

Cambridge University Press

978-1-107-40908-8 - Materials for Photovoltaics: Materials Research Society Symposium

Proceedings: Volume 836

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## **Dye-Sensitized Solar Cells**

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Mater. Res. Soc. Symp. Proc. Vol. 836 © 2005 Materials Research Society

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### Progress in Producing Large Area Flexible Dye Sensitized Solar Cells

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#### ABSTRACT

Dye sensitized nanocrystalline TiO<sub>2</sub> solar cells have been reported with over 11% efficiency and are extremely promising as very low cost and lightweight photovoltaic sources. However, most reports are for cells of low area fabricated on glass, which withstands processing temperatures of ~450°C. In this paper, we describe the fabrication and performance of cells made on flexible ITO-coated polyethylene terephthalate (PET) substrates with 6" x 3" dimensions. To improve the efficiency in the cells, we enhanced the ITO current collection efficiency with metallization fingers. The fingers resulted in a >10 fold increase in short-circuit current under normal solar illumination compared to cells without metallization. Further improvements were realized by passivating the metallization fingers at the metal/polymer electrolyte interface.

#### INTRODUCTION

Dye sensitized solar cells (DSSC) are usually prepared by first depositing colloidal TiO<sub>2</sub> onto a transparent conductive oxide coated glass substrate. The colloidal layer is then sintered at ~450°C to form a porous pure anatase layer 5-10 μm thick. Next, the layer is exposed to a solution of a sensitizing dye carrying -COO<sup>-</sup> functional groups, which are believed to bind to the Ti<sup>4+</sup> surface sites. The Ru(II) complexes usually employed as sensitizing dyes apparently undergo electron transfer to the Ti(IV) sites on nearly the optical time scale, leaving the oxidized sensitizer, a process which has been argued to protect the dye against slower irreversible photodegradative pathways. These sensitized electrodes may be used as the photoanode in regenerative photoelectrochemical (PEC) cells. The regenerative redox couple is typically I<sup>-</sup>/I<sub>3</sub><sup>-</sup> in a liquid nonaqueous electrolyte. Grätzel and co-workers were the first to have reported >11% solar conversion efficiencies for small area devices [1].

At its current state of development, at least in the published literature, the DSSC has relied mostly on the use of glass substrate materials. Glass is used because it is optically transparent and it can withstand the high temperature annealing currently required to achieve high photoactivity of the nanoporous TiO<sub>2</sub>. However, lightweight polymer substrates are clearly advantageous for portability, adaptability and ease of handling. Furthermore, the use of liquid electrolytes is unacceptable due to sealing difficulties and inhomogeneous electrolyte distribution, especially if a flexible version of the DSSC is to be realized [2].

It is the purpose of this study to evaluate DSSCs in a flexible, large-area cell configuration. To achieve this, we have employed a commercial ITO-coated polymer as the substrate rather than glass. The electrolyte is based on a plasticized polyvinylidene difluoride (PVDF) composition derived from a material used in flexible Li-ion batteries. Cells were nominally 6"x3" (active area somewhat lower), which is much larger than has been reported previously for flexible DSSCs. However, such large areas are essential for most practical applications.

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## EXPERIMENTAL DETAILS

### Baseline cell

The basic DSSC cell design is a trilayer laminate with a polymer gel electrolyte. The supporting substrate was a commercially available polyester (polyethylene terephthalate, PET) coated with ITO provided by CPFilms, Inc. The lowest available sheet resistance is 60 ohms/sq. We obtained this in 5 mil thickness. The maximum temperature without significant distortion is given by the manufacturer as 150°C. Substrates were cut to the desired cell size, in this case 6"x3". The photoanode was spray coated while heating to 95°C with 5-10 microns of a Degussa P25 nanocrystalline TiO<sub>2</sub> photoanode precursor slurry, with the carrier solvent evaporating on contact. The TiO<sub>2</sub> slurry consisted of 36g TiO<sub>2</sub>, 165ml deionized water, 2.1ml acetyl acetone, and 0.15g of polyethylene glycol. The PET/ITO/TiO<sub>2</sub> substrates were then annealed at 150°C under flow of O<sub>2</sub> for 8 hours. Following annealing, the coated substrates were transferred to an Ar atmosphere glove box, heated to 95°C to drive off remaining water. They were then placed in a sensitizing dye solution (cis-(SCN)<sub>2</sub>bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium, or "N3") in anhydrous ethanol (0.045g/100 ml). The films remained in the dye for several hours and were then rinsed several times with ethanol. The dye-sensitized films appeared dark purple color.

The counter electrodes were made by dc magnetron sputter coating PET|ITO substrates with titanium (~40 nm) and then platinum (~60 nm) to provide a uniform adherent metallization.

The electrolyte was a plasticized polymer based on polyvinylidene difluoride, PVDF (Solvay Solef 21216). The PVDF was combined with plasticizer solvents (propylene carbonate, PC, and ethylene carbonate, EC) and redox electrolyte (t-butyl ammonium iodide plus I<sub>2</sub>) in the weight ratio 1:1.2:3.0:0.95:0.03. The PVDF was ground in a mortar with a small amount of the plasticizer until a smooth slurry was formed and then allowed to stir overnight with the rest of the plasticizer. The semisolid electrolyte was then placed on the Pt counter electrode and heated at 90°C for about 5 minutes following which the TiO<sub>2</sub> was placed on top face down and clamped in place for several hours to set. The two opposite facing electrodes were offset to allow for contacts and edge sealing. Finally the cells were cleaned and sealed with Dow Corning RTV 9-1363 adhesive along the edges to prevent entry of water and oxygen. Edge contacts were reinforced with a wire adhesive mesh. Cell assembly and sealing were conducted in the argon-controlled glove box.

### Metallization of baseline cells

To improve current collection on the 6" x 3" solar cells, metallization fingers were deposited onto the PET/ITO substrates before TiO<sub>2</sub> deposition. The metallization fingers were made by sputter-depositing a metal onto the PET/ITO through an aluminum stencil mask. The metallization pattern consists of 7 fingers, each 2.5" long and 0.1" wide, along with 0.25" wide busbar along the edge of the PET/ITO. The resulting loss of area from depositing the grid is approximately 13%.

Cells were assembled in an identical manner to the baseline cell. Several kinds of metallization grid treatments were compared: 1) a "thick" 100 nm Ir grid with a 50 nm Ti adhesion layer made by dc magnetron sputtering, 2) a "thin" ~1 nm semitransparent Ir grid, 3) a Ir grid with a layer of TiO<sub>2</sub>, and 3) the entire substrate and grid structure with a 100 nm layer of

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sputtered TiO<sub>2</sub>. The TiO<sub>2</sub> coated grids, configuration 3), were made by a wet oxidation process in which the Ir grids were first coated with 100 nm Ti in the same pump-down cycle. The substrates were then introduced into a furnace at 150°C under a flow of oxygen bubbled through DI water.

## RESULTS AND DISCUSSION

### Cell characteristics

The current-voltage (I-V) characteristics of the cells were measured using a potentiostat in the dark and under outdoor sunlight, ~40 mW/cm<sup>2</sup>. A compilation of the dark current responses of the cells with different grid treatments is shown in Figure 1. The bare metallization grids, which were deposited onto the ITO to reduce the sheet resistance, caused a marked increase in the dark current. This is a result of the oxidation/reduction reaction of the iodide redox system at the metal/electrolyte interface. Such reactions effectively create a short-circuit in the cell.

Since the metallizations need only create a lower resistance current path for electrons on the ITO, it should be possible to passivate the metal/electrolyte interface by adding an additional resistive layer on the metallization surface (see below). Sputtering Ti onto the Ir grids during the grid deposition process produced grids with a Ti/Ir/Ti structure. The top Ti layer was converted to TiO<sub>2</sub> by a wet oxidation process. Cells made from the resulting substrates showed markedly reduced dark current on polarization between -0.6 to 0.6V. Metallizations were also passivated by reactive dc sputter deposition of TiO<sub>2</sub> over the entire active area, a process which reduced the dark current even more, and below that observed for cells without grids.

The I-V characteristics of the cells were greatly affected by the grid structures. Examples are shown in Figure 2. Cells without grids had very low photocurrents, on the order of 5 mA at short-circuit. Open-circuit photovoltages exceeded 0.6V, however. Introducing the grids increased the short circuit photocurrents approximately 10-fold, but the photovoltage, the point where  $I_L + I_D = 0$ , was reduced to less than 0.4V due to the large dark currents. The most effective treatment was passivation of the grids and the ITO with a thin layer of sputtered TiO<sub>2</sub>. This reduced the dark current to the level of the ungridded cells, increasing the photovoltage to >0.5V. Photocurrents for these cells were on the order of 60 mA at 0V.

As a demonstration, we fabricated 16 cells with the sputtered TiO<sub>2</sub> passivation over the photoanode substrate and arranged them into a series-parallel array, shown in Figure 3, by making interconnects between them. The total active area of each cell (without grid) is 5.5" x 2.5" = 13.75 in<sup>2</sup> = 88.71 cm<sup>2</sup>. The opaque grids cover 12.7% of the ITO, producing a real active area per cell of 77.4 cm<sup>2</sup>. Before assembly, and up to one month after their fabrication, cells were tested under solar illumination. Typical output of the as-prepared individual cells is shown in Figure 2. The maximum power point of ~8 mW/cm<sup>2</sup> resulted in a single cell efficiency of 0.25%. However, some of the cells to be used in construction the array gave less than optimal performance, possibly due to leakage of the edge seals. Nevertheless, this was the first demonstration of a complete array of individual, externally connected DSSC cells on flexible polymer substrates.

A test of the array of 16 cells in sunlight at a measured intensity of 25 mW/cm<sup>2</sup> provided a V<sub>oc</sub> of 2.51-2.56V and an I<sub>sc</sub> of 0.095-0.12 amps. The V<sub>oc</sub> represents four cells in series and the I<sub>sc</sub> four cells in parallel. The values are close to those expected for this run of cells under the given intensity.

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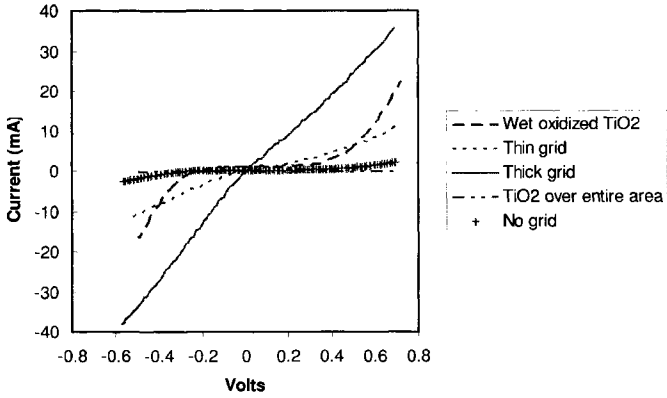
### **Current Collectors in DSSCs**

The current collection at the transparent conducting oxide layer is a major source of power loss in the DSSC and other photoelectrochemical cells of this basic design. Typical transparent conducting oxide layers on polymer substrates, for example, are on the order of 100 ohms/sq. The effect can be seen by considering two solar DSSC solar cells, one with an area of 1 cm<sup>2</sup> and the other with an area of 100 cm<sup>2</sup>. Consider under identical illumination conditions that both cells are generating a current density of 10 mA/cm<sup>2</sup>. Thus, the total current that must be withdrawn from the 1 cm<sup>2</sup> and 100 cm<sup>2</sup> cells is 10 and 1000 mA, respectively. The resistive contribution from the transparent oxide is roughly the same for the two square sizes. Thus, the IR loss is approximately 100 times greater in the larger cell.

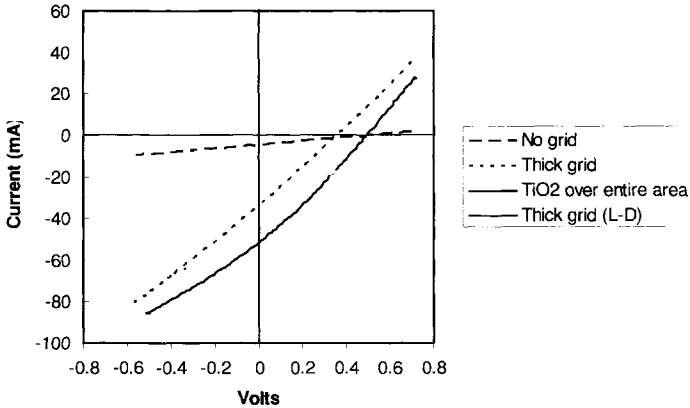
A well-established method to reduce the sheet resistance on traditional solar cells is to employ current collection metallization patterns, in the form of strips, grids, etc. These are able to collect current over smaller local areas and direct it to a current collection busbar via a low resistance metallization pathway. The patterns can be designed to occlude a minimum fraction of the active area while maximizing the overall reduction in resistive losses [3].

In the case of the DSSC, these metallization lines need to be disposed in direct electrical contact with the transparent conductive oxide, which is in turn disposed on the inner surface of the front transparent substrate. Figure 4A illustrates this arrangement schematically. It is seen, however, that current (electrons) collected on the grid is available at the grid/electrolyte interface. There, electrons can react with the I<sub>3</sub><sup>-</sup>, reducing it to I<sup>-</sup>. This in effect creates a short-circuit in the cell and reduces the current flowing through the external circuit. We observe in Figure 1 and 2 that, while the placement of metallization fingers on the ITO does indeed generate a large “dark current” indicative of this short-circuiting, large increases in the short-circuit photocurrent are still realized with this approach.

The cell design in Figure 4B further provides metallizations in which the metal/conductive oxide interface is preserved, but the metal/electrolyte reaction is prevented or suppressed. This could be achieved by several approaches, such as 1) using a metallization in which the electrochemical reduction of the redox species is extremely slow, 2) coating the metallization with an ion exchange material which rejects the redox species, or 3) coating the metallization with an electrical insulator. Figure 4 illustrates this modification with an insulator. Very recently 10 x 10 cm<sup>2</sup> DSSCs have been reported on glass with a 4.3% solar conversion efficiency using Ni grids to reduce the sheet resistance of the FTO (F-doped tin oxide) to 0.28 ohms/sq [4]. These cells employed very low sheet resistance FTO to begin with (4.8 ohms/sq) compared to ~60 ohms/sq that we are able to obtain on PET [3] and a TiO<sub>2</sub> processing temperature of 450°C. They also employed a liquid electrolyte.



**Figure 1.** Dark current vs. voltage for 6"x3" cells with and without Ir grids. Thin and thick grids correspond to 1 nm and 100 nm.



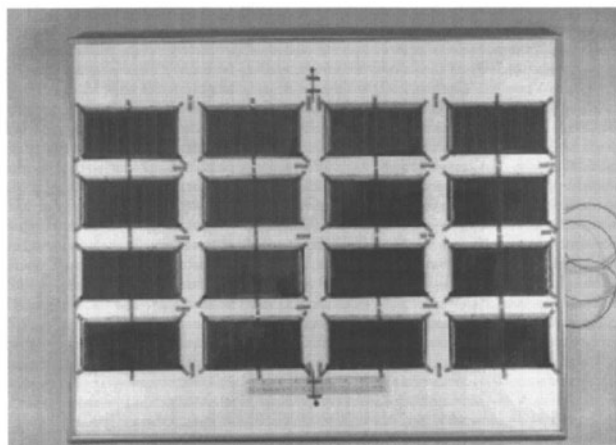
**Figure 2.** Photocurrent vs. voltage for cells with and without Ir metallization grids. The L-D trace subtracts the large dark current from the total current in the light. Also shown is the output of a cell with a uniform dense layer of TiO<sub>2</sub> sputtered over the entire grid and active area.

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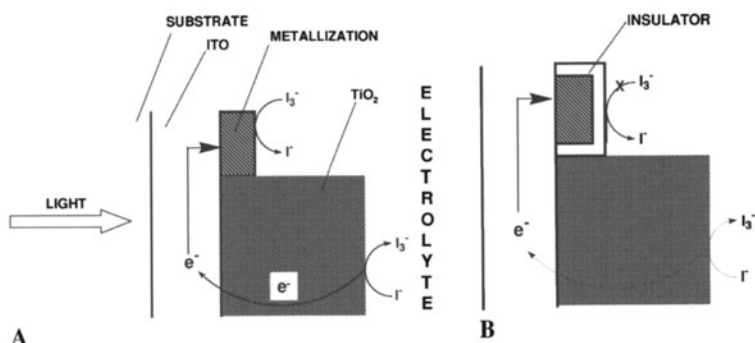
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**Figure 3.** DSSC 16-cell panel. Cells are arranged in 4 parallel sets of 4 cells in series. (Ruler is 8" long).



**Figure 4.** An interior cross section of the photoactive, current collection and electrolyte elements of a DSSC, along with the metallization segments. A. metallization creating a short-circuit at the metal/electrolyte interface. B. Addition of insulation on the metal surface prevents back reaction with redox system.

We employed Ir as the metallization since it is a very conductive noble metal which will not corrode in contact with the electrolyte. However, it is also an excellent electrocatalyst, which results in a large dark current. Recently Ni was used as the metallization grids [4], which was shown to give lower dark currents than Au or Pt. In our work, cells were generally improved by insulating the Ir metallization, either by a layer of  $\text{TiO}_2$  directly on the grids or over the entire active surface. Preliminary results also indicate that the cells with a dense, thin  $\text{TiO}_2$  layer over the entire surface had a longer shelf-life. This is to be expected since the conductive oxides



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available on plastics tend to be of lower density and generally poorer quality than that obtainable on glass using higher processing temperatures.

## CONCLUSIONS

There are several areas for improvement of these large area flexible cells before they can be considered as viable candidates for portable power. In particular, we would like even closer spaced and finer conductive grids to reduce the ITO sheet resistance further. These would be produced by photolithographically defining the pattern, then possibly by electroplating of Ni, which has been shown to produce low dark currents in DSSCs. We also seek flexible substrates that can endure higher processing temperatures, such as high  $T_g$  plastics or microsheet glass. A related issue is with the quality and high sheet resistance of current commercially available ITO coated PET, which is much inferior to what is available on glass. Indeed, to scale up these cells on flexible substrates will require new developments in these areas. Further improvements in the electrolyte conductivity and effective thickness might be realized in order to optimize the efficiencies of laminated devices. Finally, DSSCs in general have yet to undergo the kind of durability testing that will be required for the wide range of environmental operating conditions.

## ACKNOWLEDGMENTS

This work is partially supported by the DOE (DE-FG02-98ER82567), NASA (NAS5-01173 & NNC04CA98C), United States Air Force (AFRL/MLQD, F08630-02-C-0074) and MDA (AFRL/VSSV FA9453-04-M-0283).

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3. See, for example, A. R. Burgers, *Prog. Photovolt: Res. Appl.* **7**, 457 (1999).
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