IMPROVING THE EFFICIENCY AND THE LONG TERM STABILITY OF A DYE SENSITIZED SOLAR CELL

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ABSTRACT

Nanocrystalline dye sensitized solar cells are photochemical cells with a process similar to that of natural photosynthesis, where the dye acts as the chlorophyll. Dye sensitized solar cell (DSSC) is a renewable energy technology that uses solar radiation with dye as a photo sensitizer to convert light directly to electricity, but there have been a problem with the long term stability of the cell, while an efficiency of 11 % have been achieved. A research work to fabricate two solar cells; using tomato seed and zobo leaves as dye for each cell was carried out at Engineering and Material Development Institute (EMDI) Akure, Ondo State, Nigeria. The solar cell sensitized with the zobo dye produced an open voltage of 0.389 V, at a fill factor of -33.8765, which further gave a short circuit current density of -0.000236 and the efficiency calculated to be 0.0031. While the solar cell sensitized with the tomato dye produced an open voltage of 0.334 V, at a fill factor of -44.4027, which further gave a short circuit current density of -0.000236 and the efficiency calculated to be 0.0035.

INTRODUCTION

Climate change is one of the major environmental problems that affect our society. At present annually more than 40 billion Tons of greenhouses gases are exhausted to atmosphere and the tendency is to the rise; the main reason for this situation is the high and uncontrolled use of fossil resource in energy generation. Developing an environmental friendly and reliable energy technology is a necessity. Solar energy emerged as possible solution to confront this problem. This technology permits a direct conversion of sunlight into electrical power without exhaust of both greenhouse gases and another polluting agent. [1] Actually silicon technology is market leader in photovoltaic technologies; however since a pioneering dye-sensitized solar cells (DSSCs) have become one important and promising technology in photovoltaic field. DSSCs have given rise to new solar cells generation being replaced with classical solid-state homo and hetero-junction device by a

new concept with a nano-working electrode in photo-electrochemical cell. [2]

Dye sensitized solar cells are a third generation technology in the area of photovoltaics. They are classified as a type of thin-film solar cell, meaning that they require only a small amount of material per cell compared to the first solar cells, making DSSCs lighter and more physically resilient than their first generation counterparts. They use a process similar to photosynthesis to produce electrical energy, making them an example of biomimicry. [3]

Dye sensitized solar cells are a promising technology because they are inexpensive resilient, making them ideal for large scale and small scale application. However they have lower efficiencies than most other types of solar cells. This disadvantage is offset by their low cost and greater resilience and flexibility.

The basic idea of what a cell looks like at a magnified view is shown in the Figure 1.

The process by which the cell creates electrical energy can be represented by the following series of redox reactions [4]:

$$Dye + hv \rightarrow Dye^* \tag{1}$$

 $Dye + TiO_2 \rightarrow TiO_2 + Dye^*$ (2)

 $TiO_2 + CE \rightarrow TiO_2 CE^* + Energy$ (3)

 $Dye^* + I^- \rightarrow Dye + I_3^- \tag{4}$

$$I_3^- + CE \longrightarrow I^- + CE \tag{5}$$

$$Overall hv \to Energy \tag{6}$$

Where hv represents light and CE represents electrode.

As illustrated when light is shined on the stained TiO_2 an electron from the conjugated system of the dye structure becomes excited equation (1). When an electron reaches a certain excitation state, the dye will give up the electron to the TiO_2 equation (2). And travel through the load to the platinized counter electrode, creating electrical energy equation (3). The iodide/triodide electrolyte solution reactivates the dye so it is able to undergo the process again by giving an electron back to the dye equation (4) and picking another electron up from the counter electrode equation (5).

Oxide semiconductor materials have good stability under irradiation in solution. However, stable oxide semiconductors cannot absorb visible light because they have relatively wide band gaps. Sensitization of wide band gap oxide semiconductor materials, such as TiO₂, ZnO, and SnO₂, with photosensitizes, such as organic dyes, inorganic dyes, or natural dyes, that can absorb visible light has been extensively studied in relation to the development of photography technology since the late nineteenth century[5-8]. In the sensitization process. photosensitizes absorbed onto the semiconductor surface absorb visible light and excited electrons are injected into the conduction band of the semiconductor electrodes.

In this work, dye sensitized solar cell was fabricated using two different dyes with different sensitizer impregnation time to show its effect in efficiency. And also, iodide-triodide liquid electrolyte was used, and compared with another research work [9] where resin polymer electrolyte was used.

AIM AND OBJECTIVE

- To fabricate two dye sensitized solar cells ZnO/TiO₂/tomato dye and ZnO/TiO₂/zobo dye.
- To compare the efficiency and long term stability of both cells.
- To compare the efficiency and long term stability of the cells with liquid iodidetriodide electrolyte with the cells from the work with Resin polymer gel electrolyte
- To motivate researchers to fabricate dye sensitized solar cell using Resin polymer gel electrolyte
- To educate the general public about renewable energy, for power generation.

METHODOLOGY

Dye sensitized solar cell were fabricated on transparent conducting under photovoltaic operation. The conductive glass is indium tin oxide (ITO) due to low cost and stability. The TiO_2 Nano particles were fabricated by the aqueous hydrolysis of titanium alkoxides precursors, followed by autoclaving at temperature up to 240°C to archive the desired Nano particles dimensions and crystalline (anatase). The Nano particles are deposited as a colloidal suspension by screen printing.

Note that Indium tin oxide conducting glass should not be touched with bare fingers. When finger prints and other contamination are present we wash with ethanol, then allow to dry.

The procedures shown below are steps followed in the fabrication porocss of the dye sensitized solar cell.

Cleaning the ITO Glass

First the ITO was carefully washed with detergent and water, and then rinsed with distilled water. After rinsing with distilled water, the ITO glass is placed in a chamber. Finally, methanol is poured in the chamber, and the chamber is placed in an ultrasonic cleaning device to complete the cleaning process.

Deposition of Zinc Oxide by spray pyrolysis

A solution with 0.1 molarity was prepared by mixing zinc acetate salt of 99.9995 % purity with distilled and de-ionized water in a capillary tube. The solution was mixed with the magnetic stirrer for 15 mins. The surface tension of the obtained solution was deduced by the height of the solution in the capillary tube.

Spray pyrolysis was the process in which the ZnO is deposited by spraying 10 ml of the zinc acetate solution on the conducting surface of the heated ITO, where the constituent reacts to form the chemical compound. The procedure was carried out in a fume chamber and gun. The ITO was placed on heat; such that the conductive side faced up, the nozzle was fixed 5 cm from the ITO holder. The ITO was heated to 260° C, then the solution is sprayed on it until it cools to 220° C. This process is repeated until the 10 ml zinc acetate is sprayed on the ITO glasses used as the conduction electrodes for the two cells.

Titanium Deposition by screen printing

First we stir well the Nano crystalline TiO_2 pastes before use, not shake in order to avoid the formation of bubbles. The TiO_2 paste was prepared by mixing titanium dioxide salt with 5 ml of acetic acid. The thickness of the adhesive tape will determine the thickness of the titanium dioxide deposited on the glass we use scotch magic tape from 3m having a thickness of ~50 µm. This type

can be easily removed from the glass without leaving traces of adhesive materials.

The transparent pastes are made to give a layer of $2 - 3 \mu m$, for a single layer of tape. So a low dry-out of the solvent and a progressive heating is necessary to ensure optimal adhesion of the titanium dioxide layer onto the zinc oxide thin filmed ITO glass.

The deposition process itself consisted of spreading out a given volume of $\sim 10 \text{ ml/cm}^2$ of titanium dioxide paste with a plane glass slide. The electrode turns white or slightly translucent upon drying.

Note: There should be no signs of peeling off and also on the back side of the glass electrode and check if there are no air bubbles visible. Approximately 2.0 g of TiO₂ salt is mixed

with 10 ml of acetic acid. A TiO_2 layer was screen printed on the sprayed ZnO thin film, on the conducting side of the ITO glass and then annealed at 450° C for 30 mins.

Annealing Process

The annealing process allows the titanium dioxide Nano crystals to melt partially together in order to ensure electrical contact and mechanical adhesion on the glass. Good results have been obtained using a hot air blower to heat up the electrode at 450° C for about half an hour. While heating up the electrode it first turned brownish, sometimes it releases fumes and later it turns yellowish-white due to the temperature dependent band gap narrowing in the pure titanium dioxide. This is the sign that the annealing process is completed. The annealing process is carried out using the carbolyte machine.

Sensitizer Impregnation

The zobo which is a natural dye was dissolved in pure ethanol in a concentration of 20 mg of dye per 100 ml of solution, while the tomato dye was mashed before dissolving it in an ethanol solution. Put slowly the sintered electrode into the sensitizer's solution, its face up. The impregnation process was done at room temperature for 30 mins for the zobo dye sensitizer and 45 mins for the tomato dye sensitizer.

Note: No water should enter sensitizer solution, no water should contact impregnated electrodes otherwise the electrode is useless. Once stained, electrodes area is sensitive to ambient humidity they turn orange color after several weeks of ambient exposure such orange colored electrode cannot work properly.

Carbon Deposition

The method used to deposit the carbon electrode was through the deposition of soot from a burning candle. Started with an ITO glass plate matching the size of the TiO_2 electrode being used for the assembly.

After lighting the candle, the ITO glass was held above the candle flame with the conducting side facing the down, about 10 cm above the flame. The carbon from the combustion of wax is carried in the smoke and makes a black deposition on the conductive side of the ITO glass.

The process is very fast, so don't overdo it. A homogeneous gray to black layer is enough.

Allow the glass plate to cool on a suitable surface before further processing.

Sealing Electrodes

When the electrodes were put together, the active sides of the anode and the cathode will be facing each other. In other words, the stained TiO_2 will face the carbon of the counter-electrode. The gap left between the two glass plates will be filled with electrolyte during the next step.

Electrolyte Filling

The gap between the two electrodes was filled with electrolytes to complete the Dye Solar Cell. This is

performed by injecting the iodide triodide electrolyte into a small opening between the ITO glasses carrying both electrodes, with the different dyes and allow the electrolyte to fill the cell with capillary effect.

It is best to fill the cells with electrolyte as soon as the electrodes are put together. The stained thin film will otherwise be exposed to air for too long and possibly degrade.

Completing the Cell

Excess liquid was wiped off with a paper towel and the cell was manipulated carefully to avoid skin contact with the electrolyte.

The Dye Solar Cell is now operational and will last until the electrolyte solvent evaporates.

Since the assembly is open to ambient air, the performance of the cell will decrease over time. This assembly however will give plenty of time to measure and demonstrate the electrical output of the photovoltaic device.

RESULTS AND DISCUSSION

FOR TOMATO DYE

TABLE 1.1: for the current to voltage in darkreaction

| Voltage_1 (V) | Current_1 (A) |
|---------------|---------------|
| +3.438494E-04 | -6.353009E-07 |
| +1.114312E-01 | +1.861659E-04 |
| +2.224305E-01 | +1.865597E-04 |
| +3.336730E-01 | +2.827760E-04 |
| +4.447159E-01 | +3.423128E-04 |
| +5.557644E-01 | +4.657056E-04 |

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| +6.670106E-01 | +8.664844E-04 |
|---------------|---------------|
| +7.780282E-01 | +1.270817E-03 |
| +8.890325E-01 | +2.027389E-03 |
| +1.000162E+00 | +2.857973E-03 |

TABLE 1.2: for the current to voltage in lightreaction

| +1.67E-01 | -1.14E-02 |
|-----------|-----------|
| +2.22E-01 | -1.14E-02 |
| +2.78E-01 | -6.14E-03 |
| +3.34E-01 | -3.16E-03 |
| +3.89E-01 | -3.16E-03 |
| +4.45E-01 | +3.58E-03 |
| +5.00E-01 | +6.22E-03 |

Table 1.4 for the current to voltage curve forlight reaction

| +1.420346E-04 | +4.352408E-09 |
|---------------|---------------|
| +1.117178E-01 | +3.645927E-04 |
| +2.225788E-01 | +1.953811E-04 |
| +3.337425E-01 | +3.337843E-04 |
| +4.448222E-01 | +6.280288E-04 |
| +5.557271E-01 | +8.522584E-04 |
| +6.666557E-01 | +1.462236E-03 |
| +7.779317E-01 | +2.369534E-03 |
| +8.890170E-01 | +3.510679E-03 |
| +1.000158E+00 | +4.761126E-03 |

From the graphs in Fig 2 and 3 the liquid dye sensitizer (from tomato) shows that at the wavelength set at 300 nm there is an absorbance of 3 % and shows decrease in absorbability as the wavelength increases (Fig 2). And also at a wavelength set at 300 nm there is a transmittance of 0.01 % which increases as the wavelength increases (Fig 3).

| Voltage_1 (V) | Current_1 (A) |
|---------------|---------------|
| -2.36E-04 | -1.45E-02 |
| 5.58E-02 | -1.33E-02 |
| 1.12E-01 | -1.20E-02 |
| 1.67E-01 | -1.01E-02 |
| 2.22E-01 | -7.89E-03 |
| 2.78E-01 | -5.24E-03 |
| 3.34E-01 | -2.71E-03 |
| 3.89E-01 | 5.77E-04 |
| 4.45E-01 | 3.98E-03 |
| 5.00E-01 | 7.00E-03 |

FOR ZOBO DYE

Tables 1.3 for the current voltage for darkreaction

| -2.36E-04 | -1.70E-02 |
|-----------|-----------|
| +5.58E-02 | -1.56E-02 |
| +1.12E-01 | -1.38E-02 |

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In Fig. 4 and 5, the liquid dye sensitizer (zobo dye) shows that at the wavelength set at 300 nm there is an absorbance of 3 % and shows decrease in absorbability as the wavelength increases. And also at a wavelength set at 300 nm there is a transmittance of 0.04 % which increases as the wavelength increases. In Fig. 6 the graph shows an IV curve of the dye sensitized solar cell using tomatoes dye placed in a dark room and Fig. 7 shows the cell under Illumination. Likewise, Fig 8 and 9 shows the dye sensitized solar cell using zobo dye, placed in a dark room and under illuminicence respectively. Both cells had a voltage of 4 to 5 V under illuminicence.

EFFICIENCY OF THE CELLS

TOMATOES DYE

Solar conversion efficiency can be determined by the relation below

 $\eta = \frac{voc * jsc * ff * 100}{100}$

Where

 η is the solar conversion efficiency

Voc is the voltage of the open circuit

Jsc is the short circuit current density of the cell

Ff is the fill factor of the cell in percentage

Therefore

$$\eta = \frac{0.334 \times (-0.000236) \times (-44.4027) \times 100}{100}$$

 $\eta = 0.0034999 \approx 0.35 \%$

ZOBO DYE

Solar conversion efficiency can be determined by the relation below

$$=\frac{voc*jsc*ff*100}{100}$$

Where

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ŋ is the solar conversion efficiency

Voc is the voltage of the open circuit

 J_{sc} is the short circuit current density of the cell

Ff is the fill factor of the cell in percentage

Therefore

$$\eta = \frac{0.389 \times (-0.000236) \times (-33.8765) \times 100}{100}$$

$$\eta = 0.0031 \approx 0.31 \%$$



Figure 1 Magnified image of a typical dye sensitized solar cell



Fig 2 Graph of liquid absorbance of the dye from tomato



Fig 3 Graph of liquid transmittance of the dye from tomato



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Fig 4 Graph of liquid absorbance of Zobo dye



Fig 5 Graph of transmittance of liquid in zobo dye



Fig 6: I.V curve for the solar cell in dark for tomato dye



Fig 7: I.V curve for the solar cell in light for tomato dye.



Fig 8: I.V curve for the solar cell in dark for zobo dye.



Fig 9: I.V curve for the solar cell in light for zobo dye.



Fig. 10: Plot of efficiency against time of DSSCs with liquid electrolyte and resin-polymer electrolyte with different concentration of gamma-butylrolactone, showing the difference in stability of the different solar cell [5]

CONCLUSION

In conclusion the stability factor of the cell tells more of its reactivity between the sensitizer dye and the redox electrolyte which does not reduce as a result of the reduction power of the electrolyte. DSSC technology has an efficiency of above 11 % with a band gap for sensitizer of over 3.2 ev. For this work the cell with zobo dye achieved a short circuit current density of -0.000236 mA cm⁻² and an efficiency of 0.31 %, while the cell with tomato cell achieved a short circuit density of -0.000236 and the efficiency of 0.35 %, showing that the tomato dye sensitized solar cell with the impregnation time of 45 mins has a higher j_{sc}, fill factor and hence efficiency than the zobo dye sensitized solar cell with impregnation time of 30 mins. In comparison with a cell fabricated with resin polymer electrolyte; it shows that cells with resin polymer gel electrolyte are more stable and last longer.

[1] O'Regan, M. Grätzel., (1991). "A low cost high efficiency solar cell based on dye sensitized colloidal TiO₂". Nature, Vol. 353, pp. 737–740.

[2] William A. Vallejo L., Cesar A. Quiñones S. and Johann A. Hernandez S., (2011). "The Chemistry and Physics of Dye-Sensitized Solar Cells", Solar Cells -Dye-Sensitized Devices, Prof. Leonid A. Kosyachenko (Ed.), ISBN: 978-953-307-735-2, In Tech, Available from: <u>http://www.intechopen.com/books/solar-cells-dye-</u> <u>sensitizeddevices/</u> the-chemistry-and-physics-of-dyesensitized-solar-cells

[3] Massimo A; Dentico; Lonny G; Philip L; Kalewalani B (2010) "Dye sensitized solar cell Appropedia atom feed

[4] Gratzel, Michael, (2001) "Photoelectrochemical cells' nature, 114, 338-334.

[5] Rajeshwar, K. P. Singh, J. DuBow, (1978) Electrochim. Acta 23 1117—1144.

REFERENCE

[6] Danzmann, H.J., K. Hauffe, Ber Bunsen: (1975) Phys. Chem. Chem. Phys. 79 438–453.

[7] Anderson S., E.C. Constable, M.P. Dareedwards,J.B. Goodenough, A. Hamnett, K.R.Seddon, R.D.Wright, (1979) Nature 280 571—573.

[8] Hamnett A., M. Dare-Edwards, R. Wright, K. Seddon, J. Goodenough, (1979) J. Phys. Chem. 83 3280–3290.

[9] Geun, W.P; Chul, G.H; Jae, W.J. (2012) Korean Chemistry Society. Vol. 33, No. 12 4093 http://dx.doi/10.5012/bkcs.2012.33.12.4093