IMPROVEMENT IN PHOTOVOLTAIC PARAMETERS BY EMPLOYING DIP COATED BLOCKING LAYER IN PHOTOANODE OF DSSC

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Abstract: Dye-sensitized solar cell (DSSC) is fabricated by using screen printed titania as photoanode, quasi-solid state electrolyte and xylenol orange dye as photosensitizer. Further, the impact of blocking layer on photoanode has been analyzed in terms of change in power conversion efficiency of the cell. The selective and combined influence of blocking layer on photoanode was determined in terms of improvement in V_{oc}, J_{sc} and finally conversion efficiency (η) of DSSC. It is found that the effect of blocking layer on photoanode increased power conversion efficiency of DSSC more than two times. Further, the use of ionic polymeric iodide/triiodide redox electrolyte imparts stability to device.

KEYWORDS: blocking layer, xylenol orange, quasi-solid polymeric electrolyte, efficiency.

I. INTRODUCTION

Solar energy harvesting through dye-sensitized solar cells is attracting global community for converting solar energy into electrical energy as it is easy to fabricate, cost effective and eco friendly [1-2]. It may become a potential alternative to commercial solid-state semiconductor solar cells. However, their photo conversion efficiency is less than 13% because of the intrinsic limitation in charge transport [3]. The photoanode of a DSSC is prepared by screen printing the mesoporous oxide semiconductor film with high specific surface area on a transparent conducting oxide (TCO) [4-5]. Here the challenge lies in working with liquid electrolyte to restrict the leakage which otherwise limits long term durability of the cell. The only option left under these circumstances is to use quasi solid electrolyte which not only restricts leakage of electrolyte but also imparts stability of device [6].

The use of xylenol orange (XO) organic dye as sensitizer in dye sensitized solar cell has been reported by T. Matsuhara et al. [7] wherein they have used aqueous solution of XO in 0.1 M acetic acid for sensitization. The cell fabricated with this dye shows 2.2 mA/cm^2 J_{sc}, 0.44V V_{oc}, 0.7 FF and 1.3% conversion efficiency (at illumination intensity of 57mW/cm^2). They have used aqueous solution of dye for sensitization of photoanode and liquid state electrolyte for greater efficiency but with reduced the stability.

Nanocrystalline TiO_2 layer on photoanode plays a very important role in the DSSC device which is prepared by various methods like doctor blading, spin coating, screen printing etc. [8]. Blocking Layer (BL) was applied as barrier layer at fluorine doped tin oxide glass (FTO)/TiO_2 interface to increase the functional properties of the cells [9-10] by charge transfer resistance at the blocking layer/electrolyte interface. Loss of electron near the FTO substrate was effectively prevented by the presence of the BL [11]. The thickness of TiO_2 BL creates resistance in series giving rise to an electron barrier that reduces the charge collection efficiency. Therefore, the thickness of BL should be optimized to utilize its desired properties. It should not be too thin or too thick. This kind of precise optimization limits the use of BL in photoanode in DSSC. Here we report a systematic investigation of the role of the BL in inhibiting electron back recombination (the notion of the BL in an operating DSSC is illustrated in schematic figure1)

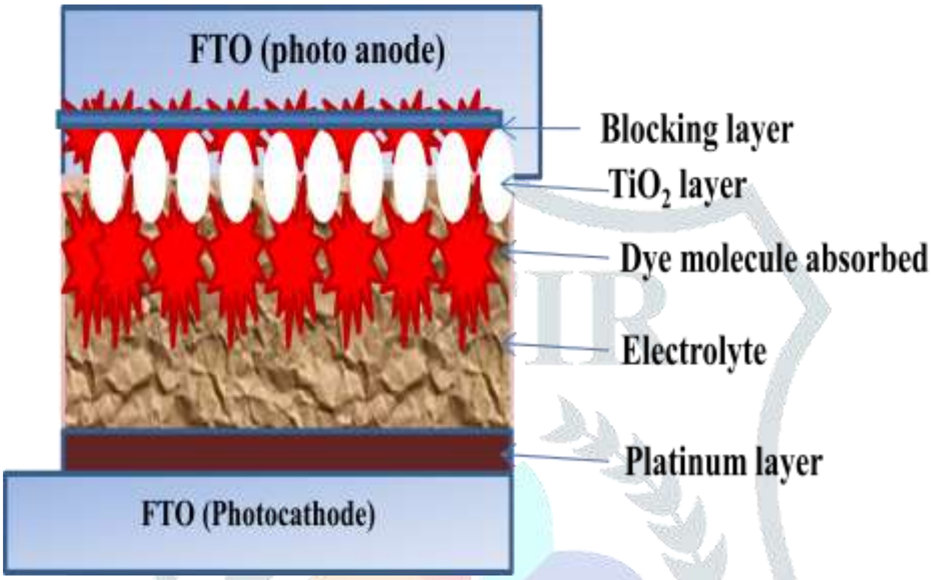


Figure 1-Assembled DSSC

Worldwide researchers are working on to improve the stability of DSSC which limits its commercialization. In present communication we have adopted a new approach of fabricating DSSC wherein photoanode incorporated with the BL and quasi solid state ionic polymeric electrolyte (I^-/I^-_3). The use of quasi solid state ionic polymeric electrolyte imparts stability to cell by addressing the issue of sealing. The blocking layer of nc-TiO2 was prepared by dip coating technique. The structural, optical and the photovoltaic properties of the fabricated DSSC devices with and without blocking layers have been studied and compared.

II. EXPERIMENTAL DETAILS

2.1 MATERIALS AND REAGENTS USED

nc-TiO_2 (Degussa P25 Rutile: Anatase/ 85:15, 99.9%, 20nm) procured from Nanoshel LLC, Wilmington, Delaware. Hydrogen hexchloro platinate (H_2PtCl_6) procured from Fluka (CAS 16941-12-1), USA for preparation of counter electrode, 1-Butanol procured from E Merk (CAS 71-36-3) to be use as solvent for preparation of blocking layer solution and screen printable paste xylenol orange (CAS N0. 3618-43-7) dye procured from Loba Chemie, Mumbai to be used as sensitizer in DSSC.

2.2 DEVICE FABRICATION

2.2.1 PREPARATION OF PHOTOANODE (WORKING ELECTRODE)

Fluorine-doped tin oxide (FTO) was used as conducting substrate to be used as photoanode (working electrode) and photocathode (counter electrode). It is cleaned with seven step cleaning process i.e. de-ionized water washing, 2-propanol in ultrasonic Bath (Model Sonicator SG-3042) cleaning with air drying. Finally it was ultra cleaned in Plasma Cleaner (Model: Harrick Plasma PDC-002) for 5 minutes prior to film preparation.

To prepare BL solution and screen printable TiO_2 paste; three beakers of 100ml each were taken. In one beaker 2g of titanium oxide was mixed with 10 ml of 1-butanol. In second beaker 2g titanium oxide was mixed with de-ionized water. In third beaker, 1g of ethyl cellulose was mixed with 10ml of 1-butanol. All three solutions were stirred separately for overnight at room temperature. Now all three solutions of separate beakers were mixed together in one beaker and allowed further stirring for 2 hours so that homogeneous mixture can be prepared. 2g of crushed polyethylene glycol (PEG) was added to this homogenous solution and stirring was kept overnight.

Finally the cleaned substrates were dipped in this solution to get the blocking layer. This BL was sintered at 450° C for one hour in muffle furnace (make Bio Technic India Model PTT1$). At last 2ml of turpenol was added into the solution with continued stirring till it turned into a viscous screen printable paste. Manual screen printing process was adopted using 100 mesh screen to prepare active layer of titania paste. The paste was applied on two different substrates i.e. with BL FTO and without BL FTO. Both types of screen printed substrates were sintered at 450° C for 1 hour in muffle furnace. Finally both type of screen printed substrate dipped for overnight in 1mM XO dye prepared in methanol solvent.

2.2.2 PREPARATION OF PHOTOCATHODE (COUNTER ELECTRODE)

Cleaned FTO substrate (as in section 2.2.1) was coated with H_2PtCl_6 diluted in methanol (1:10) by using hot water bath technique. In this technique solvent evaporated with leaving behind strong coating of platinum over the FTO substrate. This process is carried out when temperature around 70° C is attained. This coated substrate is now sintered in muffle furnace at 450° C for one hour for preparation of photo cathode.

2.2.3 PREPARATION OF QUASI SOLID STATE ELECTROLYTE

Optimized standard procedure adopted for preparation of quasi solid state electrolyte referred in [6]. During the process, a solvent mixture of GBL & NMP was taken in which KI (0.5M) & I_2 (0.1M) was added into it. Further, a thin sheet of PVB was immersed into it for at least for two hours so that it can be used as electrolyte for DSSC. It is very soft in semi solid form at the time of placing over photoanode which acts as sealants of DSSC architecture also. That is why this electrolyte termed as quasi solid state electrolyte.

2.2.4 ASSEMBLING OF DSSC DEVICE

For fabrication of DSSC; the quasi solid state electrolyte was sandwiched between photoanode and photocathode using binder clip as shown in figure 2.

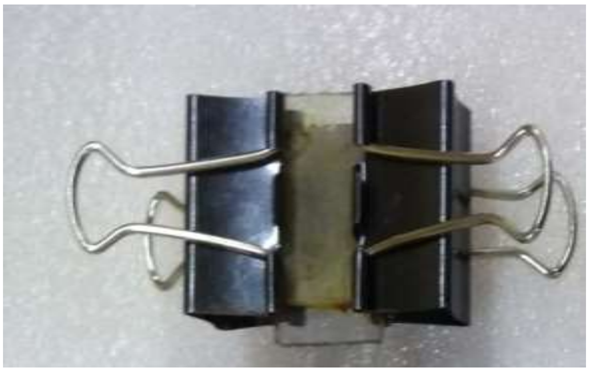


Figure 2-Fabricated sandwiched DSSC

III CHARACTERIZATIONS

3.1 OPTICAL CHARACTERIZATIONS

The UV-VIS optical absorption of photoanodes was recorded using photodiode array spectrophotometer (Model: Specord S-300 analytic jena). The optical spectra of nc-TiO_2 screen printed photo anode with and without BL was recorded for the wavelength range 200 nm -1100 nm before and after sensitization with xylenol orange dye.

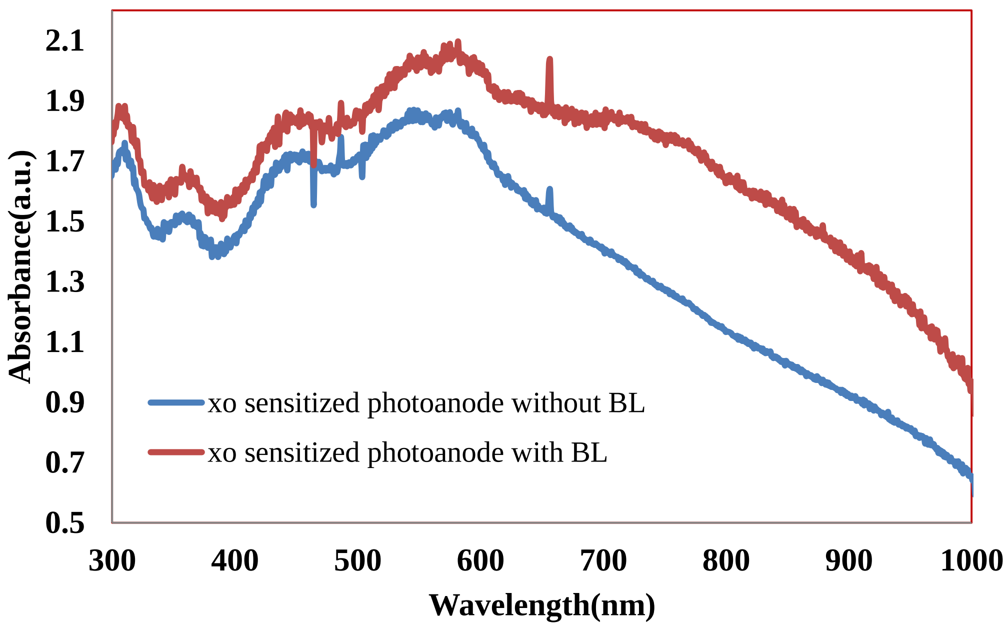


Figure 3 UV-Vis absorption spectra of Photoanode

It is clear from absorbance that photoanode incorporated with BL have wide spectral response as shown in figure 3. Significantly the improvement in absorption can be observed for entire range. Especially the enhancement in longer wavelength region indicates the photon of higher wavelength (prominent contribution in solar spectrum) can also be absorbed. Also the improved absorption suggests that blocking also increased the amount of dye loading.

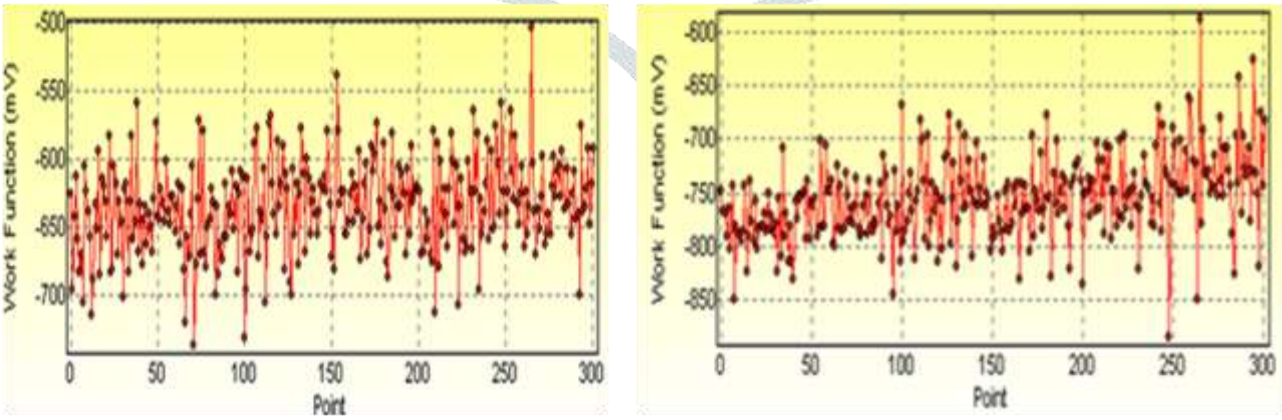
3.2 KELVIN PROBE STUDY

Kelvin probe measurements of both type of photoanode employing 2 mm dia gold plated probe were studied using a Kelvin probe setup (SKP5050) from KP Technology, Scottland. It is a non contact measurement process for the contact potential difference between a reference probe and surface of sample in the form of capacitor. If the contact made between probe and sample via back contacts, the Fermi level of the sample and the reference electrode equalize and results in generation of an electrical charge on the respective surfaces. The resulting contact potential difference ΔU relates to the work function [12]. Effect of BL can be studied from following table-1.

Table 1: Kelvin Probe Analysis

Photoanodes	Work Function in Dark (eV)	Work Function in light (eV)	Mean vibrating contact potential difference (in dark) (V_{cpd}) (mV)	Mean vibrating contact potential difference (in light) V_{cpd} (mV)
Without BL	5.0	4.46	-25	-756
With BL	4.8	4.34	-17	-636

Kelvin probe is an indirect determination technique of very small charges that makes it very useful tool in characterization of high resistive materials. The scanning was carried out in dark as well as with white light LED which provides the surface potential difference in terms of work function and surface photo voltage (SPV). It is clear from table that photoanode with BL have increased conductivity.



a) with BL b) without BL

Figure 4 Kelvin Probe measurements of photoanode

3.3 ELECTRICAL CHARACTERIZATION

HP semiconductor parameter analyser (model 41458) was used for electrical characterization of fabricated DSSC structure in actual field condition having incident solar radiation of 100 mW/cm^2. The I-V characteristics of fabricated devices are shown in figure 5 and various photovoltaic parameters are tabulated in table-2.

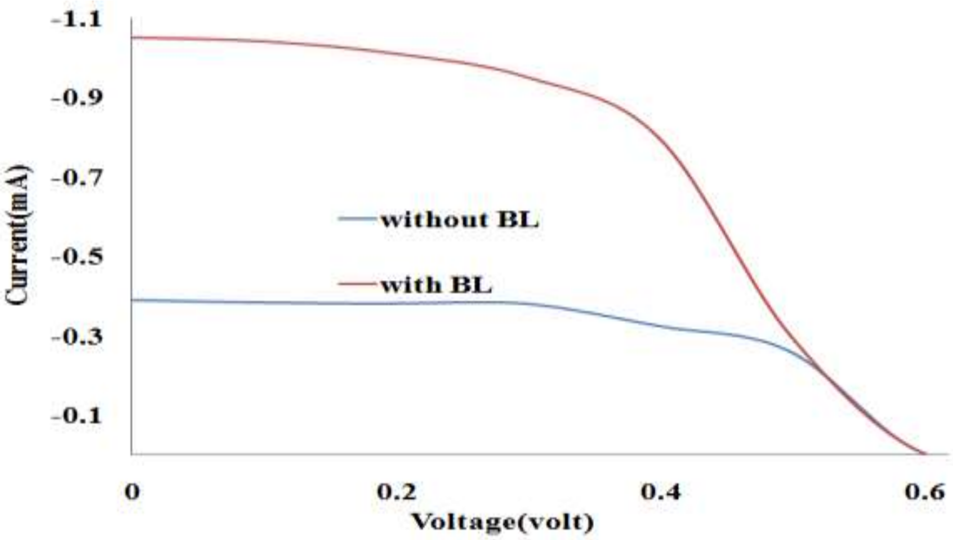


Figure 5: current-voltage characteristics of DSSC fabricated with BL and without BL

It is clear from the I-V characteristics of fabricated devices that there is a considerable improvement in the magnitude of photo current in the device with BL. This is clear evidence that use of BL has reduced the electron recombination which is a major source of current loss in DDSCs. Not much difference was observed in the values of voltage in both the cases. The improved fill factor indicates the better quality of cell.

Table2: photovoltaic parameters of fabricated devices

Device Configuration	V_{oc} (volt)	I_{sc} (mA)	Fill Factor (FF)	η (%)
Photoanode without BL	0.61	0.39	0.54	0.13
Photoanode with BL	0.62	1.05	0.56	0.36

IV RESULTS AND DISCUSSIONS

The optical absorption spectrum of the photoanode having BL on FTO glass substrate was enhanced due to BL which has a higher refractive index than TiO_2 layer only. BL has a compact structure as it is prepared by dip coating technique so it possesses high packing density and correspondingly high refractive index as it is seen from absorbance. Photoanodes having BL have low surface potential difference in terms of work function & surface photo voltage (SPV). It is evident from the lowering of work function increases with dye loading as blue shift in 3D Surface mapping. The lowering of work function & electro negativity due to BL imparts overall improvement in the performance of the cells with successive increase in conversation efficiency i.e. from0.13 % to 0.36%.

BL improved electron injection that results enhanced I_{sc} 0.39 mA to 1.05 mA. It seems clearly the BL being able to inhibit back reaction, results in improved performances of the solar cell. [13-14]

Usually liquid electrolytes are frequently used in making efficient solar cells but use of liquid electrolyte imparts leakage problems leading to poor durability of DSSC. It is the major limiting factor in commercialization of this technology. In the present device, we have used clear polymer electrolyte consisting of iodide/triiodide couple which not only imparts durability to the cells, but it also acts as a binder in keeping both the electrodes intact together along with the device structure. Cells fabricated in this way, retain their characteristics for longer time in comparison to liquid electrolyte system based cell.

V CONCLUSION

The BL prepared by dip coating technique on FTO substrate has been successful in enhancing the photocurrent of the DSSC device more than two times. BL is effective irrespective of the physical characteristics of the active layer (shape, size and size distribution).

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