LOTS-DSC

Long Term Stability of Dye Sensitised Solar Cells for large area power applications

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Abstract

In this three-year project the project partners have worked on the long-term stability and efficiency of nanocrystalline Dye-sensitized Solar Cells (nc-DSC).
Accelerated ageing tests on nc-DSC show that, to first order, a separation between the effects of the stress factors visible light soaking, UV-illumination and thermal treatment on the long-term stability can be made. The corresponding mechanisms are of electrochemical, photochemical and pure chemical nature respectively.
It has been further proven that 2-valent salts like MgI_2 and CaI_2 as additives to the electrolyte have a strong stabilising effect during UV-illumination. Tests under continuos light soaking for several thousand hours demonstrate the ability of nc-DSCs to operate for at least 5 – 10 years under outdoor illumination conditions without major degradations. Continuos and periodic thermal tests according to IEC 1215 norms are promising but with 30% to 40% loss in efficiency still critical.
Certified AM1.5 efficiencies up to 8.2% have been reached for nc-DSC on areas larger 1 cm^2, i.e. 2.5 cm^2.
A 2-Dimensional electrical model describing the contributions of the various cell components to the electrical behaviour has been developed.

Objectives

To be able to commercialise the nanocrystalline Dye sensitised Solar Cell (nc-DSC) technology for large area power applications it needs to be clear what module lifetimes and efficiencies can be obtained. Therefore, the two main objectives of this three-year project were defined as follows:

- To demonstrate that a 10 year outdoor module lifetime is achievable.
- To demonstrate that a module efficiency of 10 % is feasible.

These objectives corresponded to Task 1: Stability and Task 2: Efficiency,

In Task 1, the measurable objectives were:

- Accelerated testing procedures for nc-DSC are worked out.
- Devices (cells on masterplates) with an AM1.5 efficiency of 5 %, V_{oc}, I_{sc} and FF within 10 % reproducibility.

- The feasibility of a lifetime of over 10 years is demonstrated.
- The components and processes to obtain more stable nc-DSC are identified.

In Task 2, the measurable objectives were:

- A laboratory device (single cell) with an efficiency of 10% on an area of 1 cm^2.
- A computer model describing the contributions of the various cell components to the electrical behaviour.
- Knowledge about the maximum obtainable laboratory and module efficiencies.

During the project, the objectives followed the definition of the project subtasks:

Task 1: STABILITY
Subtask 1.1: Testing of state-of-the art devices
Subtask 1.2: Development of advanced testing methods
Subtask 1.3: Influence of components on stability
Subtask 1.4: Influence of component interaction on stability
Subtask 1.5: Fabrication routes for advanced components
Subtask 1.6: Influence of processing on stability
Subtask 1.7: Stability testing of improved devices

Task 2: EFFICIENCY
Subtask 2.1: Verification
Subtask 2.2: Computer model
Subtask 2.3: Module efficiency

Concept of Masterplates

From the numerous fabrication concepts that can be considered for nc-DSC, it was decided to use the original cell concept consisting of two glass plates as front and back electrode. The partners agreed upon using masterplates as the main vehicle of process and material development. The approach of a common design used by all partners was chosen to create a basis for compatibility of testing conditions and creating a comparable set and format of measurements and processing data.

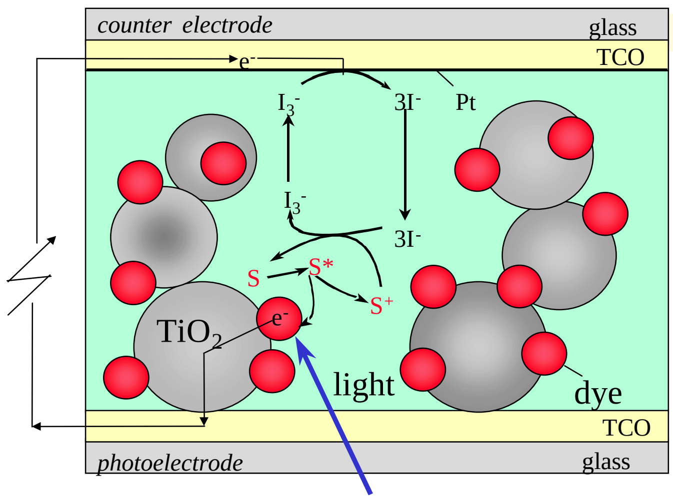


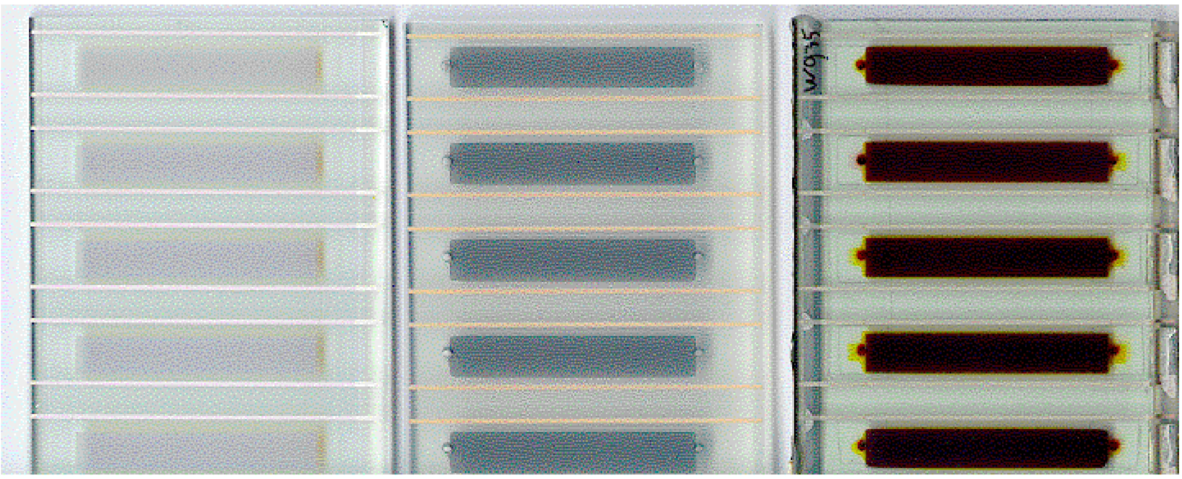
Figure 1. *Cell concept*

The main features of the masterplates design were fixed to:

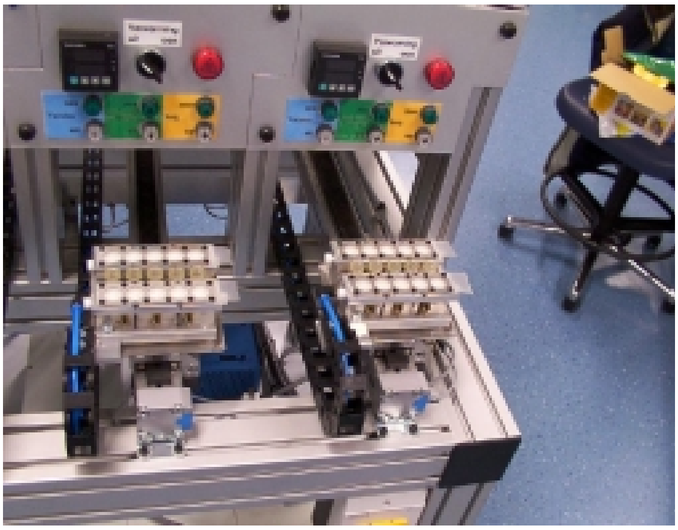
Size of base SnO_2:F (LOF-TEC8, 3 mm, 8 Ohm/square) substrates:	75 x 100 mm^2.
Number of cells:	5
Active area	50 x 8 mm^2
Spacing of cells:	20 mm
Contacts	Ag-lines (screen printed)

The masterplates were processed exclusively batch-wise in large numbers, leading to the reproducibility required for the testing procedures.

TiO_2 screen printing   Platinum printing   coloration / electrolyte / final seal



5 test cells (4 cm^2) on master plate



Coloration method

(after sealing; fusing)

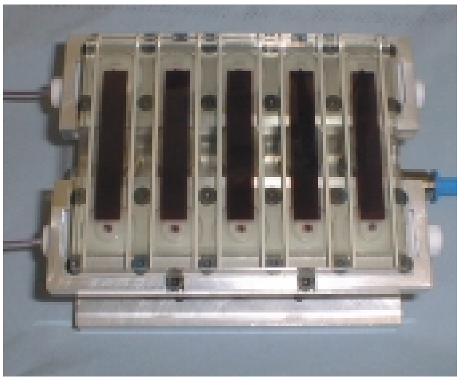


Figure 2. *Manufacturing of Dye-sensitised Solar Cells on a masterplate*

As a typical example, the efficiency data of two masterplates sealed with Surlyn 1702® are presented in Table 1. The results indicate that for all measured photovoltaic parameters the reproducibility for 5 cells on one masterplate can be achieved with an accuracy of ± 7.5%.

Table 1. *Table with efficiency data of two masterplates. Short-circuit current density J_{sc}, open-circuit voltage V_{oc} and fill factor FF are also given.*

Masterplate cell number	**J_{sc} $mA \cdot cm^{-2}$**	**U_{oc} V**	**FF %**	**Efficiency % @1000W/m²**
4408-1	10.54	0.679	65.9	4.7
4408-2	10.94	0.672	66.0	4.8
4408-3	12.12	0.670	66.0	5.4
4408-4	11.20	0.667	66.7	5.0
4408-5	12.12	0.665	65.5	5.4
4401-1	12.25	0.705	56.0	4.8
4401-2	11.85	0.703	58.1	4.8
4401-3	11.69	0.700	57.6	4.7
4401-4	12.20	0.697	56.9	4.8
4401-5	12.39	0.690	62.0	5.3

The design of the standard masterplates used for all the stability tests was not optimised for high efficiency. In particular, the distance (12 mm) between the current collecting silver fingers and, therefore, the series resistance in the TCO layer is too large resulting in lower fill factors. In order to overcome the series resistance losses in the TCO, an improved design of the original concept was developed. The masterplate still consists of five cells with a reduced size of 50 x 5 mm^2 and a 8 mm distance between the current collecting fingers.
Maximum efficiencies up to 8.18 % under Standard Test Conditions (AM1.5-G, 1000 W/m^2, 25 ^oC) were measured for cells with an active area of 2.5 cm^2 at the PV calibration laboratory of the Fraunhofer/ISE. The results of 4 cells on one masterplate are shown in Table 2 and the I-V record of the best cell is shown in Figure 3.

Table 2. *Measured I-V parameters at Standard Test Conditions (AM1.5-G, 1000 W/m^2, 25 ^oC at ISE*

MP C/Cell	**Area (cm^2)**	**I_{sc} mA**	**J_{sc} mA/cm^2**	**V_{oc}**	**FF (%)**	**η(%)**
Background Copper plate + mask						
1835	2.47	36.77	14.89	0.733	71.2	7.78
1836	2.5	37.61	15.05	0.728	71.3	7.80
1838	2.49	38.12	15.31	0.728	69.9	7.80
1839	2.36	36.82	15.60	0.727	71.3	8.10
Black background + mask						
1835	2.47	36.33	14.71	0.733	71.7	7.73
1836	2.5	37.34	14.94	0.727	71.4	7.76
White background + mask						
1838	2.49	38.44	15.44	0.726	71	7.97
1839	2.36	37.19	15.76	0.725	71.6	8.18

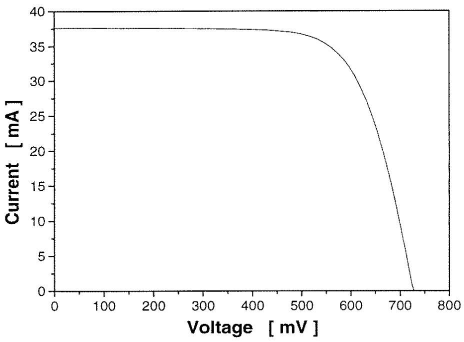
Fraunhofer Institut Solare Energiesysteme

PV CALIBRATION LABORATORY

I-V Record AM 1.5 global, 1000 W/m^2, 25°C **Date :** 16.07.2001

Material : DSC **Category :** solar cell **Ext. ID :** 1839

Manufacturer : ECN / FMF **Customer :** ECN / FMF (Hinsch)



Area	=	2.36 cm^2
V_{OC}	=	725.7 mV
I_{SC}	=	37.35 mA
J_{SC}	=	15.82 mA/cm^2
V_{MPP}	=	563.6 mV
I_{MPP}	=	34.24 mA
P_{MPP}	=	19.30 mW
FF	=	71.2 %
η	**=**	**8.18 %**

Measurement Uncertainties :

Area : ≤ ± 0.2 % V_{OC} **:** ≤ ± 0.5 % I_{SC} **:** ≤ ± 2.0 % **FF :** ≤ ± 1.5 % η **:** ≤ ± 3.0 %

Remarks : Back side of cell was painted white.

Measurement Parameters

Simulator :	Single source DC simulator	**Order-Nr. :**	024ECN0601
Ref. Cell :	IS21F	**Int. Id :**	ECN839
Operator :	GS	**Data File :**	ECN839wd.XAT

Operator Approved

Figure 3. *I-V record for a 8.18 % cell as measured under Standard Test Conditions at Fraunhofer /ISE, Freiburg.*

Characterisation and Ageing

The work presented in this report focuses on the intrinsic chemical stability of the nc-DSC. To develop appropriate accelerated ageing test procedures for nc-DSC for useful extrapolations to real outdoor conditions, stress factors are separately applied to the nc-DSC: visible light, UV-light and temperature.
For this purpose, 8 stability test stands for visible (6) and UV-light (2) soaking are developed for long-term stability testing of masterplates. A representative example of two visible light soaking test stands is shown in Figure 4 (left). One unit consists of automated measurement facilities for 80 cells, i.e. 16 masterplates (See Figure 4, right). Every week, the cells are automatically characterised in the illumination sites. Data is electronically transferred to a central database at FMF Freiburg, where further data analysis takes place.

On-line characterisation

Sulphur lamp: 400 nm to 800 nm, 1 “sun” intensity

Figure 4. *Two sulphur lamp stands installed at ECN. Six of such facilities have been installed at the project partners (left).*
Photos of continuous illumination and characterisation sites for continuous light soaking experiments. At each site 16 master plates containing in total 80 test cells are operated under 1 sun equivalent sulphur lamp spectra. Masterplates in opened drawer are shown (right).

Long-term Stability testing

Accelerated ageing tests on large numbers of dye-sensitised solar cells show that, to first order, a separation between the effects of visible light soaking, UV-illumination and thermal treatment on the long-term stability can be made. The corresponding mechanisms are of electrochemical, photochemical and pure chemical nature respectively.

- Intense visible light soaking with “2.5 sun” equivalent intensity is not a dominant stress factor. Cell stability up to 8300 hours has been demonstrated under these conditions. This result corresponds to the number of turnovers of which can be expected in at least 10 years outdoor equivalent operation.
- A serious improvement in stability under strong UV-light illumination has been reached by using MgI_2 or CaI_2 as stabilising additives to the electrolyte. As can be seen in Figure 5, 3300 hours of stability under this condition was demonstrated in cases where sufficiently high concentrations of MgI_2 or CaI_2 are used (El 6 and 7). It should be noted that the initial performance for cells containing these non-optimised electrolyte solutions is lower than for cells without the stabilising additives. 3300 hours of stability corresponds to at least 3 year outdoor equivalent operation without (!) additional UV-filter. In combination with a simple UV-filtering top-layer, dye-sensitised solar cells can therefore be UV stabilised for real (10-year) long-term outdoor operation.

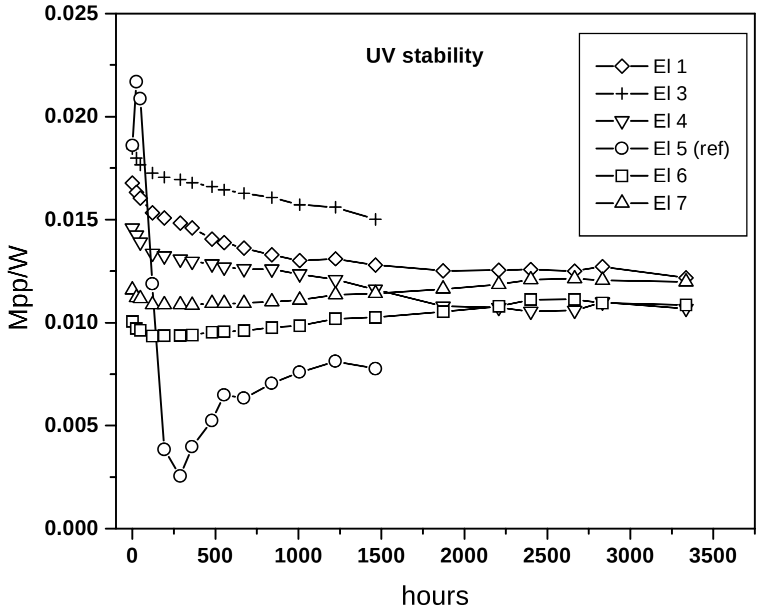


Figure 5. *Stability data (maximum power point (Mpp) measured under 1 sun) of 4 cm^2 cells on masterplates aged with a UV-light tester (cell temperature 38 ^{o}C). Electrolyte no. 5 is the (unstable) reference without additive. The other electrolytes (E1-E7) contain different concentrations of MgI_2 or CaI_2*

- The long-term extrapolation of the thermal stability achieved so far is still most critical. The results from the stability tests are very promising: a less than 10 % relative decrease from 5.5% efficient Surlyn 1702 sealed solar cells after 2000 hours at 60 ^{o}C and 30% decrease in maximum power of 4.5% efficient glass-sealed cells after 900 hours at 85 ^{o}C (see Figure 6). Further experiments at higher temperatures in the range 80 - 100 ^{o}C have still to be made to determine thermal activation energies and the reliability of the sealing technology. Also, the upper module temperatures in outdoor condition of nc-DSCs depending on location and module mounting (roof, stand-alone, facade) have to be determined.

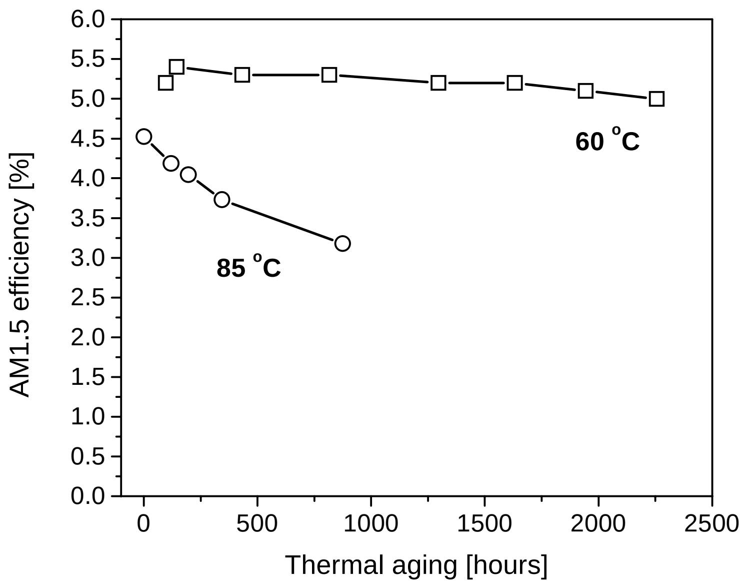


Figure 6. *Best stability results (efficiency) achieved so far for thermal ageing at 60 ^{o}C and 85 ^{o}C without light soaking. The electrolyte in the cells of the 60 ^{o}C test is based on dimethylpropyl imidazolium iodide (DMPII), LiI, I_2, 4-tertiarbuytlpyridin (4TBP) and propionitrile. In the 85 ^{o}C case, the electrolyte also contained MgI_2 in the following composition: 1.5 M hexylmethyl imidazolium iodide (HMII), 0.12 M MgI_2, 0.02 M I_2, 0.6 M TBP in propionitrile solvent.*

- The stability results obtained from tests under combined thermal stress and light soaking show some striking differences in stability for different electrolyte solvents. For instance, cells containing methoxyacetonitrile show poor stability behaviour under these conditions, while propionitrile seems to be a good choice for further research. A typical example for cells containing propionitrile-based electrolytes is shown in figure 7, where after 3400 hours of ageing, a decrease in maximum power of less than 15% has been obtained. For cells with an efficiency of 5-6 %, the decrease of the maximum power point is somewhat faster, around 30-40 % after 4000 hours of illumination.

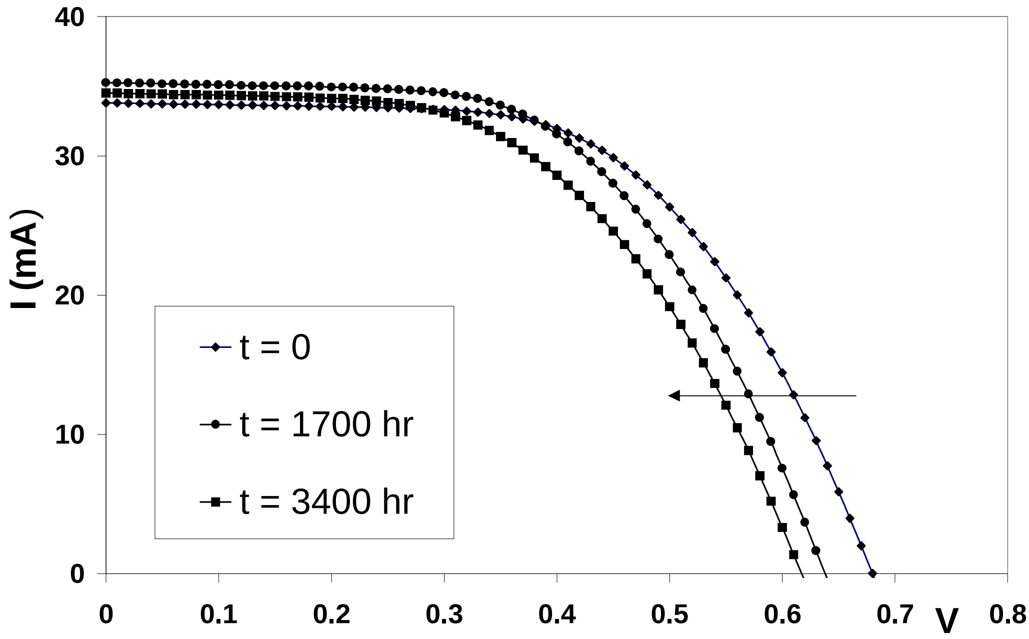


Figure 6. *I-V results from 1 sun equivalent continuous light soaking at 45 ^{o}C cell temperature. Electrolyte composition: 0.6 M HMII, 0.1 M LiI, 0.05 M I_2, 0.5 M TBP in propionitrile (chemicals used as received)*

Electrical Modelling

A two-dimensional (2-D) electrical model describing the contributions of the various cell components to the electrical characteristics has been developed.

A simplified scheme of the nanoporous structure, which is treated as if the TiO_2 film is a continuous medium, is used for modelling. Based on material parameters, the model permits the determination of steady-state charge-carrier distributions, the calculation of I-V curves under illumination, dark characteristics and the spectral response of a DSC. The results are described in J. Phys. Chem. B, 2001, 105, 4895-4903.

Furthermore, a model was developed which allows the evaluation of Electrical Impedance spectra, measured at 1 sun equivalent illumination and open circuit conditions. It has been shown that EIS can be used as a suitable characterisation tool for monitoring small changes of the internal cell parameters, which might occur under long-term operation. Results will be published in a forthcoming paper.

Outlook

Stability

Reference can be made to the Standard Test Conditions required for thin film- and crystalline silicon modules (IEC 1646:1996 and IEC 1215:1993).

Before commercialisation of DSC for outdoor application, IEC 1646 has to be fulfilled in the current or somewhat modified form. Based on the project results, it can be stated that no stopping criteria for the further developing of long-term stable DSC has been found.

In general, the authors have the impression that long-term stability of dye sensitised solar cells is not an intrinsic problem of the technology but can be improved further by better understanding of the degradation mechanisms and the chemical balancing of the electrolyte components and by further improving the sealing technology.

Efficiency

It has been shown in this project that energy conversion efficiencies up to 8 % can be achieved for unit cells with active areas of 2.5 cm^2. Scientifically, there is no reason why efficiencies of 15% or higher can not be achieved in dye sensitised solar cells. This requires new cell concepts and materials, which need further investigations in detail.

Up-scaling of this technology from laboratory sized cells to large sized modules normally leads to some loss in efficiency. Module manufacturing of individual cells generally results in a loss of active area with respect to total area, leading to lower current densities. Furthermore, at larger sizes series resistance losses, leading to lower fill factors are often observed.

The future challenge is to find technological solutions for the optimisation of the ratio [active cell area / total area], thereby maintaining the current density and minimise the resistance losses. On the other hand, non-active areas can also be used to improve the light management of the cell, for instance by applying scattering sealants or white reflecting spaces.

Publications

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