION COMPARISON TESTS

4.6.1.1 *Europium(II) tellurium oxide 5 minute alternating illumination – $9.06 \mu\text{m}$*

Due to Eu(II) exhibiting promising results regarding dark current production as well as good current retainment while being affected by an increasing voltage, it is decided to further test the effects of particle size with regards to dark current production and overall DSSC performance. The particle size has been decreased from $30.7 \mu\text{m}$ to $9.06 \mu\text{m}$ by using a pestle and mortar. Figure 42 and Table 27 illustrates the current density produced by using Eu(II) with a particle size of $9.06 \mu\text{m}$ while illuminating the DSSC in one minute intervals for 5 minutes. When comparing the J/V graphs of Figure 27 and Figure 42 it can be seen that the lower particle size Eu(II) produced an average current density of 0.04 mA/cm^2 which is double

the current density produced by the Eu(II) DSSC with a particle size of 30.7 μm . This occurred due to the available surface area of the Eu(II) particles have been increased from 16430 cm^2/g to 41880 cm^2/g , which results in higher dye-loading on the particles. A concerning change in J/V characteristics is the sudden drop in current density as voltage is increased. Even though the new particle size obtained higher J_{sc} , the overall effectivity of the DSSC is lower than the Eu(II) DSSC with the larger particle size. This indicates that particle size is a factor regarding resistance to a change in voltage. The 9.06 μm Eu(II) obtained a maximum efficiency of 0.0012 % where the 30.07 μm Eu(II) obtained a maximum of 0.0039 %. The smaller particles of the Eu(II) semiconductor may hinder movement of electrons through the crystal structure, thus when implementing a bias as well, may lead to significant current losses.

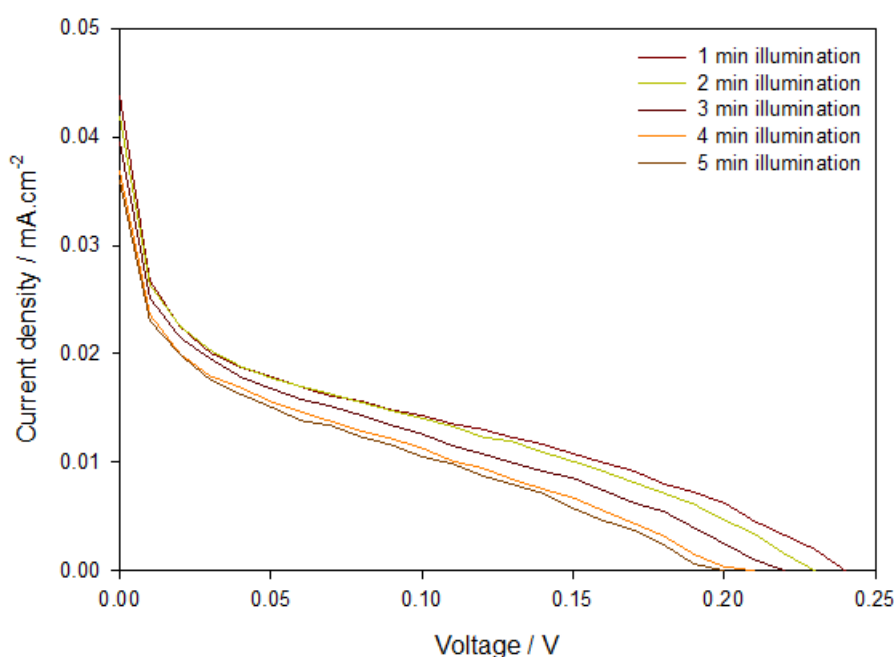


Figure 42 - J/V curve of finer Eu(II) during alternating illumination ($140 \text{ mW}/\text{cm}^2$) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 27 - J/V characteristics of finer Eu(II) during alternating illumination ($140 \text{ mW}/\text{cm}^2$) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_{M} (mA/cm^2)	V_{M} (V)	P_{M} (mW/cm^2)	FF	η (%)
1	0.044	0.24	0.012	0.14	0.0016	0.15	0.0012
2	0.042	0.23	0.012	0.13	0.0015	0.16	0.0011
3	0.040	0.22	0.010	0.13	0.0013	0.82	0.0009
4	0.037	0.20	0.009	0.12	0.0011	0.15	0.0008
5	0.036	0.20	0.010	0.11	0.0011	0.15	0.0008

Figure 43 and Table 28 illustrates the dark current produced by the 9.06 μm Eu(II) semiconductor after every minute of illumination. For the following dark current density results, the baseline was added of the DSSC which exhibits the current density produced prior to any illumination. By adding the baseline of the DSSC an interesting comparison can be made between the J_{sc} of the DSSC before and after illumination. The J_{sc} produced before any illumination is 0.006 mA/cm^2 , while after being introduced to light, a J_{sc} of 0.012 mA/cm^2 was produced. As the particle size is decreased, the surface area of the Eu(II) has increased significantly, resulting in a more porous structure which can be a factor to electron entrapment within the structure. This indicates that the short circuit dark current density has doubled after the DSSC has been treated with light. While the J_{sc} increased, the V_{oc} decreased by 0.05 V, thus resulting in a lower P_m and η as can be seen in Table 28.

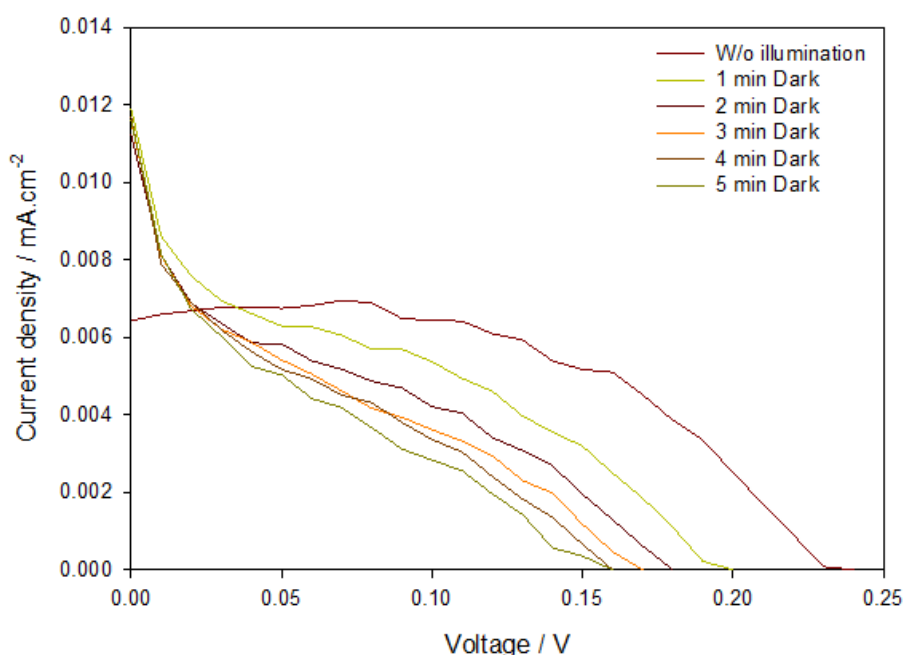


Figure 43 - J/V curve of finer Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 28 - J/V characteristics of finer Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.006	0.23	0.005	0.16	0.0008	0.55	0.0006
1	0.012	0.20	0.005	0.12	0.0006	0.23	0.0004
2	0.011	0.18	0.004	0.11	0.0004	0.22	0.0003
3	0.012	0.17	0.003	0.11	0.0004	0.18	0.0003
4	0.012	0.16	0.004	0.08	0.0003	0.18	0.0002
5	0.012	0.16	0.004	0.08	0.0003	0.16	0.0002

4.6.1.2 Titanium dioxide 5 minute prolonged illumination

Figure 44 and Table 29 illustrates the effect of continuous illumination for 5 minutes on the overall performance of the TiO₂ DSSC. As seen in Figure 44, the broad J/V curve can still be seen which exhibits satisfactory resistance to the increase in volage until the P_m is reached, resulting in a prominent decrease until the current density reaches zero. When compared to the alternating illumination times in Figure 23, it can be seen that degradation of the cell did occur after 5 minutes. The DSSC experienced constant illumination, meaning that the electron injection never stopped or “paused” while a dark current had to be measured. Without this intermediate stoppage of illumination, a higher strain on the dye to provide excited electrons to be injected into the DSSC cycle can be witnessed.

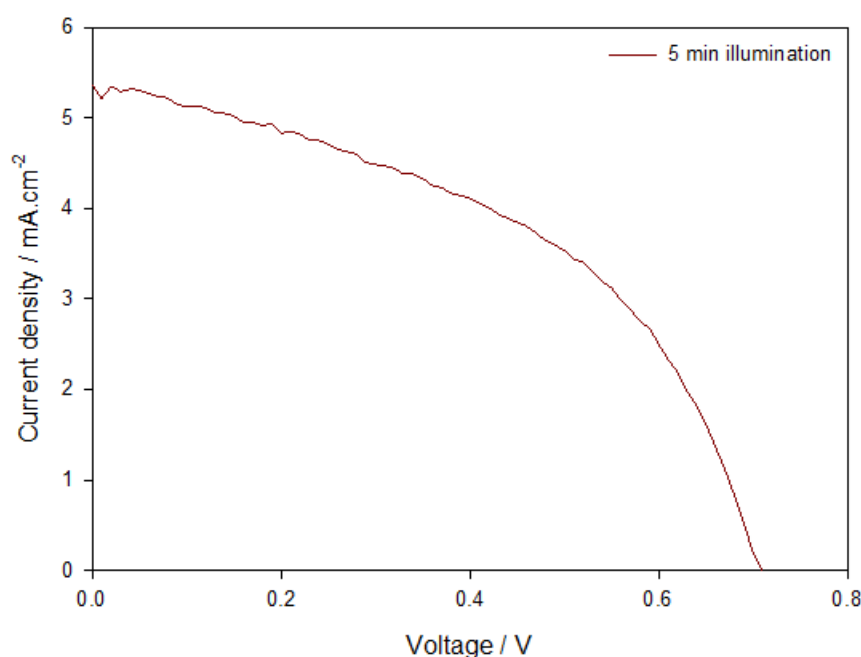


Figure 44 - J/V curve of TiO_2 after 5 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 29 - J/V characteristics of TiO_2 after 5 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
5	5.372	0.71	3.408	0.52	1.7722	0.47	1.2700

Figure 45 and Table 30 illustrates the dark current produced of the TiO_2 DSSC after being continuously illuminated for 5 minutes. As seen in Table 30, the DSSC exhibited no significant P_m nor η , which is quite interesting, because it was expected that a longer illumination time would possibly increase the dark current produced within the semiconductor however, this is not the case with TiO_2 . As the sensitizer became more exhausted due to the lengthened illumination period, when the illumination stopped, the movement of excited electrons also stopped. As time progressed, it can be seen that the V_{oc} of the TiO_2 DSSC also decreased. In comparison to the baseline of the TiO_2 prior to any illumination, the V_{oc} of 0.09 V is only 47 % of the V_{oc} obtained by the baseline measurement.

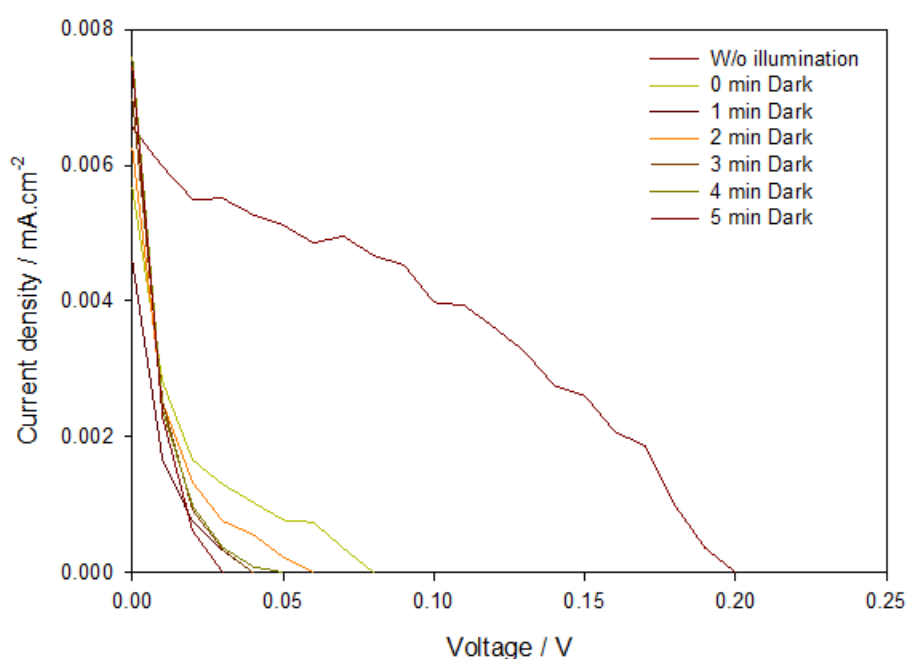


Figure 45 - J/V curve of TiO_2 dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 30 - J/V characteristics of TiO_2 without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.007	0.19	0.004	0.12	0.0004	0.12	0.0003
0	0.006	0.09	0.001	0.06	0.0000	0.09	0.0000
1	0.005	0.04	0.002	0.01	0.0000	0.09	0.0000
2	0.006	0.06	0.001	0.02	0.0000	0.07	0.0000
3	0.007	0.04	0.003	0.01	0.0000	0.09	0.0000
4	0.008	0.04	0.002	0.01	0.0000	0.08	0.0000
5	0.007	0.03	0.002	0.01	0.0000	0.10	0.0000

4.6.1.3 Titanium dioxide 3 minute prolonged illumination

Figure 46 and Table 31 illustrates the effect of continuous illumination for 3 minutes on the overall performance of the TiO_2 DSSC. When comparing the J_{sc} of the TiO_2 that was illuminated for 5 minutes with the TiO_2 that was illuminated for 3 minutes, it can be seen that the 5 minute test achieved a J_{sc} 1.2 % higher than the J_{sc} given in Table 31. It can be seen that a longer illumination time did produce a better DSSC performance, but it was only by a

small increase. Only a difference of 0.09 can be seen when comparing the two efficiencies of the DSSCs even though the DSSC in Figure 44 was illuminated for two minutes longer.

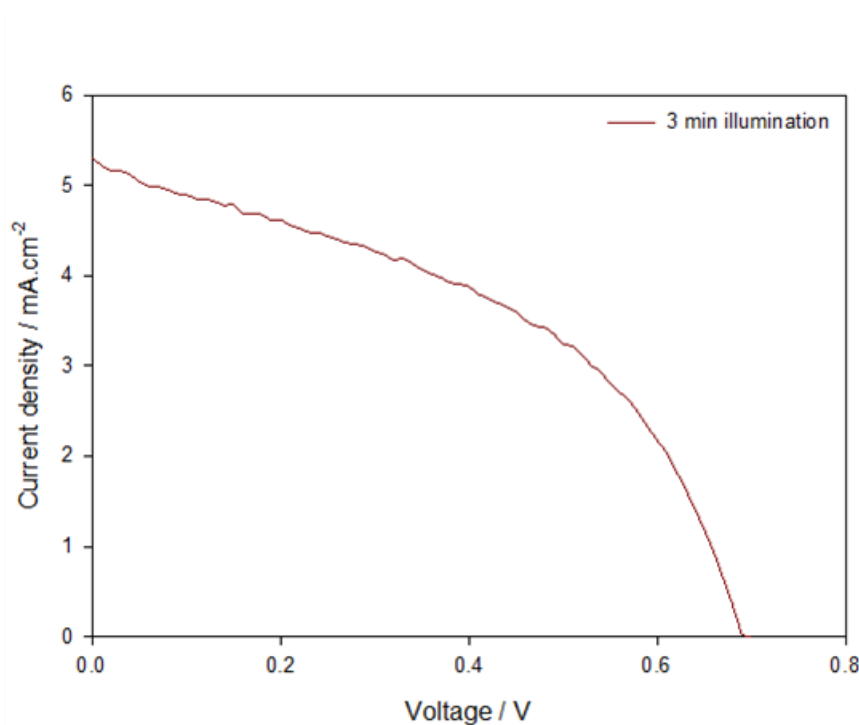


Figure 46 - J/V curve of TiO_2 after 3 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 31 - J/V characteristics of TiO_2 after 3 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
3	5.308	0.69	3.440	0.48	1.6512	0.45	1.1794

Figure 47 and Table 32 illustrates the dark current produced of the TiO_2 DSSC after being continuously illuminated for 3 minutes. Just as seen with the dark current density produced when the TiO_2 DSSC was illuminated for 5 minutes, no P_m nor η could be determined. The moment any amount of voltage was introduced, the current density instantly changed to zero. The same exhaustion discussed at Figure 45 is the reason that no efficiency or power could be seen from this DSSC.

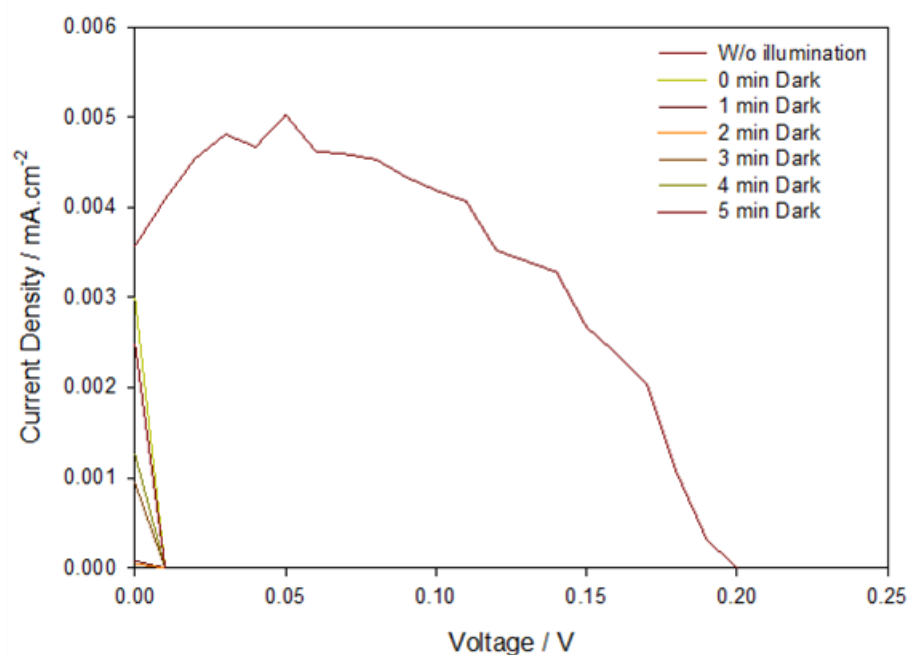


Figure 47 - J/V curve of TiO_2 dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 32 - J/V characteristics of TiO_2 without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.004	0.19	0.003	0.14	0.0005	0.66	0.0003
0	0.003	0.01	0.003	0.00	0.0000	0.00	0.0000
1	0.000	0.00	0.000	0.00	0.0000	0.00	0.0000
2	0.000	0.00	0.000	0.00	0.0000	0.00	0.0000
3	0.001	0.00	0.001	0.00	0.0000	0.00	0.0000
4	0.001	0.00	0.001	0.00	0.0000	0.00	0.0000
5	0.002	0.01	0.002	0.00	0.0000	0.00	0.0000

4.6.1.4 Europium(II) tellurium oxide 5 minute prolonged illumination – 9.06 μm

Figure 48 and Table 33 illustrates the effect of continuous illumination for 5 minutes on the overall performance of the finer Eu(II) DSSC. In Figure 48 it can be seen that the current density produced is still extremely sensitive when the voltage is increased. The finer Eu(II) produced a current density of 0.056 mA/cm² when illuminated continuously for 5 minutes. When comparing this to the J_{sc} obtained in Figure 42 after 5 minutes of alternating illumination, it can be seen that the J_{sc} produced is larger by 55.56 %. This is contradicting to what has

been seen when using a TiO_2 as the semiconductor. As illumination time is increased without intermediate stoppage, so does the J_{sc} when using the finer Eu(II) as the semiconductor. This could be due to the electron entrapment theory discussed at Figure 43. The amount of excited electrons situated within the semiconductor could possibly be released as time progresses, hence illustrating an increase in current flow as illumination time is increased.

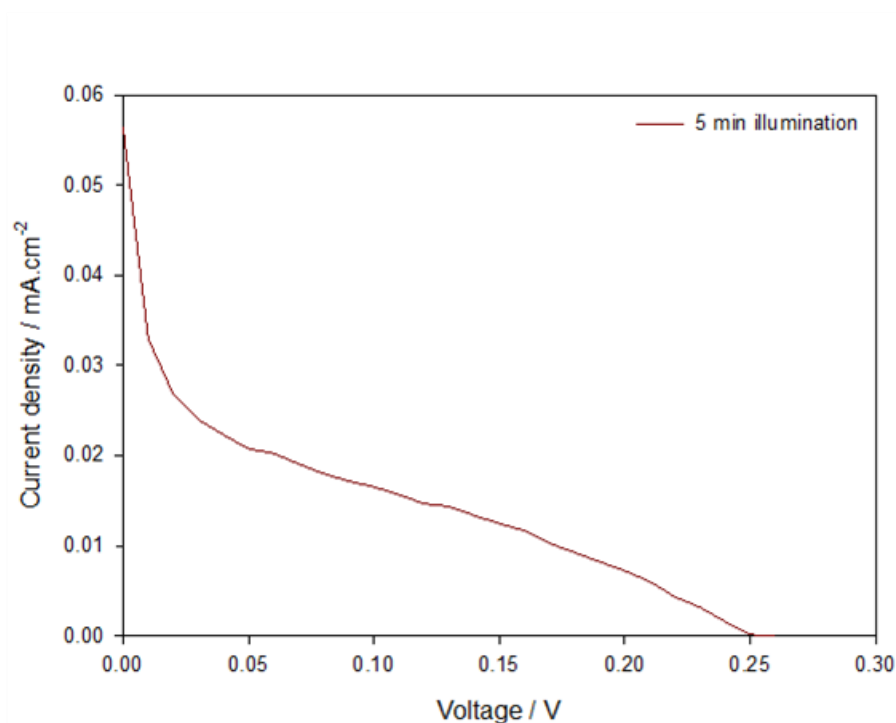


Figure 48 - J/V curve of finer Eu(II) after 5 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 33 - J/V characteristics of finer Eu(II) after 5 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
5	0.056	0.26	0.013	0.14	0.0019	0.13	0.0013

Figure 49 and Table 34 illustrates the dark current produced of the finer Eu(II) DSSC after being continuously illuminated for 5 minutes. Again, when comparing the J_{sc} of the dark current density with the baseline dark current density, the J_{sc} produced is double than what the baseline indicated. This was also seen in the alternating illumination time test in Figure 43 however, the sensitivity with respect to voltage increase still lowers the overall efficiency and P_m to only a fraction of what is produced by the baseline. When comparing the TiO_2 's performance in Figure 45 with the finer Eu(II) 's performance, it can be seen that the finer Eu(II) had an average V_{oc} of 0.16 V whereas the TiO_2 had an average V_{oc} of 0.04 V . The finer Eu(II) consisted over a much more promising J/V performance than the TiO_2 .

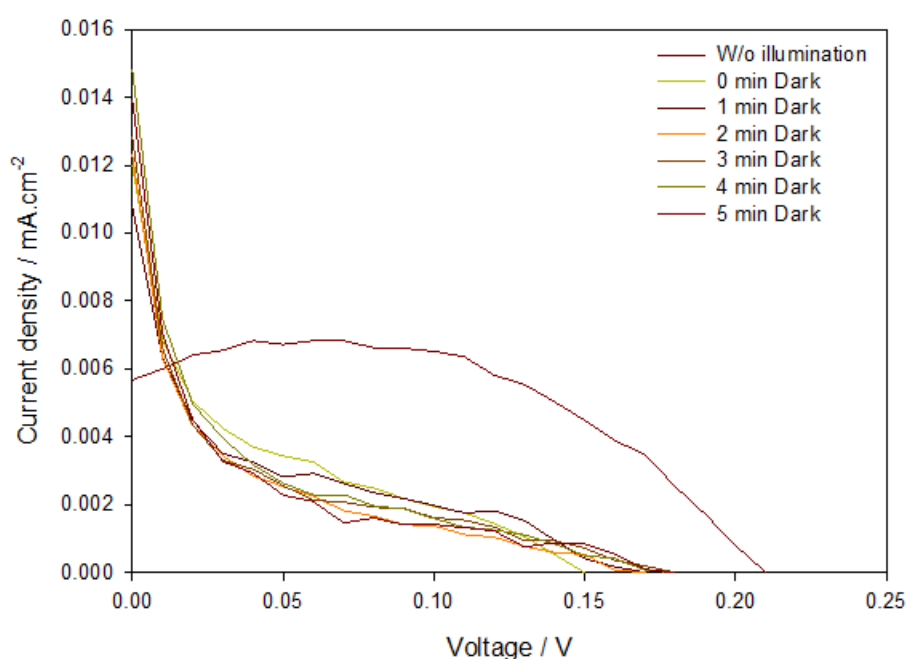


Figure 49 - J/V curve of finer Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 34 - J/V characteristics of finer Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.006	0.21	0.006	0.13	0.0007	0.60	0.0005
0	0.012	0.15	0.002	0.08	0.0002	0.11	0.0001
1	0.011	0.16	0.002	0.12	0.0002	0.12	0.0002
2	0.012	0.16	0.001	0.1	0.0001	0.07	0.0001
3	0.013	0.17	0.002	0.09	0.0002	0.08	0.0001
4	0.015	0.17	0.002	0.09	0.0002	0.07	0.0001
5	0.014	0.17	0.001	0.12	0.0001	0.06	0.0001

4.6.1.5 Europium(II) tellurium oxide 3 minute prolonged illumination – 9.06 μ m

Figure 50 and Table 35 illustrates the effect of continuous illumination for 3 minutes on the overall performance of the finer Eu(II) DSSC. When comparing Figure 48 and Figure 50 it can be seen that by illuminating the cell for 2 minutes longer, the J_{sc} increased from 0.036 mA/cm² to 0.056 mA/cm² and the V_{oc} increased from 0.19 V to 0.26 V. This indicates that as illumination time increased, so does the overall performance of the Eu(II) DSSC. The number of excited electrons entering the DSSC increases as more excited dye molecules transfer the electrons

to the semiconductor. Degradation of the cell must be kept in mind when increasing the illumination time. As seen from the alternating as well as the 5 minute illumination experiments, the new particle size Eu(II) could possibly have a higher electron flow due to the larger area created to accept excited electrons from the sensitiser.

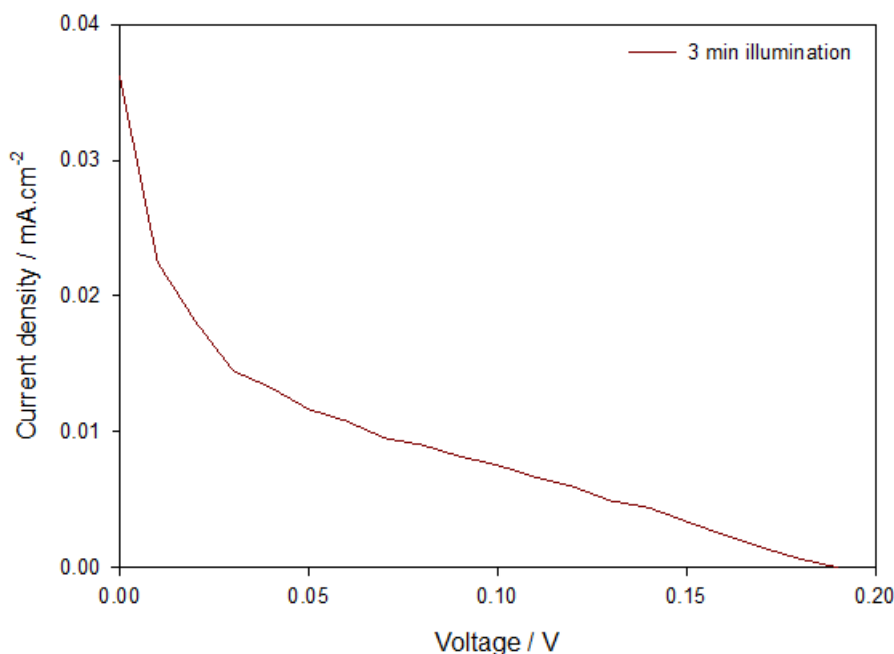


Figure 50 - J/V curve of finer Eu(II) after 3 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 35 - J/V characteristics of finer Eu(II) after 3 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
3	0.036	0.19	0.008	0.1	0.0008	0.11	0.0005

Figure 51 and Table 36 illustrates the dark current produced of the finer Eu(II) DSSC after being continuously illuminated for 5 minutes. When comparing the J_{sc} 's obtained in Table 36, it can be seen that the dark current density has doubled in comparison to the baseline dark current density prior to illumination. However, the DSSC is extremely sensitive to an increase in voltage which resulted in a η of 0 % at one and two minutes of darkness and again at 4 and 5 minutes of darkness.

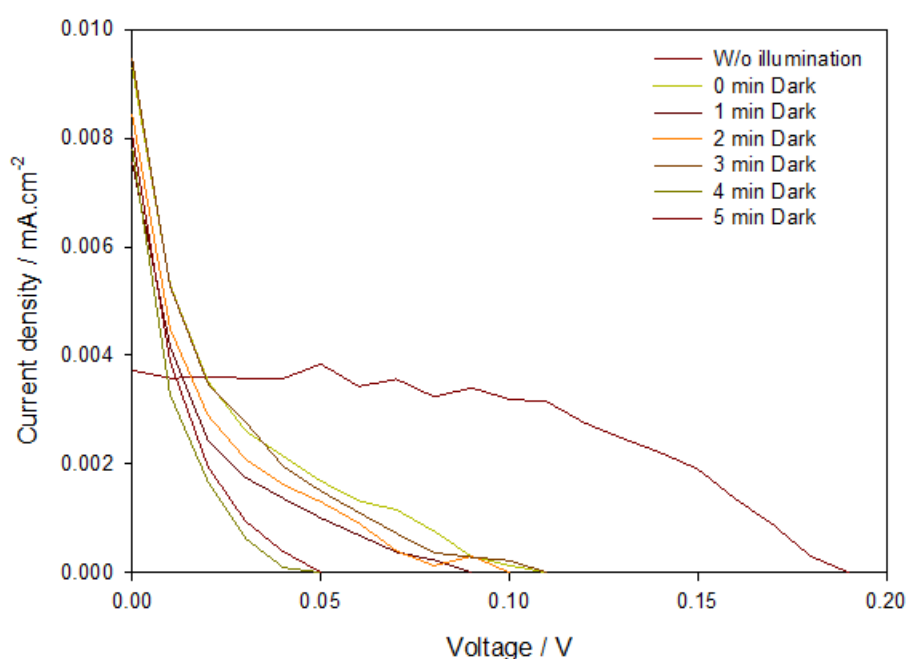


Figure 51 - J/V curve of finer Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 36 - J/V characteristics of finer Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.004	0.18	0.003	0.11	0.0003	0.50	0.0002
0	0.009	0.11	0.002	0.04	0.0001	0.09	0.0001
1	0.008	0.09	0.001	0.04	0.0001	0.08	0.0000
2	0.008	0.1	0.001	0.05	0.0001	0.08	0.0000
3	0.009	0.11	0.003	0.03	0.0001	0.08	0.0001
4	0.008	0.04	0.002	0.02	0.0000	0.10	0.0000
5	0.008	0.05	0.002	0.02	0.0000	0.10	0.0000

4.6.1.6 Europium(II) tellurium oxide 5 minute prolonged illumination – 30.70 μ m

Figure 52 and Table 37 illustrates the effect of continuous illumination for 5 minutes on the overall performance of the bigger particle Eu(II) DSSC. When comparing the trend of Figure 48 with Figure 52, it can be seen that the current density doesn't react as aggressively towards the increase of voltage as the current density in Figure 48. When comparing the DSSC parameters between the Eu(II) with a particle size of 9.06 μ m and the Eu(II) with a particle size of 30.07 μ m, the J_{sc} obtained decreased from 0.056 mA/cm² to 0.018 mA/cm² and the V_{oc}

increased from 0.26 V to 0.27 V. Again, the amount of pores as well as surface area to accept electrons from the sensitiser has significantly decreased, thus resulting in a current decrease. When comparing the η of both DSSCs, it can be seen that the finer Eu(II) DSSC achieved an efficiency of 0.013 % while the bigger particle Eu(II) achieved a η of 0.0008 %.

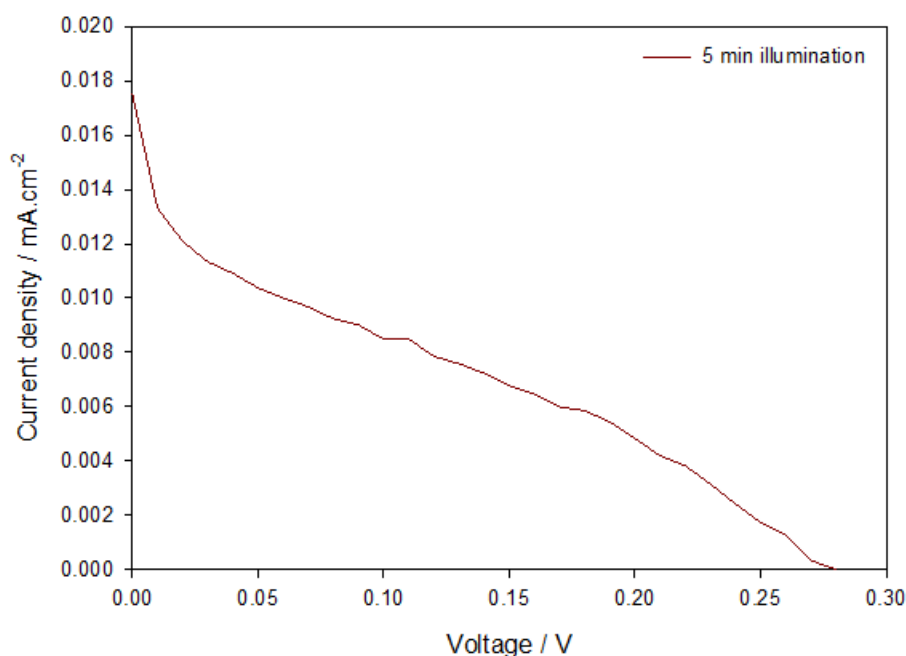


Figure 52 - J/V curve of Eu(II) after 5 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 37 - J/V characteristics of Eu(II) after 5 minutes of illumination (140 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
5	0.018	0.27	0.006	0.18	0.0011	0.22	0.0008

Figure 53 and Table 38 illustrates the dark current produced of the $30.70 \text{ }\mu\text{m}$ Eu(II) DSSC after being continuously illuminated for 5 minutes. When comparing the dark current density produced between the $30.70 \text{ }\mu\text{m}$ sample and the $9.06 \text{ }\mu\text{m}$ sample, it can be seen that the J_{sc} produced by the $30.07 \text{ }\mu\text{m}$ Eu(II) is between 0.003 mA/cm^2 to 0.006 mA/cm^2 while the $9.06 \text{ }\mu\text{m}$ produced J_{sc} in a range of 0.011 mA/cm^2 to 0.016 mA/cm^2 . This indicates that the decrease in particle size of the Eu(II) leads to an increase of J_{sc} with and without illumination. When comparing the V_{oc} of the two Eu(II) semiconductors, it can be seen that the $9.06 \text{ }\mu\text{m}$ Eu(II) had a much lower V_{oc} of 0.16 V, while the $30.70 \text{ }\mu\text{m}$ Eu(II) consisted over a V_{oc} ranging between 0.19 V to 0.26 V as total time without illumination ensued. When comparing the baseline

current density prior to any illumination with the dark current density after illumination, it can be seen that there was no increase in J_{sc} . This indicates that the larger particle Eu(II) doesn't consists over the potential ability of electron retainment, which can be supported by the fact that the semiconductor isn't as porous as the structure with the $9.06\ \mu\text{m}$ particle size.

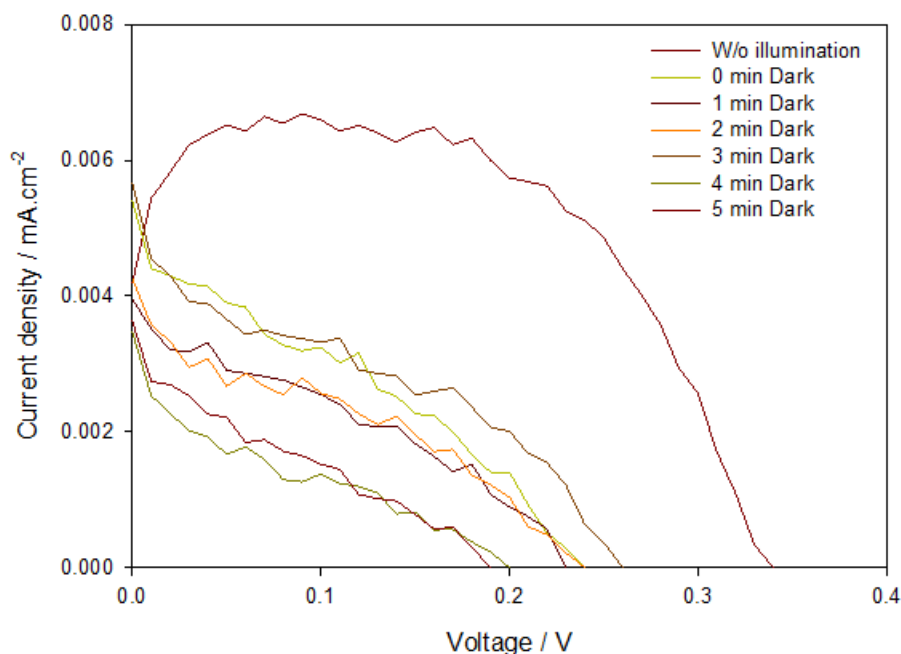


Figure 53 - J/V curve of Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 38 - J/V characteristics of Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.004	0.33	0.006	0.22	0.0012	0.88	0.0009
0	0.005	0.24	0.003	0.12	0.0004	0.30	0.0003
1	0.004	0.23	0.002	0.14	0.0003	0.32	0.0002
2	0.004	0.24	0.002	0.14	0.0003	0.31	0.0002
3	0.006	0.26	0.003	0.17	0.0004	0.31	0.0003
4	0.003	0.20	0.001	0.13	0.0001	0.21	0.0001
5	0.004	0.19	0.001	0.11	0.0002	0.23	0.0001

4.6.1.7 Europium(II) tellurium oxide 3 minute prolonged illumination – $30.70\ \mu\text{m}$

Figure 54 and Table 39 illustrates the effect of continuous illumination for 3 minutes on the overall performance of the Eu(II) DSSC. When comparing the J_{sc} of Figure 52 with the J_{sc} of

Figure 54 it can be seen that the illumination time of 3 minutes produced a higher J_{sc} of 0.032 mA/cm^2 which indicates that the Eu(II) DSSC with a particle size of 30.70 μm suffered greatly from photodegradation. When compared to the J_{sc} produced by the 9.06 μm Eu(II) DSSC in Figure 50, the J_{sc} obtained by the 30.70 μm Eu(II) DSSC was 88.89 % of the J_{sc} obtained while using the smaller particle size variant however, as illumination time progressed, the 9.06 μm Eu(II) DSSC performed better while the 30.70 μm started to degrade quickly. It is possible due to the fact that bigger semiconductor particles are more susceptible to corrosion by illumination, which results in the semiconductor cracking or even reacting with the electrolyte.

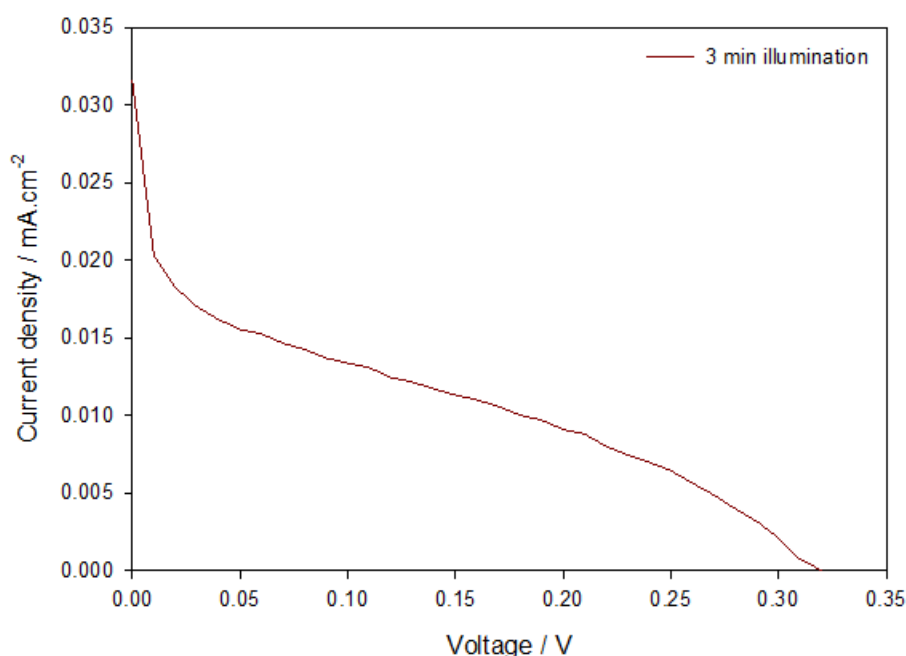


Figure 54 - J/V curve of Eu(II) after 3 minutes of illumination ($140 \text{ mW}/\text{cm}^2$) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 39 - J/V characteristics of Eu(II) after 3 minutes of illumination ($140 \text{ mW}/\text{cm}^2$) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
3	0.032	0.39	0.009	0.21	0.0018	0.15	0.0013

Figure 55 and Table 40 illustrates the dark current produced of the Eu(II) DSSC after being continuously illuminated for 5 minutes. When comparing the J_{sc} produced with the baseline it can be seen that no additional J_{sc} was conserved after illumination however, the V_{oc} did decrease with 0.07 V after illumination which could be a result of photodegradation. When comparing the J/V curves obtained in Figure 55 with the J/V curves while using 9.06 μm Eu(II) in Figure 51, it can be seen that the 30.70 μm consisted over a V_{oc} of 0.3 V which is 275 %

larger than the average V_{oc} retained in Figure 51. So as seen from the data, the overall DSSC performance without illumination is better with a larger particle size of Eu(II). However, the major increase of J_{sc} with a decrease in particle size can lead to promising results if the V_{oc} of the cell can be increased as well.

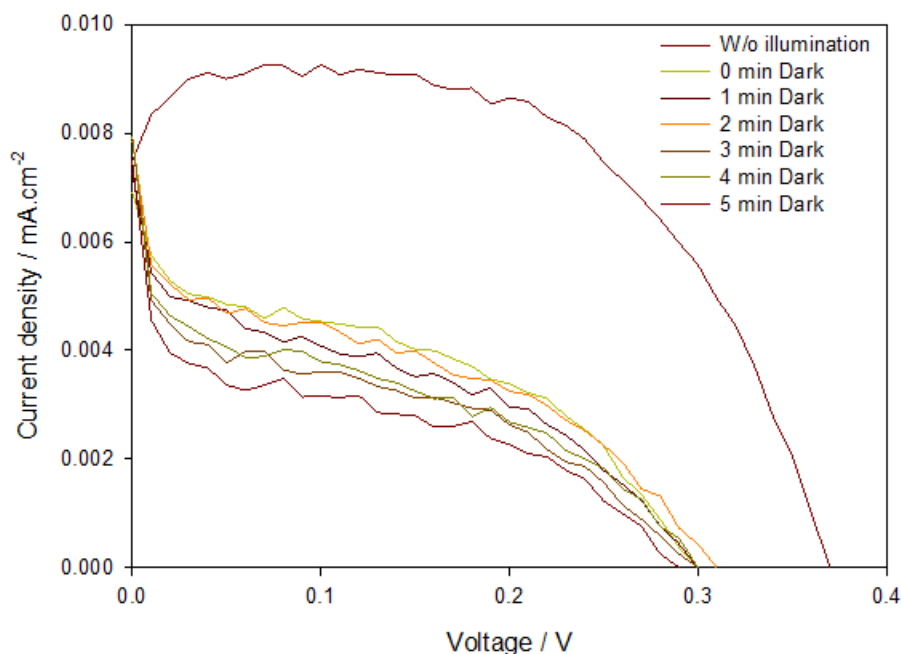


Figure 55 - J/V curve of Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 40 - J/V characteristics of Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.007	0.37	0.008	0.24	0.0019	0.68	0.0014
0	0.007	0.30	0.003	0.22	0.0007	0.33	0.0005
1	0.007	0.30	0.003	0.19	0.0006	0.29	0.0005
2	0.008	0.31	0.003	0.21	0.0007	0.27	0.0005
3	0.008	0.30	0.003	0.19	0.0006	0.23	0.0004
4	0.008	0.30	0.003	0.19	0.0006	0.24	0.0004
5	0.007	0.29	0.003	0.18	0.0005	0.22	0.0003

4.7 INFLUENCE OF EU(II) PARTICLE SIZE – 100 MW/CM²

Experiments done in chapter 4.6 have been repeated while using a light intensity of 100 mW/cm². Results obtained while using a lower light intensity followed identical trends seen in chapter 4.6, but with lower currents than the 140 mW/cm² experiments. The comparison tests done between the Eu(II)TeO₆ with a particle size of 9.06 μm and the Eu(II)TeO₆ with a particle size of 30.07 μm can be found in Appendix E: 100 mW/cm² illumination comparison test of finer Eu(II). After observing the reoccurring trend between the 30.70 μm and 9.06 μm Eu(II) DSSC in both the 140 mW/cm² and 100 mW/cm² experiments, it is noted that as the particle size decreases, the dark current density during no illumination increases. The reason behind this is due to the newly obtained porous structure and layer created by the finer Eu(II) as the photoanode. Electron entrapment may occur during illumination in this newly finer porous structure of Eu(II), which is only slowly released as the active electrons from the sensitiser is stopped as illumination is halted. Eu(II) as a semiconductor has shown that even though the TiO₂ consisted over a particle size of 11.3 μm, it couldn't exhibit any current retainment without illumination, which in retrospect adds another characteristic of Eu(II) that is absent in TiO₂

5. CONCLUSION & RECOMMENDATIONS

5.1 CONCLUSION

The main outcomes of this study was to establish an infrastructure for DSSC manufacturing coupled with accurate and precise testing procedures as well as obtaining a rigid basis of knowing how DSSC manufacturing works. Another outcome was to indicate whether europium might add additional properties to DSSC performance.

The following objectives have been stated in Chapter 1.2 with the purpose to identify the effect it will have on the performance of the DSSC:

- Effect of sensitising time
- Effect of extended illumination time
- Effect of spacer size
- Effect of different dyes
- Effect of light intensity
- Effect of electrolyte preparation
- Effect of photoanode preparation

It can be concluded that the sensitising time of the semiconductor in the dye significantly affects the total current produced. It was seen that a sensitising time of 18 hours delivered the highest current out of all other sensitising times. The increase in illumination time illustrated the effects of photodegradation quite well, where the results indicated that continuous illumination affected the semiconductor negatively. When the two spacer sizes were compared, the findings agreed to what was stated in literature, stating that a thicker spacer negatively affects the DSSC's performance. As seen in literature, ruthenium dyes are still the leading sensitisers used in DSSCs and the results in this report indicated the same verdict where N719 outperformed the other 3 sensitisers in terms of efficiency and max power output. When the light intensity was lowered, the overall performance of the DSSC decreased as well while retaining the same trend patterns of a J-V curve. The TBP additive contributed significantly to the increase in performance of the DSSCs however, it is concerning that the TBP affects the conduction band of the semiconductor by creating a smaller energy gap between the LUMO of the dye and the conduction band of the semiconductor. This can result in excited electrons falling back to steady state instead of moving through the porous structure of the semiconductor. Lastly, the semiconductor paste concentration played a significant role regarding DSSC performance. The ethanol became saturated when the 3.88 M semiconductor paste sample was created, this led to issues such as film cracking and uneven photoanode surfaces.

It can be concluded that europium introduces an increase in dark current production to DSSC performance however, when using europium as the semiconductor, the current produced is so low that it can't be used as a photovoltaic cell yet. The europium semiconductors showed intriguing effects such as conservation of V_{oc} with or without illumination as well as better conservation of current produced than TiO_2 . A noteworthy remark is the increased dark P_m and PCE in $Eu(II)TeO_6$ over its illuminated counterpart.

Even though the TiO_2 DSSCs outperformed the europium based DSSCs during illumination, it was seen that as illumination was lengthened, the dark current and performance exhibited by the TiO_2 DSSCs diminished while the europium(II) tellurium oxide DSSCs still produced a measureable power. Due to the fact that only the semiconductor was changed to observe this dark current conservation indicates that europium consists over certain characteristics that influence the flow of electrons within the DSSC. It is believed that the conduction band of the $Eu(II)$ – and $Eu(III)TeO_6$ is much higher than the TiO_2 semiconductor, which supports the low current seen being produced by the europium semiconductors. The TiO_2 semiconductor performed quite well and consistent as expected, but parameters such as cathode thickness, different electrolyte solutions and semiconductor thickness can be optimised to increase the performance of the TiO_2 DSSCs.

5.2 RECOMMENDATIONS

An important factor to note is that these europium cells were constructed on the premises of what increased the TiO_2 's DSSC efficiency. It might be that europium DSSCs would perform more efficiently under different parameters. It is highly recommended that an entire performance analysis should be done on europium as the main semiconductor.

When investigating each component of the DSSC, a few general recommendations can be made. When observing Figure 18, it can be seen that as the concentration of N719 dye was increased, so did the efficiency of the cell increase. A summary of recommendations have been identified and evaluated:

- It is highly recommended to investigate the performance of DSSCs when using dye concentrations higher than 1 mM.
- Regarding semiconductor layer thickness, the DSSCs prepared with the laboratory equipment presently available achieved a thickness of 20 - 30 μm which is quite large, thus new techniques should be implemented to decrease the semiconductor thickness [227].
- For this research topic, the platinum cathode thickness was kept constant at 100 nm however, studies show that when decreasing the cathode thickness, a possible performance increase in DSSCs can be observed [235].

- Only two spacer thicknesses were tested in this research topic however, other spacer thicknesses can be studied as well to optimise the DSSC's performance.
- Quartz substrates can be used as a replacement for glass substrates to reduce the total reflected light, which will lead to an increase in DSSC performance.
- The conduction band of the europium (II) and (III) tellurium oxide must be identified and altered to increase total current produced.
- The HOMO and LUMO levels of the sensitisers should be studied to ensure that the electron injection force needed between the sensitiser and europium tellurium oxide is as low as possible.
- The conductivity of the europium tellurium oxide is quite low in comparison to TiO_2 , but reduced graphene oxide can be added to increase the conductivity.
- It was seen that decreasing the particle size resulted in higher current densities, but it is highly recommended to find methods to decrease the particle size even further.

For this research, the DSSC was built around the general TiO_2 DSSC standard, which is probably not identical to what europium tellurium oxide requires to produce notable current. It is highly recommended that the effect of semiconductor concentration should be investigated again, but from the perspective of europium tellurium oxide. To compensate for europium tellurium oxide's low current densities, a hybrid cell between TiO_2 and europium can also be researched to possibly obtain qualities of both semiconductors in one DSSC. It was now seen that europium does bring additional effects into DSSC operation, further research should emphasise on this finding.

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APPENDIX

APPENDIX A: UNCERTAINTY ANALYSIS FOR CHAPTER 4.2

For Figure 23:

Illumination time (min)	Standard deviation at specific voltages	0 V	0.05 V	0.1 V	0.15 V
1		0.22	0.21	0.21	0.20
2		0.32	0.30	0.30	0.29
3		0.22	0.21	0.20	0.20
4		0.24	0.26	0.23	0.30
5		0.26	0.28	0.30	0.33

For Figure 24:

Dark interval time (min)	Standard deviation at specific voltages	0 V	0.05 V	0.1 V	0.15 V
1		0.0017	0.0014	0.0018	0.0014
2		0.0015	0.0016	0.0015	0.0014
3		0.0016	0.0019	0.0017	0.0015
4		0.0020	0.0017	0.0017	0.0015
5		0.0015	0.0018	0.0016	0.0018

For Figure 25:

Illumination time (min)	Standard deviation at specific voltages	0 V	0.05 V	0.1 V	0.15 V
1		0.0018	0.0008	0.0009	0.0011
2		0.0033	0.0015	0.0013	0.0014
3		0.0026	0.0011	0.0012	0.0010
4		0.0026	0.0012	0.0012	0.0011
5		0.0033	0.0015	0.0013	0.0014

For Figure 26:

Dark interval time (min)	Standard deviation at specific voltages	0 V	0.05 V	0.1 V	0.15 V
1		0.0024	0.0001	0.0004	0.0004
2		0.0015	0.0004	0.0004	0.0007
3		0.0014	0.0008	0.0008	0.0007
4		0.0016	0.0009	0.0012	0.0011
5		0.0011	0.0010	0.0012	0.0011

For Figure 27:

Illumination time (min)	Standard deviation at specific voltages	0 V	0.05 V	0.1 V	0.15 V
1		0.0020	0.0027	0.0023	0.0022
2		0.0015	0.0020	0.0018	0.0015
3		0.0003	0.0010	0.0011	0.0010
4		0.0004	0.0011	0.0012	0.0015
5		0.0014	0.0017	0.0019	0.0022

For Figure 28:

Dark interval time (min)	Standard deviation at specific voltages	0 V	0.05 V	0.1 V	0.15 V
1		0.0029	0.0028	0.0028	0.0028
2		0.0025	0.0025	0.0028	0.0027
3		0.0028	0.0030	0.0030	0.0046
4		0.0024	0.0023	0.0025	0.0018
5		0.0024	0.0028	0.0029	0.0029

APPENDIX B: J/V CURVES – 100 MW/CM²

Appendix B gives information relevant to Chapter 4.2 J/V curves – 140 mW/cm²

APPENDIX B1: TITANIUM DIOXIDE J/V CURVE

Figure 56 and Table 41 illustrates the effect of one minute alternating illumination at 100 mW/cm² on the performance of the DSSC using TiO₂ as the semiconductor. The DSSC was illuminated for 5 minutes while testing the dark current at every one minute by switching off the light source and waiting for 15 seconds before measuring the current. The following

experiments were done to determine whether the change in light intensity from 140 mW/cm² to 100 mW/cm² had any effects on the performance of the DSSC.

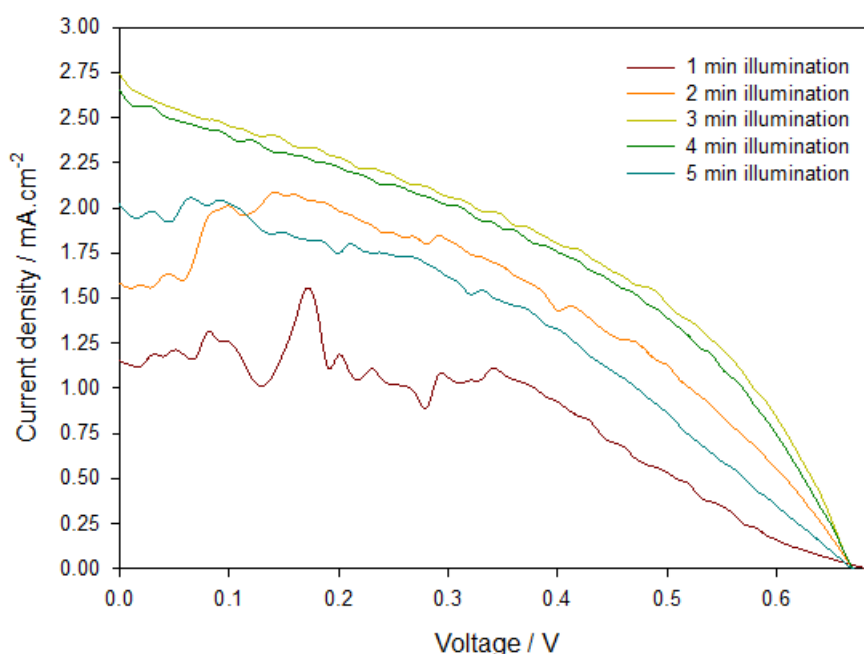


Figure 56 - J/V curve of TiO₂ during alternating illumination (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 41 - J/V characteristics of TiO₂ during alternating illumination (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J _{sc} (mA/cm ²)	V _{oc} (V)	J _M (mA/cm ²)	V _M (V)	P _M (mW/cm ²)	FF	η (%)
1	1.152	0.68	1.028	0.37	0.3804	0.48	0.3804
2	1.584	0.67	1.432	0.42	0.6014	0.57	0.6014
3	2.740	0.67	1.536	0.49	0.7526	0.41	0.7526
4	2.652	0.67	1.528	0.47	0.7182	0.40	0.7182
5	2.020	0.67	1.444	0.37	0.5343	0.40	0.5343

Figure 57 and Table 42 illustrates the dark current produced after every minute of illumination for a total of 5 minutes while using TiO₂ as the semiconductor. Even though the light intensity was lowered during the illumination time, the dark current produced hasn't changed significantly when comparing the results obtained in Table 42 with Table 20. The only noteworthy difference is the decrease in V_{oc} where the experiment using a light intensity of 100 mW/cm² obtained an average V_{oc} of 0.11 V while the average V_{oc} observed in Table 20 was 0.18 V. Due to the decrease in V_{oc}, the P_m decreased significantly during no illumination. The P_m produced in Table 20 is more than double than what can be seen in Table

42, which indicates that the light intensity has an influence over the performance of the cell during no illumination.

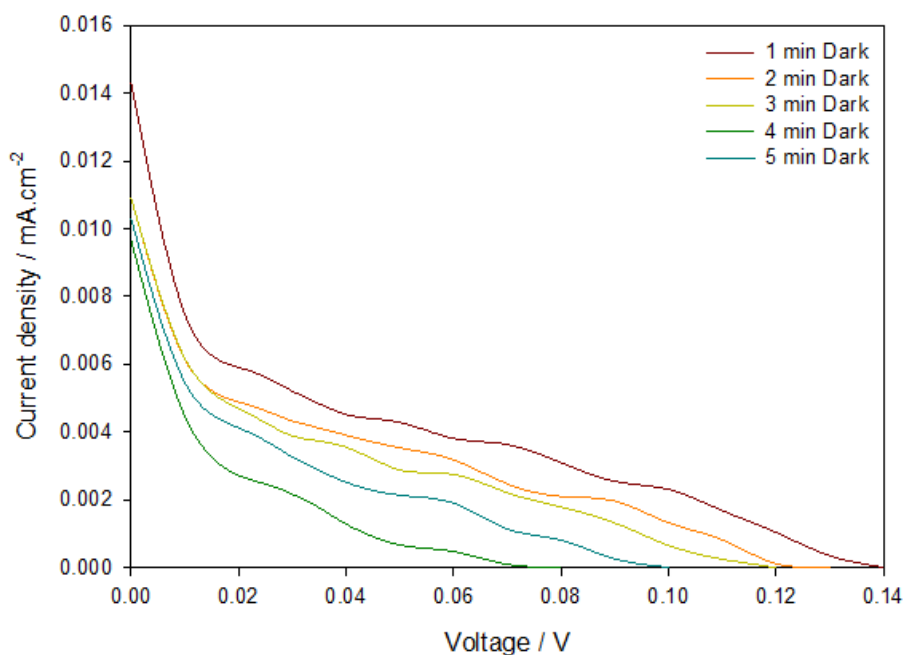


Figure 57 - J/V graph of TiO₂ dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 42 - J/V characteristics of TiO₂ without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without Illumination (min)	J _{sc} (mA/cm ²)	V _{oc} (V)	J _M (mA/cm ²)	V _M (V)	P _M (mW/cm ²)	FF	η (%)
1	0.014	0.14	0.004	0.07	0.0003	0.13	0.0003
2	0.011	0.12	0.003	0.06	0.0002	0.14	0.0002
3	0.011	0.11	0.003	0.06	0.0002	0.13	0.0002
4	0.010	0.07	0.002	0.03	0.0001	0.09	0.0001
5	0.010	0.10	0.002	0.06	0.0001	0.12	0.0001

APPENDIX B2: EUROPIUM(III) TELLURIUM OXIDE J/V CURVE

Figure 58 and Table 43 illustrates the effect of one minute alternating illumination at 100 mW/cm² on the performance of the DSSC using Eu(III) as the semiconductor. Identical to what has been seen by the TiO₂ DSSC, the J_{sc} of the Eu(III) DSSC seen in Figure 58 is only 30-35 % of the J_{sc} obtained by the Eu(III) DSSC when a light intensity of 140 mW/cm² was implemented. Both DSSCs still exhibit the same reaction to when a bias is implemented into the DSSC cycle. The current density decreases significantly the moment the voltage is

increased. It can be seen in Figure 58 that after one minute of illumination, barely any current was produced. This exhibits the same characteristic as seen in the TiO_2 's J/V curve, but just more drastically. Eu(III) as a semiconductor already showed difficulty of injecting an excited electron into the DSSC cycle, by decreasing the light intensity, the probability of getting an excited electron to move into the DSSC cycle became even more difficult.

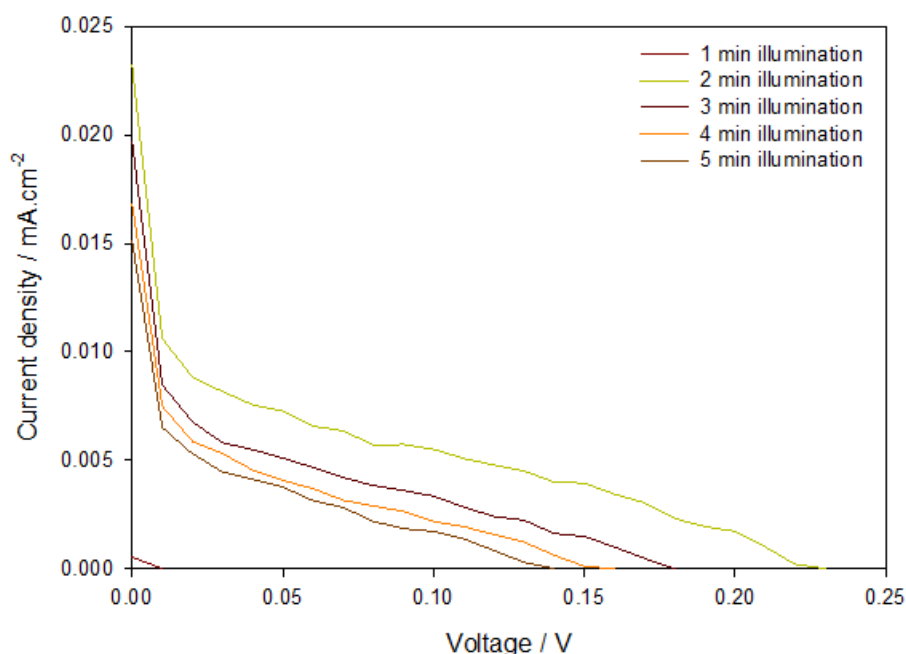


Figure 58 - J/V curve of Eu(III) during alternating illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 43 - J/V characteristics of Eu(III) during alternating illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
1	0.001	0.01	0.001	0.00	0.0000	0.00	0.0000
2	0.023	0.23	0.004	0.15	0.0006	0.11	0.0006
3	0.020	0.18	0.003	0.10	0.0003	0.08	0.0003
4	0.017	0.16	0.003	0.09	0.0002	0.09	0.0002
5	0.015	0.14	0.003	0.07	0.0002	0.09	0.0002

Figure 59 and Table 44 illustrates the dark current produced after every minute of illumination for a total of 5 minutes using Eu(III) as the semiconductor. The Eu(III) DSSC that was illuminated with a light intensity of 100 mW/cm^2 only produced 40 - 50 % of the J_{sc} dark current in comparison to the Eu(III) in Figure 26. This indicates the notion stated when observing the dark current between the TiO_2 DSSCs to be true and that the dark current generated is

depended on the light intensity used. It can be seen that when comparing the J_{sc} of Figure 58 and Figure 59 that only minute 2 and 3 had a significant difference of 50 %. Whereas minute 4 and 5 had only a 29.50 % and 13 % difference in current density. Even though TiO_2 had more current flowing through the DSSC cycle, Eu(III) and TiO_2 still consisted over a relatively similar dark J_{sc} . Just as seen in the 140 mW/cm^2 tests, the Eu(III) DSSC conserved V_{oc} much more effectively than TiO_2 . Eu(III) retained and even had an increase in V_{oc} without illumination, but TiO_2 only consisted over 16 % of the V_{oc} it had during illumination.

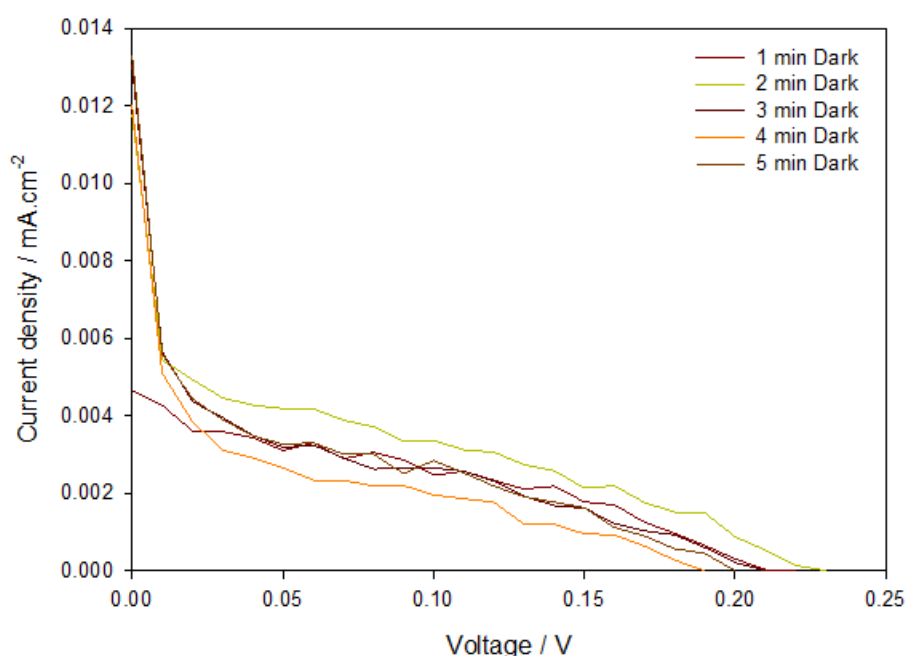


Figure 59 - J/V curve of Eu(III) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 44 - J/V characteristics of Eu(III) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without Illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
1	0.005	0.22	0.002	0.14	0.0003	0.30	0.0003
2	0.012	0.23	0.003	0.12	0.0004	0.14	0.0004
3	0.013	0.21	0.003	0.11	0.0003	0.10	0.0003
4	0.012	0.19	0.002	0.12	0.0002	0.09	0.0002
5	0.013	0.20	0.003	0.1	0.0003	0.11	0.0003

APPENDIX B3: EUROPIUM(II) TELLURIUM OXIDE J/V CURVE

Figure 60 and Table 45 illustrates the effect of one minute alternating illumination at 100 mW/cm^2 on the performance of the DSSC using Eu(II) as the semiconductor. Again it can be seen in Figure 60 that there was a small delay in current produced after one minute however, this effect was much more prominent when observing the Eu(III) and TiO_2 DSSC. Eu(II) is the only semiconductor that did not undergo significant losses as the light intensity decreased and even showed an increase in V_{oc} by 29 %.

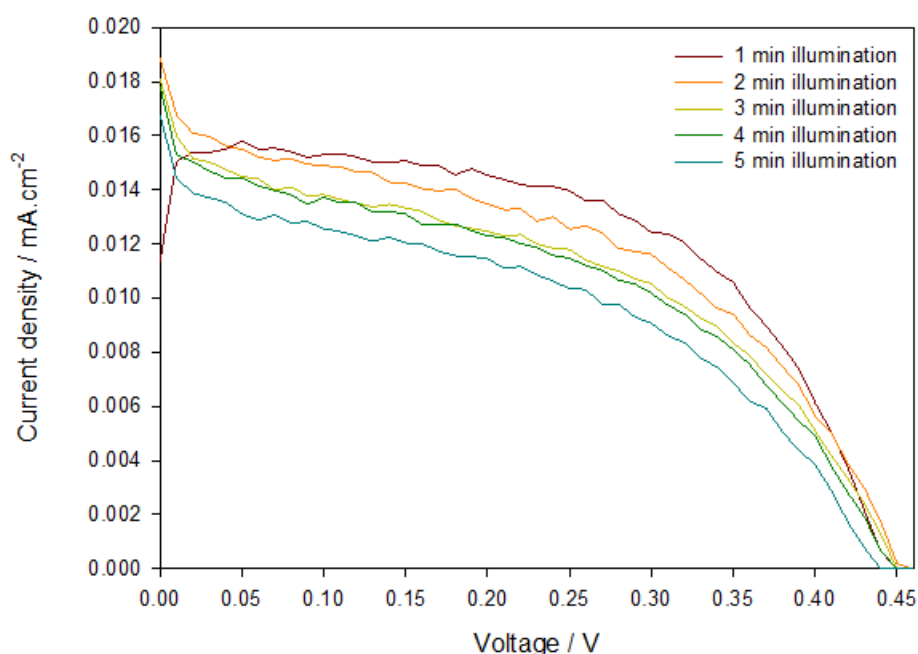


Figure 60 - J/V curve of Eu(II) during alternating illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 45 - J/V characteristics of Eu(II) during alternating illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
1	0.011	0.44	0.012	0.32	0.0039	0.77	0.0039
2	0.019	0.45	0.011	0.31	0.0035	0.41	0.0035
3	0.018	0.45	0.011	0.30	0.0032	0.39	0.0032
4	0.018	0.45	0.010	0.30	0.0031	0.38	0.0031
5	0.017	0.44	0.010	0.28	0.0027	0.38	0.0027

Figure 61 and Table 46 illustrates the dark current produced after every minute of illumination for a total of 5 minutes using Eu(II) as the semiconductor. When comparing the η obtained in Table 45 with the η obtained Table 46, it can be seen that the Eu(II) DSSC barely lost efficiency

even though no illumination was present, this indicates that even though no active light is being absorbed by the sensitiser, electrons are still being injected into the DSSC cycle while no light is present. When comparing Eu(II)'s J/V curves with Eu(III)'s J/V curves, the Eu(II) DSSC is much more resistant to an increasing voltage which is a pinnacle characteristic for an effective working DSSC. This can be seen as well by comparing the fill factor of the two europium semiconductors. Eu(II) obtained a fill factor of 0.48 without illumination while Eu(III) obtained fill factors between 0.1 – 0.14 without illumination. Even when comparing the dark current J/V curves of Eu(II) to TiO₂ it can be seen that Eu(II) still consists over an effective broad J/V pattern without illumination while the TiO₂ DSSC significantly decreased in current density as voltage increased.

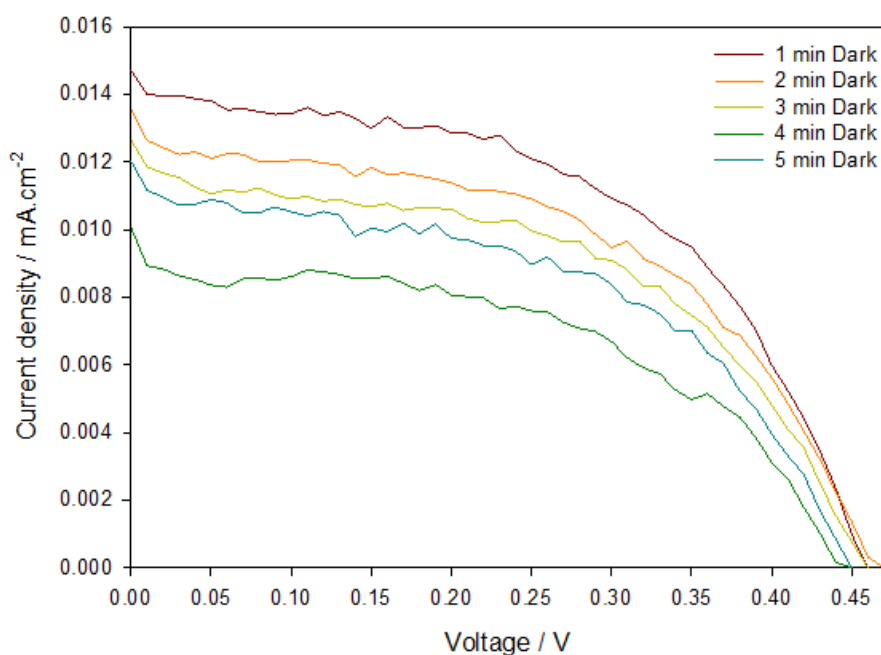


Figure 61 - J/V curve of Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 46 - J/V characteristics of Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without Illumination (min)	J _{sc} (mA/cm ²)	V _{oc} (V)	J _M (mA/cm ²)	V _M (V)	P _M (mW/cm ²)	FF	η (%)
1	0.015	0.46	0.011	0.31	0.0033	0.49	0.0033
2	0.014	0.46	0.010	0.31	0.0030	0.48	0.0030
3	0.013	0.46	0.008	0.33	0.0028	0.48	0.0028
4	0.010	0.44	0.007	0.29	0.0020	0.46	0.0020
5	0.012	0.45	0.007	0.29	0.0025	0.47	0.0025

APPENDIX B4: TITANIUM DIOXIDE J/V CURVE – UV RANGE

Figure 62 and Table 47 illustrates the effect of only illuminating the DSSC with an ultraviolet light (280-315 nm) at 100 mW/cm² while using TiO₂ as the semiconductor. The DSSC was illuminated for one minute before measuring the current density produced. It can be seen in Table 47 that the J_{sc} obtained by only using UV light is 1.05 mA/cm² which is 38 % of the max J_{sc} produced when using the Xe light source used in the solar simulator. This indicates that TiO₂ is still more dependant on the visible spectrum of light rather than UV light.

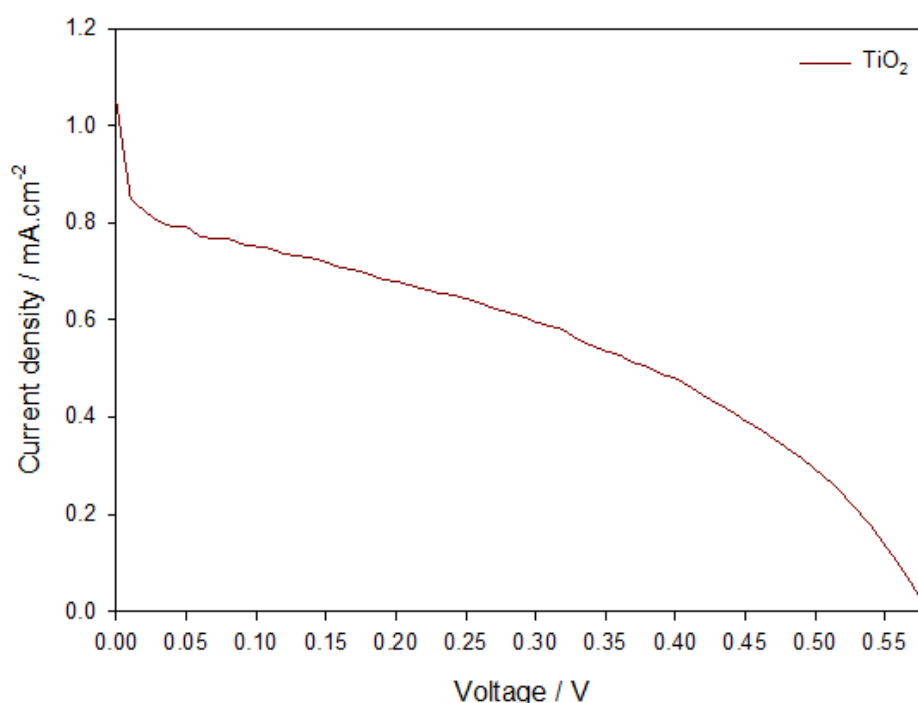


Figure 62 - J/V curve of TiO₂ during UV irradiation (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 47 J/V characteristics of TiO₂ during UV irradiation (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Semiconductor	J _{sc} (mA/cm ²)	V _{oc} (V)	J _M (mA/cm ²)	V _M (V)	P _M (mW/cm ²)	FF	η (%)
TiO ₂	1.048	0.58	0.480	0.40	0.1920	0.32	0.1920

APPENDIX B5: EUROPIUM(II)/EUROPIUM(III) TELLURIUM OXIDE J/V CURVE – UV RANGE

Figure 63 and Table 48 illustrates the effect of only illuminating the DSSC with an ultraviolet light (280-315 nm) at 100 mW/cm² while using Eu(III) or Eu(II) as the semiconductor. The DSSCs were illuminated for one minute before measuring the current density produced. When

comparing the maximum J_{sc} obtained by Eu(III) in Figure 58 with the J_{sc} obtained when only illuminating Eu(III) with UV light, the newly obtained J_{sc} is only 13 % of the maximum J_{sc} . This still shows that Eu(III) is dependant on the visible spectrum of light as seen in Figure 30 as well. The J_{sc} produced by Eu(II) in Figure 63 is 0.006 mA/cm² which is only 32 % of the maximum J_{sc} obtained in Figure 60. When comparing the UV J/V curve of Eu(II) when illuminated with an intensity of 140 mW/cm² and 100 mW/cm², the Eu(II) UV absorption ratio to entire light spectrum stayed constant regardless of light intensity which is what was expected.

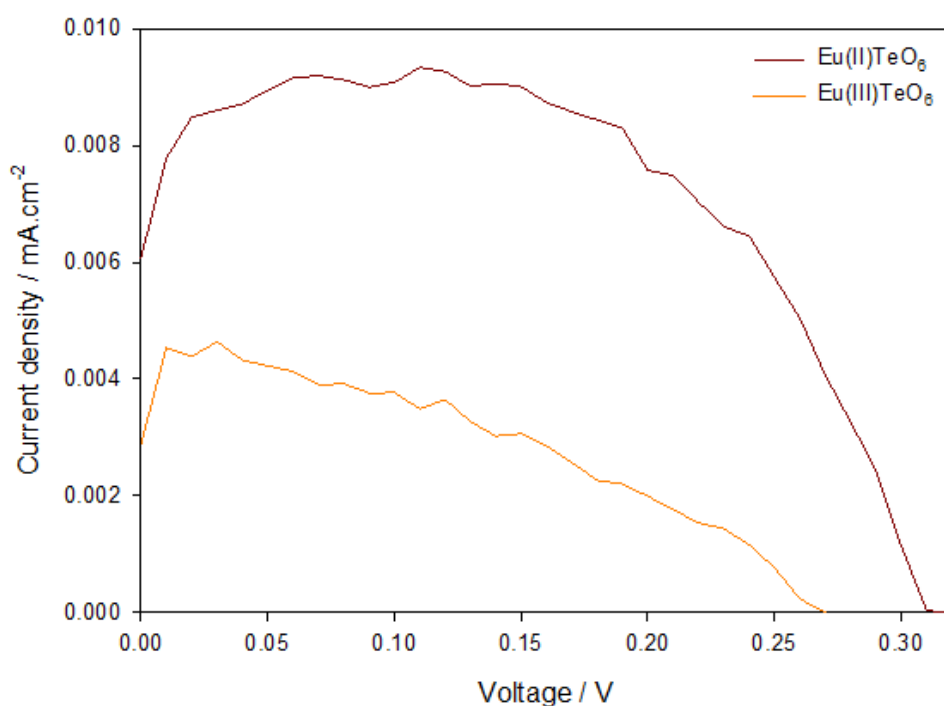


Figure 63 - J/V curve of Eu(III) and Eu(II) during UV irradiation (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 48 - J/V characteristics of Eu(III) and Eu(II) during UV irradiation (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Semiconductor	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
Eu(ii)	0.006	0.31	0.008	0.19	0.0016	0.84	0.0016
Eu(iii)	0.003	0.27	0.003	0.15	0.0005	0.59	0.0005

APPENDIX C: CHRONOAMPEROMETRY - 100 MW/CM²

Appendix C gives information relevant to Chapter 4.3 Chronoamperometry – 140 mW/cm²

APPENDIX C.1: TITANIUM DIOXIDE CHRONOAMPEROMETRY

Figure 64 illustrates the effect of voltage on the dark current produced by TiO₂ DSSCs. Each DSSC was illuminated for one minute at 100 mW/cm², then 15 seconds was given for the solar simulator to completely shut down before measuring the dark current produced while being affected by a bias (Voltage). The same phenomena occurred as what was seen in Figure 31, the current density produced decreased as the voltage is increased. When comparing Figure 31 with Figure 64 it can be deduced that if the light intensity is increased during illumination, the dark current produced will also be higher. The reason for this is that more electrons are simultaneously excited when using a light with a higher intensity, thus when stopping illumination, more electrons need to revert back to a steady state which results in a larger dark current being observed. The TiO₂ DSSCs in Figure 64 that were put under 0.01, 0.02 and 0.03 V produced current densities of 0.0046 – 0.0055 mA/cm², while the TiO₂ DSSCs in Figure 31 produced current densities in a range of 0.0095 – 0.0115 mA/cm².

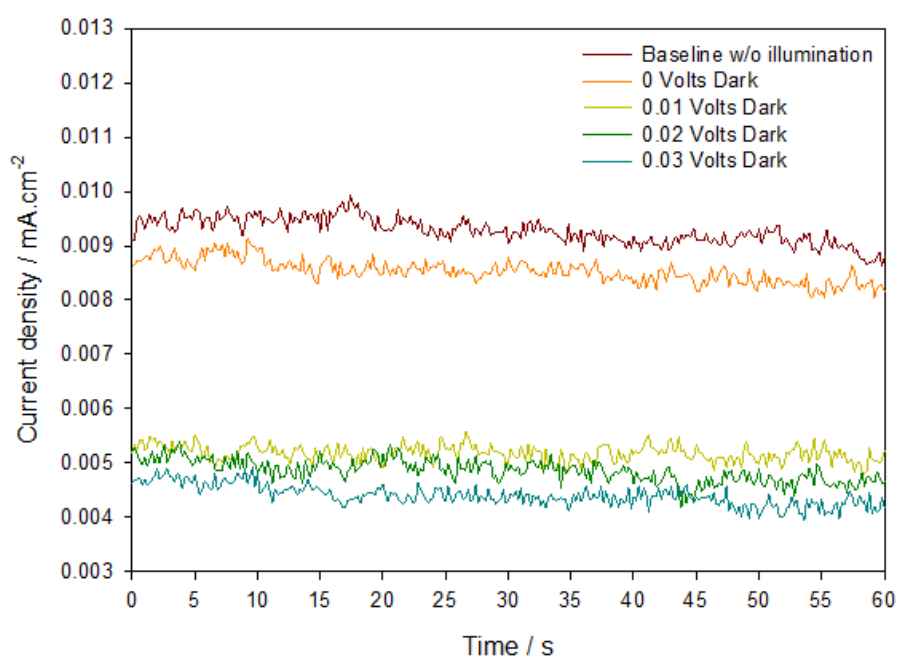


Figure 64 - Effect of voltage on dark current produced - TiO₂ (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

APPENDIX C.2: EUROPIUM(III) TELLURIUM OXIDE CHRONOAMPEROMETRY

Figure 65 illustrates the effect of voltage on the dark current produced by Eu(III) DSSCs. The chronoamperometry process for Eu(III) is done exactly as described by the TiO₂'s

chronoamperometry. Again, it can be seen that the DSSC that was put under a higher voltage, produced lower current densities. When comparing Figure 64 with Figure 65 it can be seen that the Eu(III) DSSCs did not deviate as much to the change in voltage as what the TiO₂ DSSCs did. TiO₂'s 0.03 V and 0 V DSSCs consisted over a 0.004 mA/cm² difference, while Eu(III)'s DSSCs all grouped together in a range of 0.001 mA/cm² regarding each DSSC. The Eu(III) DSSCs exhibited more resistance against the changing bias, which could be an indication of excited electrons still being released from the semiconductor even though no illumination is present to create excited dye molecules.

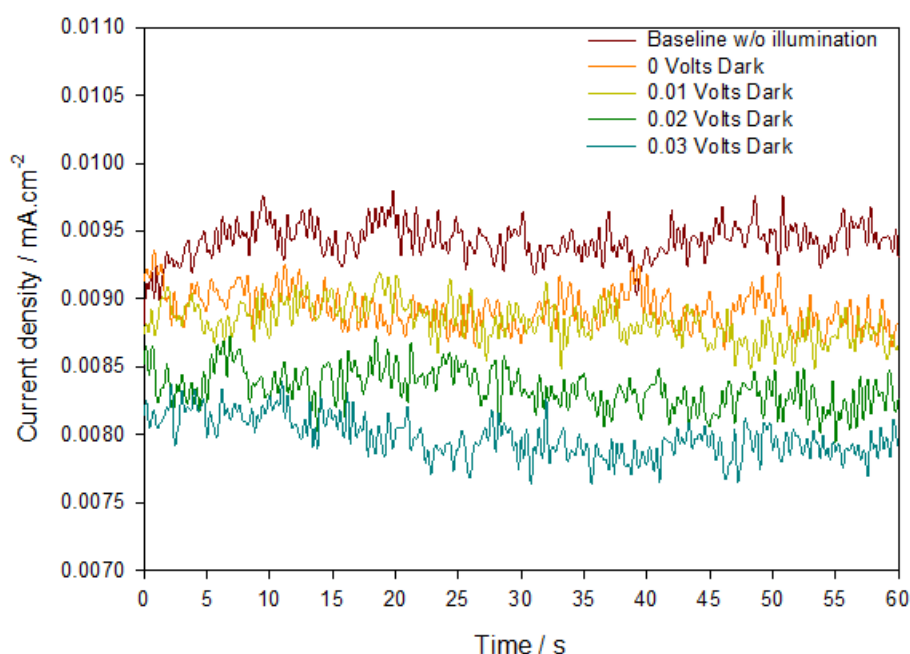


Figure 65 - Effect of voltage on dark current produced - Eu(III) (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

APPENDIX C.3: EUROPIUM(II) TELLURIUM OXIDE CHRONOAMPEROMETRY

Figure 66 illustrates the effect of voltage on the dark current produced by Eu(III) DSSCs. The chronoamperometry process for Eu(II) is done exactly as described by the TiO₂ chronoamperometry. Just as seen by the Eu(III) chronoamperometry, regardless of a change in voltage, the Eu(II) DSSCs stayed within a 0.001 mA/cm² from each other showing little change due to the increase in voltage however, there is still a small current density decrease of 0.0003 mA/cm² as voltage increases. When comparing Eu(II)'s chronoamperometry with TiO₂'s chronoamperometry, Eu(II) produced a current density of 0.001 mA/cm² larger than TiO₂ even though the TiO₂ DSSCs generate more than a factor of 5 the current density that Eu(II) produced during illumination.

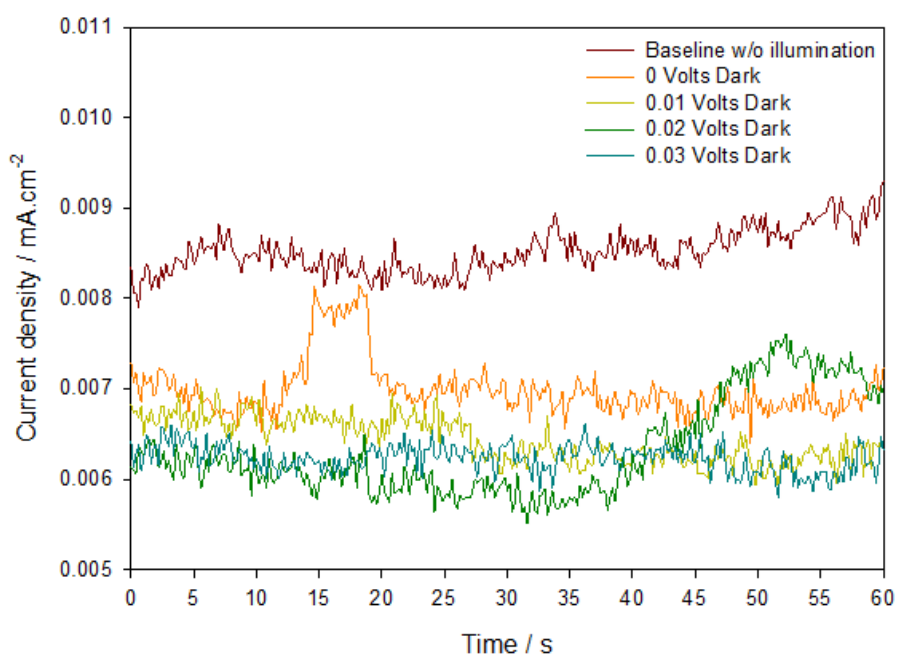


Figure 66 - Effect of voltage on dark current produced - Eu(II) (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

APPENDIX C.4: TITANIUM DIOXIDE CHRONOAMPEROMETRY – LONG EXPOSURE

Figure 67 illustrates the current density produced during illumination as time progresses. The chronoamperometry process for the 100 mW/cm^2 tests are done exactly as described by the TiO_2 's chronoamperometry at Figure 34. The current density trend observed here can be exactly seen in Figure 34 as well. The current density reaches a maximum of 2.844 mA/cm^2 at 133 seconds before slowly decreasing as time progresses. The reason behind this trend is identical to the explanation found at Figure 34.

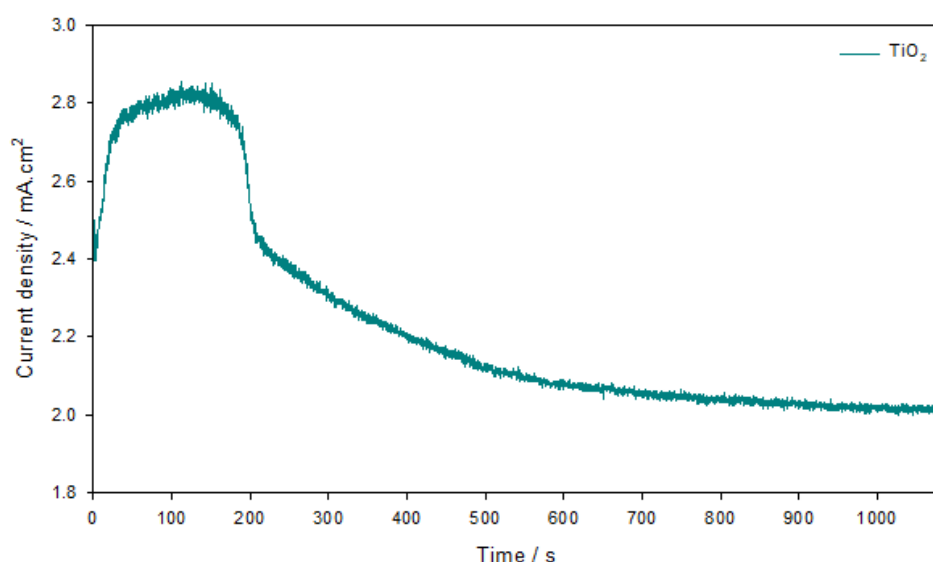


Figure 67 - Current density during illumination as time progressed - TiO_2 (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution

Figure 68 illustrates the dark current produced after being illuminated for 18 minutes with a light intensity of 100 mW/cm^2 . The initial measurement was only taken 15 seconds after the solar simulator was switched off to ensure complete darkness. It can be seen in Figure 68 that the electrolyte and sensitizer is exhausted after such long illumination time, hence the dark current is so low when compared to the baseline of the DSSC prior to any illumination. This can be supported by the decline of current density at the later stages in Figure 67.

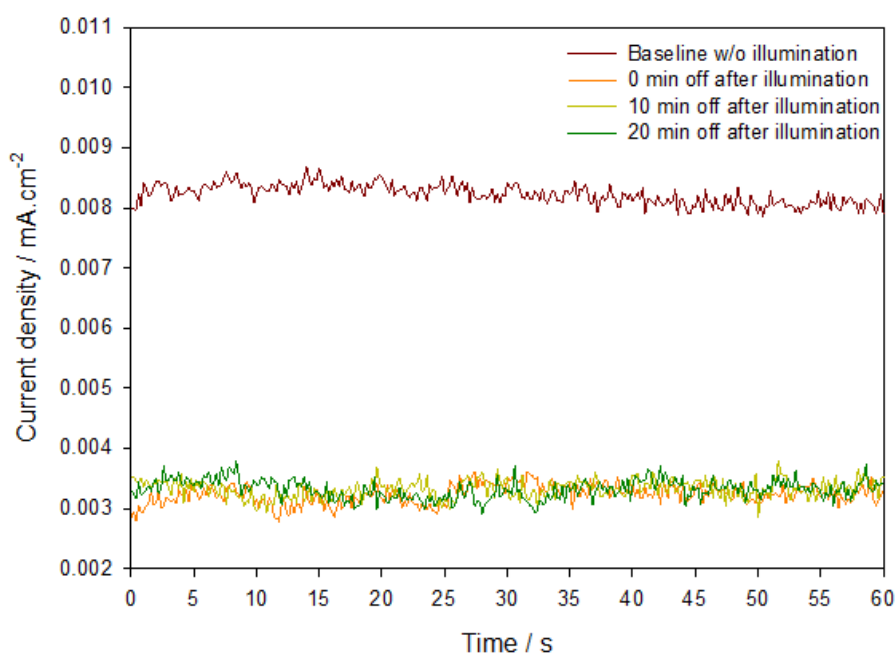


Figure 68 - Dark current produced after long exposure to light - TiO_2 (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution

APPENDIX C.5: EUROPIUM(III)/EUROPIUM(II) TELLURIUM OXIDE CHRONOAMPEROMETRY – LONG EXPOSURE

Figure 69 illustrates the current density produced during illumination as time progresses while using Eu(III) and Eu(II) as semiconductors. The chronoamperometry process for Eu(III) is done exactly as described by the TiO_2 's chronoamperometry at Figure 34. In Figure 69 it can be seen that Eu(II) maintained its current density quite well when comparing it to Eu(III). Eu(II) initially produced a current density of 0.011 mA/cm^2 where Eu(III) produced a lower current density of 0.0078 mA/cm^2 which started to significantly decrease at 100 seconds.

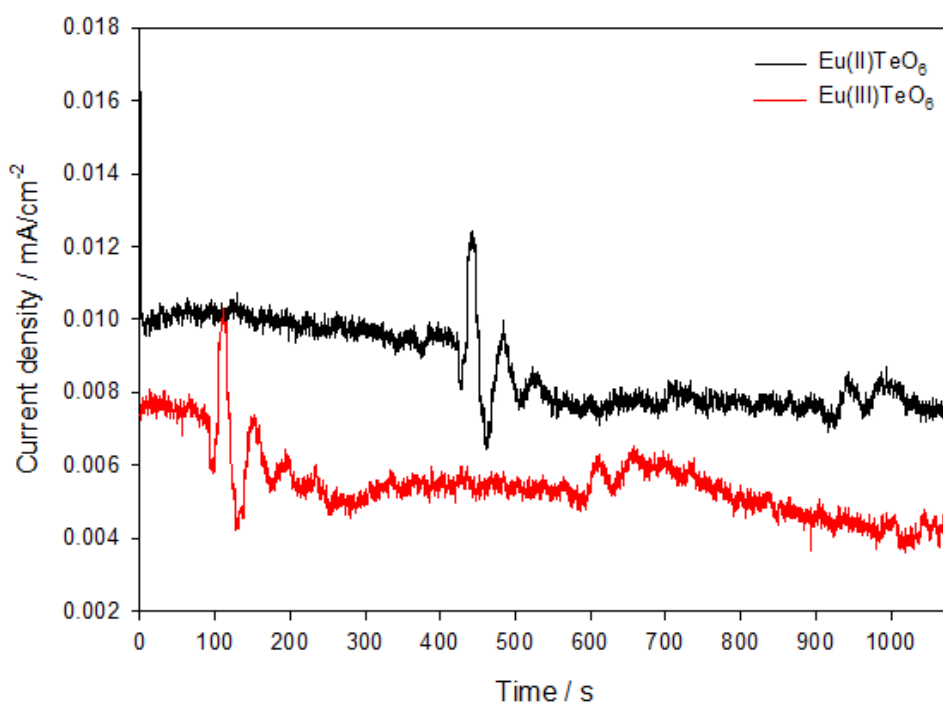


Figure 69 – Current density during illumination as time progressed - Eu(III) and Eu(II) (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Figure 70 illustrates the dark current produced after being illuminated for 18 minutes with a light intensity of 100 mW/cm^2 . Just as seen in Figure 37, regardless of extending the darkness time period, the dark current density produced was consistent around 0.0055 mA/cm^2 for both the 10 minute and 20 minute test. The current density produced right after illumination produced higher results than the two tests mentioned previously and produced a current density of 0.0065 mA/cm^2 . The baseline of Eu(III) exhibits inconsistency, which means that the electron movement through the DSSC system is obstructed at certain points such as the excitation step from sensitiser to semiconductor.

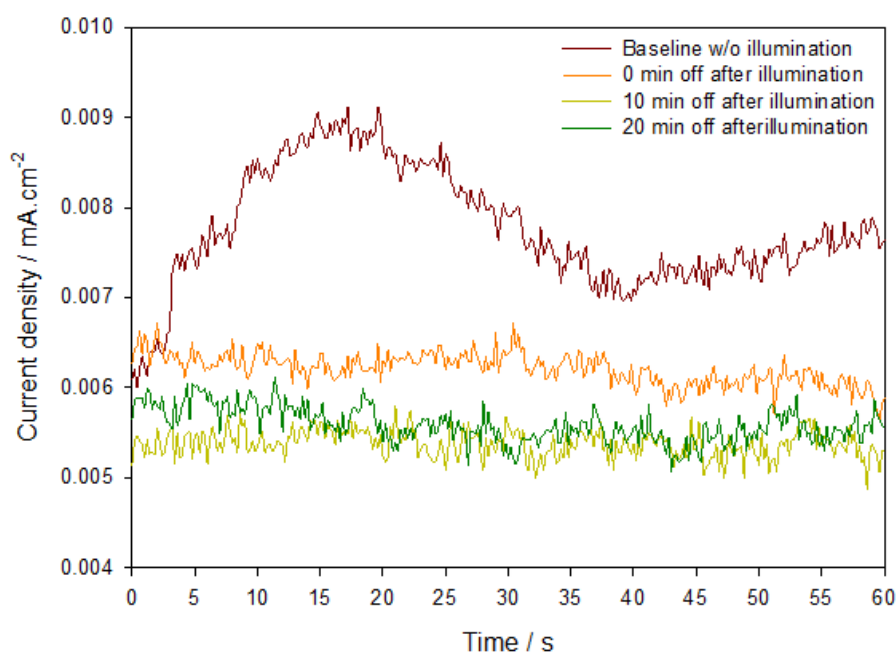


Figure 70 - Dark current produced after long exposure to light - Eu(III) (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Figure 71 illustrates the dark current produced after being illuminated for 18 minutes with a light intensity of 100 mW/cm^2 . When comparing all three semiconductors, it can be seen that Eu(III), Eu(II) and TiO_2 got a decrease in dark current after illumination when compared to their baselines. This indicates exhaustion of the electrolyte and excited dye molecules after such a long illumination time. It can be seen in Figure 71 that as time increased without illumination, the current density decreased as the electron cycle started to slow down within the DSSC.

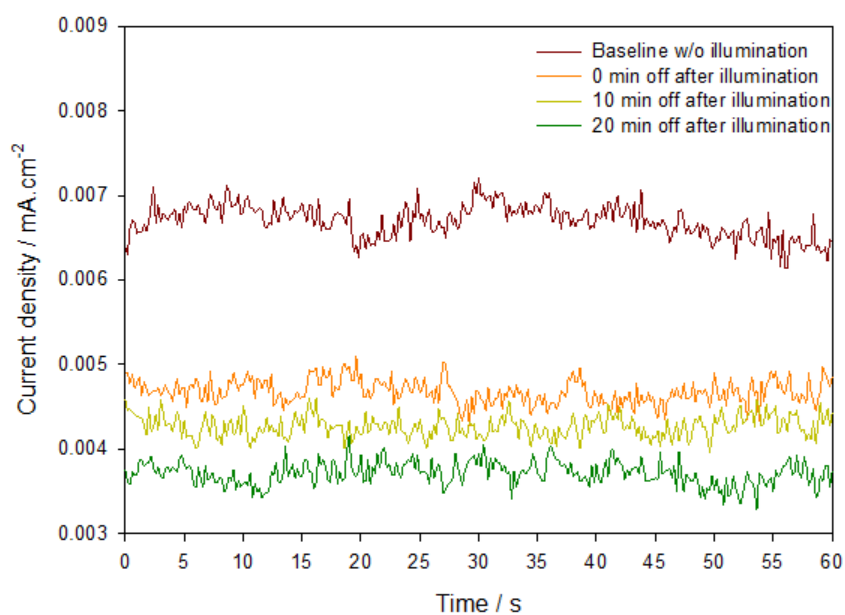


Figure 71 - Dark current produced after long exposure to light - Eu(II) (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

APPENDIX D: INCIDENT PHOTON TO CURRENT CONVERSION EFFICIENCY – 100 MW/CM²

Appendix D gives information relevant to Chapter 4.4 Incident Photon to Current conversion efficiency – 140 mW/cm².

APPENDIX D.1: TITANIUM DIOXIDE IPCE

Figure 72 illustrates the IPCE obtained by using different sources of light with different wavelengths. Light filters were attached to the solar simulator to only allow a specific wavelength to be shined onto the surface of the DSSC. A DSSC only came into contact with one type of wavelength to ensure no excitation is carried over when testing a new wavelength, thus meaning there was one DSSC test per wavelength. The DSSC was illuminated for one minute before a measurement was taken. The trends followed by both Figure 39 and Figure 72 are quite identical when compared to each other however, the IPCE obtained by the TiO₂ at 100 mW/cm² is larger than the IPCE observed in Figure 39. This can be explained by looking back to equation 3.6 which indicates the power of light is part of the denominator, this means having a lower light intensity will be advantageous to the IPCE.

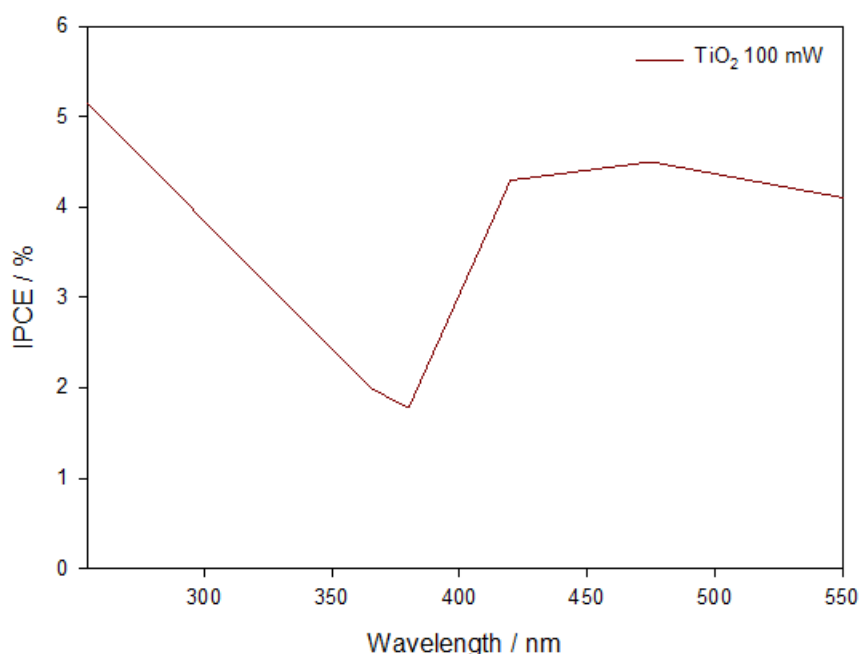


Figure 72 - IPCE at 0 volts (100 mW/cm²) while using TiO₂ paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

APPENDIX D.2: EUROPIUM(III) TELLURIUM OXIDE IPCE

Figure 73 illustrates the IPCE obtained by using different sources of light with different wavelengths. The IPCE of Eu(III) was tested by using the exact same process as described

in the TiO_2 's IPCE paragraph. When comparing Figure 40 with Figure 73 it can be seen that the IPCE produced while using a 100 mW/cm^2 light intensity is higher than the IPCE produced while using a light intensity of 140 mW/cm^2 . When comparing the trends of the two IPCE graphs, it can be seen that the IPCE still increases as the wavelength is increased. This indicates that Eu(III) is more dependant on the visible spectrum of light than the UV range, which is an agreement to what was observed in Figure 40.

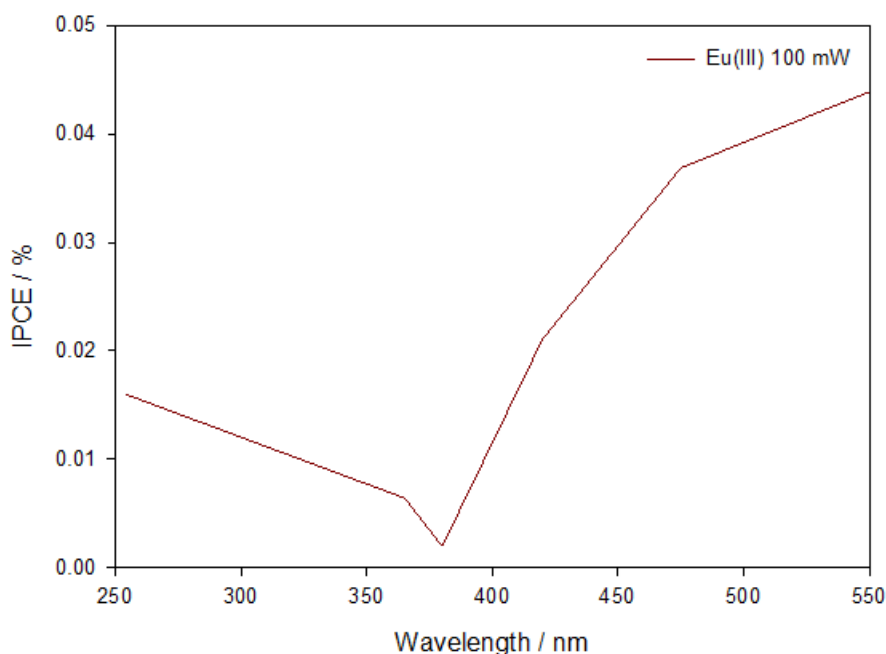


Figure 73 - IPCE at 0 volts (100 mW/cm^2) while using Eu(III) paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

APPENDIX D.3: EUROPIUM(II) TELLURIUM OXIDE IPCE

Figure 74 illustrates the IPCE obtained by using different sources of light with different wavelengths. The IPCE of Eu(II) was tested by using the exact same process as described in the TiO_2 's IPCE paragraph. The IPCE produced in Figure 74 is double than the IPCE produced in Figure 41. With regards to the trend of the IPCE curve, both Figure 41 and Figure 74 move identical alongside the change in wavelength. As can be seen in Figure 74, Eu(II) is still heavily dependant on the UV spectrum of light, with achieving a maximum IPCE of 0.048% at 254 nm . As stated at Figure 41, the short wavelength of UV light might penetrate the semiconductor which creates excited electrons within the Eu(II) . These excited electrons could possibly be trapped within the crystal structure of Eu(II) before being transferred to the rest of the DSSC cycle.

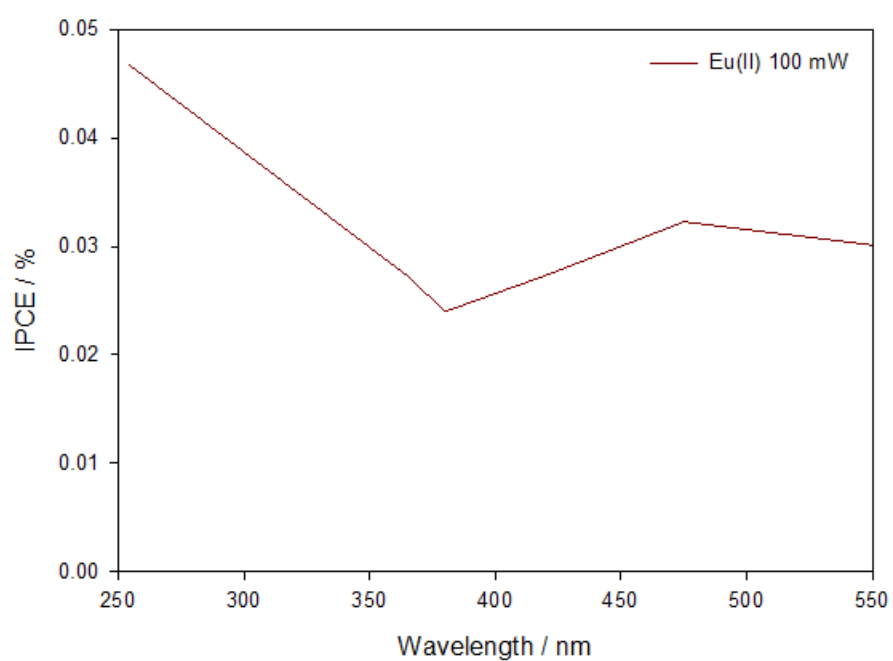


Figure 74 - IPCE at 0 volts (100 mW/cm^2) while using Eu(II) paste as the semiconductor, N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

APPENDIX E: 100 MW/CM² ILLUMINATION COMPARISON TEST OF FINER EU(II)

Appendix E gives information relevant to Chapter 4.6 Influence of Europium(II) tellurium oxide particle size

Europium(II) tellurium oxide 5 minute alternating illumination – 9.06 μ m

The following experiments done are identical to the tests done in the previous results chapter however, the light intensity has been lowered to 100 mW/cm² to indicate if a change in light intensity has any effect on the performance of the DSSC. Figure 75 and Table 49 illustrates the effects of alternating illumination for 5 minutes with a light intensity of 100 mW/cm² on the performance of the finer Eu(II) DSSC. As the light intensity lowered from 140 mW/cm² to 100 mW/cm², the J_{sc} of the DSSC has lowered as well from an average J_{sc} of 0.04 mA/cm² as seen in Figure 42 to an average J_{sc} of 0.036 mA/cm². The reoccurring trend still occurs as the voltage is increased, the current density drastically decreases as well.

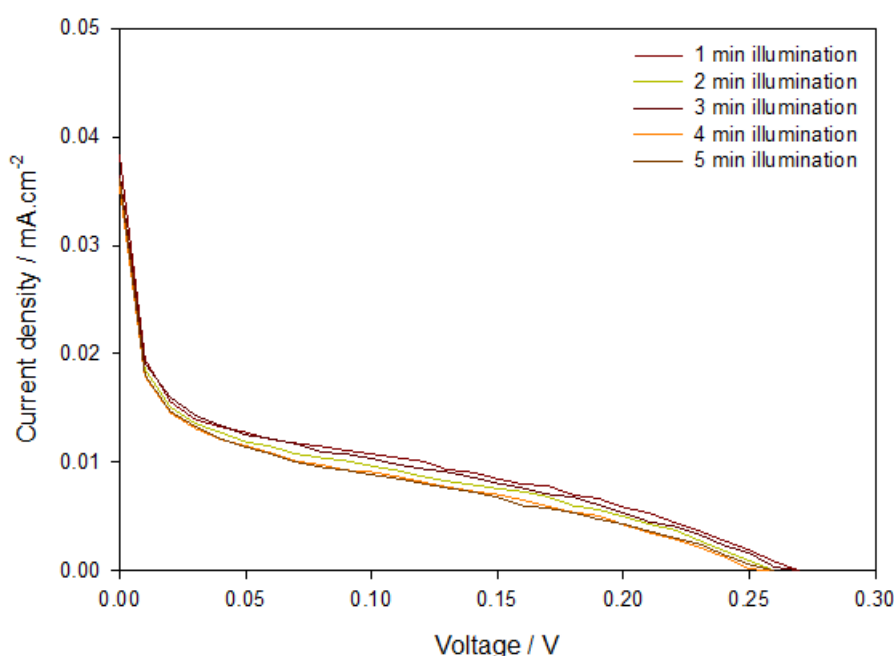


Figure 75 - J/V curve of finer Eu(II) during alternating illumination (100 mW/cm²) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 49 - J/V characteristics of finer Eu(II) during alternating illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
1	0.038	0.27	0.008	0.17	0.0013	0.13	0.0013
2	0.036	0.26	0.007	0.16	0.0012	0.12	0.0012
3	0.036	0.26	0.007	0.18	0.0012	0.13	0.0012
4	0.035	0.25	0.007	0.15	0.0011	0.12	0.0011
5	0.036	0.26	0.007	0.15	0.0010	0.11	0.0010

Figure 76 and Table 50 illustrates the dark current density produced after every additional minute of illumination. The baseline only consists over a J_{sc} of 0.003 mA/cm^2 which is four times smaller than the average dark current density J_{sc} produced, which is 0.013 mA/cm^2 . This shows potential that excited electrons are still moving through the entire DSSC without the cell being illuminated, indicating that the semiconductor is transporting electrons into the system without the assistance of the sensitizer however, due to the drastic decrease in current density as voltage is increased, the fill factor obtained without illumination is extremely low ranging between $0.16 - 0.19$.

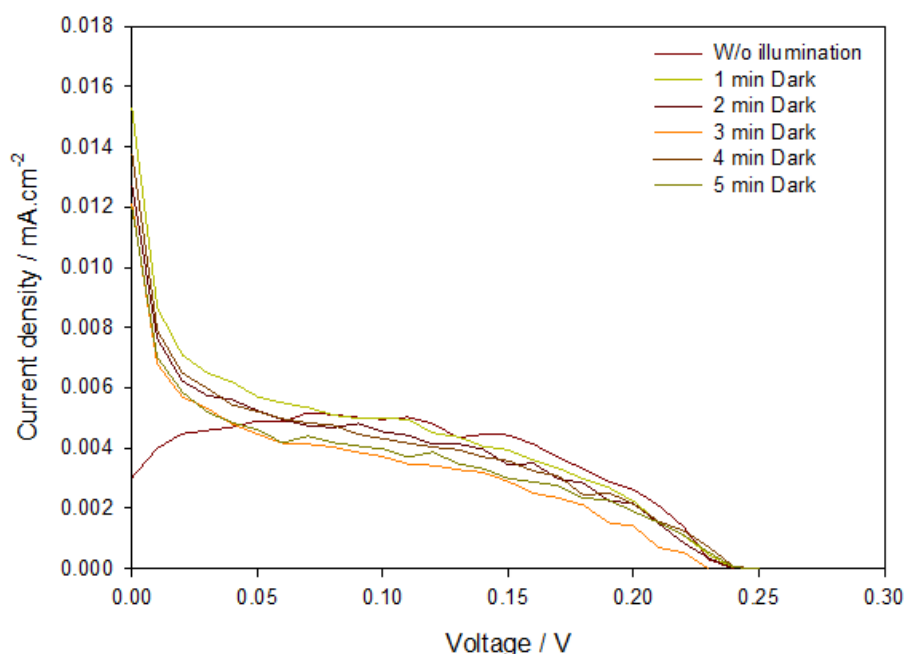


Figure 76 - J/V curve of finer Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 50 - J/V characteristics of finer Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.003	0.24	0.004	0.15	0.0007	0.94	0.0007
1	0.015	0.24	0.004	0.15	0.0006	0.16	0.0006
2	0.013	0.24	0.004	0.16	0.0006	0.19	0.0006
3	0.012	0.23	0.003	0.14	0.0004	0.16	0.0004
4	0.014	0.24	0.004	0.15	0.0005	0.16	0.0005
5	0.012	0.24	0.003	0.17	0.0005	0.16	0.0005

Titanium dioxide 5 minute prolonged illumination

Figure 77 and Table 51 illustrates the J/V curve of the TiO₂ DSSC after being continuously illuminated for 5 minutes with a light intensity of 100 mW/cm². When comparing the η produced by using a light intensity of 140 mW/cm² in Figure 44 with the η produced while using a light intensity of 100 mW/cm², it can be seen that the efficiency decreased from 1.27 % to 0.84 %. As light intensity is decreased so does the quantity of excited dye molecules decrease as well, resulting in less electrons being transported into the semiconductor layer. The J_{sc} has also decreased from 5.37 mA/cm² to 3.14 mA/cm² when comparing Figure 44 and Figure 77.

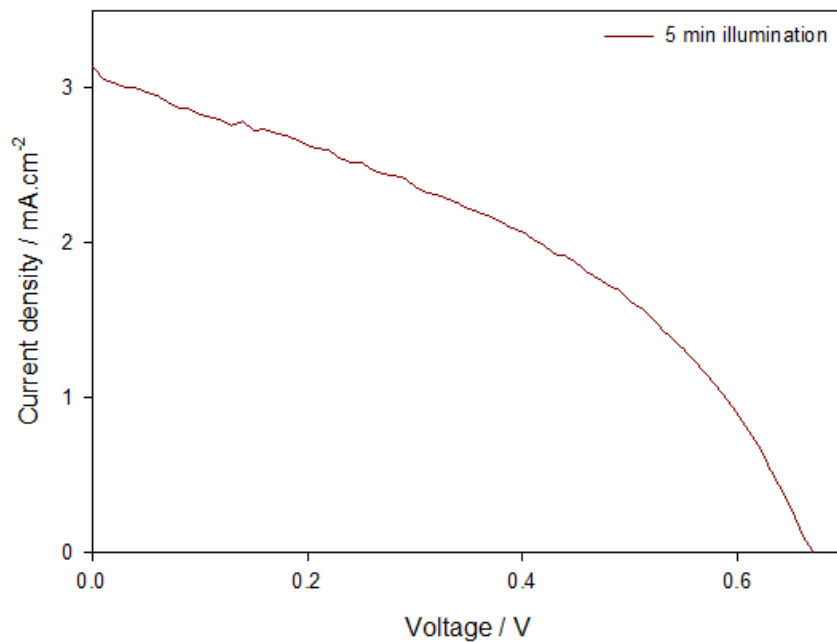


Figure 77 - J/V curve of TiO_2 after 5 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 51 - J/V characteristics of TiO_2 after 5 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
5	3.144	0.67	1.916	0.44	0.8430	0.40	0.8430

Figure 78 and Table 52 illustrates the dark current density produced as time increases without illumination after the DSSC has been illuminated for 5 minutes. Just as seen in the 140 mW/cm^2 light intensity tests, no P_m could be calculated because the moment the voltage got added, the current density instantly decreased to zero. This indicates that there are little to no excited electrons left within the DSSC.

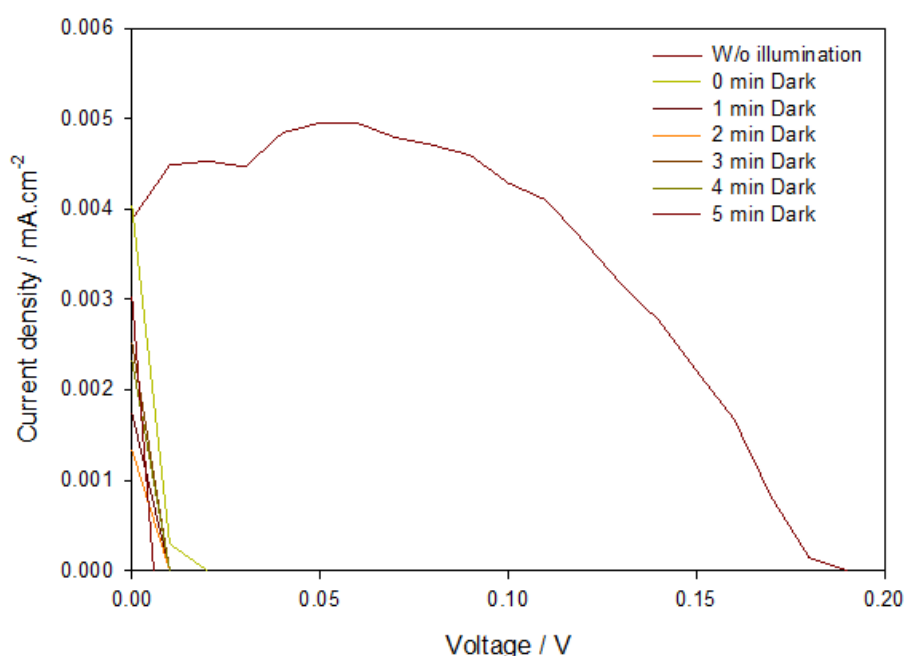


Figure 78 - J/V curve of TiO_2 dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 52 - J/V characteristics of TiO₂ without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J _{sc} (mA/cm ²)	V _{oc} (V)	J _M (mA/cm ²)	V _M (V)	P _M (mW/cm ²)	FF	η (%)
W/o illumination	0.004	0.18	0.004	0.11	0.0005	0.64	0.0005
0	0.004	0.01	0.000	0.01	0.0000	0.06	0.0000
1	0.002	0.01	0.002	0.00	0.0000	0.00	0.0000
2	0.001	0.00	0.001	0.00	0.0000	0.00	0.0000
3	0.003	0.01	0.003	0.00	0.0000	0.00	0.0000
4	0.002	0.01	0.002	0.00	0.0000	0.00	0.0000
5	0.003	0.01	0.003	0.00	0.0000	0.00	0.0000

Titanium dioxide 3 minute prolonged illumination

Figure 79 and Table 53 illustrates the J/V curve of the TiO₂ DSSC after being continuously illuminated for 5 minutes with a light intensity of 100 mW/cm². It can be seen that the J_{sc} produced by only illuminating the cell for 3 minutes is 2.77 mA/cm² which is 88.17 % of the J_{sc} obtained when illuminating the TiO₂ DSSC for 5 minutes. When comparing the η of the two illumination times, it can be seen that there is only a 0.0114 % difference, with the illumination time of 5 minutes obtaining a higher efficiency. This indicates that the DSSC's performance increased as illumination time increased, indicating the the electron flow within the DSSC was still in the progress of reaching its peak performance.

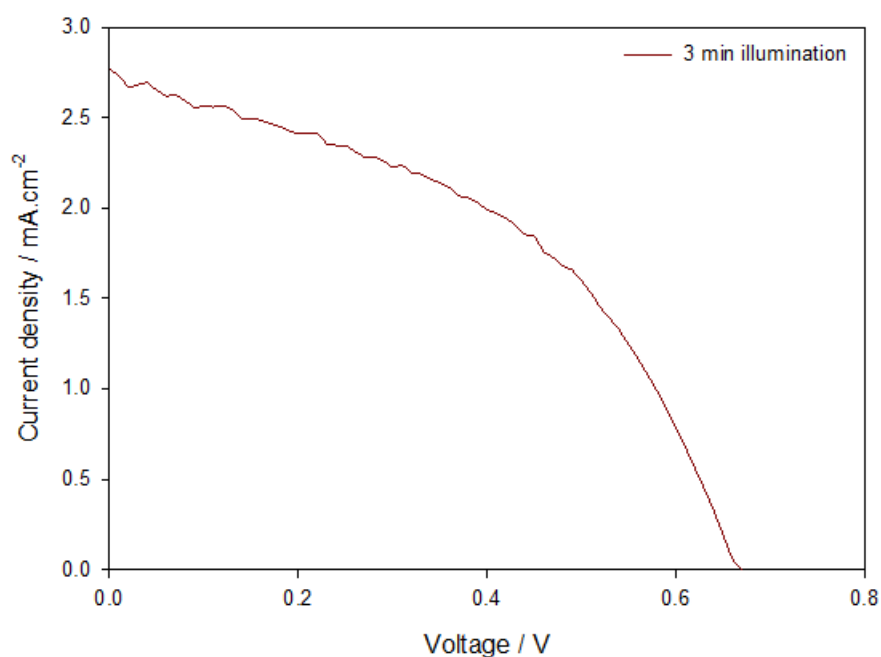


Figure 79 - J/V curve of TiO_2 after 3 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 53 - J/V characteristics of TiO_2 after 3 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
3	2.772	0.66	1.848	0.45	0.8316	0.45	0.8316

Figure 80 and Table 54 illustrates the dark current density produced as time increases without illumination after the DSSC has been illuminated for 3 minutes. Just as seen by the 140 mW/cm^2 tests, the TiO_2 DSSC couldn't produce any current as the voltage was added, resulting in a P_m and η of zero.

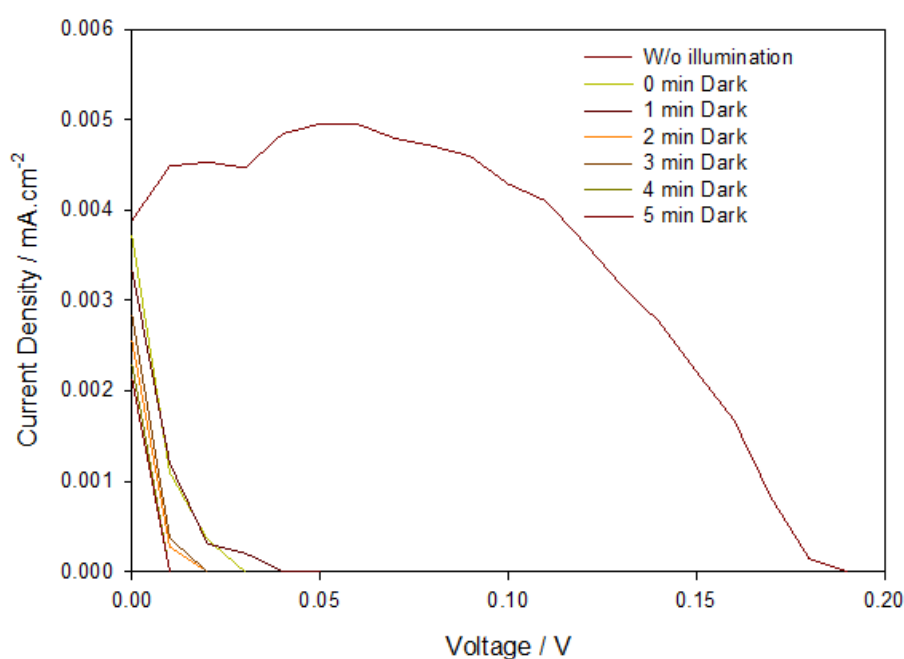


Figure 80 - J/V curve of TiO_2 dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 54 - J/V characteristics of TiO_2 without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.008	0.23	0.007	0.16	0.0011	0.61	0.0011
0	0.004	0.03	0.001	0.01	0.0000	0.11	0.0000
1	0.003	0.04	0.001	0.01	0.0000	0.09	0.0000
2	0.003	0.01	0.000	0.01	0.0000	0.08	0.0000
3	0.003	0.01	0.000	0.01	0.0000	0.09	0.0000
4	0.002	0.01	0.002	0.00	0.0000	0.00	0.0000
5	0.002	0.01	0.002	0.00	0.0000	0.00	0.0000

Europium(II) tellurium oxide 5 minute prolonged illumination – 9.06 μm

Figure 81 and Table 55 illustrates the effect of illumination with a light intensity of 100 mW/cm² for a continuous 5 minutes on the overall performance of the finer Eu(II) DSSC. When comparing the overall performance of the finer Eu(II) under a light intensity of 140 mW/cm² with the finer Eu(II) DSSC that was illuminated with a light intensity of 100 mW/cm² it can be seen that there was a decrease in J_{sc} from 0.056 mA/cm² to 0.048 mA/cm² and a decrease in

η from 0.0013 % to 0.0008 %. This indicates that as the light intensity is decreased, so does the current density as well as η decrease.

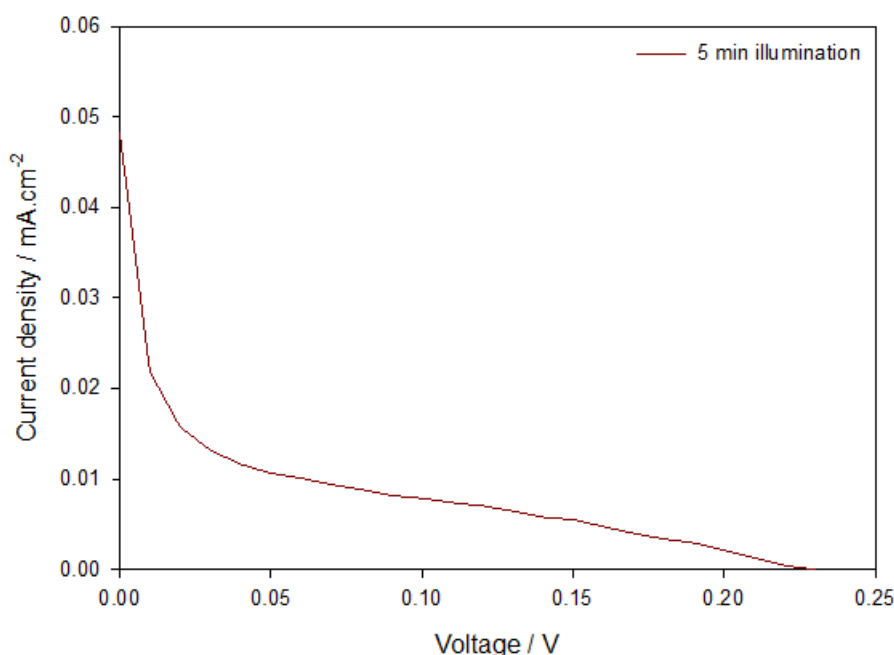


Figure 81 - J/V curve of finer Eu(II) after 5 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 55 - J/V characteristics of finer Eu(II) after 5 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
5	0.048	0.23	0.007	0.12	0.0008	0.08	0.0008

Figure 82 and Table 56 illustrates the dark current density produced after the finer Eu(II) DSSC has been illuminated for 5 minutes. When comparing the J_{sc} 's produced without illumination to the baseline of the DSSC prior to any illumination contact it can be seen that there was an increase from 0.006 mA/cm^2 to 0.016 mA/cm^2 directly after illumination. It can also be seen in Table 56 that after being left for 4 minutes in complete darkness, the J_{sc} reached a maximum of 0.046 mA/cm^2 which is roughly eight times larger than the J_{sc} obtained prior to illumination. This indicates that even after being without illumination for 4 minutes there is still a large amount of electrons moving through the DSSC. This can be an indication of entrapped electrons only being released into the DSSC after 4 minutes without illumination however, the finer Eu(II) does still suffer from an increase in voltage, resulting in a low η of 0.0001 %.

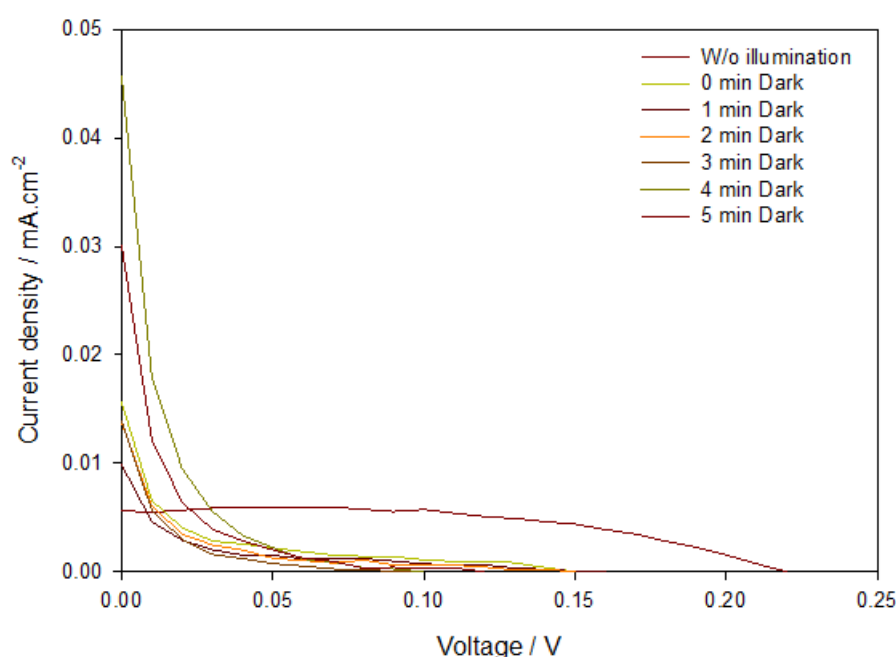


Figure 82 - J/V curve of finer Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 56 - J/V characteristics of finer Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.006	0.22	0.004	0.15	0.0007	0.53	0.0007
0	0.016	0.15	0.001	0.09	0.0001	0.05	0.0001
1	0.010	0.16	0.001	0.08	0.0001	0.06	0.0001
2	0.014	0.15	0.001	0.08	0.0001	0.04	0.0001
3	0.014	0.10	0.003	0.02	0.0001	0.04	0.0001
4	0.046	0.10	0.009	0.02	0.0002	0.04	0.0002
5	0.030	0.12	0.006	0.02	0.0001	0.04	0.0001

Europium(II) tellurium oxide 3 minute prolonged illumination – 9.06 μm

Figure 83 and Table 57 illustrates the effect of illumination with a light intensity of 100 mW/cm² for a continuous 3 minutes on the overall performance of the finer Eu(II) DSSC. When comparing Figure 81 with Figure 83 it can be seen that the J_{sc} is lower when the DSSC was only illuminated for 3 minutes however, the V_{oc} of the DSSC that was only illuminated for 3 minutes was higher than the V_{oc} obtained by the finer Eu(II) that was illuminated for 5 minutes. When comparing the trend that the J/V curve shows of the two Eu(II) DSSC's, it can be seen

that the current density of the Eu(II) DSSC that was only illuminated for 3 minutes, did not decrease as drastically when to voltage was added in comparison to the Eu(II) DSSC that was illuminated for 5 minutes.

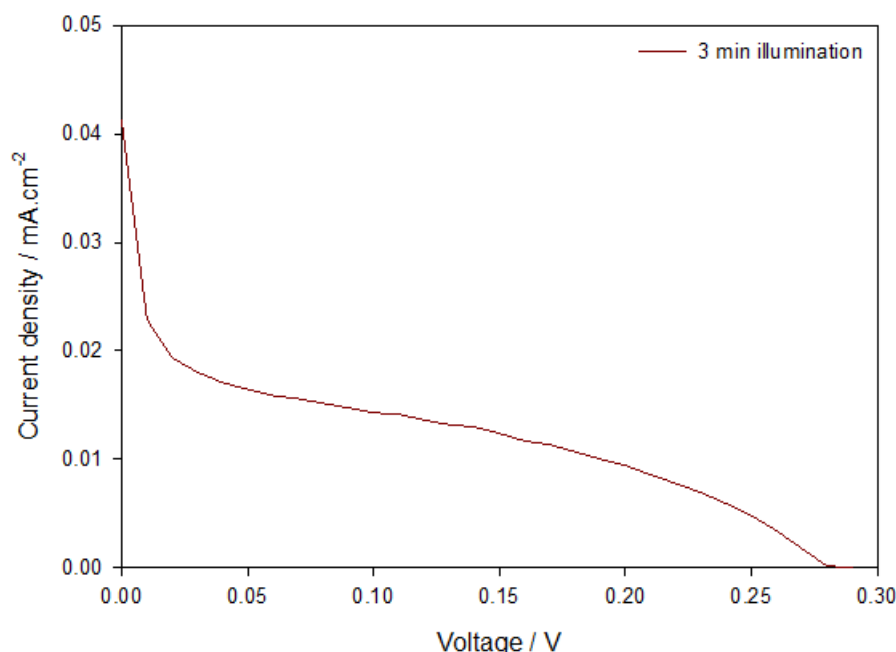


Figure 83 - J/V curve of finer Eu(II) after 3 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 57 - J/V characteristics of finer Eu(II) after 3 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
3	0.041	0.29	0.011	0.17	0.0019	0.16	0.0019

Figure 84 and Table 58 illustrates the dark current density produced after the finer Eu(II) DSSC has been illuminated for 3 minutes. Again it can be seen that the J_{sc} after illumination consists over an average value of 0.016 mA/cm^2 whereas the base J_{sc} prior to illumination was only 0.012 mA/cm^2 however, due to the ongoing drastic decrease of current density seen with the Eu(II) DSSCs with a particle size of $9.06 \mu\text{m}$, the efficiency of the DSSC is still lower than the efficiency calculated prior to illumination.

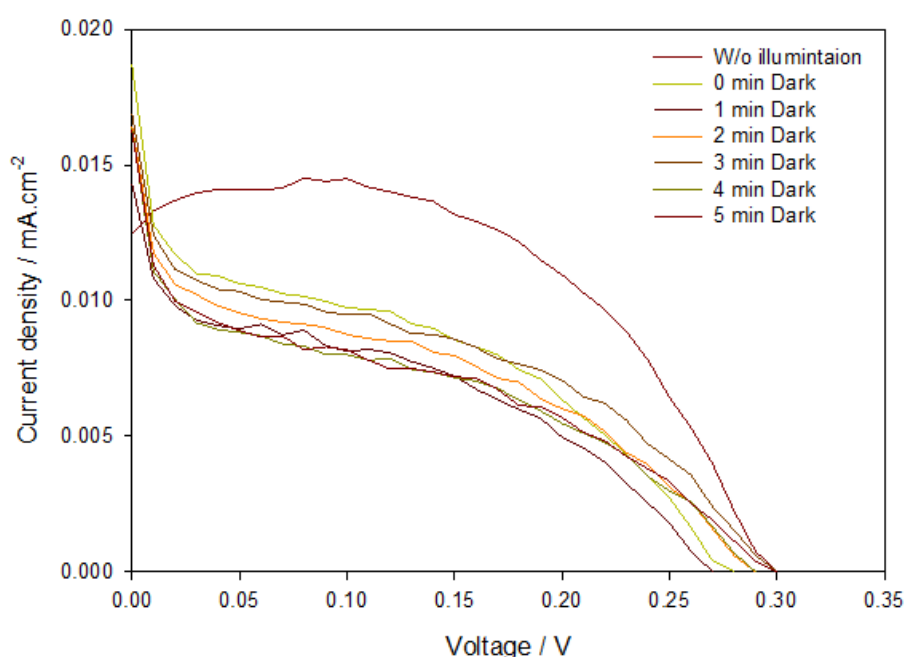


Figure 84 - J/V curve of finer Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 58 - J/V characteristics of finer Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.012	0.29	0.011	0.2	0.0022	0.60	0.0022
0	0.019	0.27	0.008	0.17	0.0014	0.27	0.0014
1	0.014	0.27	0.007	0.15	0.0011	0.28	0.0011
2	0.016	0.29	0.007	0.18	0.0013	0.27	0.0013
3	0.017	0.30	0.007	0.19	0.0014	0.28	0.0014
4	0.016	0.29	0.007	0.17	0.0011	0.24	0.0011
5	0.016	0.29	0.006	0.19	0.0012	0.24	0.0012

Europium(II) tellurium oxide 5 minute prolonged illumination – 30.70 μ m

Figure 85 and Table 59 illustrates the effect of illumination with a light intensity of 100 mW/cm² for a continuous 5 minutes on the overall performance of the 30.70 μ m Eu(II) DSSC. Again as seen in the previous tests of the 30.70 μ m Eu(II) DSSC, the J_{sc} significantly decreased as particle size is increased. The J_{sc} obtained by the 30.70 μ m Eu(II) DSSC is 0.01 mA/cm² which is only 20 % of the J_{sc} obtained by the finer Eu(II) DSSC however, the bigger particle Eu(II) exhibits much more resistance to an increase of voltage than the 9.06 μ m Eu(II).

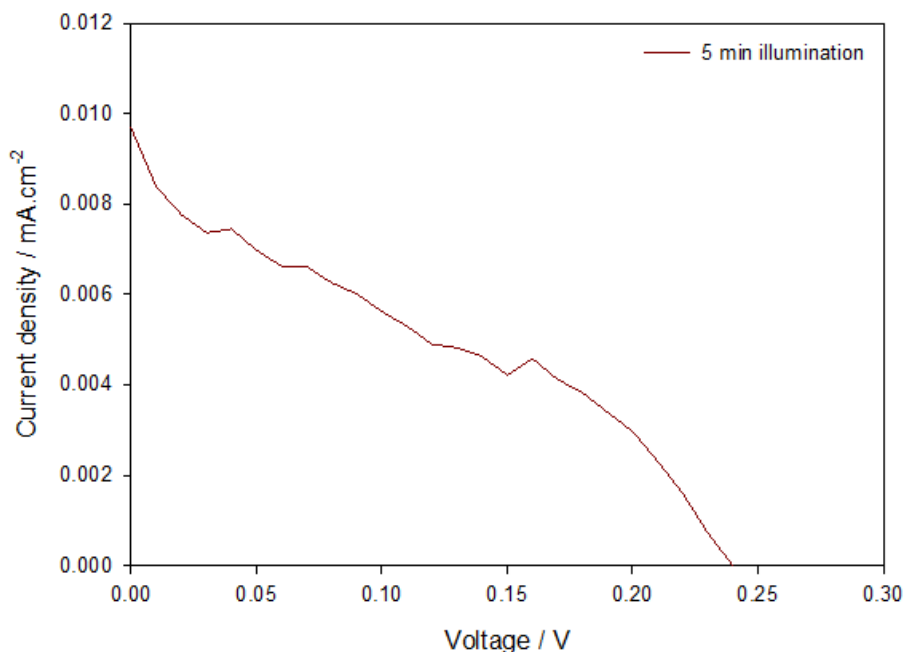


Figure 85 - J/V curve of Eu(II) after 5 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 59 - J/V characteristics of Eu(II) after 5 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
5	0.010	0.24	0.005	0.16	0.0007	0.32	0.0007

Figure 86 and Table 60 illustrates the dark current density produced after the $30.70 \mu\text{m}$ Eu(II) DSSC has been illuminated for 5 minutes. When compared to the baseline of the DSSC, it can be seen that the J_{sc} has decreased from 0.006 mA/cm^2 to an average of 0.004 mA/cm^2 , which shows that there wasn't an increase of excited electrons within the DSSC after illumination. When comparing the two versions of Eu(II) with the TiO_2 semiconductor, it can still be noted that only the Eu(II) DSSCs have obtained a relative noteworthy dark current density in comparison to its baseline.

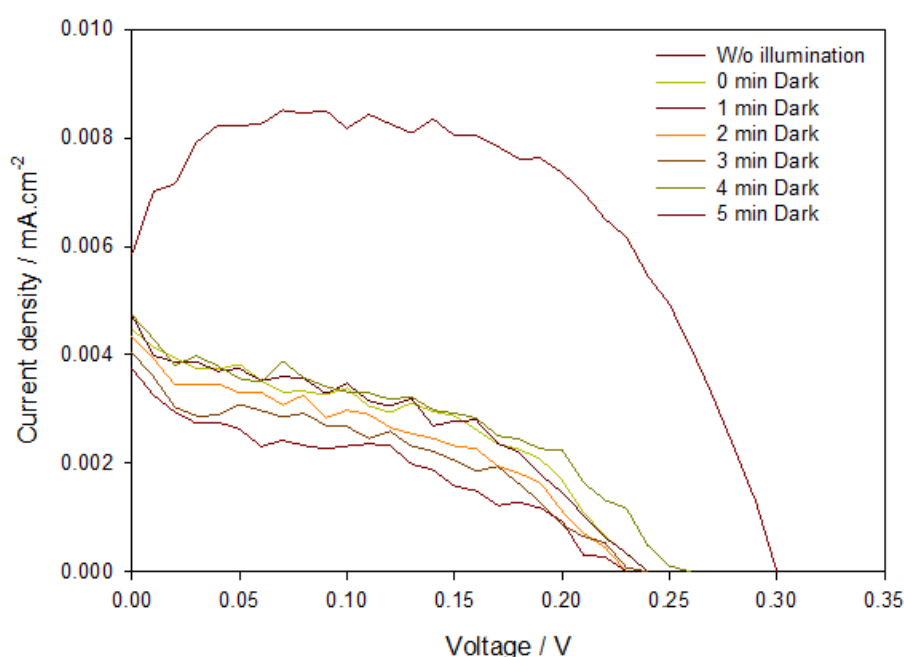


Figure 86 - J/V curve of Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 60 - J/V characteristics of Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.006	0.29	0.007	0.2	0.0015	0.86	0.0015
0	0.004	0.24	0.003	0.15	0.0004	0.41	0.0004
1	0.005	0.24	0.003	0.16	0.0004	0.40	0.0004
2	0.004	0.23	0.002	0.16	0.0004	0.37	0.0004
3	0.004	0.23	0.002	0.17	0.0003	0.35	0.0003
4	0.005	0.25	0.003	0.16	0.0005	0.38	0.0005
5	0.004	0.23	0.002	0.12	0.0003	0.33	0.0003

Europium(II) tellurium oxide 3 minute prolonged illumination – 30.70 μ m

Figure 87 and Table 61 illustrates the effect of illumination with a light intensity of 100 mW/cm² for a continuous 3 minutes on the overall performance of the 30.70 μ m Eu(II) DSSC. When compared to the Eu(II) DSSC that was illuminated for 5 minutes in Figure 85 it can be seen that the J_{sc} of the 3 minute illuminated Eu(II) DSSC was larger with a value of 0.014 mA/cm² in comparison to the J_{sc} value of 0.01 mA/cm². This indicates that photodegradation occurred as illumination time was increased. This result occurred with the 30.70 μ m Eu(II) DSSC,

whereas the J_{sc} increased for the 9.06 μm Eu(II) DSSC indicating that a smaller particle size promotes better electron transport and conservation of current.

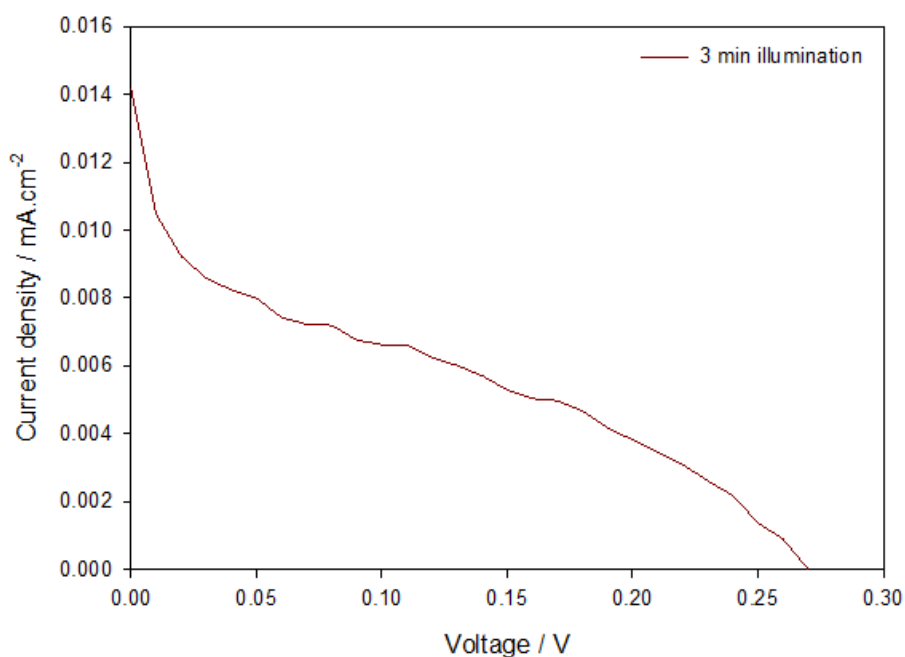


Figure 87 - J/V curve of Eu(II) after 3 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 61 - J/V characteristics of Eu(II) after 3 minutes of illumination (100 mW/cm^2) while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Illumination time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_M (mA/cm^2)	V_M (V)	P_M (mW/cm^2)	FF	η (%)
3	0.014	0.27	0.005	0.17	0.0008	0.22	0.0008

Figure 88 and Table 62 illustrates the dark current density produced after the 30.70 μm Eu(II) DSSC has been illuminated for 3 minutes. Again it can be seen that there was no increase in J_{sc} after being illuminated when compared to the baseline prior to illumination.

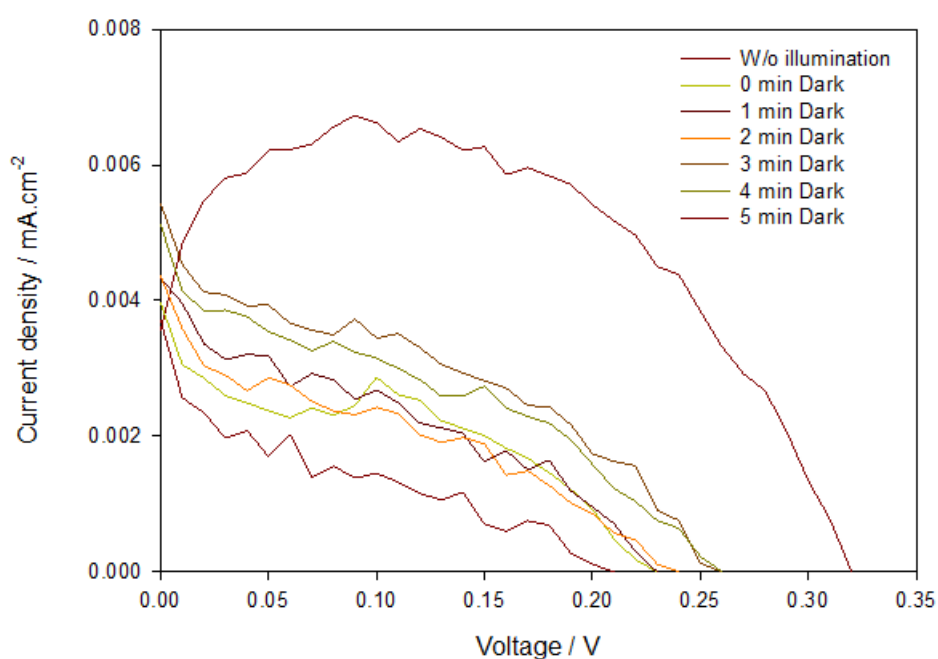


Figure 88 - J/V curve of Eu(II) dark current while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Table 62 – J/V characteristics of Eu(II) without illumination while using N719 as the dye, scotch tape as the spacer and a 0.5 M Li iodide and 0.05 M iodine electrolyte solution.

Time without illumination (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	J_M (mA/cm ²)	V_M (V)	P_M (mW/cm ²)	FF	η (%)
W/o illumination	0.004	0.32	0.005	0.22	0.0011	0.97	0.0011
0	0.004	0.22	0.003	0.12	0.0003	0.34	0.0003
1	0.004	0.23	0.002	0.18	0.0003	0.30	0.0003
2	0.004	0.23	0.002	0.15	0.0003	0.28	0.0003
3	0.005	0.25	0.002	0.18	0.0004	0.32	0.0004
4	0.005	0.25	0.003	0.15	0.0004	0.32	0.0004
5	0.004	0.21	0.001	0.14	0.0002	0.22	0.0002