NEW CONCEPTS AND MATERIALS FOR WORLD-CLASS DYE SENSITIZED SOLAR CELLS

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ABSTRACT: Several areas are explored for dye-sensitized solar cells (nc-DSC) in the field of new concepts and materials, fabrication protocols for TiO_2 and scatterlayers, metal oxide blocking layers and low temperature processes of platinum deposition. The combined efforts have led to maximum power conversion efficiencies under full sunlight of 11 % for areas < 0.2 cm^2 and 10.1 % for a cell with an active area of 1.3 cm^2 which is the highest efficiency ever measured for a nc-DSC with an active area > 1 cm^2.
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1 INTRODUCTION

For a successful introduction of nano-crystalline dye sensitised solar cells (nc-DSC) [1] for outdoor applications, specifically for large area power applications, several factors are of importance: technical performance and manufacturability, costs, design, market demand and long term stability. Important progress has been made on production technology [2] and stability [3], but relatively little progress has been made in efficiency since the breakthrough paper by O'Regan and Grätzel in 1991 [4].

Since 2002, a consortium consisting of 4 universities (EPFL, Imperial College, Cracow University, Freiburger Materials Research Center), 3 research institutes (ECN, FhG/ISE, IVF Sweden) and 1 industrial partner (Greatcell Solar SA) cooperate in the framework of the European project NANOMAX. The activities in NANOMAX are focussed on demonstrating new DSC cell concepts, cell materials and fabrication protocols aiming at increasing the efficiency to 12 % under Standard Test Conditions (AM1.5, 1000 W/m^2) and improvement of the long-term stability of the liquid junction dye-sensitized solar cells and modules. Furthermore, a technical evaluation of the processing and cost analyses have been made to demonstrate the potential of nc-DSC as a low cost thin film PV technology.

Work on nc-DSC started with the optimisation of cells with a standard photoelectrode design (Concept ST), i.e. a single sensitizing dye adsorbed on high surface area nc-TiO_2 (Fig.1). During last years a number of new possibilities for configuring nc-DSC have been announced. One concept that reveals a lot of attention is the combination of a relatively thin high surface transparent TiO_2 layer with a (white) light back scattering layer (Concept Sc). Other approaches involve the use of nanocrystalline oxides with reduced electron surface recombination by modifying the oxide surface with very thin tunneling barrier layers (capped oxides).

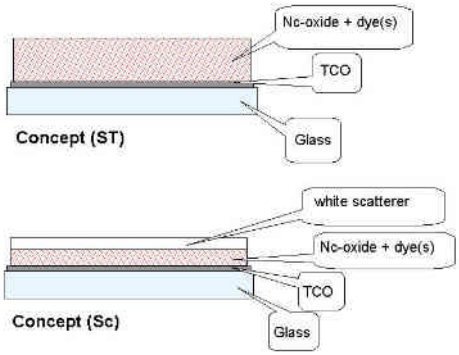

Figure 1. Schematic presentation of two nc-DSC concepts under investigation. The counterelectrodes are not shown for clarity.

Part of the NANOMAX consortium follows a common approach for the processing of nc-DSC on so called "masterplates" [4] in semi-automated baselines with a common design and size to create a basis for comparability of testing conditions and a comparable format for measurement and processing data. Exploratory research on new concepts and cell materials is carried out first on laboratory cells of smaller area (< 1 cm^2).

In this contribution, we will report on the progress in the NANOMAX project towards achievement of world record performances for nc-DSC with active cell area of > 1 cm^2.

2 EXPERIMENTAL

2.1 Measuring objects: single cells and masterplates

The detailed fabrication procedure for the nanocrystalline TiO_2 photonanodes and the assembly of complete, hot-melt sealed cells is described in previous work of EPFL [3].

The detailed fabrication procedure for masterplates can be found in refs. [2] and [5]. A representative picture of a completed masterplate is shown in Fig. 2.

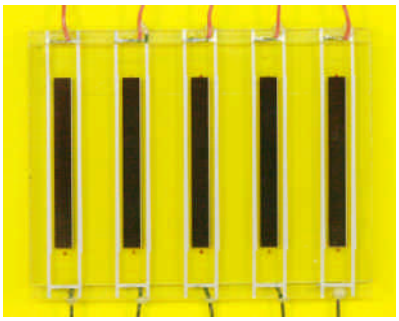

Figure 2. "Masterplate" containing five single nc-DSC with an active area of 50 x 5 mm^2.

3 RESULTS

3.1 Materials development

The materials that are used for testing the concepts as shown in Fig. 1 are various nanocrystalline metal oxides, new dyes, electrolytes and novel additives. In this section, a brief summary is given of the materials and fabrication methods that have been developed and characterized in working devices.

Nanocrystalline materials

Nanocrystalline TiO_2

Screenprintable TiO_2 pastes are used for the manufacturing of small sized cells and masterplates. The colloids are synthesised following sol-gel procedures via either acidic or basic preparation procedures [6]. Changing the synthesis conditions does influence primary particle sizes. Home-made TiO_2 colloids and commercial colloids like P25 (Degussa) are transformed into screenprintable pastes, based on formulations containing terpineol and ethylcellulose as organic media/binders.

Scattering layers

For the scatterlayers, powders are used with particle sizes between 100 and 400 nm. Most of these materials are commercially available. The powders that are used in a number of experiments are: ZrO_2 (Degussa), TiO_2-anatase (Fluka), TiO_2-Rutile (Bayer), TiO_2-Anatase (ECN home-made) and TiO_2-anatase (CCI, Japan). In addition, TiO_2 layers containing spherical voids acting as scattering centers in the film itself have been prepared and shown to be effective. Usually, relative increase of around 10 % in photocurrent is observed after application of the different types of scatterlayer.

Capped oxides

A 'wet-chemical 'method is used for coating the TiO_2 particles with metal oxides, with higher band gap, acting as insulator barriers [7]. Different metal oxides (Al_2O_3, ZrO_2, SiO_2, CeO_2 and MgO) have been applied of which Al_2O_3 and MgO coated TiO_2 layers have shown improved efficiencies) compared to bare TiO_2 films.

Other oxides

There has been wide interest in replacing TiO_2 with other metal oxides such as Nb_2O_5, ZnO and SnO_2. SnO_2 has been investigated as an alternative since it has a band gap and conduction band edge quite similar to that of TiO_2 but shows faster transport of electrons. It has been found that interfacial recombination dynamics is at least 3 orders of magnitude faster for SnO_2. Conformal coatings on SnO_2 result in retardation of the recombination dynamics by a factor of 10, which is insufficient to achieve efficient device function comparable to devices based on TiO_2.

Dye

In most of the experiments, $Ru(dcbpy)_2(NCS)_2$ with 2 protons (cis-di (thiocyanato)-N,N' - bis (2,2"bipyridyl-4,4'-dicarboxylate)Ru(II) bis- tetrabutylammonium), also known as N719, is used as the standard 'red' dye and is obtained from several suppliers i.e GSA, Solaronix SA, and EPFL.

Other sensitising « red » dyes which were made available by EPFL and GSA are $Ru(dcbpy)_2(NCS)_2$ with 0 (N712), 1 and 1.5 H+. By adjusting the number of protons in the dye, it is possible to modulate the current density and V_{oc} to optimum values. It has been further shown by EPFL that improved performances (up to 1 % absolute) could be obtained after repetitive purification of N-719 from GSA. Furthermore, hydrophobic dye Z907 is of interest in view of the promising results obtained with this dye regarding long term stability at elevated temperatures. The presence of the aliphatic chains prevents/inhibits water adsorption to TiO_2 and could retard recombination with I_3^- [3].

Novel Ru-photosensitizers were synthesized containing tetradentate ligands to shift the absorption more to red/infrared part of the spectrum as compared to N719. However, the new Ru complexes containing tetradentate ligands did not show the expected improvement in solar cell efficiency so far, due to solubility limitations preventing efficient coloration of the TiO_2 surface area.

Electrolytes

The electrolyte mixtures that have been used in high-efficiency cells mainly consist of alkylimidazolium iodides or Tetraalkyl ammoniumiodides, LiI, I_2 and surface additives such as *tert*-butylpyridin (TBP), Benzimidazole derivatives (benzimidazole, N-Methylbenzimidazole) in solvents such as acetonitrile, propionitrile or mixtures of acetonitrile and valeronitrile.

Novel additives

A number of additives have been discovered, which facilitate self-assembly of the N-719 dye at the TiO_2 surface, rendering it more impermeable resulting in reduced dark current of the cell. Examples are carboxylic and phosphonic acid derivatives. In addition, several cationic species have been investigated. Amongst those, guanidinium thiocyanate, had shown the most promising results in terms of efficiency. Replacing in the standard high efficiency electrolyte compositions LiI by guanidinium thiocyanate reduces the dark reduction current at the mesoporous TiO_2 electrode significantly, resulting in an increasing cell voltage (> 800 mV) and overall efficiency of the device (5-10 % relative).

Platinum counterelectrodes

As the standard counterelectrode, SnO_2:F substrates coated with a catalytic amount of platinum are used.

The standard counterelectrodes of the masterplates are obtained by screenprinting a platinum based paste,

after which a heat treatment is applied to obtain homogeneous layers of Pt on SnO_2:F.

Another way is to apply the Pt-layer by solvent casting of organic platinum containing solution and subsequent heat treatment. Charge Transfer (CT) resistances are < 1 • .cm^2.

In addition, an alternative method to manufacture Pt counter electrodes at low temperatures is investigated at CUT, resulting in a fine, nanoparticle size layer of a selected metal on the support. Optimisation of this process has now led to counterelectrodes with a suitable CT resistance (~1.5 • .cm^2) to be applied in nc-DSC.

3.2 I-V characteristics for single cells

A large number of small test cells (< 1 cm^2) have been prepared to test the materials described in section 3.1 and to apply improved fabrication protocols. Concept (Sc) (See Fig.1) was chosen as the main working horse.

This has resulted in non-certified AM1.5 power conversion efficiencies of 11.0 % in full sunlight for cells prepared at EPFL with an active area < 0.2 cm^2 using an optimal set of materials (dye, electrolyte and TiO_2+scatter layer) and improved fabrication protocols. One of the aims of the consortium is to achieve a certified world record efficiency on cell areas > 1 cm^2. Attempts to translate the high efficiency results from the small sized cells to single cells with active areas > 1 cm^2 has recently resulted in a 1.3 cm^2 device with a non-certified AM1.5 power conversion efficiency of over 10 % measured in the EPFL laboratories using well established standard measuring techniques. This value is significantly higher than the 8.2 %, currently regarded as the world record efficiency for a nc-DSC with an area > 1 cm^2 [8]. The I-V curve for this top device is shown in Figure 3.

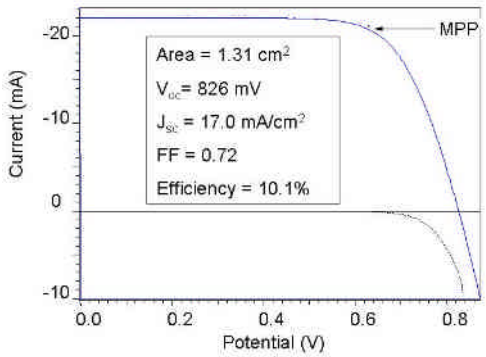

Figure 3. I-V characteristics of the 1.3 cm^2 nc-DSC top-cell, with antireflector coating (EPFL cell); Dye: N719 ($1H^+$) 4 times purified; Electrolyte: 0.6 M Butyl, Methyl Imidazolium iodide (BMII), 0.1 M Guanidinium Thiocyanate, 0.03 M I_2, 0.5 M Tert-butylpyridin in acetonitrile. MPP = Maximum Power Point

The high efficiencies were achieved by judiciously increasing the total TiO_2 layer thickness to 20 micron and modifying the basic particle size of the base TiO_2 layer to 20 nm. The layer is made up of a transparent 16 micron thick TiO_2 layer and a 4 micron thick scattering layer. Improving the purity of the N719 sensitizer by repeating chromatography using GSA Dye as the basis and using high transmission TCO-glass (Nippon Sheet Glass, 10 Ohm/square) with an antireflector coating further increases the photocurrent, while the photovoltage is increased to over 800 mV by adding the self-assembling additive, Guanidinium thyocyanate, to the electrolyte (see section 3.1 under electrolytes).

3.3 I-V characteristics of masterplate cells

Part of the consortium follows a standardized approach for the processing of nc-DSC on so-called "masterplates". Masterplates are constructed on semi-automated baselines now available at ECN, FMF/ISE and IVF, with the aim to reach a high yield and reproducibility to investigate the small deviations that can be expected upon changing material parameters/production pathway.

The cell design shown in Figure 2 was optimized to minimize resistance losses through the TCO substrates thereby maximizing the Fill Factor.

A large number of masterplates has been made up to now. Representative I-V data for cells using Concept (Sc) fabricated at ECN are shown in Table 1 using SnO_2:F substrates as the front electrode from different suppliers varying in sheet resistance and transmission. LOF-TEC 8 glass (3mm, 8 Ω/•) and LOF-TEC 15 glass (2.3mm 15 Ω/•) are SnO_2:F substrates commercially available (from Hartford Glass Company) while Sx TCO glass (1mm, 9 Ω/•) is a research sample obtained as a kind gift from Solaronix SA (Aubonne, Switzerland).

Table 1. I-V characteristics for masterplate cells (active area 2.5 cm^2) measured at 0.95 sun equiv. illumination. Three types of SnO_2:F substrates are used for the front electrode (FE). The cells consist of 10 µm TiO_2 (ECN home made nanocolloids) + 5 •m TiO_2 anatase 400 nm scattering layer (supplier CCI), N719 (Solaronix) was used as received, 0.6 M BMII, 0.1 M LiI, 0.05 M I_2, 0.5 M TBP in Acetonitrile/Valeronitrile (85/15 v/v), Pt-coated SnO_2:F (LOF-TEC8).

SnO_2:F FE	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)
TEC 8	12.4	720	69	6.4
TEC15	13.4	725	67	6.9
Sx TCO	14.3	725	69	7.5

The transmission of the SnO_2:F substrates in the wavelength region where the dye absorbs increases in the order TEC 8 < TEC15 < Sx TCO which is reflected in the measured current densities increasing from 12.4 mA/cm^2 TEC8 to 14.3 mA/cm^2 for Sx TCO. A maximum power conversion efficiency of 7.5 % was achieved for the highest transmission glass. It should be noted that there appears a gap in performance between the smaller sized single cells and the cells fabricated on masterplates. An important difference lies in the use of dyes of different quality. It has been shown that "high purity" dye based on the GSA batch is of superior quality as compared to non-purified dyes that have been used "as received" in the masterplate fabrication.

3.4 TCO-less concept

In a new concept, nc-TiO_2 layers are deposited on a glass substrate without SnO_2:F resulting in a better optical efficiency. A secondary electrode, consisting of a porous metal, is deposited on top of the TiO_2 layers and acts as the current collecting layer. Cells of this novel TCO-less design were made on masterplate level. Proof-of-principle was demonstrated for this concept with

efficiencies of around 3.5 %. Further work is needed to drive this concept to a higher performance.

3.5 Technical Evaluation, cost analysis

The objective of the consortium is to work on new concepts and materials for dye-sensitised solar cells in order to improve the efficiency and stability and to demonstrate the low cost perspectives of this technology. The latter includes that the most promising concepts and materials should also be analysed from a manufacturing point of view. It has been shown in the former sections that the best performing cells up to now are based on the "sandwich" concept (Sc). The basic difference of single cells on masterplate and module production is, apart from the size-related issues, the complexity involved in realising current collectors and/or serial connections. The evaluation of the producibility of critical process steps of the sandwich concept as well as upscaling issues is ongoing in NANOMAX.

Preliminary cost calculations for manufacturing of dye PV "sandwich" modules for different relatively small production capacities (1-4 MW_{peak}/year) have been performed. Although different approaches were applied (high labour, semi-automated processing vs. higher level of automation) the common result is that the production costs for devices based on concept (Sc) with the present material costs would be 120-150 Euro/m^2. The detailed cost distributions show that the production costs of the technology mainly come from materials (50-70 %). Consequently, a major cost reduction in the nc DSC PV technology can be obtained via reducing material costs. The TCO glass and the dye are the main material costs. It is expected that these components will come down to at least half the present prices once large-volume dye PV production is running. The high cost of the materials also highlights the importance of minimising waste (especially of the dye), using thin TiO_2 films, and advantages of TCO less designs.

The manufacturing costs depend on the module efficiency. The percentage active area TiO_2 on a module will depend upon the module design. A TiO_2 coverage of 75 % is realistic. Taking a masterplate efficiency (7.5% active area, corresponding to 5.6 % module efficiency) and the present forecast manufacturing costs (120-150 Euro/m^2), the manufacturing costs would be 2.1-2.7 Euro/W_{peak}. If the efficiencies obtained on the test cells could be transferred to the modules (11 % corresponding to ~ 8% module efficiency), the manufacturing costs would end up as low as 1.50 Euro/W_{peak}. Of course, the real cost of PV is in terms of kWh/Wp/annum or kWh/Sqm/annum. It is in this respect that DSC has advantages over every other photovoltaic technology. DSC provides higher power availability. For instance angular sensitivity measurements show that DSC devices have approximately 20% improvement in angular performance compared to equivalent crystalline silicon devices. Calculations, based on real time exposure by GSA show that DSC modules produce usable power even when heavily shaded. DSC module when 50% completely parallel shaded produces just over half the power of an unshaded module. The shading studies show that V_{mpp} is virtually unaffected by parallel shading so there is no risk of inverter shut-down. The quantitative benefit of these light harvesting advantages of DSC are being measured. It is expected that the real value of DSC in the market place will be power availability combined with a price competitive with any other PV technology.

4 CONCLUDING REMARKS

Several new areas are explored in the field of new concepts and materials, fabrication protocols for TiO_2 and scatterlayers, metal oxide blocking layers, low temperature processes of platinum deposition (electrical modeling and advanced characterization). The combined efforts have led to maximum power conversion efficiencies under full sunlight of 11 % for areas < 0.2 cm^2 and 10.1 % for a cell with an active area of 1.3 cm^2. Although this value is not yet certified by a calibration institute, the result can be considered as the highest efficiency ever measured for a cell with an area > 1 cm^2. Work is in progress to enhance the efficiency of nc-DSC further to values beyond 12 %. To obtain this result, new panchromatic sensitizers are needed to increase the photocurrent from currently 15-18 mA/cm^2 to > 20 mA/cm^2 and minimizing the surface recombination loss to maintain a high voltage (> 800 mV) and FF (>0.7).

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