I-V performance analysis of flexible back Illuminated Dye Sensitized Solar Cells (DSSCs) with various platinum catalyst contents

Shamsudin N H1,2, Shafie S1,3, Ab. Kadir M Z A1,4,5, Ahmad I6, Chachuli S A M3,7 and Sulaiman Y3

1Department of Electrical and Electronic Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.
2Faculty of Electrical Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, Durian Tunggal 76100, Melaka, Malaysia.
3Institute of Advanced Technology, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.
4Institute of Power Engineering, Universiti Tenaga Nasional, Putrajaya Campus, Kajang 43000, Selangor.
5Centre for Electromagnetic and Lightning Protection (CELP) Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.
6Department of Electronic System Engineering, Malaysia-Japan International Institute of Technology(MJIT),Universiti Teknologi Malaysia, Kuala Lumpur 53400, Malaysia.
7Faculty of Electronic Engineering and Computer Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, Durian Tunggal 76100, Melaka, Malaysia.

E-mail: nurhazahsha@gmail.com

Abstract: Flexible based Dye Sensitized Solar Cells (DSSCs) in nanotechnology revolution have always been in the thick of things where fabrication method and achieving good performances are concerned. Such concerns were adjudicated by improvising four(4) innate DSSCs structures composed of photoanode, semiconductor, electrolyte and counter electrode. This paper aims to observe the impact of changing Platinum(Pt) volumes on the counter electrodes of DSSCs by conducting tests on 0.2mm Titanium (Ti) foil based photoanode DSSCs. The deposition of Pt was varied into 70µl, 50µl and 30µl accordingly by spin coating technique at 1500 rpm. All samples were synthesized, deposited with Pt and assembled before being tested under solar light simulator of 1000W/cm². Samples with 70µl Pt deposition indicated a higher efficiency (Ƞ) of 2.83%, even though it allowed less light penetration, while the 30µl Pt deposition sample provided efficiency (Ƞ) of 0.88% with more light penetration.

Keywords: Dye Sensitized Solar Cells; flexible; Platinum; Titanium; spin coating.

1. Introduction

Amidst a rapidly growing solar photovoltaic industry, the high costs incurred by solar PV including manufacturing, transportation, assembling, installation and maintenance are increasing yearly. In addition to that, the engagement of PV particularly on Silicon is getting tedious. A few obstacles must be faced by Silicon based PV such as the complicated synthesis with high amounts of energy required to manufacture the final product of cells, higher recombination losses due to the morphological structures of the grain boundaries which hinder the continuous flow of electrons in the cells and the large losses of material [1]. These worrying circumstances are decreasing because of the high efficiency of Silicon film performances and their well-known non-toxicity to the environment.
Many studies initiated on organic photovoltaic (OPV) cells, which is an alternative photovoltaic system for utilities [2-4]. Among the OPV and hybrid cells is the notable nanotechnology empowerment called dye sensitized solar cells (DSSCs) discovered by [5] which is led to the ‘photosynthesis’ concept. The components of DSSCs differed according to materials composition with cells performance being determined by harvesting and consuming light energy in the solar region spectrum before converting into current. While Silicon pure cells and amorphous thin film cells struggled with a scarcity of accommodating huge expenditure on production both on a large scale as well as limited easy options processing methods and tools, DSSCs offer low cost diversification and modification ranging from materials usage, preparation methods, fabrication, synthesis and assembling [6-8]. They also emphasize roll to roll manufacturing scale capability via its flexible substrate preparation.

The exploration of conventional DSSCs was done by researchers, mostly on glass sheets coated with material elements either Indium Tin Oxide (ITO) or Fluorine Tin Oxide (FTO) due to their high efficiency [9, 10] before shifting to critical issues such as higher costs, heavy weight, robustness, shape deformability and brittleness. It is obvious that the bottlenecks from the prolonged utilization of glass substrate are for the full implementation and application of the DSSCs to provide compatible resources for the roll-roll scale production. Therefore, the most frequently used polymer substrates which are Indium Tin Oxide (ITO) Polyethylene naphthalate (PEN) and Polyethylene terephthalate (PET) [11] are tailored as an approach to tackle the problem head on. It is highlighted that polymer formation is however linked to unfavourable changes in temperature that is <150°C [12, 13].

The resurgence of polymer substrates in flexible DSSCs applied numerous TiO$_2$ nanoparticles preparation and deposition methods, for example binder free pastes [13-15], EPD [16, 17], UV technique [18] and mechanical compression [19, 20]. [21, 22] modified TiO$_2$ nanoparticles film preparation by applying ball milling with 3% and 4.2% efficiency respectively to improve cell adhesion for better dye adsorption. The technique was improved by adding with HCL solution [23] that gave 5% efficiency. PV fabrication on ITO-PEN by [24] achieved the highest efficiency of 8.1% by combining TiO$_2$ nanoparticles pastes modification and press method without any high temperature process and vacuum equipment imposed on this 0.25cm$^2$ cell area. However, the low temperature in polymer substrates was associated with substantial and hypothetically detrimental changes in TiO$_2$ colloidal chain upon partial organic binder dissipation, arising in inferior levels of chemical bonding that are thought to trigger inflammatory conditions for instance, the fracture formation in the film throughout the drying process, short circuit due to electrolyte drainage and the easy absorption of impurities into the substrates.

Affected by these undesirable concerns, metal-based substrates, mostly are StSt and Ti are becoming attractive referral options for further expansion in flexible area. Researches exhibited that metal manage to sustain heat up to 500°C and are highly stable with low sheet resistance and low cost. [25] found that StSt and Carbon steel indicated better stability compared to others (Zn, Cu) after observing the corrosion rates for 11 weeks consecutively, as well as soaking and encapsulation tests. But, the findings in [26] discovered that StSt fabricated with complete cell encountered major instability performance whereby about 80% to 90% degradation were detected in only a few hours under 1000mW/cm$^2$ illumination. Similar findings also proved that Ti and Inconel were significantly likely to sustain its stability features, even after being soaked for 1000 hours. [27, 28] investigated on the electrochemical properties of Ti in comparison to FTO and StSt, whereby Ti displayed outburst traits in ability to deter electrolyte erosion, to endure thermal heating while maintaining low sheet resistance, laboriously oxidized in aerophilic surroundings and to possess good light reflectance. The efficiency recorded for both studies were 5.45% and 3.2% respectively. In fact, [29] did surface modification on StSt substrates by sputtering different layers of Ti foil to produce 6.9% efficiency that are able to drastically reduced high electrons transfer resistance and hinder chemical interaction between electrolyte and anode substrate.
Despite all the excellent elements of Titanium, there is a major aspect of concern that is the inhibition of light to be absorbed from the front-side of the developed cell. Therefore, channelling the absorption to the counter electrode side would be the most practical approach so far. Studies have emphasized that the counter electrode must constitute a fast, high optical transparency, an effective charge transfer ability and conductive properties of catalytic materials that manage to properly regulate the redox reaction of electrolyte while permitting high absorption rates of visible light spectrum, particularly during back illumination as well [30, 31]. For that reason, Platinum (Pt) is selected amongst other catalytic materials such as Carbon (C), polymer and Alloy, as it complies with the aforesaid criteria [32].

Therefore, this paper is intended to analyse the experimental studies on Titanium (Ti) foil as anode conductive material of dye sensitized solar cells (DSSCs) that is carried out within the parameter constraints. The parameter constraints are in accordance with variable Pt volumes ranging from a minimum of 30µl, a standard of 50µl and a maximum of 70µl specifically to effectuate the anticipated optimal power conversion efficiency performances. The counter electrode is deposited with Pt using the spin coating method, whereas the photoanode is deposited with TiO\textsubscript{2} using the Doctor Blade method.

2. DSSCs Working Process Flow

Figure 1 shows the DSSCs operational system. Intrinsically, the process is initiated as soon as the sunlight rays hit the dye molecules. The photon particles in the rays thus invigorate the dye molecules (D) to produce excited dye (D*). In this stage, the dyes are activated from their non-conductive state (ground state) to excited state in overcoming the energy bandgap of semiconductor. In a substantial way, this process is followed by the oxidation of the excited dye (D+). The electrons generated are then injected into TiO\textsubscript{2} semiconductor’s conduction band. After the process, the electrons travel to the transparent conducting oxide (TCO) and anode to complete the external circuit. In the electrolyte, the iodide ions undergo oxidation to form triiodide ions and donate electrons to the dye to reinstate it to its initial state. This forward charge transfer ended when the triiodide ions migrate to the cathode to form iodide ions again through the reduction process. Meanwhile, the TiO\textsubscript{2} nanoparticles film, as the forward reaction occurs, the residual electrons would cause the annihilation of the oxidized dye and triiodide ions. This in turn will regenerate the neutral dye molecules and iodide ions respectively. DSSCs efficiency would be lowered as a result of these dark reactions.

![Figure 1](image-url)
3. Experimental Setup

Materials
Materials purchased were as follows: Titanium sheet (ASTM B265, Combat), Flourine Tin Oxide (FTO) coated glass (< 15ohm/sq.; > 83 %; Zhuhai Kaivo Optoelectronic Technology Co., Ltd.), Titanium (IV) Oxide anatase, Ethyl Cellulose, Alpha terpineol Hexachloroplatinic Acid Hexahydrate (H2PtCl6•6H2O), Ruthenizerhipsillic N719 dye (Sigma Aldrich Co USA), Iodolyte AZN 150 (Solaronix, Switzerland), Isoprophyl Alcohol, Ethanol, Hydrogen Peroxide 30% (R&M Chemicals).

Materials and Sample Preparation

![Flowchart of Materials and Samples Preparation](image)

Figure 2. Flowchart of Materials and Samples Preparation

Figure 2 illustrates the stages of experimental work from the materials and samples preparation until the final stage of samples testing. The TiO2 nanoparticles paste was prepared by synthesizing all materials as stated in the previous section. Starting with the mixing of 0.17ml of acetic acid, 0.84ml of DI water and 2.5ml of ethanol into TiO2 powder, the ethyl cellulose was also stirred with ethanol to be mixed with the TiO2 nanoparticles solution later. The DI water and ethanol were added sequentially for 60 seconds while grinding with a pestle and mortar several times until homogeneity was achieved. The 17 ml ethanol was then added to the solution together with the previously stirred ethyl cellulose and alpha terpineol as well. The blended materials were stirred recurrently and sonicated at room temperature for hours, followed by evaporation to acquire the slurry white paste of TiO2 nanoparticles. In the meantime, both FTO Glass substrates and the Titanium sheet were washed thoroughly for 10 minute using detergent, DI water, ethanol and IPA.

For anode construction, the (2x2.5)cm2 of Titanium sheet was initially treated with H2O2 solution to prevent Titanium surface corrosion. It was done by sintering the treated Titanium at 450°C after permeating the Titanium into H2O2 solution at 70°C for 30 minutes on the hotplate. When the treatment process was over, the treated Titanium was layered with the white slurries of TiO2 nanoparticles using the Doctor Blade method. The TiO2 layered anodes were then heated at 80°C to eliminate any humidity that could affect the cell outcome during current-voltage measurement. The anodes were prepared for heating at 450°C for 30 minutes. When the TiO2 layered anodes were cooled to 80°C, they were instantly soaked with a solution of hydropillic N719 dye in 50ml of ethanol and acetonitrile in a ratio of 1:1. After being soaked overnight with the dye solution, they were taken out to be cleaned with ethanol.

The cathode part of the cells was set up by depositing Pt on the FTO glass. The platinized cathode was constructed onto the FTO glass substrates using spin coating technique. A 60µm of a transparent polymer film (Surlyn Dupont 1472) was affixed between the cell’s anode and cathode. Once the cells were assembled, the commercial Iodolyte AZN-150 electrolyte was injected into the 0.05cm vacant space between the anode and the cathode.

The UV light solar simulator 1000mW/cm2 with AM 1.5 light intensity was illuminated at the (1x1)cm2 TiO2 cell area in order to measure the efficiency performance from the current versus the
voltage curve. Meanwhile the image and thickness of TiO$_2$ nanoparticles were characterized by field emission scanning electron microscopy (FESEM). The absorption spectra of TiO$_2$ nanoparticles was conducted by UV-Vis-NIR (Perkin Elmer, Lambda 35).

4. Results and Discussions

Figure 3 shows the condition of samples after being treated with H$_2$O$_2$. After H$_2$O$_2$ treatment, the Titanium foil turned yellow due to surface oxidation removal from the substrate. The treated samples are deposited with TiO$_2$ nanoparticles paste using Doctor Blade method. The deposition is applied around the active area which is white in color as shown in Figure 3 b).

![Figure 3. Samples condition; a) After H$_2$O$_2$ treatment b) TiO$_2$ nanoparticles paste deposition](image)

After sintering at 450°C in a furnace, the foils were immersed in N719 dye solution as displayed in Figure 4. It is also observed that the colour of the active area changed from white to purple when the samples were taken out after immersing with N719 Dye solution for 24hours.

![Figure 4. After 24 hour Dye Adsorption](image)

![Figure 5. The FESEM image showing a) a cross section of the deposited TiO$_2$ layer onto Ti foil b) TiO$_2$ nanoparticles](image)
The significance of TiO\textsubscript{2} nanoparticles film in determining the I-V performance on the samples was also investigated using the FESEM and UV-Vis analysis as presented in Figure 5 and Figure 6. The cross section of TiO\textsubscript{2} nanoparticles film measured by FESEM was in a range of 13.26 µm to 13.56 µm as shown in Figure 5 a). The observed thickness is sufficient in giving more electron collection by providing higher surface area for dye adsorption. When the dye amount is increased, more electrons are collected which would rise the current density (Jsc), thus allowing good efficiency performance for the tested samples. Meanwhile, the image from FESEM analysis views the porosity of TiO\textsubscript{2} nanoparticles as shown in Figure 6. This is to confirm the porous nature of TiO\textsubscript{2} nanoparticles in the fabricated samples which was advantageous for higher dye adsorption in supplying electrons, thereby increasing Jsc.

Figure 6. The Optical Absorption Spectra of bare TiO\textsubscript{2} and TiO\textsubscript{2} immersed with dye

Figure 6 gives the absorbance peak at 340 nm wavelength for the bare TiO\textsubscript{2} sample as observed by UV-Vis spectroscopy. However, the absorption give rise to 380 nm after the TiO\textsubscript{2} was immersed with dye N719. The dye immersion is able to intensify the light absorption which provides more photoelectrons to the sample.

Figure 7. I-V curves characteristics deposited at different values

Table 1. IV parameters for 30µl, 50µl and 70µl Pt deposition

| Pt coating | Jsc(mA/cm\textsuperscript{2}) | Voc(V) | FF | \(\eta\) (%) |
|------------|-------------------------------|-------|----|-------------|
| 70µl       | 4.87                          | 0.72  | 0.82| 2.83        |
| 50µl       | 2.12                          | 0.74  | 0.68| 1.06        |
| 30µl       | 1.86                          | 0.75  | 0.63| 0.88        |

As shown in Figure 7 and Table 1, the results generated show that the sample which was deposited with a 30µl of Pt is more likely to depreciately provide Jsc of 1.86 mA/cm\textsuperscript{2} than sample which was
deposited with a 50µl layer of Pt, with Jsc of 2.12 mA/cm². The thinner Pt coating with lower Jsc suggests there could be a slower catalytic process occurrence within the redox electrolyte that rapidly generated high recombination, giving low efficiency of 0.88%.

There was also a huge disparity of Jsc between the 30µl Pt coating and the 70µl Pt coating which is the highest Jsc achieved at 4.87 mA/cm² with 2.83% efficiency. This shows that the light still experiencing major amount of light penetration even though after thicker coating of Pt. Meanwhile Voc for the different coating are almost the same, ranging from 0.72V to 0.75V. The fill factor (FF) provided enhancement from 0.63 to 0.82 with the increase of Pt layer coating. Such increments clearly reveal that the Ti substrates reduce the internal resistance.

5. Conclusion

This outcome of this research clearly indicates that the most reliable way to enhance sample performance while considering Pt deposition is to use a thicker Pt coating, instead of a thinner one. The sampling was also successfully performed, since it was carried out with a higher volume of Pt deposition instead of a lower one. The enhancement of Jsc was also contributed by the characteristic of TiO\textsubscript{2} nanoparticles layer as deposited onto Ti foil.

Acknowledgments

The authors would like to acknowledge and thank Universiti Putra Malaysia(UPM), Universiti Teknikal Malaysia Melaka(UTeM) and the Ministry of Education (MOE), Malaysia for the support and assistance rendered towards the successful completion of this research paper. This research work is funded by a University Putra Malaysia Grant (9629800).

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