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Efficient solid-state dye sensitized solar cells fabricated on a compact TiO_2 barrier layer preventing short-circuit current

J. Bandara * and H. C. Weerasinghe

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

Abstract

A dye sensitized solid-state solar cell (DSSC) was fabricated consisting of a dense TiO_2 (D) and a nanoporous TiO_2 (P) layers. The dense TiO_2 layer of the DSSC type TiO_2(D)/TiO_2(P)/Dye/CuI prevents the short circuit problem, which normally encounter in DSSC while the poor dye adsorption of the dense TiO_2 film is compensated using a porous TiO_2 layer. The dense TiO_2 film provides the opportunity of optimizing the performance of the second porous layer and the overall cell performance. i.e. TiO_2(D)/Dye/CuI solar cell delivers Isc = 1.20 mA and Voc = 345 mV while solar cell consisting of a porous TiO_2 layer on the dense TiO_2 layer (TiO_2(D)/TiO_2(P)/Dye/CuI) delivers Isc = 6 mA and Voc = 500 mV.

I. INTRODUCTION

Dye-sensitized photoelectrochemical cells (PEC) constructed using nano-porous films of TiO_2 are gaining recognition as promising photovoltaic devices for conversion of solar energy [1]. In a dye sensitized PEC with nano-porous TiO_2, the charge on the dye molecule, which had transferred an electron into the conduction band, is scavenged by a redox species present in the electrolyte. Such dye-sensitized solar cells (DSCs) with a liquid electrolyte can be unstable for long time operations due to solvent evaporation and degradation. In this regard, efforts have been made to replace the liquid electrolyte with inorganic p-type semiconductors [2-4], ionic conducting polymers [5], organic hole transport materials [6,7] and molten salts [8,9]. The dye sensitized solid-state solar cells (DSSC) of ionic conducting polymers and molten salts present low conversion efficiencies compared with the liquid DSC because of the low conductivity and poor contact between the dye and electrolyte used. Tennakone et al. [2,4,10] and Gratzel et.al. [11] successfully employed the DSSCs using p-type

* Corresponding author

semiconductors. However, the DSSCs often met problems of short-circuit and mass transport limitations of the ions resulting in low conversion efficiencies compared with the liquid version. The attempts have been made to overcome short-circuit problem using different techniques, i.e. by the insertion of oxide film and by deposition of the organic layers onto spin coated TiO_2 films [12-14]. The electrodes for DSSC have been prepared using a mixture of TiO_2 powder and Ti-isopropoxide [10]. However, the films prepared by such methods are often dense causing decrease of dye loading. However, it was noticed that the DSSCs could be fabricated using thin and dense TiO_2 films with Ti-isopropoxide alone. The such solid state cells (TiO_2 (D)/Dye/CuI) showed better rectification, however poor dye adsorption by the dense TiO_2 layer results in low Isc. Therefore, in this work we investigated the possibility of applying a thin dense TiO_2 film using Ti-isopropoxide in-between conducting glass and the porous TiO_2 layer and fabricate a solar cell type (TiO_2 (D)/ TiO_2 (P)/Dye/CuI). The devices fabricated with a dense TiO_2 layer acts as a barrier for short-circuiting problem while the porous layer enhances the dye adsorption. The advantage of thin film preparation by the method described in this article is that the dense TiO_2 layer between conducting glass and the porous TiO_2 layer provides the opportunity of optimizing the properties of the second TiO_2 layer i.e. porosity, surface area etc, and thereby improve the cell performances. However, the electrode preparation methods reported in literature do not provide such a vast variation of electrode properties. In addition, the porous TiO_2 layer can be replaced with a suitable other oxide i.e. ZnO or $SrTiO_3$ to obtain a higher photovoltage than expected for a porous TiO_2 layer.

2. EXPERIMANTAL

In DSSC, the TiO2 electrodes without a compact layer has been made mixing Titanium tetra-isopropoxide and Degussa TiO2 powder [2]. The electrode described in this article consists of a compact and a porous TiO2 layers and they were prepared by a similar method described in reference with some modifications [2,15]. Titanium tetra-isopropoxide (5ml, Aldrich) mixed with propan-2-ol (15 ml) and acetic acid (5.5 ml) followed by addition of water dropwisly (25 ml). Few drops of the suspension were spread on a 150°C heated conducting tin oxide glass plate, puffed off the loosely bound crust and the suspension was again spread. After three cycles, the film was sintered at 450°C for 15 minutes, loose crust on the surface was wiped off, and the process was repeated until the film resistance ~ 50 –100 kΩ. Four-probe method [16] was not successful in measuring the film resistance due to high resistance of the TiO2 film. Therefore the following indirect method was employed to measure the film resistance. 1 cm2 Pt plated conducting glass was pressed on to the 1 cm2 area of TiO2 film and the resistance across the film was noticed. By SEM analysis, the film thickness was noticed at particular film resistance. Therefore, the film resistance measurement technique described above can be used to prepare thin films with different TiO2 thickness. On the dense TiO2 film, a porous Degussa TiO2 layer, which was prepared mixing 500 mg of Degussa TiO2, 50 ml of conc. HNO3 and 2 ml of H2O in an agate motor, was applied by doctor blade method [17]. The films were dyed keeping them immersed in a 5.0 X 10^{-4} M

solution of cis-bis(thiocyanate)bis(2,2'-bipyridyl 4,4'-dicarboxylate) ruthenium(II) in ethanol for 6 hours. CuI was prepared dissolving 1 g of CuI in 30 ml of acetonitrile [2, 10] and 15 mg of triethylamine hydrothiocyanate (THT). The dye-coated plate was placed on a hot plate (~110 °C) and the CuI solution was lightly spread over the dyed surface. A Pt sputtered conducting tin oxide glass plate pressed into the CuI surface served as the back contact. The energy conversion efficiency was measured under simulated sunlight (AM 1.5, 1000 Wm^{-2} illumination) and the incident photons to photocurrent conversion efficiency (IPCE) were measured using a solar cell evaluation system. Rectification curves in the dark were recorded using dyed cells with both dense and porous TiO_2 films after coating of CuI. Electron micrographs are taken with a LEO-1400 model Scanning Electron Microscope (SEM).

3. RESULTS AND DISCUSSION

The SEM images of ~ 50 kΩ and ~ 100 kΩ resistance TiO_2 compact layers are shown in Fig.1a and 1b respectively. The formation of big TiO_2 clusters size ranging 3 – 4 mm with some void spacing is clearly visible in ~ 50 kΩ resistance electrode. Big TiO_2 clusters look amorphous and XRD analysis (not shown) confirmed the amorphous nature of TiO_2 clusters. In the SEM image shown in Fig.1b for ~ 100 kΩ resistance electrode, smaller TiO_2 particles could clearly observed and most of the void spaces are not observed, probably due to filling of void spaces by the smaller amorphous TiO_2 particles. The cross section of ~ 100 kΩ TiO_2 film shown in Fig.1c confirms the compact nature of the electrode. The thickness of ~ 50 and 100 kΩ TiO_2 dense film calculated from SEM analysis are ~ 1 and 2 μm respectively.

The solar cells made entirely with a dense TiO_2 film (TiO_2 (D)/Dye/CuI cell) having ~ 50 kΩ resistance (thickness ~ 1 μm) or a porous film prepared by Degussa TiO_2 (TiO_2(P)/Dye/CuI) did not give measurable Isc and Voc at an illumination intensity of 1000 Wm^{-2}. However increasing the film resistance to ~100 kΩ of the dense TiO_2 layer (thickness ~ 2 μm), the solar cell generated an Isc of 1.3 mA cm^{-2} and a Voc of 345 mV and the cell consisting of both ~100 kΩ dense TiO_2 layer and a porous TiO_2 layer (TiO_2 (D)/TiO_2 (P)/Dye/CuI cell) showed an Isc of 6 mA cm^{-2} and a Voc of ~500 mV at the same illumination intensity. Also for the solar cell TiO_2(D)/TiO_2(P)/Dye/CuI fabricated with a dense film having ~ 50 kΩ and ~ 75 kΩ resistance, the generated Isc and Voc are as follows; for ~ 50 kΩ dense film, Isc and Voc are ~ 0.2 mA cm^{-2} and ~ 40 mV respectively and for ~ 75 kΩ dense film, Isc and Voc are ~ 1.3 mA cm^{-2} and ~ 200 mV respectively. I-V characteristic of the DSSC consisting entirely dense TiO_2 film having resistance ~ 100 kΩ (TiO_2(D)/Dye/CuI) and the similar dense film with a porous TiO_2 film (TiO_2(D)/TiO_2(P)/Dye/CuI) are shown in Fig.2. The maximum energy conversion efficiency and the fill factor derived from the Fig.2 are 0.12% and 28% respectively for the cell TiO_2(D)/Dye/CuI while for TiO_2(D)/TiO_2(P)/Dye/CuI cell, the corresponding values are 1.74% and 58% respectively. The optimum Isc and Voc reported here are superior to the Isc

(2.5 mA/cm^2) and Voc (375 mV) values reported in [2] for a solar cell without a TiO_2 barrier layer under similar conditions.

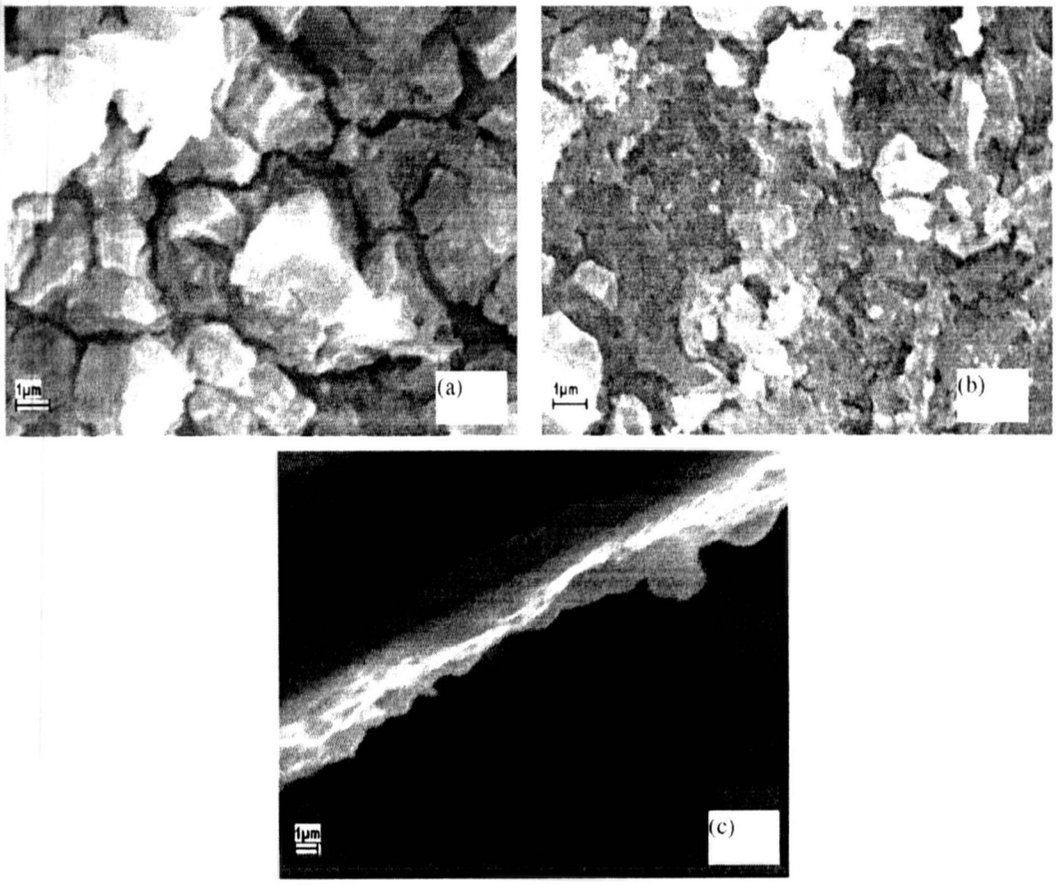

Figure 1. The SEM images of (a) ~ 50 kΩ and (b) ~ 100 kΩ resistance compact TiO_2 layers and (c) the cross section of ~ 100 kΩ resistance compact TiO2 film.

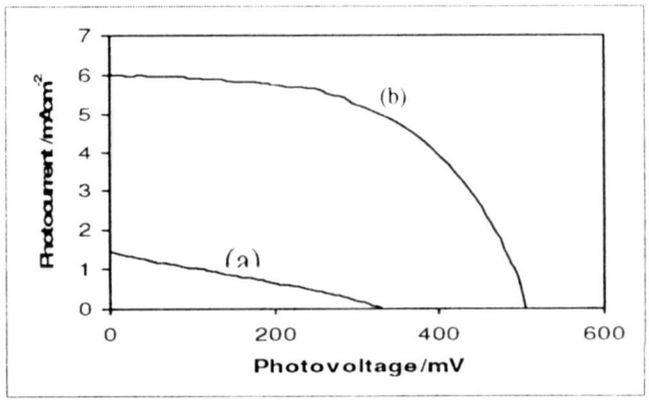

Figure 2. I-V characteristic of the DSSC consisting (a) entirely dense TiO_2 film having resistance ~ 100 kΩ (TiO_2(D)/Dye/CuI) and (b) the similar dense film with a porous TiO_2 film (TiO_2 (D)/TiO_2(P)/Dye/CuI)

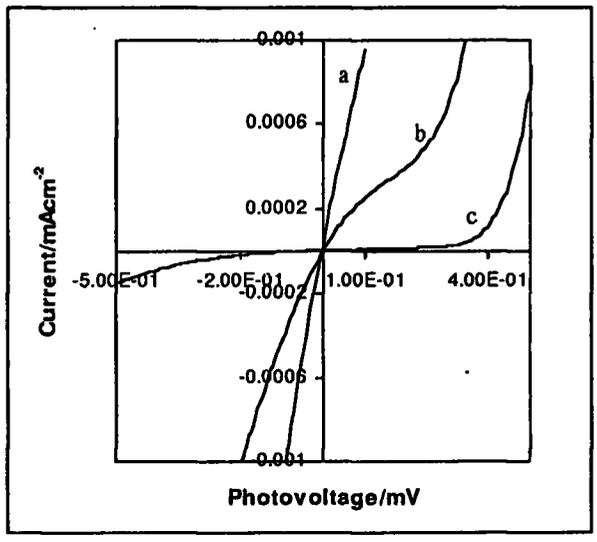

Figure 3. Dark I-V characteristics of DSSC made from (a) TiO2(D)/Dye/CuI, (b) TiO2(D)/Dye/CuI and (b) TiO2(D)/TiO2(P)/Dye/CuI. For curve (a), the resistance of the dense TiO2(D) layer is 50 kΩ while for curves (b) and (c), 100 kΩ TiO2(D) films were employed.

The dark I-V curves for the cells in the forward and reverse bias directions are presented in Figure 3 For the dense TiO_2 film with ~ 50 kΩ resistance (curve a), rectification characteristics needed for functioning as a photovoltaic device is absent. However, rectification has been improved for the dense film with ~ 100 kΩ resistance (curve b), which justifies the observed higher Isc and Voc for such electrodes than lower resistance electrodes. A dramatic increase in rectification was observed in the presence of both a porous TiO_2 layer and a dense TiO_2 film with ~ 100 kΩ resistance (curve c). Therefore, it can be concluded that the presence of both dense and porous films was found to be necessary for good rectification action.

Figure 4 shows the action spectra of the DSSC made from entirely of dense TiO_2 (curve a) film and containing both dense and porous TiO_2 layers (curve b). The photocurrent action spectra of both cells give a peak at ~540 nm with the maximum IPCE 5% and 20% (corrections were not made for losses) respectively for TiO_2(D)/Dye/CuI and TiO_2(D)/TiO_2 (P)/Dye/CuI solar cells and matches the absorption spectra of Ru-dye. The lower IPCE of the cells made entirely from dense TiO_2 could be due to poor dye adsorption of the dense TiO_2 film. Dye adsorption studied revealed that in the presence of both porous and dense layers, amount of dye adsorption was 5.53×10^{16} molecules cm^{-2} while for the dense layer alone the dye-adsorbed amount was 5.13×10^{15} molecules cm^{-2}. Therefore, the poor cell efficiency of TiO_2(D)/Dye/CuI can be understood on the basis of dye adsorption amount.

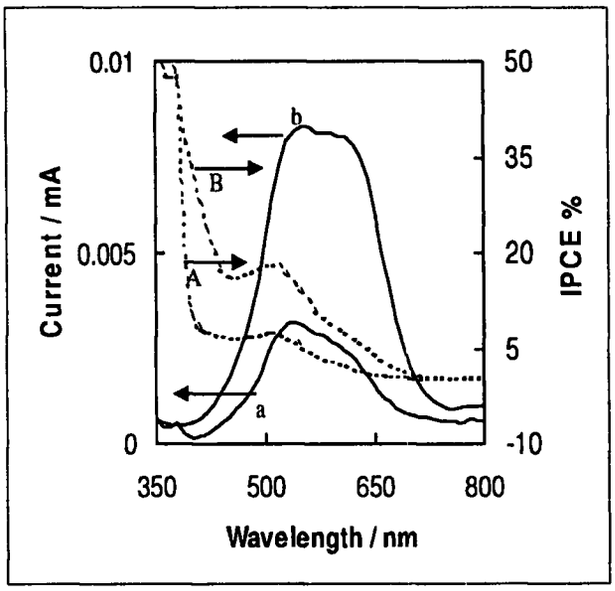

Figure 4. Photocurrent action spectra of (a) TiO2(D)/Dye/CuI, (b) TiO2(D);TiO2(P)/Dye/CuI and IPCE of the cells (A) TiO2(D)/Dye/CuI, (B) TiO2(D);TiO2(P)/Dye/CuI.

The results presented above clearly indicated that the presence of a compact TiO2 layer increases the solar cell performance. It was observed that the variation of thickness and resistance of the compact TiO2 layer results in change in both Isc and Voc. The optimum resistance and thickness were found to be ~ 100 kΩ and ~ 2 μm respectively. As the resistance increases above ~ 100 kΩ, Isc begins to decrease while Voc remains almost the same value.

The possible explanation could be that as the resistance and thickness increases, the compact layer itself acts as a barrier for electron flow and hence charge recombination increases. The decrease in compact layer thickness and resistance i.e. electrode with ~ 75 kΩ resistance and ~ 1.5 μm results in decrease in both Isc and Voc and the SEM images shown in Fig.1 justifies the above results. As shown in Fig.1, the voids spaces are clearly noticeable for SEM image of ~ 50 kΩ and no voids spaces are clearly noticeable for ~ 100 kΩ resistance TiO_2 compact layer. The void space present in 1 mm thin film (~ 50 kΩ) may get filled with CuI and could act as short circuit paths in DSSCs resulting in lower Isc and Voc for the solar cells constructed with those films. However, for ~ 100 kΩ resistance electrode, void spaces are not observed, probably due to filling of void spaces by the smaller amorphous TiO_2 particles resulting in blocking the short-circuit paths. However, the void space cannot be filled indefinitely with a thicker layer of TiO_2 as it leads to increase the resistance of the barrier. Therefore, we assume that the optimum resistance and thickness is the results of two competing effects of voids filling and barrier resistance. It was noticed that both the efficiency and the fill factor increase as the incident light intensity decreases. At the light intensity of 100 Ωm^{-2}, the efficiency is 1.9% compared to the 1.7% at illumination intensity of 1000 Ωm^{-2}. This is the general behavior of solar cells with short-circuit paths and these recombination

losses could be either due to recombination via void spaces or due to surface recombination [2,14]. However, the efficiency difference with the variation of light intensity reported in this article for the electrode TiO_2(D)/TiO_2(P)/Dye/CuI is less than the efficiency at different light intensities reported in literature [2, 14], suggesting that the short-circuit paths have been reduced drastically.

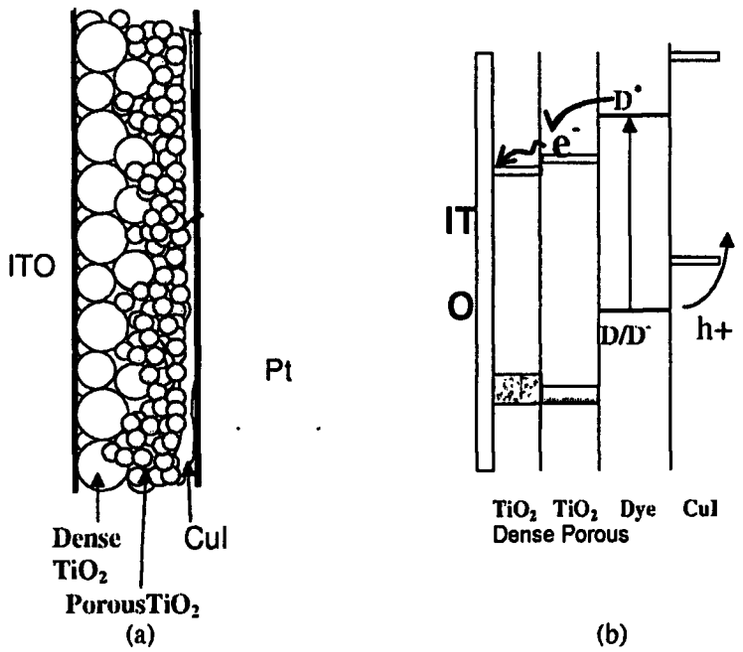

Figure 5. (a) Schematic diagram illustrating the structural morphology of the DSSC of TiO2(D);TiO2(P)/Dye/CuI, (b) An energy level diagram showing the relative positions of the bands of TiO2, CuI and ground and excited energy levels of the dye.

Schematic diagram illustrating the structural morphology, energy level diagram showing the relative positions of the TiO_2, dye, CuI are shown in Fig.5 and the function of the compact TiO_2 layer can be explained as follows. As shown in Figure 5, the electrode was consisting of both dense and porous TiO_2 films. The dye was mainly adsorbed on the porous TiO_2 layer, which was perfectly separated from the conducting glass by the dense TiO_2 film. As Ru-dye was coated mainly on the porous TiO_2 layer, the photocurrent generation could occur mainly via the excitation of dyes of the porous TiO_2 layer. Photoexcited dye at the porous TiO_2 surface injects an electron into the CB of TiO_2 and a hole is transferred to CuI. The electron crosses to the CB of dense TiO_2 layer traversing through the porous TiO_2 layer. The CB position of the compact TiO_2 layer was found to be situated below or close to the CB position of porous TiO_2 layer. Therefore, the band energies facilitate the crossing of an electron from the CB of porous TiO_2 layer to the CB of dense TiO_2 layer leading to well separated electron and hole minimizing charge recombination. However, the major problem in DSSC is the short-circuiting due to penetration of CuI and makes direct contact with the conducting glass. The dense TiO_2 layer acts as a barrier for penetration of CuI into conducting

glass and short-circuiting. However, thickness and the resistance of the barrier layer were found to be the crucial parameters when fabricating the electrodes for solid-state dye sensitized solar cells. The highest solar cell efficiency was observed when the thickness and the resistance of the dense TiO_2 layer were ~ 2 μm and 100 kΩ respectively. Decrease in thickness/resistance causes short-circuiting problem while increase in thickness/resistance causes movement of photo-injected electrons more difficult leading to poor cell efficiency. However, the electrode with a dense TiO_2 film having optimum thickness and resistance provides opportunity to modify the properties of the second porous layer very easily for DSSCs to optimize the Voc and Isc. In addition, fabrication of such electrodes is much easier than the earlier reported methods [2,10]. Preliminary results indicated that the coating of porous ZnO or $SrTiO_3$ layer on dense TiO_2 layer leads to higher Voc and Isc.

4. CONCLUSION

According to the results presented above, efficiency of the DSSC with the electrodes consisting of both dense and porous films is higher than that of DSSC made entirely of the dense films while DSSC made entirely from the porous TiO_2 film or dense film with low resistance/thickness showed negligible photocurrent and photovoltage. The higher efficiency was originated as a result of the dense TiO_2 layer prevents short-circuiting problem, while the porous layer enhances the dye adsorption amount. The thickness and the resistance of the dense TiO_2 layer were found to be the major factors, which determine the overall cell performance. The dense TiO_2 layer with the correct thickness and the resistance provides opportunity to modify the properties of the second porous layer very easily for DSSCs to optimize the Voc and Isc.

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