

Dye Sensitized Solar Cells: A New Prospective to the Solar to Electrical Energy Conversion. Issues to be Solved for Efficient Energy Harvesting.

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Abstract

Dye-sensitized solar cells (DSSCs) are placed in third generation photovoltaics and are proposed as alternatives to conventional solar cells of silicon. DSSCs have numerous advantages over silicon based solar cells such as low materials cost, ease of production, and efficiencies out performing amorphous silicon solar cells. As these cells can be printed on glass, they can uniquely offer a high degree in freedom for the design and the optical appearance of a building-integrated module. The cell concept is believed to reduce the production costs and energy payback time significantly compared to standard silicon cells or other thin film cells. Although the efficiency record of single cell is 12% the conversion efficiency on larger areas is still an issue to be solved before this technology will follow the production line. Along with the up-scaling of DSSCs, open circuit voltage and fill factor of DSSCs may rapidly decrease with the increase of shunt current and internal resistance. If the design methods and techniques of these cells are not optimized appropriately, the efficiency of the cell is likely lower than 1% when the size is up to 10cm x 10cm. In this work we present studies on the DSSC efficiency depending on their size. We focus on the efficiency of cells in shape of long strips with varying their length from 1 to 20 cm while their width is always kept constant to 1 cm. Extensive studies on the open circuit voltage - Voc, short circuit current density- Jsc, fill factor - ff and overall efficiency - n% of the cells will be presented.

Keywords: Dye sensitized solar cells, quasi-solid state electrolyte, high efficiency, nanocomposite materials.

Introduction

Utilization of renewable energies is of major importance because of the increase in fossil energy costs in combination with carbon dioxide reduction preventing global warming. The importance of the solar energy can be considered as the sustainable energy which may successfully satisfy a part of the energy demand of future generations. Handling this opportunity of solar energy utilization is a big bet for the future. Besides the development of new clean techniques to the electrical power generation is urgently important in order to protect global environment and assure economic growth of sustainable resources [1]. Taking into account the present status in photovoltaic technology, some improvements have to be made which are summarized in three basic fields: (a) in costs, (b) in their applicability and (c) sustainability [2]. Although the cost per peak watt of crystalline silicon solar cells has significantly dropped, it is still expensive compared to the conventional grid electricity resources [3]. Silicon wafers made of pure semiconducting material to avoid limitations in energy conversion are still expensive. For this reason developments on potentially cheaper solar cells based on environmentally friendly procedures is an interesting prospective. Almost two decades ago, dye sensitized solar cells (DSSCs) were proposed as low cost alternatives to the

conventional amorphous silicon solar cells, owing to the simplicity of their fabrication procedures, practically under ambient conditions with mild chemical processes [4]. DSSCs are placed in the category of third generation photovoltaics (PV) where new trends in the photovoltaic technology are applied. In the 1st generation PV cells, the electric interface is made between doped n-type and p-type bulk silicon. 1st generation PV cells provide the highest so far conversion efficiency. The 2nd generation PV cells are based on thin film technology. These cells utilize less material and they thus drop the production cost, however, they are less efficient than the bulk cells. Both 1st and 2nd generation cells are based on opaque materials and necessitate front-face illumination and moving supports to follow sun's position. Thus they may be either set up in PV parks or on building roofs. 3rd generation solar cells, are based on nanostructured (mesoscopic) materials and they are made of purely organic or a mixture of organic and inorganic components, thus allowing for a vast and inexhaustible choice of materials [5]. Because of their mesoscopic character, it is possible to make transparent cells, which can be used as photovoltaic windows [6]. Photovoltaic windows can be functioned by front-face light incidence but also by diffuse light and even by back face light incidence. Also because of their mesoscopic nature, 3rd generation solar cells are easy to make at ambient conditions, not necessitating severe measures of purity, thus dropping production cost. Among the different possibilities

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of 3rd generation solar cells DSSC have the most promising prospect. The overall efficiency of ~12% (for laboratory small size) placed DSSCs as potential inexpensive alternatives to solid state devices [7]. Since the pioneer work of M. Grätzel and co-workers [4] an intense interest to the development of such kind of solar cells has been recorded because of their low cost, simple preparation procedures and benign methods of construction compared with conventional methods applied in first and second generation photovoltaic technology [8]. Although the solar to electrical energy conversion efficiencies recorded for DSSCs are lower than those measured for silicon based solar cells, a high potential for improvement in their efficiency, stability and commercialization has been announced till nowadays [9].

The working principle of a DSSC substantially differs from that of a conventional solar cell based on silicon. In silicon solar cell a *p-n* junction by joining semiconductors of different charge carriers' concentration in a very close contact is necessary. In this case the processes of light absorption and charge transport are caused in the same material. In DSSCs, these fundamental processes are occurred in different materials which avoid the premature recombination of electrons and holes [10]. As these processes do not happen at the same material ultrapure materials are not required for a high performance DSSC. DSSCs are composed of four major components: a nanostructured n-type semiconductor, typically TiO₂, a dye-sensitizer to absorb visible light, an electrolyte, which creates the interface with the semiconductor and a counter electrode carrying an electrocatalyst, which facilitates transfer of electrons to the electrolyte. Figure 1a

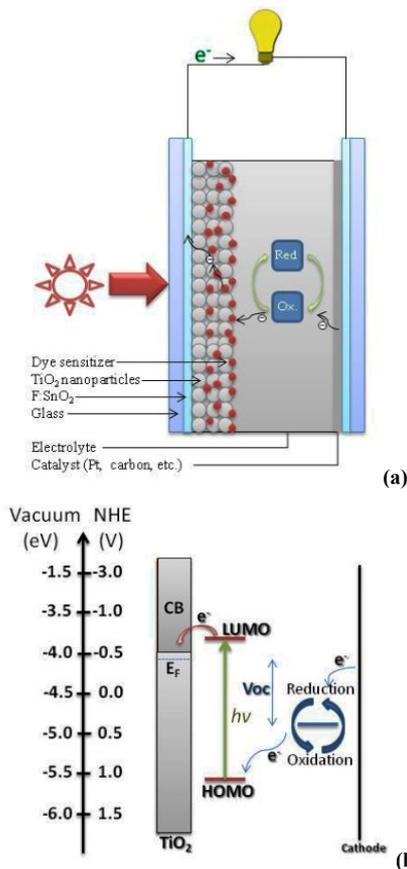


Fig. 1. a) Principle of operation for a DSSC and (b) an energy diagram of DSSC's operation.

illustrates the basic principle of cell operation while Figure 1b the energetics of DSSC operation.

While many research groups investigate the working principles of DSSCs and new developments have been achieved concerning their efficiency and large scale applications, new companies founded in the meanwhile try to carry DSSC technology in market place evaluating all process steps are needed for industrial production [11]. Experimental results for small size solar cells cannot directly applied in large scale DSSCs as the efficiencies measured for small size solar cells cannot be repeated in large scale [12]. This is caused by the high internal resistance of FTO substrates which eliminates their efficiency and it is found to be drastically decreased. Below are referred some of the main issues which have to be taken into account before DSSCs go to a production line:

- Large area deposition of TiO₂ layers. The layers have to be homogeneous and uniform.
- New methods for dye staining and electrolyte filling.
- Electrical interconnection of individual cells. A major factor for limited efficiency of the DSSC is the ineffective contacts on FTO glass. The external connections of the individual cells are also a problem.
- Sealing process for modules in case of liquid electrolytes.
- Long-term stability of at least 10 years for outdoor use.
- Evaluation costs, which is believed to be approximately 10% of that needed for silicon solar cells.

Moreover, for the durability of the cells, it was considered necessary to replace the liquid electrolyte with quasi-solid state, solid, polymer electrolytes or p-type inorganic semiconductors as the manufacturing cost and convenience of preparation is highly simplified [13-15].

In this work we demonstrate the major issue of cell size which is a limiting factor to cell efficiency and overall a problem to the DSSC commercialization. We study the effect of cell size to the open circuit voltage, short circuit current density; fill factor and overall efficiency of the cells. Our studies are limited to strip like cells which are the structural units for big size solar cells and modules.

2. Experimental

2.1. Materials.

Lithium iodide, iodine, 1-methyl-3-propylimidazolium iodide, hydrogen hexachloroplatinate(IV) hydrate (H₂PtCl₆), poly(propylene glycol)bis(2-aminopropyl) ether, 3-isocyanatopropyltriethoxysilane and all solvents were purchased from Sigma-Aldrich. 3- *Cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium),N719 was purchased from Solaronix S.A, Switzerland. SnO₂:F transparent conductive electrodes (FTO, TEC15) 15 Ohm/square were purchased from Hartford Glass Co., USA. Commercial ultra pure titanium isopropoxide (TTIP, 97%, Aldrich), Triton X-100 (polyoxyethylene-10- isooctylphenyl ether) surfactant (99.8%, Aldrich), glacial acetic acid (AcOH, Aldrich) were used to make precursor TiO₂ sols.

2.2 Preparation of TiO₂ films sensitized with dye.

TiO₂ thin films were deposited by following a previously reported procedure [16,17]. Briefly, for 12.5 ml solution, 1.8 g of Triton X-100 were mixed with 10 ml of ethanol, followed by addition of 0.8 ml of glacial acetic acid and 0.9 ml of titanium isopropoxide under vigorous stirring. After a few minutes stirring, FTO glasses were dipped in the above sol and withdrawn with 2cm/sec. The films were heated up to 500°C for 30 minutes using 20°C/min heating ramp rate. The above procedure for TiO₂ films was repeated several times in order to make films with thickness around 1.5 microns (based on cross-sectional FE-SEM images). The size of TiO₂ electrodes was varied from 1x1 cm² to 1x20 cm² with always kept the one dimension constant. TiO₂ films were finally immersed in t-butanol/acetonitrile (1/1 v/v) solution of N719 (the dye concentration was 5x10⁻⁴ M) in order to sensitize the TiO₂ electrode in the visible.

2.3 Preparation of quasi-solid state electrolyte for dye-sensitized solar cells.

In the construction of the solar cells a quasi-solid state electrolyte was used. This was chosen as a promising approach to DSSC technology as it combines the high ionic conductivity of liquids while it reduces the risk of leaks and minimizes sealing problems in the cells. For the gel electrolyte applied to the DSSCs, we used a hybrid organic-inorganic material which was prepared according to a procedure described in previous publications [18-20]. Briefly, poly(propylene glycol)bis(2-aminopropyl ether) of molecular weight 230 and 3-isocyanatopropyltriethoxysilane (ICS; molar ratio ICS/diamine=2) react in a vessel (acylation reaction), producing urea connecting groups between the polymer units and the inorganic part. The gel electrolyte was synthesized by the following procedure: 0.7grams of the functionalized alkoxide precursor were dissolved in 2.4 grams of sulfolane under vigorous stirring. Then, 0.6 ml AcOH were added followed by 0.3M 1-methyl-3-propylimidazolium iodide, 0.1M LiI and 0.05M I₂ in a final molar ratio AcOH:LiI:MPIIm:I₂ = 2.5:0.1:0.3:0.05. After six hours stirring, one drop of the obtained sol was placed on the top of the titania electrode with adsorbed dye molecules and a slightly platinized FTO counter electrode was pushed by hand on the top. The platinized FTO glass was made by exposing it to a H₂PtCl₄ solution (5mg/1ml of ethanol) followed by heating at 450°C for 10 minutes. The electrodes tightly stuck together by Si-O-Si bonds developed by the presence of the hybrid material.

2.6 Electrical characterization of the DSSCs.

For the *J-V* curves, the samples were illuminated with Xe light using a Solar Light Co. solar simulator (model XPS 400) equipped with AM 0 and AM 1.5 direct Air Mass filters to simulate solar radiation at the surface of the earth. The light intensity was kept constant at 750 W/m² measured with a CMP 3 Kipp & Zonen pyranometer. Finally, the *I-V* curves were recorded by connecting the cells to a Keithley Source Meter (model 2601) which was controlled by Keithley computer software (LabTracer). The cell active area for these measurements was varied from 1 to 20 cm² while masks and back reflectors were not used in the measurements. For each cell size, we have made three devices which were tested under the same conditions in

order to avoid any misleading estimation of their efficiency. Cell performance parameters, including short-circuit current (*I*_{sc}), open circuit voltage (*V*_{oc}), maximum power (*P*_{max}), fill factor (*ff*) and overall cell conversion efficiency, were measured and calculated from each *I-V* characteristic curve.

3. Results and Discussion

While many research groups investigate the working principles of DSSCs and new developments have been achieved concerning their efficiency and large scale applications, new companies founded in the meanwhile try to carry DSSC technology in market place evaluating all process steps are needed for industrial production. Unfortunately, experimental results for small size solar cells cannot directly applied in large scale DSSCs as the efficiencies measured for small size solar cells cannot be repeated in large scale [21]. For an in depth examination of the factors may cause a decrease to the efficiency of the DSSC we constructed cells in the shape of a strip with variable size. The size was varied from 1x1 to 1x20 cm². A visual appearance of the proposed cells can be seen on the Fig.2.

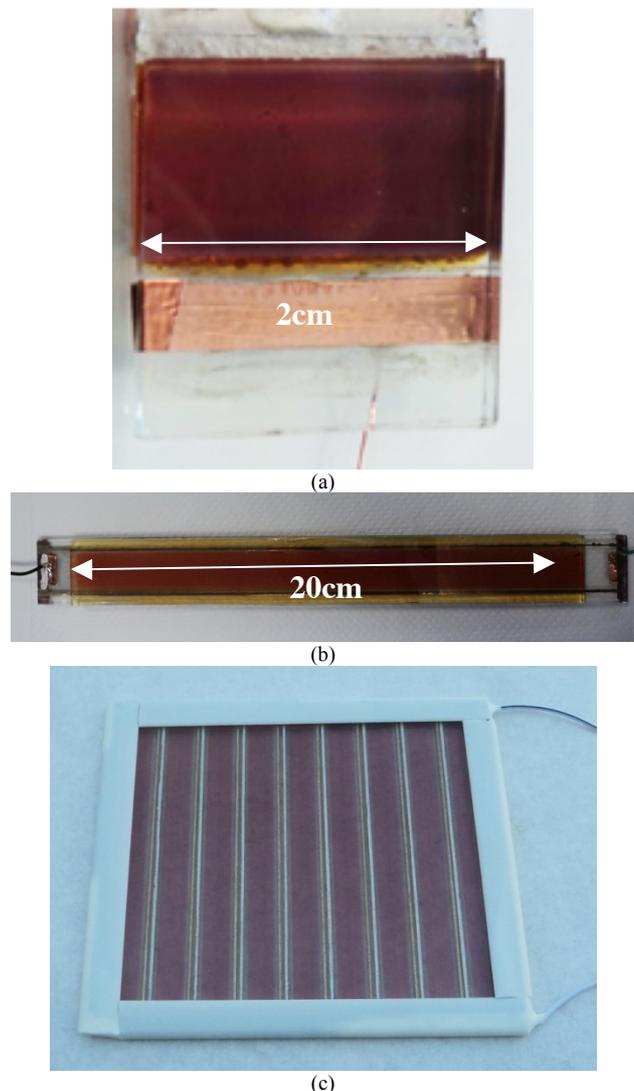


Fig. 2. Images of DSSCs in the shape of strips (a) 1x2 cm², (b) 1x20 cm² and (c) DSSC module of 20x20 cm².

As an example, we present cells of 1x2 and 1x20 cm² (Fig.2a and b) while a solar module of 20x20 cm² can also be seen on Fig.2c which obviously consisted of successive strips of 1x20 cm². We decided to keep the one dimension constant in order to limit the factors that affect to the efficiency of the cells. Usually, the optimum width of the strips is found to be varied from 0.8 to 1 cm. The results for all cell parameters are presented in Table 1.

Table 1. Solar cell parameters from *I-V* curves of DSSC strips with variable length.

Strip size (cm ²)	J_{sc} (mA/cm ²)	V_{oc} (volts)	ff^*	n (%) ^o	R_s (ohms)	R_{sh} (ohms)	T (°C)
1x1	12.2	0.76	0.62	7.7	13	1967	25
1x2	12.1	0.77	0.61	7.6	12	1345	25
1x5	12.0	0.75	0.60	7.2	10	1321	25
1x10	11.5	0.72	0.55	6.1	6	768	25
1x20	9.6	0.73	0.53	5.0	1.3	95	25

* Fill factor: $ff = \frac{(V \cdot J)_{max,p}}{V_{oc} \cdot J_{sc}}$, and ^o overall efficiency calculated from the equation: $n = \frac{V_{oc} \cdot I_{sc} \cdot ff}{A \cdot P_{light}}$ where A is the effective area of the cells. P_{inc} was kept at 750 W/m².

It can be seen that the overall efficiency for all cells is almost constant when the length was increased from 1 to 10 cm while a decrease was noticed for lengths longer than 10 cm. It can be concluded that the size of the strip affects to the efficiency of the cells when it exceeds 10 cm. The lower efficiency is achieved mainly by the lower values in J_{sc} and ff of the cells. In particular V_{oc} seems to be unaffected from the size of the cells and the J_{sc} was lower than expected values. The ff was also affected by the size of the cell mainly due to the internal in series resistance of the cell (R_s). As can be seen from data presented on Table 1 the R_s series resistance of the large size cell was lower than that obtained for small size. The values were ranged from 1.27-13 Ohms while the R_{sh} resistance has the same behavior. In the case of 1x20 cm² strip cell the value of R_{sh} was low and measured to be 95 Ohms while in the case of 1x1 cm² was 1967 Ohms which is a good value for this type of cell resistance. In all cases R_{sh} and R_s resistances of the cells were approximately calculated from the slopes of the *I-V* curves at I_{sc} and V_{oc} respectively. The temperature during the experiments was kept constant at 25°C. Experimental results on *I-V* characteristic curves for 1x2 and 1x20 cm² strip cells are presented on Fig.3 and Fig.4 respectively.

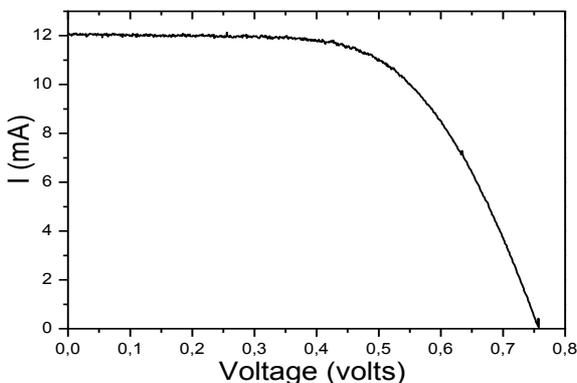


Fig. 3. *I-V* curve at simulated AM 1.5, Xe-light for 1x1 cm² DSSC strip.

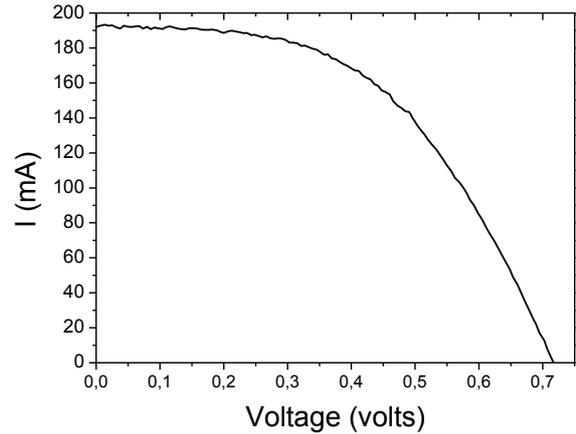


Fig. 4. *I-V* curve at simulated AM 1.5, Xe-light for 1x20 cm² DSSC strip

Similar results were obtained for cells with variable electrolyte thickness. Increased amounts of electrolyte in the cells affect to the overall efficiency. The result is obvious since the R_s expected to be higher as the material content is increased. The interesting fact to the data is that the overall efficiency of the cells is almost constant for up to 10 cm length to the strips but the overall efficiency is 10% lower when the thickness of the electrolyte is increased from 50 to 80 μm. In all cases of long cells we used silver fingers for current collection which have a resistance of 1-1.5 Ω. Therefore, we may consider that the resistance of metal fingers is another factor for efficiency limitations as they put additional resistance to the cells. The effective current collection is one of the major factors for safe measurements and conclusions. Bad contacts usually add parasitic resistances with a direct effect on the I_{sc} and ff of the cells.

The most interesting results found for three strips connection in parallel on the same glass substrate. The glass was previously etched in order to separate the one strip from the other so as three isolated conductive strips were created on the same glass. The final connection of the cells in parallel was made at the three edges using copper tape. As it can be seen from data of Fig.5

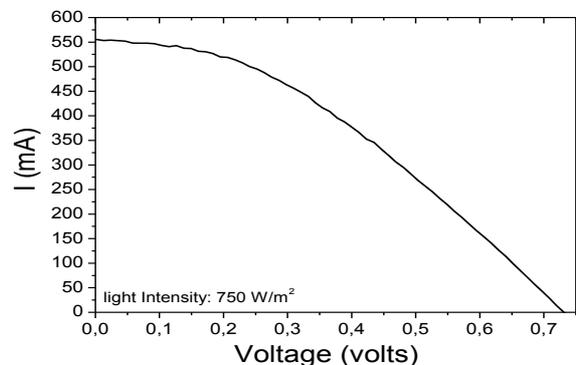


Fig.5. *I-V* curve at simulated AM 1.5, Xe-light for 3x20 cm² DSSC consisted of three strips (1x20 cm²) in parallel.

the fill factor of the module of the three cells was seriously affected while the total short circuit current of the assembly was lower of that was expected. A 35% drop to the ff value among $1 \times 20 \text{ cm}^2$ strip like cell and isolated strip cell of the same dimensions on the parallel connection was found while a 5% drop to the expected value for the I_{sc} was also monitored. The main reasons for these evidences are (a) the poor external connections of the strip like cells and (b) the difficulty to isolate the strip like cells on the same glass. The existence of electrolyte in each cell requires effective isolation between cells with no electrolyte leakage between them.

Finally, DSSCs as promising alternatives to the conventional silicon based solar cells require specific modifications and inspired connections before they can be applied to a production line. The electrolyte thickness, the efficient current collection, and effective isolation of the cells to the module are of the main issues to be solved before.

4. Conclusions

In this work we present the major advantages of using dye sensitized solar cells but also express the main issues arise from their up-scaling. The efficiency for a quasi-solid state DSSC could be as high as 7.7% and fall to 5% when the size of the cell is twenty fold larger than the initial of $1 \times 1 \text{ cm}^2$. The main factors of limitation were found to be the current collector material and structure while the internal resistance of the cell depending on the FTO glass substrate and electrolyte do also affect the overall efficiency.

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