

## DYE-SENSITIZED NANOCRYSTALLINE TiO<sub>2</sub> SOLAR CELLS ON FLEXIBLE SUBSTRATES

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**ABSTRACT:** In this paper a new concept for the dye-sensitized nanocrystalline titanium dioxide solar cell is introduced. The innovation involves the substrate which is a polymer foil instead of glass. This innovation can be a breakthrough in the processing of the nc-DSC's on an industrial scale, because polymer foils are more easy to handle in processing steps as cutting of larger entities into smaller individual modules. Moreover, the processing of foil into flexible solar cells can be realized by means of a continuous roll to roll process, whereas for the glass analogue batch processes are the general rule. This implies that for the flexible nc-DSC a higher throughput can be realized. Also, special applications requiring some flexibility of the solar cell, such as smart cards, come into play. In this paper the efficiency and stability of the nc-DSC's on polymer foil is considered in comparison to the analoga on glass.

Keywords:TiO<sub>2</sub> - 1: Plastic - 2: Stability - 3.

### 1. INTRODUCTION

A new type of solar cell based on dye-sensitized nanocrystalline titanium dioxide has been developed by M. Grätzel and coworkers [1,2]. Remarkably high quantum efficiencies have been reported for this type of solar cell (a so called nc-DSC), with overall conversion efficiencies up to 11 % [3]. This fact, in combination with the expected relatively easy and low cost manufacturing makes this new technology an interesting alternative for existing solar cell technologies.

Realisation of stable efficiencies in the order of 10 % in production, however, requires a lot of effort on the research and development side. For this reason, the first application of this type of solar cell will probably be one in which only a low power output is required, since this is easier to achieve. Less stringent efficiency requirements leave room for increased flexibility in the manufacturing process of these cells, i.e. the requirements that are put on the materials used are less severe. This results in lower manufacturing costs and more flexibility in materials choice, opening the way for alternative production processes.

One alternative concept for the nc-DSC is based on the introduction of polymer foils as a substrate instead of glass. This opens the way to attractive roll to roll production processes and special applications in which flexibility of the solar cell is to some extent required. Moreover processing and handling of polymer foil devices in general is easier than for the glass version.



### 2 WORKING PRINCIPLE AND MANUFACTURING

#### 2.1 Working principle of nc-DSC's

nc-DSC's are based on a wide bandgap semiconductor, usually TiO<sub>2</sub>, which is sensitized for visible light by a monolayer of adsorbed dye. The most frequently used dye is, for reasons of best efficiencies, cis-(NCS)<sub>2</sub>bis(4,4'-dicarboxy-2,2'-bipyridine)-ruthenium(II).

The photoelectrode in such a device consists of a nanoporous TiO<sub>2</sub> film (approx. 10µm thick) deposited on a layer of transparent conducting oxide on glass (Fig.1). The counter electrode also consists of SnO<sub>2</sub>:F coated glass on which a small amount of platinum catalyst is deposited.

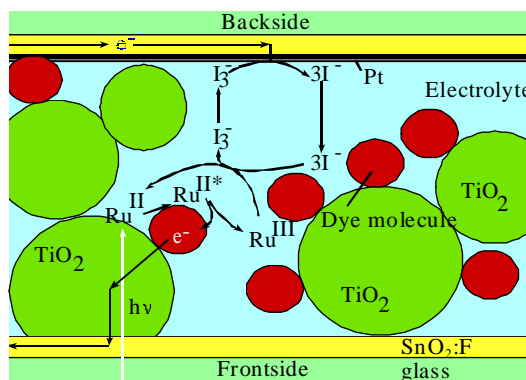


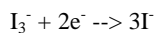
Fig. 1. Working principle of a nc-DSC.

In a complete cell, photo- and counter electrode are clamped together and the space between the electrodes and the voids between the TiO<sub>2</sub> particles are filled with an electrolyte. This electrolyte consists of an organic solvent containing a redox couple, usually iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>).

A dye monolayer on a flat surface absorbs less than 1 % of the incoming light (one sun conditions). To obtain reasonable efficiencies comparable to established solar cell technologies, in the nc-DSC the surface area is enlarged by a factor of 1000, by using nanoparticles of TiO<sub>2</sub> with a diameter of approximately 10-20 nm.

The working principle of the nc-DSC is based on excitation of the dye followed by fast electron injection into the conduction band of the TiO<sub>2</sub>, leaving an oxidized dye

molecule on the TiO<sub>2</sub> surface. Injected electrons percolate through the TiO<sub>2</sub> and are fed into the external circuit. At the counter electrode, triiodide is reduced to iodide by metallic platinum under uptake of electrons from the external circuit:



Iodide is transported through the electrolyte towards the photoelectrode, where it reduces the oxidized dye. The dye molecule is then ready for the next excitation/oxidation/reduction cycle.

## 2.2 Manufacturing of nc-DSC's

In this section the general basic manufacturing technology for nc-DSC's on glass substrates is described. The first process step consists of the preparation of the photo electrode by deposition of a layer of nanocrystalline titanium dioxide onto the SnO<sub>2</sub>:F coated glass substrate. On an industrial scale this can be realized by means of screen printing of a screenprintable medium, containing a TiO<sub>2</sub> colloidal suspension. This layer is dried and sintered in a furnace at 450-550 °C to eliminate organic residues of the screen print medium and to establish electrical contact between the TiO<sub>2</sub> particles.

After cooling down of the photo electrode, it is stained by emerging the electrode in a solution of organic dye for a certain period of time.

After drying the stained photo electrode is assembled with the platinized counter electrode and a thermoplastic thin film in between (not on the active cell surface). The two electrodes are sealed together by heating up to 150°C and applying pressure.

The cell is completed by filling with electrolyte through small prefabricated holes in the counter electrode. The electrolyte is spread in the very small space between the electrodes (approx. 10µm) by capillary forces. Finally, the holes are sealed with the thermoplastic film and small cover glasses.

## 3. INTRODUCTION OF NC-DSC'S ON POLYMER FOIL

Switching from glass to polymer foil as a substrate for nc-DSC's brings about that several concessions have to be made regarding the parameters in the production process, the efficiency and the stability of the cell. Factors of concern are the following:

**Stability:** In practical tests where polymer foil nc-DSC's are used to power a watch or calculator, the power output of the cells appeared to decrease with time and eventually became zero within several weeks. The following factors could be the cause behind the observed instability:

- 1) TiO<sub>2</sub> on polymer foil substrate is sintered at a maximum temperature of 150 °C. This TiO<sub>2</sub> could exhibit instability of the mechanical integrity or residual organic materials could disturb the cell chemistry.
- 2) The use of polymer foil as a substrate introduces new parameters in the delicate cell system. Depending on chemical composition of the foil, the cell stability could be influenced by components like plasticizers or stabilizers that are leached out of the substrate by the electrolyte. In the second place, polymer foils are permeable for water vapor which can influence the cell stability in a negative way. This potential problem could either be solved by applying water

vapor barrier coatings to the foil or by modifying the cell chemistry.

- 3) The transparent conductive coating of indium tin oxide (ITO) on the polymer foil could be intrinsically instable, possibly due to temperature treatment of the foil.
- 4) The galvanic platinum on the counter electrode could be inactivated during cell operation.

**Efficiency:** the cell efficiency is related to the sinter temperature of the TiO<sub>2</sub>. In the standard process for glass cells, temperatures between 450 and 550 °C are used. In the case of polymer foil substrates lower sinter temperatures are required to avoid melting of the substrate. For regular compositions of the screen print media used, this imposes that probably not all organic material is burnt out, which can effectively block the functioning of the solar cell. In the experiments described in this paper a special screenprint medium has been applied which can be sintered at lower temperatures without introducing an adverse effect due to organic residues in the final nanoporous TiO<sub>2</sub> layer. This results in a decreased cell performance, i.e. lower currents. However, these photo electrodes still exhibit a sufficient power output for several indoor applications such as calculators, solar watches or smart cards. Table I presents several data on power consumption for these applications.

Table I: Data on power consumption of indoor applications

	current (µA)	voltage (V)	area (cm <sup>2</sup> )
calculator	2-3	1.5	2-3
watch	0.6-1	1-1.2	5-7
smart card	5-10	1.5	4-8

To be able to maintain a high temperature sintering process while using polymer foil substrates, alternative polymers could be applied. Polymers exist which are fairly stable up to temperatures around 400-500 °C, however these are not by definition good candidates to serve as a substrate for the nc-DSC. The reason for this is that in general higher temperature stability in polymers is realized by applying aromatic systems which are more or less intensely colored, filtering out a part of the incoming light. This means that a compromise foil has to be found which combines thermal stability with sufficient transmission characteristics.

In this paper efficiency and stability of nc-DSC's on polymer foil have been studied by continuous illumination and monitoring of IV-characteristics with time. Cells on polymer foil and on glass substrates manufactured by identical techniques (low temperature sintering) have been compared to study the intrinsic stability of low temperature sintered TiO<sub>2</sub> photoelectrodes.

## 4. EXPERIMENTAL METHODS

### 4.1 Cell preparation

Photo electrodes have been prepared both on glass substrates and on polymer foil, i.e. polyethyleneterephthalate (PET), by means of doctor blading [2]. The titanium dioxide paste used in this process has been developed for sintering at lower temperatures (150 °C) but has also been applied to the electrodes on glass substrates which have been sintered at 450 °C. Titanium dioxide pastes were based on commercially available P25 from Degussa or on in house synthesized colloid. The latter material was synthesized by hydrolysis of an organic titanium precursor according to the procedure described in literature [1].

The colloid was processed to produce a titanium dioxide paste that can be deposited onto glass or polymer foil substrates.

Several sintering temperatures have been applied to the photo electrodes: 150 °C for the polymer foil electrodes, 150 °C and 450 °C for the glass electrodes.

After sintering for 30 minutes the photo electrodes have been emerged overnight in a solution of  $3 \cdot 10^{-4}$  M cis-(NCS)<sub>2</sub>bis(4,4'-dicarboxy-2,2'-bipyridine)-ruthenium(II) in ethanol.

Counter electrodes have been prepared by deposition of a thin layer of a 150 mM solution of H<sub>2</sub>PtCl<sub>6</sub> in isopropanol and subsequent heating at 450°C for 30 minutes. Temperature sensitive polymer foil counter electrodes have been made by a galvanic platinisation process.

Cell assembly has been carried out according to the procedure described in section 2.2. The electrolyte composition was as follows: 0.5 M LiI, 0.05 M I<sub>2</sub> and 0.4 M tert-air-butylpyridine in methoxypropionitrile.

#### 4.2 Characterization and stability testing

Cells have been characterized at Solaronix and at ECN, using fluorescent tube lamps with a light intensity of 50-5000 lux to mimic indoor artificial light conditions. IV characteristics have been determined with a Keithley 2400 source meter. Stability tests have been carried out using the same fluorescent tube lamps and for high intensity irradiation a UV filtered xenon lamp (120.000 lux). Cells have been under continuous illumination and IV characteristics of individual cells have been monitored with time. Light intensities have been measured using a lux meter (Licor 188B integrating quantum radiometer)

### 5. RESULTS AND DISCUSSION

#### 5.1 Cell efficiency

IV measurements under 250 lux illumination of nc-DSC's on polymer substrates (PET) revealed an open circuit voltage of 0.48 V, a short circuit current of  $15 \mu\text{A}/\text{cm}^2$ , a fill factor of 67 % resulting in a "low level illumination efficiency" of 2.3 %. The light intensity of 250 lux represents low light, i.e. typical of indoor conditions. Taking into account that the averaged power demand of a calculator is  $10 \mu\text{W}$ , a polymer foil nc-DSC of the size of 5 cm<sup>2</sup> is able to deliver this amount of energy down to a light intensity of 100 lux.

A polymer foil cell exposed to 1 sun irradiation with an area of 1 cm<sup>2</sup> can deliver up to 0.7 V. The short circuit current is limited to 2 mA. Polymer foil nc-DSC's give the same voltage and, depending on the irradiation intensity, the same fill factor as the known nc-DSC's on glass substrates, which are sintered at higher temperatures. The lower sinter temperatures used during the manufacturing of the polymer foil cell apparently only affect the short circuit currents, which are lowered by approx. a factor of two relative to the glass version.

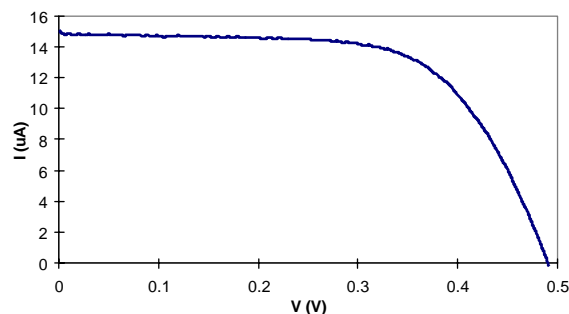


Fig. 2. IV characteristic of a nc-DSC on PET at 250 lux

#### 5.2 Results of stability testing

Figure 3 represents the short circuit current with time for several types of nc-DSC's, all under continuous illumination of approximately 4000 lux. Table II comprises the composition and relevant manufacturing data for the different cells depicted in figure 3.

Table II: Cell composition data

cell no.	T (°C)	substrate	paste
2	150	glass	P25
3	150	glass	P25
4	150	glass	P25
6	150	glass	colloid
7	450	glass	P25
11	450	glass	colloid
14	150	polymer	P25

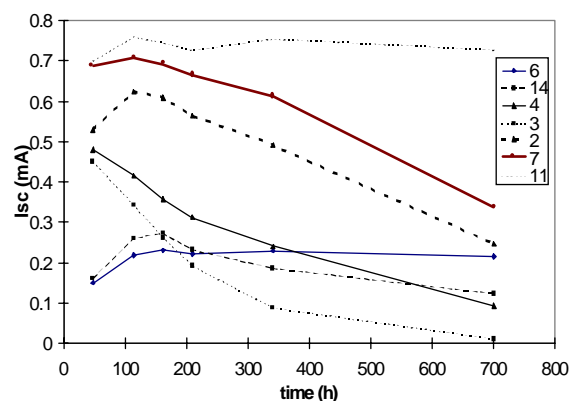


Fig. 3. I<sub>sc</sub> with time for cells (Table 1) under 4000 lux

For all cells under investigation no leaking or changes in color of the electrolyte have been observed.

From figure 3 it can be derived that under the given circumstances all cells prepared with P25 degrade within several weeks. This happens irrespectively of the sintering temperature of the titanium dioxide. However, glass cells based on a home made colloid, do not exhibit degradation during the test.

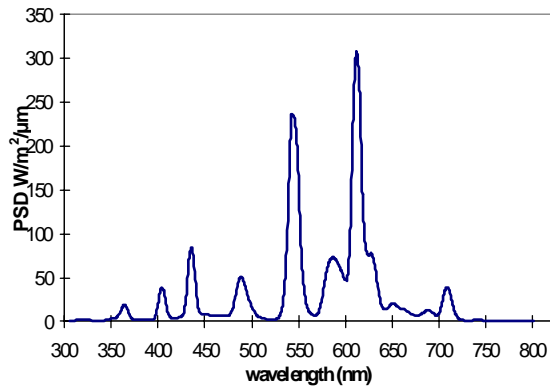


Fig. 4. Power spectral density of fluorescent tube, 4000 lux

P25 nanocrystals consist of approx. 70 % anatase and 30 % rutile crystal form, while home made colloids consists of 100 % anatase. Anatase and rutile have bandgaps of resp. 3.2 eV and 3.0 eV. The difference in degradation behavior of the two types of TiO<sub>2</sub> might be attributed to direct excitation of the P25 TiO<sub>2</sub> rutile form by the fluorescent tube with wavelengths below 400 nm (see figure 4, peak at 360 nm). This results in a generation of holes in the TiO<sub>2</sub>, which can induce oxidation and degradation of organic compounds present in the cell, such as the dye or the electrolyte solvent. The home made colloid, consisting of 100 % anatase with a bandgap of 3.2 eV will not be directly excited by the fluorescent tube lamp, which explains the improved stability of these devices as compared to P25. This theory is supported by the fact that the P25 cell made on polymer foil (No. 14) is degrading less rapidly because of the better UV absorption by the polymer foil than by the glass.

In a separate experiment, carried out at Solaronix inc., a nc-DSC on PET, consisting of home made TiO<sub>2</sub> colloid, sintered at low temperatures, have been illuminated at higher light intensity (120.000 lux, Xenon lamp), while direct excitation of TiO<sub>2</sub> was avoided by using a UV cut-off filter. The cells are operating under working conditions since an 8 kOhm resistor is connected with the cell. The voltage drop across this external load resistor is monitored continuously and plotted as a function of irradiation time (see Figure 5). At this working point, the voltage drop remains constant for a period of 2000 hours of operation indicating that these cells are stable, at least for the period of testing, which is in correspondence with the findings described above. Direct excitation of TiO<sub>2</sub> might thus be a plausible explanation for the accelerated degradation of nc-DSC based on P25-TiO<sub>2</sub>.

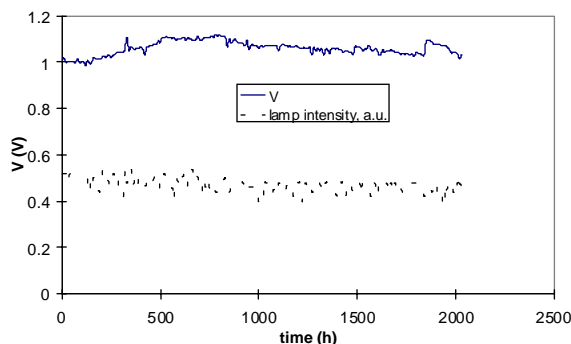


Fig. 5 Stability test carried out with an nc-DSC module of 2 cm<sup>2</sup> on PET, based on home made colloid over 2000 hrs of illumination with visible light (polycarbonate 395 nm cutoff filter) at 120000 Lux. The voltage drop measured across an external load resistor of 8kOhm and the lamp intensity are plotted as a function of time.

## 6 CONCLUDING REMARKS

nc-DSC cells on polymer foil substrates can meet the demands required by calculators, watches etc. under typical indoor conditions. From the point of view of production technology and special applications, flexible solar cells are an attractive alternative to the existing rigid systems. Though principal stability of the nc-DSC on glass has been established [4,5], the polymer foil concept is still in development. If, for example, water vapor appears to penetrate the substrate foil to an extent that influences stability, barrier coatings can be applied to overcome this problem. At this moment the synthesized colloid gives the best results regarding the cell stability on glass. The low temperature sintered colloid is a promising raw material for nc-DSC's for indoor applications. The currently used substrate PET foil is a good candidate from the point of view of light transmission, though the influence on cell stability is not well established yet. Other polymer foils which are more temperature resistant are interesting candidates to serve as a substrate for nc-DSC's.

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