

PROJECT FINAL REPORT



Grant Agreement number: 212792

Project acronym: ROBUST DSC

Project title: Efficient and Robust Dye sensitized Solar Cells and Modules

Funding Scheme: FP7-Energy-2007-1-RTD

Period covered: from 01-02-2008 to 01-02-2011

Name of the scientific representative of the project's co-ordinator¹, Title and Organisation:

Dr. J.M. Kroon

Energy Research Centre of the Netherlands (ECN)

Tel: +31 224564734

Fax: +31 224568214

E-mail: j.kroon@ecn.nl

Project website address: www.robustdsc.nl

¹ Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

4.1 Final publishable summary report

Executive summary

The main aim of the ROBUST DSC project was to develop materials and manufacturing procedures for Dye Sensitized Solar Cells (DSC) with long lifetime and increased cell efficiencies (14 % target) and module efficiencies (7% target) with the intention to accelerate the exploitation of the DSC technology in the energy supply market.

The approach focused on the development of large area, robust, efficient DSC modules using scalable, reproducible and commercially viable fabrication procedures. In parallel with this objective, more fundamental research, employing new materials and device configurations, was carried out to boost the efficiency of lab-scale devices.

The R&D in this project Robust DSC spanned over a wide range of activities varying from exploration of new materials (dyes, electrolytes, metal-oxides), device concepts, advanced characterization and modeling towards processing of large area modules, lifetime testing, standardization and analysis of commercialization aspects.

The partnership consisted of: two SMEs (3G Solar and G24i) that are committed to large-scale production of DSC, one industry (Corning) that has proven experience on inorganic frits for sealing for a variety of applications, three research institutes (ECN, Swerea IVF, ISE) with expertise in the field of long-term testing, up-scaling and module fabrication, and four academic partners, world leaders in both new DSC materials and concepts, and in fundamental research on cell function and modelling (EPFL, IMPERIAL, ICIQ, UAM).

The combined efforts of the consortium have led to a number of important achievements in Robust DSC that form an essential basis for creating an economically accessible and widely applicable solar energy technology.

- The portfolio of available sensitizing dyes and electrolyte compositions able to achieve > 10 % efficiencies for small cells have been extended tremendously, since the start of the project. Over 13 % efficiencies are obtained for single junction DSC at 0.6 sun illumination conditions for selected materials combinations. The Robust DSC project has therefore achieved unprecedented efficiency records and set new performance benchmarks, which will be of great benefit to the practical implementation and commercial development of this promising new PV technology.
- Development of a characterisation tool set and a whole cell model for predictive evaluation of device performance. The model and tool set have been completed to conditions where it can be disseminated to a wider public.
- It has been proven that hole-closure can be done by glass-frits using laser assisted sealing methods with the aim to demonstrate hermetic packaging of the DSC under all possible operating conditions
- Large Area DSC demonstrators of 900 up to 6000 cm² have been manufactured showing the potential of large scale manufacturability of DSC
- The research institutes responsible for the manufacturing of large area modules have made significant progress in the development of the processing technology, device stability and performance, resulting in two different device technologies (monolithic serial-connected modules and glass-frit sealed sandwich modules) that will be further developed towards commercialisation after ROBUST DSC.
- It has been shown that it is not straightforward to compare the results between different module manufacturers since the processing significantly affects the results.
- It has been shown that there are specific issues involved in defining the degradation of DSC devices due to the dynamic (and module-specific) behaviour of the performance. This has led to the formulation of a pre-normative standard test protocol for DSC taking into account the specific properties of the DSC concepts
- An extensive report has been written including cost of materials, evaluation of large scale manufacturability, and life cycle analysis. Additionally, calculations on the Return on Investment (ROI) are provided. Detailed life cycle analysis and energy payback calculations were completed on the module designs of all Robust DSC partners. As a result, a web tool accessible by all partners was created to assist in the analysis. The web-tool will be disseminated for continued use for all people working in the DSC field.

- Outdoor tests have been made and one year operation under Israeli outdoor conditions without any degradation of the device performance was achieved
- Modules from different partners have passed the temperature cycling and damp-heat tests with $< 10\%$ degradation of the performance, as defined by IEC 61215, the International Standard for crystalline PV devices.



This graph shows examples of DSC module prototypes that have been fabricated in the frame of Robust DSC

A summary description of project context and objectives

Dye sensitized Solar Cells (DSC) have been under intensive investigation as a new type of solar cell technology for almost 20 years now. In contrast to earlier expectations, the transfer of the technology from laboratory stage to a module production phase has turned out to be complex and time demanding. Despite the ease of the basic manufacturing principle of DSC, experience has shown that existing standard technologies such as sealing solutions or the upscaled synthesis of the dye require extensive efforts to eventual being able to manufacture successfully large-scale DSC. Despite the fact that it takes much longer to overcome these challenges, commercial interest and early investment in this technology remains strong. This is exemplified by the commercial ambitions of a significant number of small and larger sized companies operating worldwide in Europe, Asia and Australia to produce flexible and glass based DSC for short- and mid-term market areas. As an example, project partner G24i is the first company in setting-up a production line for flexible DSC and they recently launched their first flexible DSC products in 2010 for the consumer electronics market.

Between 2008 and 2011, a consortium consisting of universities (EPFL, Imperial College, University Autonoma Madrid), research institutes (ECN, FhG/ISE, Swerea/IVF AB, ICIQ) and 3 industrial partners (3GSolar, G24i, Corning) have cooperated in the frame of the European project ROBUST DSC.

The project has followed a research strategy covering the whole value chain from basic research including innovative materials development, advanced characterization, and predictive modeling to more applied technology development including aspects like up scaling of fabrication technology and accelerated and outdoor lifetime testing of representative module prototypes.

Thus the operational approach was on one hand to transform the current state-of-the-art lab-scale devices into modules (up to 7% stable efficiency, designated as development line). In addition, the performance of the lab-scale device will be boosted to >12% (designated as research line) by continuous materials development and improved fabrication protocols. Progress on the cell research line was continuously fed into the module development line immediately. The project intended to accelerate the exploitation of the DSC technology towards entering the energy market.

The ROBUST DSC consortium worked out the parallel line approach into 8 work packages (WPs) that cover the whole value chain from materials development to commercialisation aspects.

Research line:

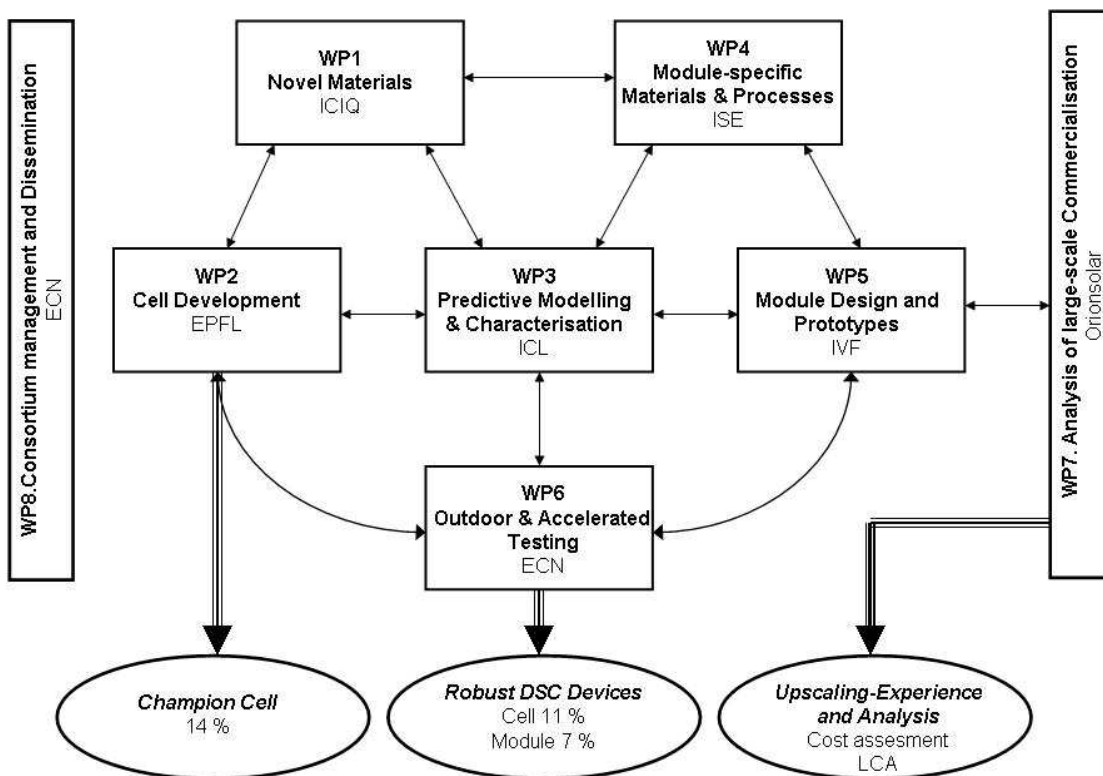
- WP 1. Novel materials
- WP 2. Cell development
- WP 3. Predictive modelling and characterisation

Development line:

- WP 4. Module-specific materials and processes
- WP 5. Module design and prototypes
- WP 6. Outdoor and accelerated testing
- WP 7. Analysis of large-scale commercialisation

Management & dissemination

- WP 8. Consortium management and dissemination



Project structure showing the interdependencies between the work packages

The overall objectives of ROBUST DSC were defined as:

- Innovative materials and concepts leading to a champion cell ($< 1 \text{ cm}^2$) power conversion efficiency (PCE) of $> 14 \%$ measured at Standard Test Conditions (STC), i.e AM1.5GN, 1000 W/m^2 , $25 \text{ }^\circ\text{C}$.
- Stable* cell ($< 1 \text{ cm}^2$) having a PCE of 11% at STC.
- Stable* module ($\sim 100 \text{ cm}^2$) reaching a 7% total area module efficiency at STC
- Demonstrator module of 900 cm^2 with a 5% total area module PCE using the most cost-effective module concept
- Predictive device models for efficiency optimisation and extrapolation of degradation pathways
- Data from outdoor field tests and accelerated lifetime tests
- Comparative evaluation of DSC performance in relation to inorganic thin film PV technologies
- Pre-normative test protocol for DSC
- Analysis of critical cost factors and roadmap how to overcome them (target 0.7 Euro/Wp)
- Life Cycle Assessment including environmental impact and analysis of the energy pay-back time
- Results from lead-user workshop with representatives from the PV industry

* Stability is defined as $< 10 \%$ degradation of the initial performance of three identical devices after exposure to 1000 hours of light-soaking under load, storage at 85°C in darkness, and temperature cycling (to be defined).

A description of the main S&T results/foregrounds (not exceeding 25 pages),

In the following section, a summary is given of the achievements obtained in the Workpackages 1 to 7:

Workpackage 1: Novel materials

The Work-package 1 was devoted to the development and study of novel materials and molecules to increase the device efficiency and stability.

The state-of-the-art devices prior to the **ROBUST** project used the well-known Ruthenium complex **N719** (Year 2008). Although the certified efficiencies using **N719** sensitizer have been demonstrated to be of 10.3% the **ROBUST** partners were able, in a reproducible way, to achieve 8-9% (Figure 1.1).

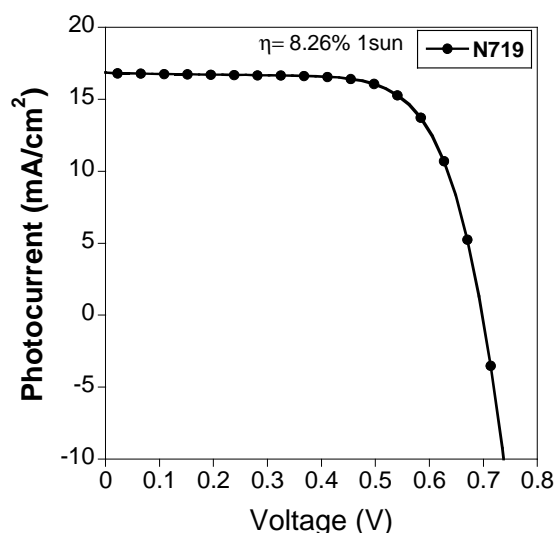


Figure 1.1 Photocurrent vs. voltage for a 0.16 cm^2 masked device using the standard **N719** sensitizer measured at 1 sun conditions. The electrolyte was composed by 1M BMII (1-butyl-3-methylimidazolium iodide), 0.03M I_2 , 0.05M LiI, 0.1M GuSCN and 0.5M tert-butylpyridine in acetonitrile:valeronitrile (85:15).

Regarding the use of the metal oxide TiO_2 paste, the consortium set a standard. It was agreed to use DyeSol© screen-printing paste to increase the reproducibility and in view of the impossibility for ICIQ and EPFL to provide large amounts of home-made pastes to all the **ROBUST** partners. Moreover, the consortium decided that ICIQ and EPFL should use parallel strategies for paste preparation in order to check-and-proof the increase in device light-to-energy conversion efficiency. Figure 1.2 shows digital images for the standard TiO_2 material used.

The first improvement was to change the sensitizer used, **N719**, by a new Ruthenium complex, which extended the light absorption into the red region of the Sun spectrum. This new sensitizer was called **C101** (Figure 1.3).

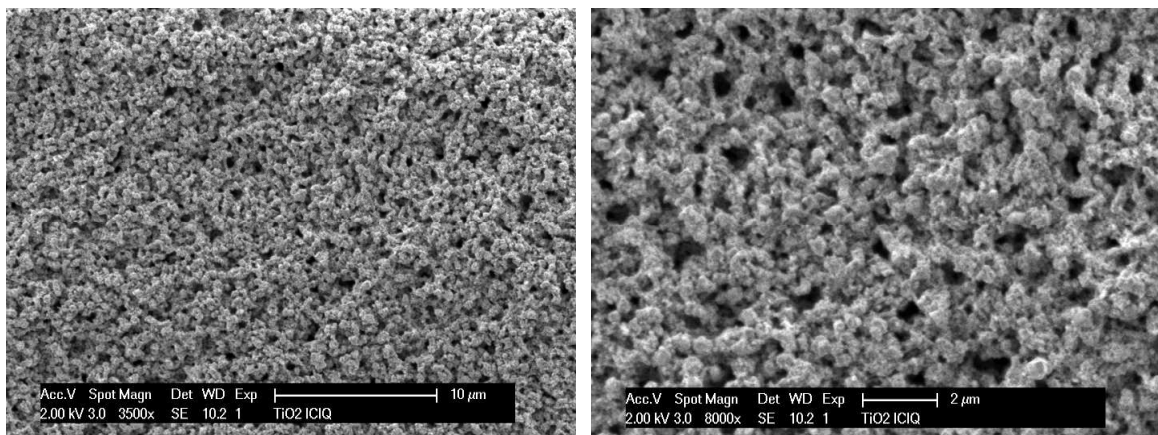


Figure 1.2. Scanning electron microscopy (SEM) digital picture of a benchmark TiO₂ film. The film thickness was 7.1 μm + 4.7 μm scatter paste.

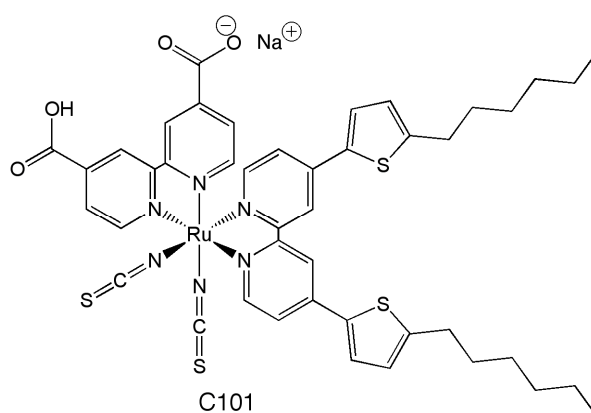
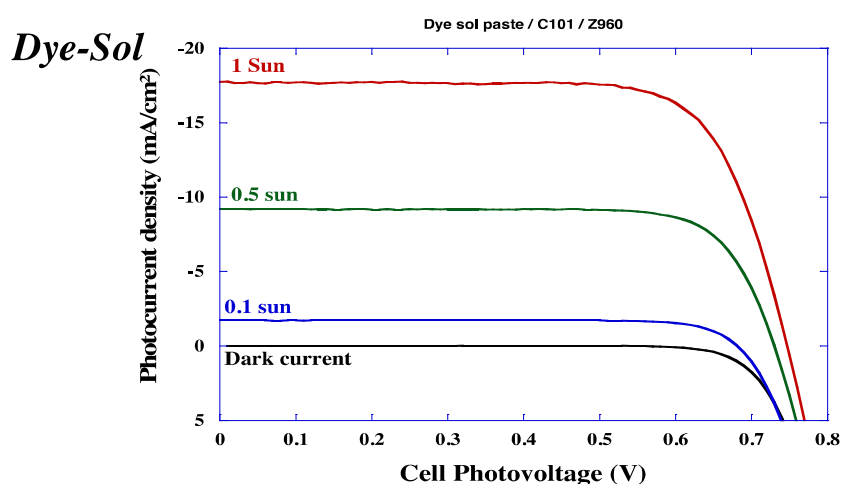


Figure 1.3. Molecular structure draw for the “red” sensitizer **C101**.

The first efficiencies achieved with the novel sensitizer overcome easily those obtained for the **N719**. As can be seen in **Figure 1.4**.



	0.1 Sun	0.5 Sun	1 Sun
<i>V_{oc}</i>	680.43 mV	729.95 mV	746.97 mV
<i>J_{sc}</i>	1.718 mA/cm ²	9.196 mA/cm ²	17.738 mA/cm ²
<i>F.F.</i>	0.797	0.771	0.738
Cell efficiency	10.02 %	10.17 %	9.88 %

Figure 1.4. Photocurrent vs. voltage curves and light-to-energy conversion efficiency when using the new **C101** dye in combination with the **Z960** electrolyte.

The **C101** sensitizer was not the only “red” absorbing dye that was introduced at **WP1**. **Partner 10** (UAM) designed and developed sensitizers, which extended the red absorption close to 700 nm by using phthalocyanines as a molecular scaffold. The consortium achieved for the first time an impressive light-to-energy conversion efficiency of 4% under standard conditions with the so called **TT1** dye (Figure 1.5).

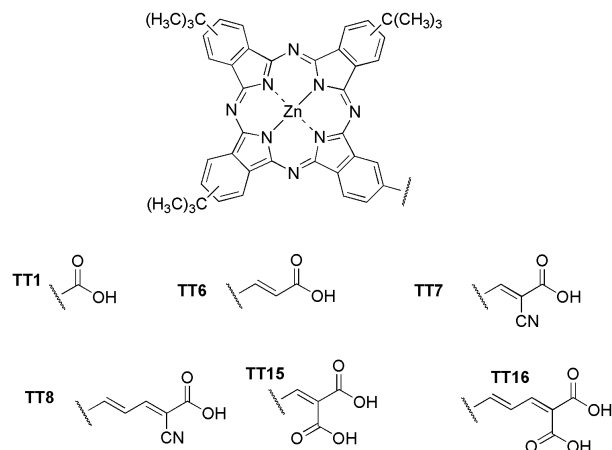


Figure 1.5. **TT1** and derivatives synthesized by **P10** for **WP1**.

Several new dyes were also synthesised to improve the **C101** efficiency but major step forward was to work on the “scatter layer” of bigger nanocrystalline particles (particles size between 300-400nm). Based on a previous publication, **WP1** focussed on optimizing the number of TiO_2 layers to increase the response into the red without losing open-circuit voltage. Doing so we were able to achieve efficiencies of 11.03% under standard conditions.

Further optimization of the scatter layer using combination of different materials gave efficiencies of 11.6%, Figure 1.6, yet the reproducibility was low and only 3 out of 9 devices were above the 11.3%.

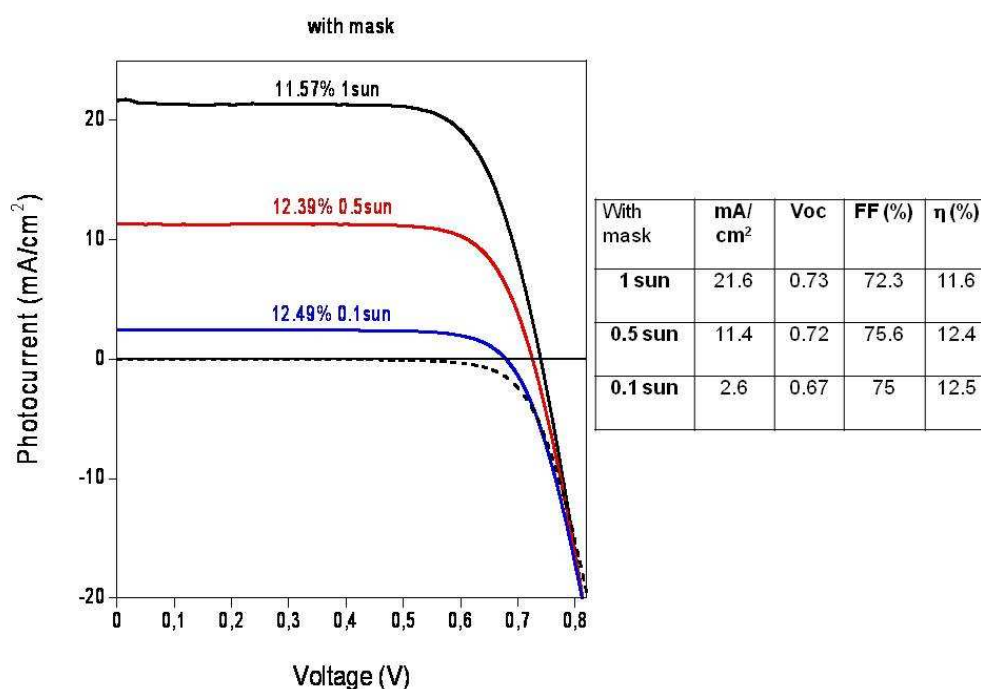


Figure 1.6. Photocurrent vs. voltage curves for a device (cell 658) composed by 8 μm TiO₂ EMI paste + 2 μm scatter TiO₂ paste + 2 μm Al₂O₃ paste. The dye was C101 (300 μM C101+300 μM chenodeoxycholic acid in Ethanol). Electrolyte Z060. Cell area 0.169 cm²

Workpackage 2: Cell development

Prior to the opening of Robust-DSC project, high efficiency devices were classically constituted of a photo-anode composed of 20 nm-based anatase TiO₂ particles sheltered by bigger particles to back reflect the unabsorbed photons. The light capture was ensured using either the N719 or the so-called black-dye which provides a panchromatic response from 400 to 900 nm. 11.1 % power conversion efficiency (PCE) has been attained with this black dye in combination with volatile electrolyte based on acetonitrile [1]. During the three year Robust DSC project, research within the framework of the work package 2 focused on activities allowing to significantly progress towards the efficiency goals of the project on the laboratory scale cell level, i.e. demonstration of 14 % PCE with a single junction device and 15 % with a tandem cell as well as 11 % with a cell that shows stable cell operation that shows stable operation using a nonvolatile electrolyte. The endeavors in both WP1 (see former section) and WP2 (this section) have concentrated on improving the 3 major components of the cells that are: the sensitizer, the mesoscopic, TiO₂'s film and the electrolyte chemistry. We expose below the major step towards realizing these three parts within the frame of RobustDSC.

Dye chemistry to reach new record efficiency

Based on the Z907Na structure, a new class of hydrophobic sensitizers was introduced employing thiophene or bis-thiophene substituents unit on the bipyridine ancillary ligand. Coded C101, C106, Z991 or B11, these new heteroleptic complexes extend the π -conjugation of the bipy-ligand inducing a red-shift of MLCT transition and increase of the molar extinction coefficient (Figure 2.1).

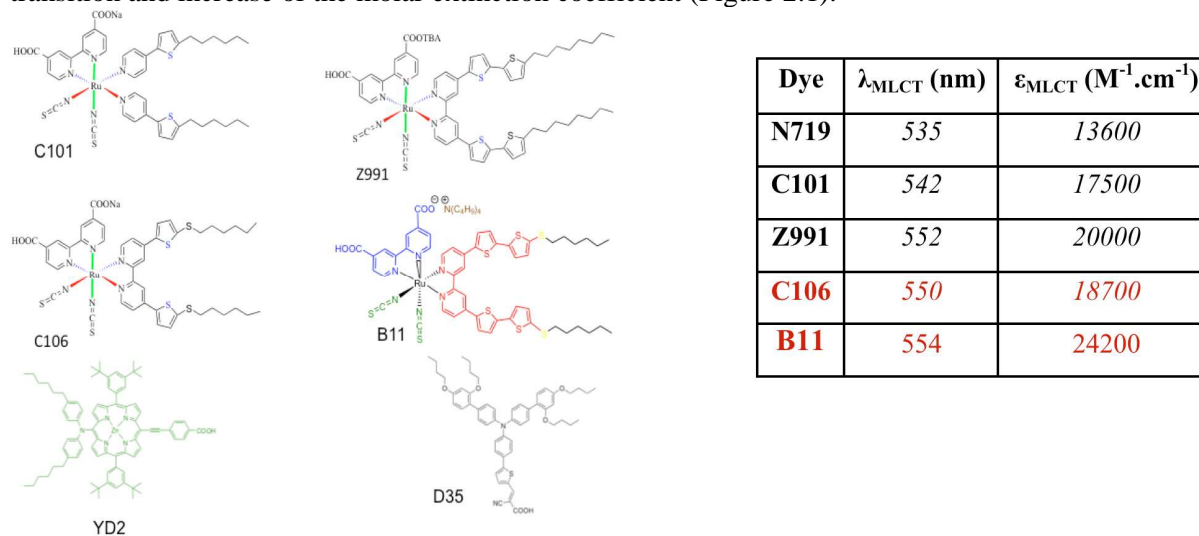


Figure 2.1. Dye structure and evolution of MLCT transition and molar extinction coefficient for C101, C106, Z991, B11, D35 and YD2 dyes.

This new generation of sensitizers obtained at high purity grade after column purification, achieve PCEs as high or above 11.5 % or above, demonstrating their great potential for high efficiency dye-sensitized solar cells. More particularly, we have demonstrated that the self-assembly of the C101 dye forming the monolayer is sensitive to the temperature of the bath solution [2]. Coloring at low temperature (4°C) proved to be effective in reducing the dynamic of back reaction as well as increasing the APCE. In this manner 11.5 % PCE has been attained. As mentioned above, the introduction of thiophene unit has been successful to augment the dye red response as well as the light absorption capability of the complex. More strikingly, by means of a careful optimization of electrolyte and dye solution composition, we achieved crossing the threshold of the 12.0 % mark using the Z991 dye yielding PCE values a high as 12.1 % or even 12.4 % under 100 mW/cm² and 50 mW/cm² illumination, respectively (Figure 2).

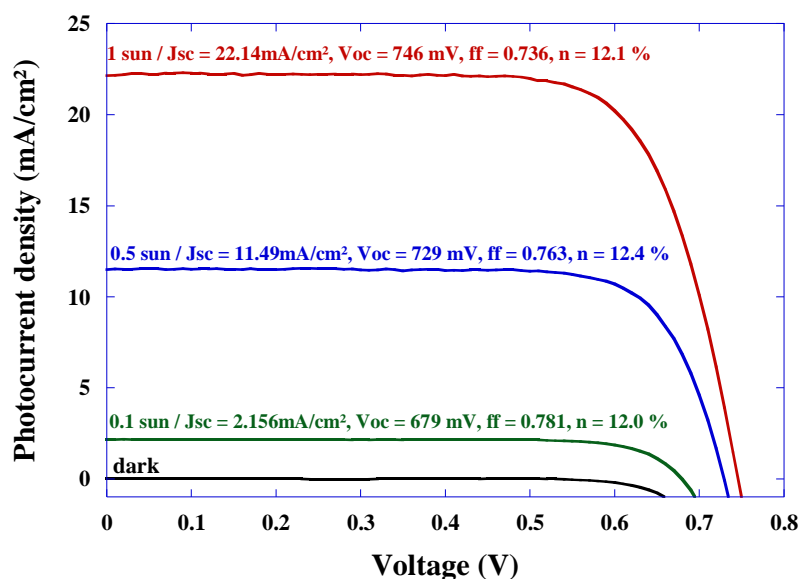


Figure 2.2. (J-V) characteristics of Z991 dye at 100, 50, 10 mW/cm² and in dark.

Besides the development of ruthenium dyes, during this project we have been able to (i) tailor the new zinc porphyrin sensitizer YD2 for which we reached an outstanding 11.0 % PCE [3] Very recently a YD2 analogue achieved 13.3 % PCE at 65 mW/cm² intensity when used in conjunction with a novel redox electrolyte based on the Co(II)/Co(III) complexes. This comes within very close reach of the 14% PCE percent target of the DSC-Robust project. The cobalt complexes employed yield remarkably high V_{oc} values, the highest obtained so far being 1.1 V, which is unprecedented for dye sensitized solar cell. (ii) Make use of two complementary sensitizers (dye cocktail), i.e. the B11 and the organic tri-aryl amine D35 dye which show synergistic properties leading to enhanced light capture. With this latter system, using a 7/1 ratio between B11 and D35, we have tailored a champion cell showing 12.2 % under standard illumination (A.M. 1.5G 100 mW/cm²) and even 12.8 % at 10 mW/cm² (Figure 2.3)

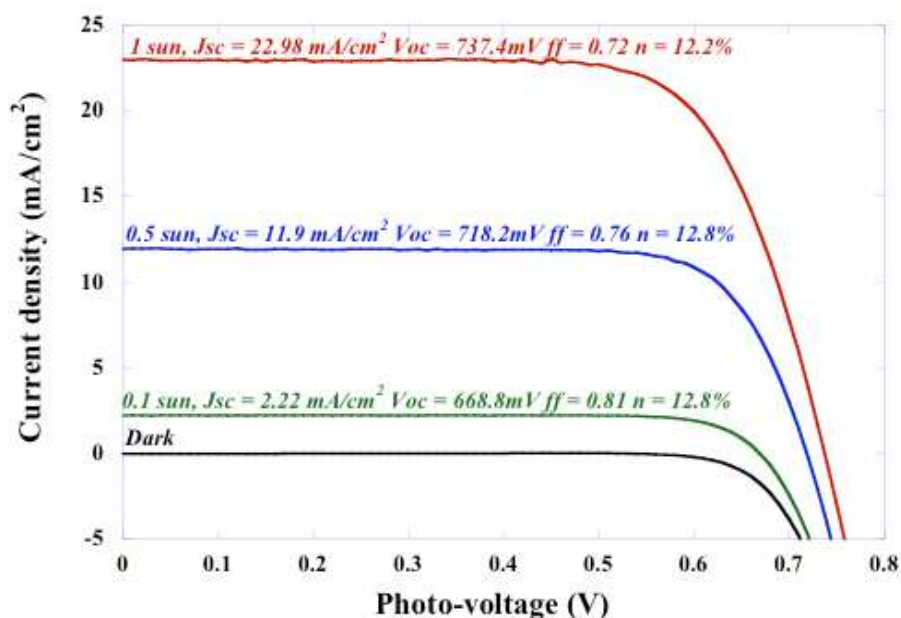


Figure 2.3: (J-V) characteristics of B11/D35 concerto system under 100, 50, 10 mW/cm² and in dark.

New TiO₂ photo-anode

The role of the TiO₂ photo-anode plays is to collect electrons from the photo-excited sensitizer. Hence, both the intrinsic and extrinsic characteristics of the TiO₂'s photo-anode control to some extent the charge injection rate, the charge transport towards the current collector, the kinetic of back-reaction with tri-iodide and finally

the light containment properties of the photo-anode. Within the framework of this project, we have been actively working on modifying the intrinsic properties of TiO_2 by introducing point defects in the anatase lattice using aliovalent substituent (Nb^{5+} , Ga^{3+} or Y^{3+}). Details are described in references [4] and [5]. We were the first to show how efficient this approach could be. In the first case, we highlighted that niobium is completely ionized in the lattice providing a precise control on the distribution of the intra-bandgap trap states. On the other hand, for the three elements, we experienced an augmentation of the charge collection efficiency after a careful optimization of the total amount of point defects introduced in the lattice.

We also showed the effectiveness to significantly reduce the recombination rate by means of reducing the electrode's dimensionality towards 1D [6]. This benefit was further borne out by extrinsically modifying the TiO_2 's properties using mesoporous beads of TiO_2 to support the sensitizer. These combine a high capacity for light harvesting with excellent electron transport resulting in the generation of high photocurrent. The BET surface area of these mesoporous beads approaches $100 \text{ m}^2/\text{g}$. One additional advantage of the beads is their ability for multiple scattering of light leading to photon containment and enhanced light harvesting in the red and near IR region of the solar spectrum. For first time, we crossed double digit efficiency with a single type of TiO_2 particles as the photo-anode the PCE reaching 10.7 % even 11.2 % PCE upon improving further light containment in the electrode (Figure 2.4).

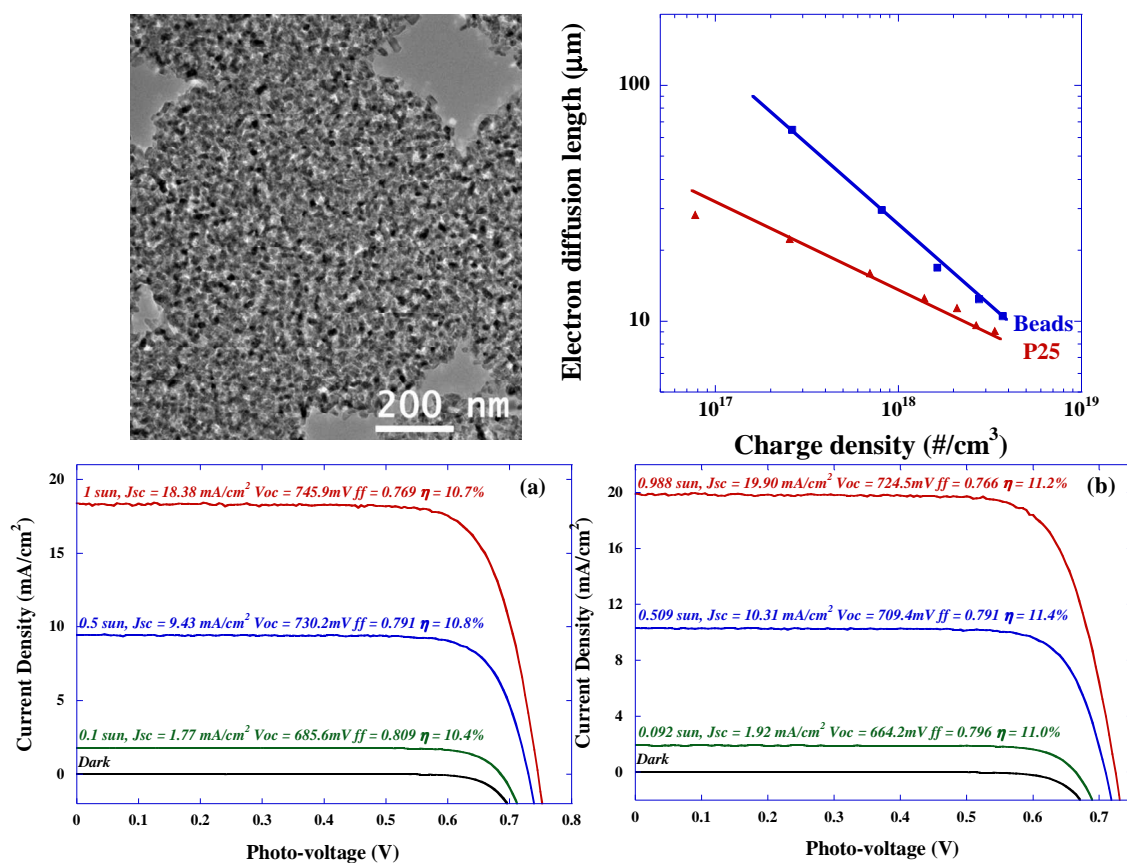


Figure 2.4. TEM micrograph of beads of TiO_2 , evolution of electron diffusion length as a function of charge density for the beads compared to the benchmark P25 particles, ($J-V$) characteristics of C106 dye in combination with a single type layer of beads (a) or using a triple layer configuration 20nm TiO_2 nanoparticles / Beads / 400 nm sized TiO_2 scattering particles.

New electrolyte system

In order to meet the very stringent objective of 11% stable cells, our strategy was focused on the elaboration of a new electrolyte system that combines at once high chemical/electrochemical stability and low viscosity to ensure fast mass transport. We have developed one new branch of low-volatile electrolyte based on butyronitrile. This solvent holds all the physical characteristics to pass successfully IEC 61646 accelerating test protocol (*ie.* melting point: $-112 \text{ }^\circ\text{C}$ and boiling point: $+118 \text{ }^\circ\text{C}$). Photovoltaic experiments employed the C106 dye from which best stability has been obtained. After optimization of electrolyte composition, at $t = 0$,

the new BN electrolyte combines a superior photovoltage of *ca.* 33 mV with greater fill factor, at the expense of the short-circuit photocurrent which was *ca.* 0.7 mA/cm² lesser with respect to the benchmark Z946 composition based on MPN. As a result, we achieved 8.8 % PCE using the BN formulation compared to 8.5 % when the robust MPN electrolyte was used. Interestingly, this is not the sole advantage held by this new electrolyte. Indeed, in the course of this accelerating protocol, the three cell characteristics exceed even those of MPN to yield an excellent PCE retention of 99 % with a maximum power conversion efficiency of 9.2 % after 350 hours of exposure ($V_{oc} = 712$ mV, $J_{SC} = 16.9$ mA/cm² and $ff = 0.76$) and 8.7 % after 1000 hours. We realized a new step forward towards high efficiency and high stability by the introduction of NaI, which shows excellent compatibility with BN. The best results in terms of efficiency vs. stability were obtained with a concentration corresponding to 50 mM of NaI (coded BN50Na). For first time, regardless of light intensity, we achieved crossing the double digit efficiency using a stable electrolyte, namely 10.0 % efficiency under standard A.M. 1.5G conditions - 100 mW/cm² illumination ($V_{oc} = 733$ mV, $J_{SC} = 17.9$ mA/cm² and $ff = 0.76$) and even 10.2 % at 51 mW/cm² ($V_{oc} = 718$ mV, $J_{SC} = 9.3$ mA/cm² and $ff = 0.78$) (Figure 5). Substantiating the photocurrents measured with our simulator, the spectral response of the IPCE shows values above 80 % quantum efficiency from 430 nm to 670 nm the maximum attaining *ca.* 92 % at 550 nm.

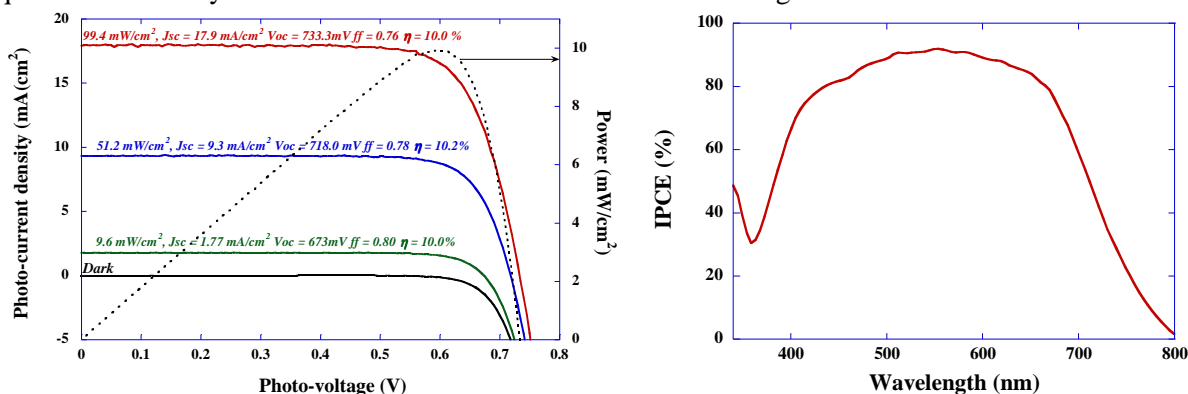


Fig 2.5. (*J-V*) characteristics and IPCE spectrum of C106-sensitized solar cells with BN electrolyte containing 50 mM NaI at 99.4, 51.2, 9.6 and 0 mW/cm² illumination (Results for a champion cell).

In contrast to lithium-based electrolytes in combination with MPN (or with BN) as solvents, by using BN50Na we successfully accomplish to obtain an excellent stability profile until 1000 hours under 60°C - 100 mW/cm² conditions while exhibiting a superior power conversion efficiency in comparison to the sodium-free electrolyte (Figure 2.6). After this ageing protocol, we achieved as high as 9.1 % PCE ($V_{oc} = 664$ mV, $J_{SC} = 18.3$ mA/cm² and $ff = 0.74$) leading to 95 % power conversion efficiency retention (Initial efficiency was 9.6 %).

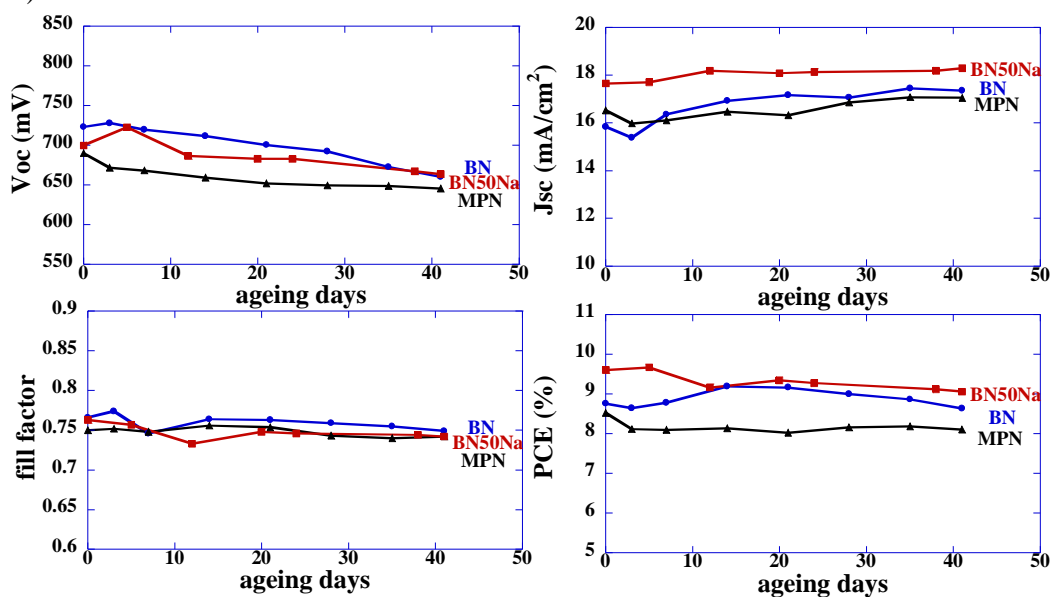


Figure 2.6. Evolution of the cell characteristics (V_{oc} , J_{sc} , ff and PCE) as a function of time of ageing ($60^{\circ}\text{C} - 100 \text{ mW/cm}^2$ illumination) for BN50Na compared to BN and MPN electrolytes.

Work still in progress, we have also taken advantage of the extended light capture ensured by our B11 / D35 concerto system. Using this newly formulated BN50Na composition, we have demonstrated outstanding 10.5 % under 100 mW/cm^2 illumination and 10.7 % under 50 mW/cm^2 light, values never achieved before with a stable electrolyte system (Figure 2.7).

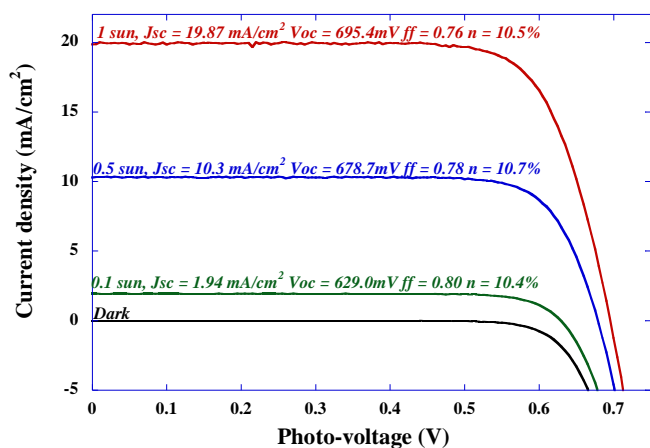


Figure 2.7. (J - V) characteristics of B11/D35-sensitized solar cells with BN electrolyte containing 50 mM NaI at 99.4, 51.2, 9.6 and 0 mW/cm^2 illumination.

Tandem Cells

The concept of a tandem hybrid concentrator solar module was demonstrated using a dye-sensitized TiO_2 solar cell (DSSCs) and a silicon p-n junction solar cell, Figure 2.8. [7]. The test system employed DSSC and Si cells with indoor AM1.5G efficiencies of 9.1 and 18.1%, respectively. A heat mirror or differential optical filter was used to selectively reflect and concentrate near-infrared light from the DSSC onto the Si cell. On the basis of outdoor testing in a 2x concentrator-reflector arrangement, the tandem system generated 93 and 96% of the output power of directly illuminated Si cells under altostratus/cirrostratus and clear sky irradiances, respectively, despite a DSSC-to-Si active area ratio of only 0.92. Similar performance is expected at higher (5-10 X) concentration ratios. The active area based PCE of the module was 16-19 %. This exceeds 15% PCE of target for tandem cells set by the DSC Robust consortium. The hybrid arrangement of visible- and IR-absorbing solar cells addresses the problem of lower performance of conventional concentrators under diffuse irradiance conditions. Si could also be replaced by another efficient flat plate IR-absorber such as CIGS or quantum dot solar cells because they operate over the same spectral range. These proof-of-concept results suggest that system level efficiencies exceeding 20% should be readily achievable in the near future with this concept.

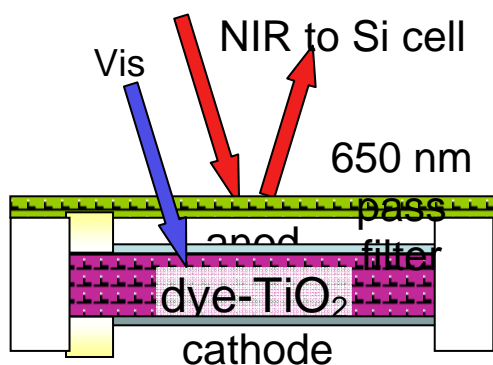


Figure 2.8. A schematic diagram of tandem hybrid solar module using a heat mirror

Acknowledgement

We gratefully acknowledge the gift of dye samples from Prof. Anders Hagfeldt, Dr. Gerrit Boschlo, Prof.

References

- [1] Y. Chiba, A. Islam, Y. Wanatabe, R. Komiya, N. Koide, L. Han, *Jpn. J. of Appl. Phys.*, 45(25) (2006) L638-L640
- [2] F. Sauvage, J.-D. Decoppet, M. Zhang, S.M. Zakeeruddin, P. Comte, Md. K. Nazeeruddin, P. Wang, M. Graetzel, *submitted*
- [3] T. Bessho, S.M. Zakeeruddin, C.Y. Yeh, E.W.G. Diao, M. Graetzel, *Angew. Chem.*, 49 (2010) 6646-6649
- [4] A.K. Chandiran, F. Sauvage, M. Casas-Cabanas, P. Comte, S.M. Zakeeruddin, M. Graetzel, *J. Phys. Chem. C*, 114(37) (2010) 15849-15856
- [5] A.K. Chandiran, F. Sauvage, E. Lioz, M. Graetzel, *Accepted*
- [6] F. Sauvage, F. Di Fonzo, V. Russo, P. Comte, C.S. Casari, A. Li Bassi, C.E. Bottani, M. Graetzel, *Nano Letters*, 10(7) (2010) 2562-2567.
- [7] G. D. Barber, P. G. Hoertz, S.H. A. Lee, N. M. Abrams, J. Mikulca, T. E. Mallouk, P. Liska, S.M. Zakeeruddin, M. Graetzel, A. Ho-Baillie, and M. A. Green, *J. Phys. Chem. Lett.* 2011, 2, 581-585

Workpackage 3: Characterization and Modelling

During this project we have made considerable progress in understanding the basic processes in DSSCs. We have focussed mainly on understanding these processes directly in terms of how they impact the efficiency of real devices. This helps keep the characterization and modeling efforts relevant to the efficiency optimization program. During the project we have developed new tools and techniques to aide characterization. We have also written a full cell simulation model (running in MatLab) which allows us to reproduce all the characterization results, and go further to predict the effects of variations not yet created in the laboratory. In the next paragraphs we will summarize the highlights of the characterization and modeling progress.

We have designed and built a fully automated system for characterizing DDSCs named TRACER (TRansient And Charge Extraction Robot). TRACER is based on complete computer control of cell conditions including applied potential, open circuit (OC) or short circuit (SC) condition, bias light, and pulsed light. Light is supplied by white and colored LEDs up to ~3 suns equivalent. The light levels and voltage on the cell can be pulsed or changed with an arbitrary wave form in ~200 ns. We have developed extensive automation software that allows sequential characterization of more than 10 parameters including the JV response, photocurrent vs light intensity, transient SC photocurrent and OC photovoltage, charge density (by charge extraction or capacitance integration) at any applied voltage or light level, large amplitude transients such as photocurrent "turn on" transients and Voc decays, and constant current transient photovoltage (CCTPV). This automated system is user friendly and often operated by undergraduates doing 6 weeks lab projects. Most recently we have built a second TRACER system capable of performing the same characterization on modules up to 10x10 cm, or single cells up to 1x19 cm. For modules this uses a unique array of 60 white diodes and 120 red diodes (figure 1a) along with low resistance switches. We have just begin to use this system on real "pre commercial" modules, but already demand is high for a larger version, now under construction.

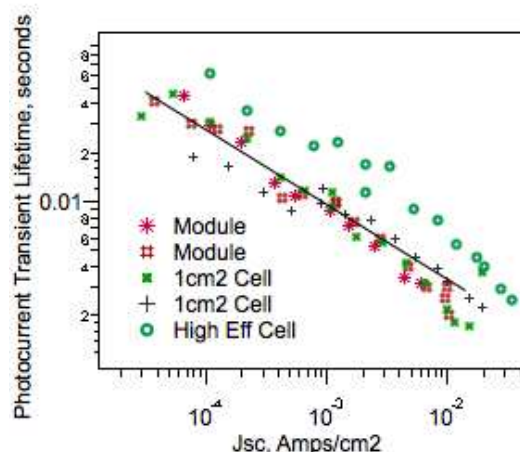


Figure 3.1 a) 15 x 15 cm LED array used in TRACERII. b) Results comparing current transport in a 10x10 cm module to the same data measured on small cells in TRACER I.

We have also built up an additional combined transient absorption (TA) and TRACER system for use when investigating the regeneration of the photo-oxidized dye. This reaction is too fast to follow by electrical signals alone. Along with this we have established a new methodology for studying this reaction in full operating cells so that the kinetic results are directly derived from and consistent with the cell efficiency. Results have allowed us to measure orders (figure 3.2) and rate constants for this reaction, specific to particular dye/electrolyte systems. These values are fed directly into the modeling (see below).

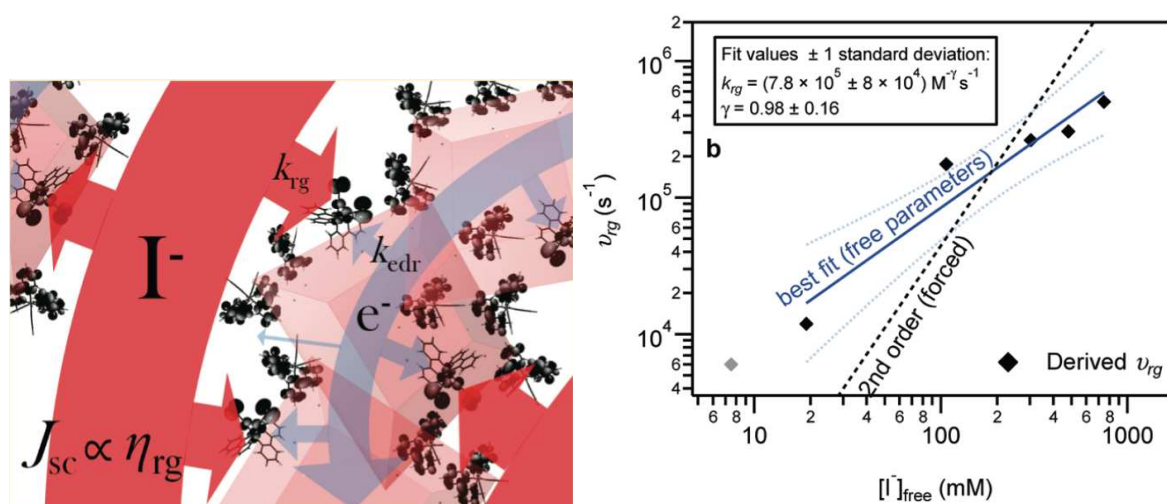


Figure 3.2 a) Schematic of the dye regeneration process and electron recombination to the dye. Black structures are the HOMO levels of the dye. Pink "crystallites" are TiO_2 . b) Recombination flux rate constant versus iodide concentration with fit showing approximately first order and clearly not second order behavior.

Using the TRACER system and model we have been able to measure the effect on J_{sc} and FF of the redistribution of the electrolyte species during operation. In stable cells using high boiling point (higher viscosity) electrolytes, the increase in iodine in the TiO_2 pores clearly reduces the electron lifetime, and the decrease in iodide increases the concentration of photo-oxidized dye. Taken together these can be significant effects, giving up to 3 times more recombination, for the same electron density, under light as compared to dark conditions. In addition we have used the temperature dependence of electron/electrolyte recombination to estimate the absolute TiO_2 conduction band edge as a function of electrolyte composition. Using front and rear spectral response measurements we have resolved the contradiction between previous very long diffusion length estimates and an empirical optimum thickness that was much shorter. However, exact theory to resolve the two remains controversial.

During the project we continued our studies of electron injection from excited dyes into TiO_2 , again focusing on standard operable cells. Studies comparing J_{sc} , TRACER data, and time resolved luminescence allowed us to show that in many standard cells, and cells from industry, the injection step is slow enough to have an efficiency <100% and thus limit the photocurrent.

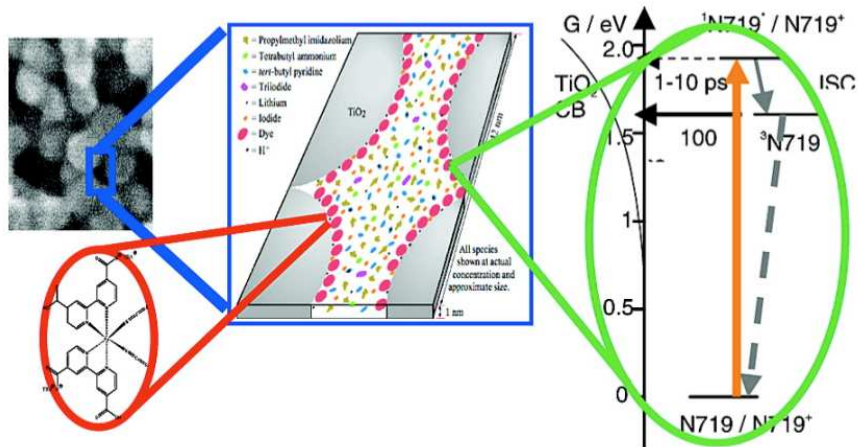


Figure 3.3. Physical and energetic schematic of the electron injection reaction.

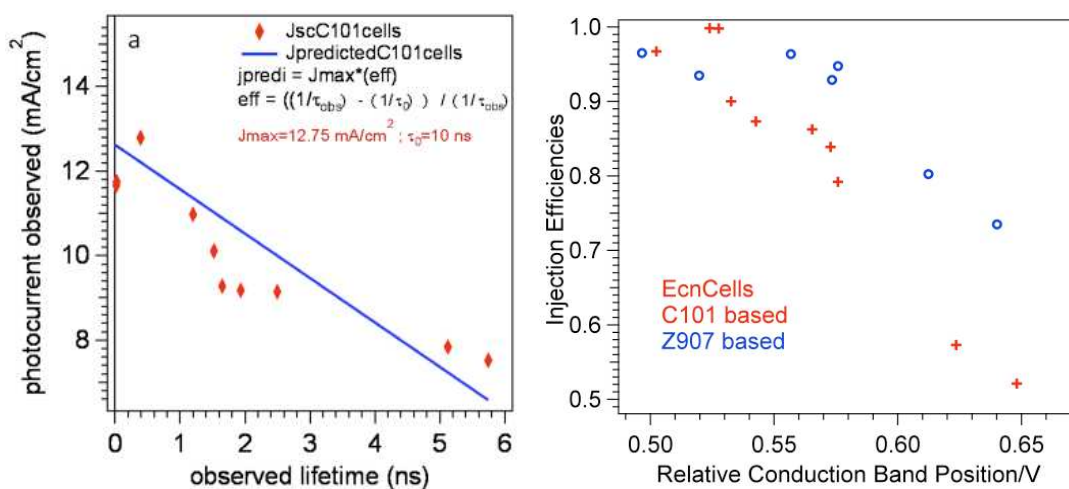


Figure 3.4 a) Plot showing the correlation between measured luminescence decay time and photocurrent in a series of 4 cm² cells from ECN. b) Plot showing how the injection efficiency (calculated from lifetimes in panel a) is determined by the position of the conduction band edge (determined from TRACER charge extraction measurements).

As part of the project we have developed a model to incorporate the kinetic results described above into a self consistent picture of DSSC operation and also to use for prediction of the effects of possible improvements and design of new experiments. The model incorporates the known features of DSSCs including trapped electron concentrations, non-linear recombination and transport, electrolyte diffusion, counter electrode potential etc. In addition, the model is useful for specific cells, where the measured transport, recombination, and regeneration rates, and the DOS of traps can all be entered. Figure 3.5 shows some of the available outputs from the model.

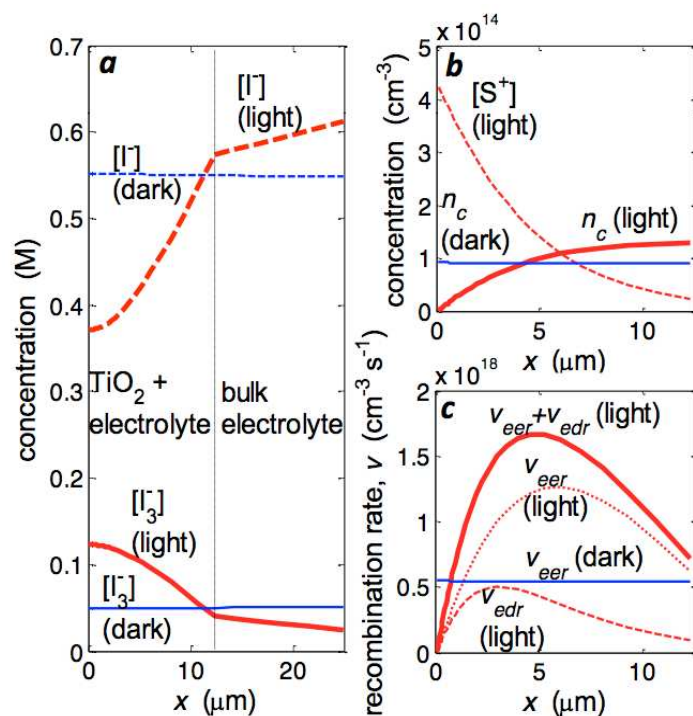


Figure 3.5 Electrolyte and electron concentration profiles and recombination flux profiles for a MPN based DSSC at short circuit under 1 sun.

In figure 3.5 a standard cell has been modeled at 1 sun intensity, short circuit conditions, with an standard solvent MPN. The results show that the depletion of iodide and build up of iodine in the pores can be significant. We also show the electron concentration and the absolute recombination flux to the electrolyte and to the photo-oxidized dye. The novel finding is that in this typical cell, the recombination to the dye is a significant fraction of all recombination at Jsc and also at Voc.

Taken together, the new methods, the results, and the modeling have allowed us to build up a self consistent model of cell. The characterization suite now allows us to take a module or cell from a commercial source and make suggestions on bringing it's efficiency closer to those of record cells. In additions, although the main limits to the efficiency of record cells remain well known (i.e. light absorption, increased Voc vs injection efficiency, and voltage loss at the regeneration step) our work has allowed us to describe additional issues such as how non-ideality determines the maximum fill factor, and the cost of heterogeneous injection and regeneration reaction conditions.

Workpackage 4: Module specific materials and processes

Objectives

The objective of work-package 4 was to work on specific development and up-scaling of materials and processes for application in the DSC modules. This included:

- up-scaling of material production to reach appropriate amounts for modules
- optimising the screen printing process and paste development
- improving the encapsulation and electrical interconnection
- developing the coloration process for modules
- defining low cost module materials for use in a demonstrator

Up-scaling of cell materials

At the beginning of the project, ECN ordered larger amounts of materials (dyes, TiO₂ pastes, electrolytes) at different commercial suppliers and distributed this to the various partners in the project for cell and module manufacturing. Fraunhofer ISE and ECN relied on subcontractor 3D-nano for providing them with paste for the catalytic back electrodes.

By increasing the physical size of the equipment used, Subcontractor 3D-nano is able to manufacture up to 8 liters of paste in a single production cycle which is more than 100 times the amount of product compared to the standard lab scale fabrication. 3D-nano provided the project partners with 1 kg of paste, which was used for the 100 cm² modules as well as for the 6000cm² demonstrator produced by Fraunhofer ISE. An excellent charge transfer resistance parameter of 0.2 Ωcm² was shown in 100 cm² modules.

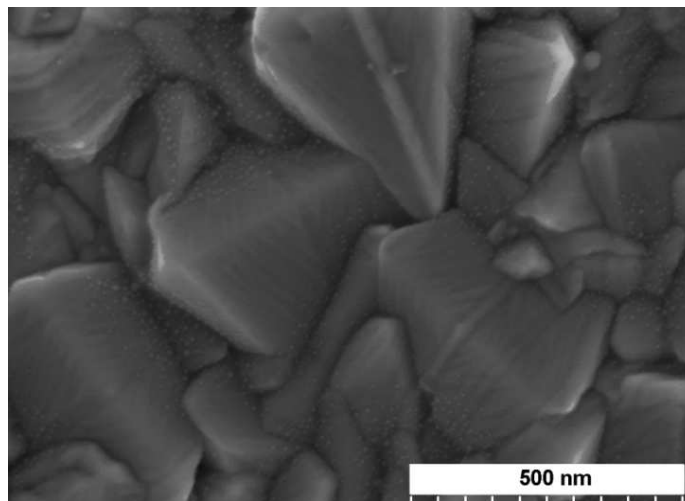


Figure 4.1 SEM image of a platinised counter electrode

The company is planning to put into practice a technology of the microreactors in near future. Major benefits of the microreactors vs. conventional batch chemistry are the safe and easy operation, fast development time and low reagent consumption during optimization. Microreactors provide strictly controlled reaction conditions thus contribute to the quality enhancement of the produced novel materials.

Screen printing and pastes

At Fraunhofer ISE, the glass frit structure was improved by using glass frit paste with a high rate of dispersion, i.e. a homogenous particle distribution, and by improving the parameters and screen mesh sizes for printing of the module electrodes. A drying procedure has been developed which prevents the inhomogeneous settling of the printed glass frit structure. The sintering temperature profile has been adjusted such, that during the melting up of the glass frit particles a good wetting and "bubble-free" solidification of the glass frit melt is possible. These improvements lead to fewer hole inclusions during fusing of the glass plates and therefore to a minimization of defects in the glass frit seal.

The printing and drying of the TiO₂ layer had to be optimised since there was no experience with the use of the Dyesol TiO₂ at Fraunhofer ISE till this project started. An astonishing flat surface of the TiO₂ photoelectrode layer was achieved. Only at the edges of the layer a small overshooting was still observed. As a flat, homogenous photoelectrode layer is crucial for achieving high photocurrents, this was regarded as an important stepping stone in the up-scaling of the screen printing process.

For application in the modules, several different platinum pastes were tested by the subcontractor 3D-nano for their printability, catalytic property and transparency. This was done using measurement techniques such as UV-vis spectroscopy, ICP-MS and SEM observation. The platinum paste which was delivered to Fraunhofer ISE showed good printing properties as well as acceptable catalytic effect. Catalytic effect increases with platinum content in the paste; this also reduces the transparency of the back electrode. Transparency of the back electrode will be important in the future for building integrated PV.

Encapsulation and electrical interconnection

At Fraunhofer ISE it was found that impurities on the glass substrate from organic origin can form hole inclusions or even channels in the glass frit, therefore decreasing the mechanical stability of the encapsulation. A new standard cleaning method was developed removing most of the impurities, if they are from organic origin.

Microscopic inspection of the fused glass frit from batch to batch showed that the fusing process is now better controlled and higher through-puts can be accomplished from batch to batch.

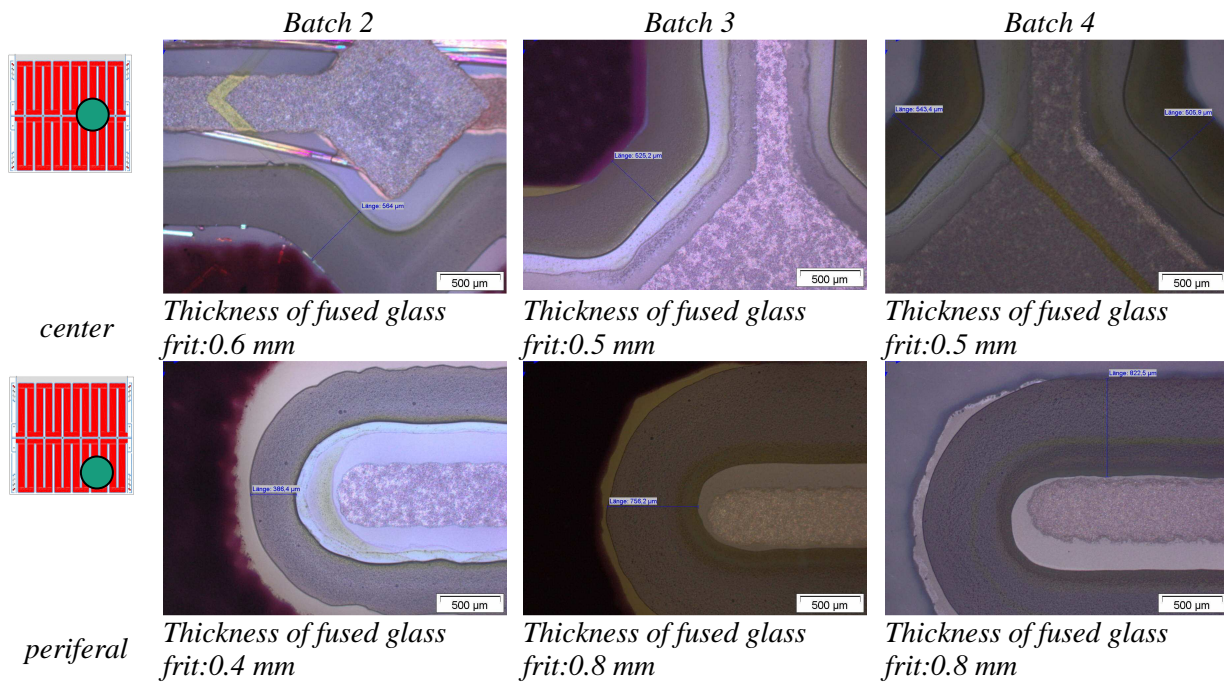


Figure 4.2

Corning's objective during the project was to demonstrate a possibility of hermetic packaging of the dye solar cell based on frit sealing technology (Vita™), or using glass sealing technology. The technology is based on the use of a high power laser delivering energy to highly absorbent frit or glass material and melt it with a fast moving laser heat source, so surrounding glass material is not heated. This enables sealing of temperature sensitive materials such as Dye sensitized solar cells. The work was focused on:

- Evaluating of the frit sealing of the edge in the presence of a liquid electrolyte, which is required for the DSC operation.
- Evaluating sealing of the filling holes with either glass seal or frit seal in order to provide a hermetic seal to the packages made with conventional technology (i.e., filling cells through holes in the glass).

Corning was able to show that the frit sealing process works in the presence of fluids. In order to minimize presence of air bubble trapped in package the cell can be overfilled with electrolyte and then sealed. Corning was able to show that the frit sealing process can be compatible with packaging fluids. During sealing the laser boils out the fluid which is in contact with the sealing surfaces. The package is sealed as if it would be dry. The boiling spot moves together with the laser and when the sealing loop is closed, almost no bubbles are trapped inside of the cell. The process works best with inorganic fluids. It was also shown that sealing in the case of a pure solvent such as methoxypropionitrile produces good results, with samples passing an 85°C test. However, sealing with HSE electrolyte and gel from Dyesol based on the same organic solvent show low yields with cell-leaking after the sealing. It was concluded that the seal fails due to organic contamination from other components of the electrolyte. Since some of the electrolytes such as the TG50 from Solaronix work well with the perimeter sealing, the final conclusion is that perimeter sealing is feasible with certain electrolytes. Special development of an electrolyte compatible with laser sealing and giving high efficiency is possible, but not in the time frame of this project.

Another set of efforts was targeting sealing holes with either glass seal or frit seal in order to provide hermetic seal to the packages made with conventional technology with filling cells through holes in the glass. For hole sealing of the final DSC package, it was shown that sealing of glass with a CTE of more than 5×10^{-6} 1/C to soda lime glass with a hole can be done with frit sealing or direct glass sealing at a fast speed and with a high yield. Sealing of higher CTE glass of more than 6×10^{-6} 1/C requires uniform heating of the sealing perimeter with gradual cooling.

Sealing of the glass package with a laser, even if the package has a hole, has a manufacturing advantage. Sealing of the package in the furnace requires two additional steps:

- staining of electrodes with dye
- filling package with electrolyte and sealing holes.

Laser sealing of the perimeter allows doing dye staining with open electrodes, which reduces time needed to process modules.

These final tests were performed with electrodes for the small test cell design from Fraunhofer ISE. The obtained cells filled with HSE electrolyte from DyeSol and coloured with the N719 dye showed a good efficiency close to 4% at 2.5 cm² active area. Unfortunately, the cell developed a leak through the perimeter. This was due to the presence of the residues of the dye at the seal path after staining. Therefore, the conclusion is that it may well be possible to make cells using this technique, but the seal area needs some advanced cleaning method (local plasma cleaning) or needs to be protected from staining by a special masking.

Coloration

At 3GSolar uniform dye staining on large cells was achieved with C101 dye. Comparisons were made between different dye materials, C101 and N719. Higher efficiency was achieved when using C101 compared to N719. Also, the RobustDSC electrolyte Z946 was compared to Dyesol HSE. This was done for as-is electrolytes and gelled versions of the electrolytes. Z946 efficiency is clearly lower than HSE, both initial and when aged in dark at 85C. However, there is noteworthy improvement of Z946 performance when aged at 85C under 1000 W/m² illumination where it closes the current density and efficiency gap with HSE after around 700 - 1000 hours of aging. C101 staining was also evaluated with DINHOP coabsorbent, better results were obtained when using DINHOP compared to the results with Chenodeoxycholic acid coabsorbent.

At Fraunhofer ISE it was found that when using pure DMSO as a solvent for the dye, the staining gets darker than for other solvents which can easily be observed by visual inspection. A drawback of using DMSO as a solvent for colouring is that it has to be removed very carefully after the colouration is finished by rinsing with ACN, since it will cause the module to be instable if any DMSO is left in the cells.

Low cost module materials

After two years of the project, it stood clear that it is not evident to define the most-efficient module concept or the most cost-effective materials. Moreover, the consortium had the opinion that the project should spend as much effort as possible on obtaining the module targets on 100 cm² devices (Deliverable 23: Stable module (100 cm²) at 7 % module efficiency). This was thus ranked as more important than to realize the demonstrator with the most promising low-cost concept. The ROBUST DSC partners therefore agreed (see Milestone 5.2) to exclude the most-promising low-cost criteria for the definition of the demonstrator. Instead, it was decided to use the existing design of 3GSolar for the 900 cm² demonstrator. In addition, at Fraunhofer ISE, it has been decided not to work on 900 cm² modules, but to focus on sizes that are interesting for building integrated photovoltaics. For this, demonstrator modules of the size 6000 cm² on single substrates have been realized.

Workpackage 5: Module designs and prototypes

The central objectives of this workpackage have been to deliver stable 100 cm² modules with module efficiencies of 7 %, and to realize a 900 cm² demonstrator with 5 % module efficiency. Stability was defined as <10 % degradation of the initial performance of three identical devices after exposure to 1000 hours of light-soaking under load, storage at 85 °C in darkness, and temperature cycling (defined to follow IEC 61215, i.e. 200 cycles from -40 to 85 °C). Moreover, the efficiency measurements should be taken at STC conditions (Standard Test Conditions, i.e. AM1.5G, 1000 W/m², 25 °C) and the device size was set to 10 x 10 cm².

There are many different designs and methods for module fabrication of DSC devices. An overview is given by Hagfeldt et al. Chem. Rev. 110, 6595-6663. In ROBUST DSC, four different module technologies from four different project partners have been investigated, as described below.

ECN	Current-collecting double glass-substrate sandwich devices
Fraunhofer ISE	Current-collecting double glass- substrate sandwich devices
Swerea IVF	Single glass-substrate monolithic serial-connected devices
3GSolar:	Large double glass-substrate single cells

Halfway through the project, ECN and Fraunhofer ISE decided to share design and process methods, i.e. three different module techniques were used during the second part of the project. Apart from the differences in module construction between the partners, further differences between the module technologies are that Fraunhofer ISE and ECN encapsulate the devices with glass-frits, whereas the others are using polymers. Swerea IVF and 3GSolar use carbon as counter electrode material, whereas Fraunhofer ISE and ECN use platinum. Moreover, there are processing details related to each design that may influence the device performance and stability.

The original strategy of ROBUST DSC was to continuously define a new set of reference material components, especially dye solution, electrolyte solution, TiO_2 paste, and conducting glass, in order to broadly advance in performance and stability among all the module partners. However, this turned out to be much more complicated than expected due to the fact that the experiences from different partners differed. The results were thus confusing and experiments had to be repeated many time-consuming times. As a result of this, a new strategy was defined after two project years, where each module manufacturer was responsible for defining its own set of reference materials that have the best possibility to achieve the project targets. This new strategy turned out successful and all module partners made significant progress in year 3.

The original objective of the demonstrator work was to realize a 900 cm^2 demonstrator with a 5% total area module efficiency (D24) using the materials for the most cost-effective module concept. After two years of the project, it stood clear that it is not evident to define the most-efficient module concept or the most cost-effective materials. The ROBUST DSC partners therefore agreed to exclude the most-promising low-cost criteria for the definition of the demonstrator.

Module results

The 100 cm^2 modules

The different modules are shown in the Figures below.



Figure 5.1. A $10 \times 10 \text{ cm}^2$ current-collecting double glass-substrate sandwich devices from ECN /Fraunhofer ISE.



Figure 5.2 A 10x10 cm² serial-connected monolithic module from Swerea IVF.



Figure 5.3 A double glass-substrate single cell from 3GSolar.

Module efficiency and stability

Each module manufacturer has tested devices according to the defined tests, i.e. 1000 h illumination, 1000 h at 85°C darkness, and temperature cycling (defined to follow IEC 61215, i.e. 200 cycles from -40 to 85°C). The latter was performed at Swerea IVF for all partners whereas the other tests were carried out by each partner, since the tests are straightforward and results can be compared. Apart from this, several additional tests were made to increase the understanding of the modules, e.g. storage in darkness at temperatures between 60°C and 80°C (ECN, Swerea IVF), illumination at elevated temperature (3GSolar and ECN), and efficiency measurements at different light-intensities (Swerea IVF).

In Table 5.1, an overview of the modules is given for the three tests that have been defined in the ROBUST DSC work plan. In Workpackage 6, some typical ageing patterns obtained by different partners are described presented in more detail

Table 5.1

Partners	Typical module efficiencies at STC (aperture area)	Stability 1000 h light-soaking	Stability 1000 h 85°C darkness	Stability temperature cycling -40 °C/85°C	Comments
ECN / ISE	4.1 – 5.3 %	Passed test, i.e. <10 % degradation	Passed test, i.e. <10 % degradation	Passed test, i.e. <10 % degradation	Illumination after high T testing results in recovery of a substantial part of the lost efficiency

Swerea IVF	4.0 %	Passed test, i.e. <10 % degradation	Failed test, 20-25 % degradation	Passed test, i.e. <10 % degradation	The module efficiencies after 1000 h illumination were 6.7 % (100 W/m ²) 6.3 % (250 W/m ²) 5.4 % (500 W/m ²) 4.0 % (1000 W/m ²)
3GSolar	5.1%	Passed test (best cell), i.e. 10 % degradation	Passed test (best cell; 85°C), i.e. 10% degradation; 12% for 6976 h	24 % degradation	<ul style="list-style-type: none"> • 5% improvement after 8970 h (i.e. >1 yr) outdoor test on Jerusalem rooftop • 22% degradation after 1008 hours of 85°C/85%RH • Light conditioning before measuring after test in dark

The 900 cm² demonstrator

The 900 cm² demonstrator has been realized by 3GSolar (Figure 5.4). It consists of four individual cells that have been assembled and electrically connected by external contacts. The device has delivered module efficiencies of 3.9 % at 1000 W/m² and 4.9 % at 500 W/m². Consequently, the project has not managed to deliver a demonstrator with 5 % module efficiency at STC. However, the 4.9 % module efficiency obtained at 500 W/m² is in fact extremely close. Additionally, it stands clear that at even lower light-intensities, the module efficiency exceeds 5 %.

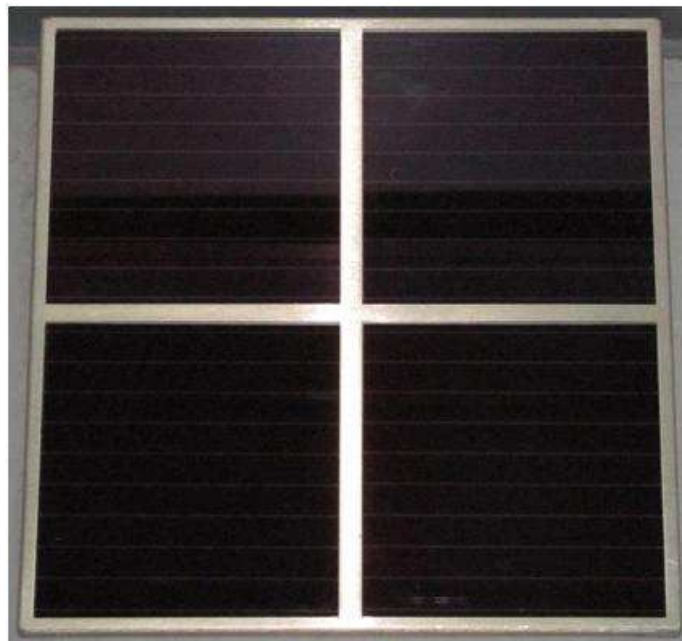


Figure 5.4 The 900 cm² demonstrator from 3GSolar.

The 6000 cm² demonstrator from Fraunhofer ISE

At Fraunhofer ISE a concept has been developed for dye solar modules, which is closely related to the manufacturing methods of the flat-glass industry. For the first time, it has been shown that DSC modules can be up-scaled on a single substrate to a size that is interesting for building integrated applications. Previously

published results on modules show externally series connection of small sub-modules; in contrast, this concept is a fully internally serial-connected module. The modules are manufactured in a multiple screen-printing process and are subsequently encapsulated in a thermal fusing step.

First prototypes were produced using a much thinner active layer than commonly applied. Moreover, the inactive area is very large, approximately 50 %. Therefore the photocurrent produced by these modules is limited. Nevertheless, first outdoor measurements at full sun show a short circuit current of 1.5 A and an open circuit voltage of 8 V. The design and manufacturing principle is the same as for the 100 cm² devices produced at Fraunhofer ISE. They therefore believe that it can be expected that stability and efficiency values will be very comparable to these in the near future.



Figure 5.5 The 6000 cm² demonstrator from Fraunhofer ISE.

Workpackage 6 Outdoor and Accelerated testing

The work performed in WP6 was divided in the following three categories:

- 6.1.** *Accelerated life time testing of cells and modules*
- 6.2.** *Outdoor long term performance testing*
- 6.3.** *Standardization of testing*

Task 6.1 Accelerated life time testing of cells and modules.

Accelerated lifetime testing of cells and modules was carried out by means of storage at elevated temperature in an oven (1000 h), continuous illumination at elevated temperature (1000 h) and temperature cycling (200 cycles between -40 and 85°C). An overview of all tests carried out for the different modules with initial efficiencies and results is given in table 5.1 under Workpackage 5.

Figure 6.1 shows a typical evolution of module IV parameters during testing at elevated temperatures (60 and 80 °C). After an initial period of 20-100 h all IV parameters stabilize except V_{OC} , which continues to decrease. FF shows a concomitant decrease caused by the change of V_{OC} .

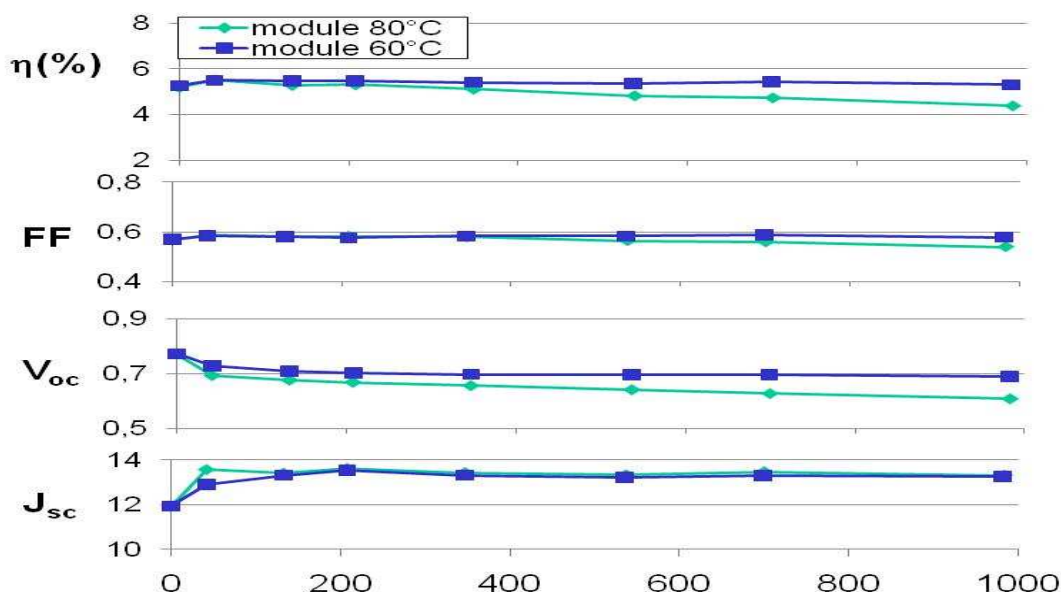


Figure 6.1 Module stability at 60 and 80°C at ECN.

The most stable cell at high temperature/dark (ECN, 4 cm²) with the best performance reached 6.7 % efficiency after 24 preconditioning at 80 °C. After prolonged ageing at 80°C during 960 h the efficiency decreased to 5.5 %. However, upon light soaking after the dark ageing test a recovery of the cell efficiency is often observed. For this most stable cell an impressive recovery to 95 % of the maximum performance (measured after 24 h preconditioning at 80°C) has been shown. As an overall result the loss in performance is only 5 % which is well below the maximum allowed 10 % in the definition of stability for the project. EPFL stable cells (< 1cm²) reached an efficiency of 9.6 % with more than 95 % retention of performance after light soaking at 60°C during 1000 h.

The monolithic series-connected devices from Swerea IVF passed the illumination and temperature cycling tests but failed in the 85°C darkness test (typically 20-25 % degradation). Further tests were carried out to understand the degradation at lower temperatures. It then stood clear that the devices are very stable for 1000 h darkness up to at least 70°C. Storage at temperatures between 70-75°C lead to degradation levels of 5-10 % in relation to the original performance. However, at higher temperatures, a threshold temperature is obviously passed since the degradation is much larger.

Another feature of the series-connected devices from Swerea IVF is that the performance, especially at lower light-intensities, is strongly activated by illumination. As an example, the module performance increased from 4.5 % to 6.4 % at 250 W/m² during the 1000 h illumination test. However, there was no difference between the initial and final performance when characterized at 1000 W/m².

6.2. Outdoor long term performance testing

A very promising result has been reached by 3GSolar in outdoor testing of their module. The performance has been stable during the period of testing of 9000 h. At ECN a decrease in FF was observed for 10x10 modules outdoor, probably due to corrosion of contacts.

6.3. Standardization of testing

DSC-specific pre-normative testing protocols have been proposed based on observations during accelerated long term testing of cells.

Some relevant observations made during (high T) ageing are the following:

- A steep initial efficiency rise followed by a slow decrease. Slow decrease is caused by a continuous V_{OC} decrease
- Acceleration of ageing by combined illumination/high T
- Arrhenius is “visible”: at 85°C ageing is faster than at 80°C for glass-glass devices, for monolithic it’s much more severe (maybe due to a change of ageing mechanism)
- Module related specific DSC issues: iodine migration under reverse bias, electrophoresis

What tests should a protocol contain?

For rooftop outdoor applications existing protocols should be followed as a start (IEC 61646) David Ginley, ISOS 2, 2009 (<http://isos.wikispaces.com/>). It is of great importance to define stability of the DSC. When the typical initial rise of efficiency upon exposure to elevated temperature is ignored, devices seem more stable than they actually are. A stabilization period of 20-100 h at the temperature of testing, in the beginning of the test is recommended to reveal the maximum achievable device performance as a reference to compare with the efficiency after completion of the durability test.

At the end of a durability test in the dark it is useful to check if the performance increases by a short period of light soaking (up to 200 h) and regular monitoring of IV parameters to get to the maximum achievable performance after durability testing.

Since illumination at high temperature (80-85°C) seems to induce extra stress (at least for ECN, ISE and 3GSolar modules), the illumination/85°C (including UV) test is highly recommended, to learn more and try to improve devices in that respect. Reverse bias is a test in the standard protocol, but deserves more attention and also electrophoresis needs further attention.

Conclusions and discussion

The monolithic series-connected devices from Swerea IVF suffer from a decreased fill-factor, and thus module efficiency, at increasing light-intensities. At 1/10 sun, i.e. 100 W/m², the fill-factor is good and a module efficiency of 6.7 % was obtained (a module efficiency of 7.0 % at 50 W/m²) after the 1000 h light-soaking. For the monolithic devices, the improvement of fill-factor at high light-intensities is the key to obtaining the 7 % stable module efficiency at STC. In order to realize this, several actions are required, e.g. to increase the conductivity of the carbon layer and the TCO layer, to use a thinner spacer layer and to use a less viscous electrolyte.

The best efficiency of the combined efforts of ECN/Fraunhofer ISE was a stable 100 cm² module of 7.10 % on active area, after 24 h at 80°C as a preconditioning. On total area (only 74 % of the total module area is active) this amounts to 5.25 % module efficiency. It should be noted that, like the Swerea modules, the fill factor is limiting at 1 sun illumination and improves considerably at low light intensities. Measured at 12 % of one sun illumination the efficiency is 5.7 %. To put this into a global perspective a review by Hagfeldt et al. can be referred to. From this review it can be concluded that historically there have been few published results containing module efficiencies in combination with data from accelerated testing of DSC modules. This review reports that most of the published module work with stability results reported module efficiencies between 3 and 4 %.

Despite the substantial progress made in module technology and improved stability/efficiency the target of a 7 % stable module has not been reached. Two relatively simple measures can be taken to get close to this target.

1. The amount of active area of the particular chosen module design is relatively small and 85 % coverage should be feasible by application of a different design (straight lines instead of meander with much more filling holes as a consequential drawback). In that case a total area efficiency of 6 % would have been reached.

2. A second improvement can be realized by application of NSG10 TCO glass with a 9 % higher transmission and a 9 % higher short circuit current (as shown in test cells, it should also be noted that for practical purposes NSG10 is still rather expensive at this moment). This would result in a stable module efficiency of 6.6 %.

To compare again to a maximum stable efficiency reported in literature this time for a small *cell* of 8.6 % (maximum after preconditioning) tested at 80°C/dark (Daibin Kuang, Adv Mat. 2007), this 8.6 % cell efficiency can be translated to a 5.9 % module efficiency when a FF of 0.65 (which is reasonable for a module) would be taken instead of 0.71 and the active area would be 74 % as in the ISE/ECN module design. It shows that a stable module efficiency between 5.2 and 6.6 %, which is feasible, can even meet with the state of the art result at cell level reported in literature.

Workpackage 7. Analysis of large scale commercialisation

Work Package 7 included the following tasks:

Cost of materials

- Identification of material cost for base materials and prediction of future price trends
- Prediction of large scale synthesis costs for specific materials (TiO₂, graphite, catalytic layers, dye, electrolyte) using data from procedures in industry and from new innovative synthesis (microreactors)

Evaluation of large scale manufacturability

- Identification of comparative production processes and machinery in industry (glass industry, display industry, printing industry, PV industry)
- Investigation of DSC module concepts for throughput in in-line process
- Estimation of investment costs and return of investment

Life Cycle Analysis

- Calculation of energy and material inputs for large scale production.
- Inventory of emissions to the environment during production, installation and disposal / recycling.
- Life cycle impact assessment (not inventory) calculating size of impact on relevant environmental indicators.
- Calculating of energy payback time for DSC modules taking into account the balance of the system for different locations and applications (roof-top, stand-alone, façade).

Material costs have a major contribution to the total cost of the DSC module. Our base calculation shows material costs of around €40.7/m², which is €0.58/W_p for 7% efficient modules.

Cost of materials for ROBUST DSC module baseline

	Cost per m² Robust DSC	Cost per W_p Robust DSC	Comments
Anode			
TCO glass	€ 7.00	€ 0.10	
TiO ₂ paste	€ 4.5	€ 0.06	assumes 90g/m ²
Ag paste	€ 3.60	€ 0.05	
Dye	€ 4.50	€ 0.06	assuming 1 g/m ²
Cathode			
Pt paste	€ 2.38	€ 0.03	

Polyurethane			
Cover glass	€ 2.10	€ 0.03	
Sealing			
Seal material	€ 5.28	€ 0.08	
Filling			
Electrolyte	€ 4.57	€ 0.07	assuming 50g/m ²
Bus Line			
Soldering	€ 0.88	€ 0.01	
Interconnection material	€ 3.60	€ 0.05	
Frame			
Al frame	€ 0.24	€ 0.003	
Liquid adhesive	€ 2.10	€ 0.03	
Total Cost	€ 40.74	€ 0.58	

The dye cost was estimated according to a quote from Johnson Matthey for 100 kg of N719 dye and updated according to the present price of ruthenium. Manufacturing charge for 100Kg of N719 is €4.1/g plus cost of metal. N719 is 8.5% ruthenium by weight. At the present ruthenium cost of €4.2/g, the cost adder is €0.36/g. Total cost per gram of N719 is therefore estimated at €4.5/g.

Review of the manufacturing cost structure reveals opportunities for further reduction. Significant gains can be achieved by dyes with increased absorption coefficient, thereby reducing consumption of both dye and titania. If titania thickness and the quantity of dye and of electrolyte are reduced by a factor of two compared to the estimations above (or alternatively, their costs per kilogram), a cost savings of €0.10/W_p is achieved.

Regarding titania, nanoparticle titania of pure anatase phase is the preferred material for dye solar cells. Researchers and suppliers of research grade materials typically use manufacturing processes that are high cost, low throughput and not easily scaled to mass production. High volume, low cost TiO₂ is available from companies like Evonik-Degussa by a process of gas phase powder synthesis (e.g. P25 and P90) but these materials are a mix of anatase and rutile phases. Despite the lack of phase purity, the Degussa and similar nano-titania products are still good candidates for mass production of modules. In addition, there is advancement in highly scalable innovative synthesis of pure phase anatase. Solaronix SA now estimates anatase titania paste at €95/kg for quantities of 30 tons per year. The company Joma International of Norway estimates anatase titania paste at less than €50/kg in quantities of 300 tons anatase powder per year in paste form (which is 1000 tons of paste at a 30% solids content).

Evaluation of large scale manufacturability

Production of the DSC module consists of eight major production stages described graphically in the flow diagram in the Figure.

First: Glass is scribed, broken and cleaned. This is a standard industrial process and the equipment for the process is available from the thin film PV industry.

Second: TiO₂ layers are screen-printed and dried. Screen printing is one of the most versatile printing processes. A varied selection of fully automatic and semi-automatic printers is available in the market. Automated printing lines that include several printing processes are available to the silicon PV industry with processing speeds of 1,440 cells per hour (Applied Materials – Baccini).

Third: Printed layers of TiO₂ are sintered at temperatures of typically 450°C to 550°C. Sintering is a standard industrial process and high-temperature belt ovens are available in the PV and a wide range of other industries.

Fourth: The TiO₂ layers are stained in dye. A batch staining process requires typically 16 hours in the lab when preparing research cells. The volume of the bath and the staining solution can be estimated for this staining time regardless of substrate size. We assume glass thickness of 2.2 mm and glass area per hour of

8000 kW per yr production / 6000 hrs net annual production time / 0.07 kW/m² = 19 m² per hour. If the gap between the glasses is 1.8 mm (dye driven between the plates by a flow system), bath volume is 19 m²/hr * 0.004 m * 16 hrs = 1.2 m³ (1200 liters) and volume of dye is 550 liters. This would be double for a more automated, faster plant of 16 MW annual production (2400 liter bath and 1100 liters dye solution).

Staining process, since it has the longest cycle time, is a potential bottleneck in industrial production of DSC's. Development of much faster staining techniques is desired for in-line production. For their pilot line, G24i achieved staining time of 6 minutes for Z907 dye, thereby enabling efficient in-line manufacturing.

Fifth: The module is sealed with organic sealing or glass frit. Thermal sealing with thermoset organic adhesives typically requires a long cure time. Glass frit sealing requires high temperature (up to 600°C). UV sealing has a cure time of less than a minute and potentially, only a few seconds. This sealing process also offers lower energy use.

Sixth: Electrolyte is filled into the cell/module using vacuum sealing or by using flow-through methods. These filling methods are widely used in production of electrochemical batteries and capacitors.

Seventh: Cells/mini-modules are assembled into modules. This process will require design of custom equipment. Extensive experience in PV module assembly exists in the PV industry.

Eighth: DSC modules require performance testing and quality control. An international standard that specifies procedures to examine the impact of mechanical, thermal and electric stress on power output and lifetime has not yet been defined for DSC modules. Various testing equipment is available in the PV industry.

Flash testing used to test PV performance and sort Si cells cannot be used with DSC because of their large capacitance. DSCs require ~20 sec per IV scan. Even on this time scale, there is hysteresis when scanning voltage from I_{sc} to V_{oc} and then back again.

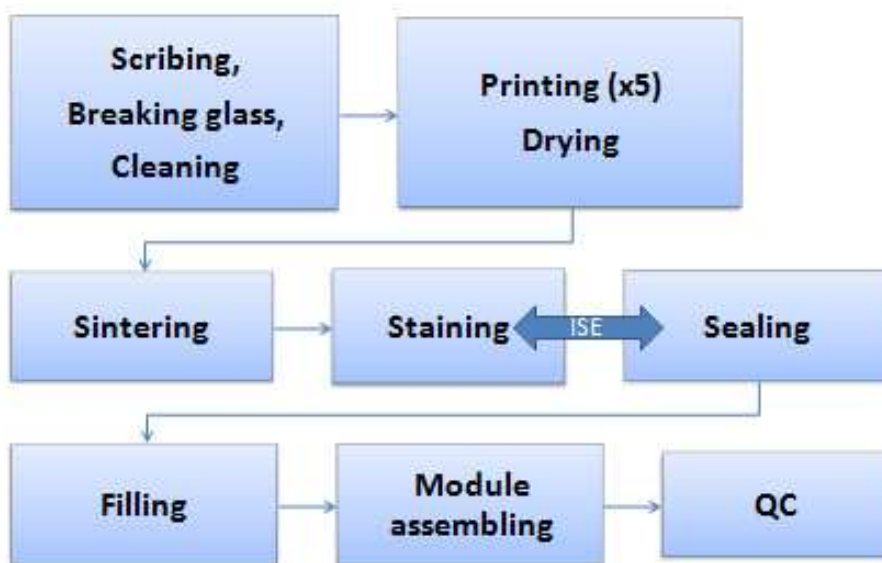


Figure: The process flow diagram of in-line production of DSC module. In the ISE design, staining is preceded by sealing.

To evaluate the efficiency of the business investment in DSC technology, we performed Return on Investment (ROI) analysis of an 8 MW production line. To calculate ROI, the benefit from the investment is divided by the cost of the investment and the result is presented in percentage form.

$$ROI = \frac{\text{Gain from Investment} - \text{Cost of Investment}}{\text{Cost of Investment}}$$

We calculated ROI for three scenarios of the production cost: a) €0.86/W, according to our initial cost analysis; b) €0.7/W, according to the target of the Robust DSC consortium, and c) €0.63/W, assuming cost reduction of materials and manufacturing presented as analyzed in the Deliverable 26 Report. For all scenarios we assume a sale price of €1.30/W for the first two years and reduction of the prices by €0.1 every consequent year. By year 5, ROI results for each scenario are a) 29%, b) 56% and c) 72%.

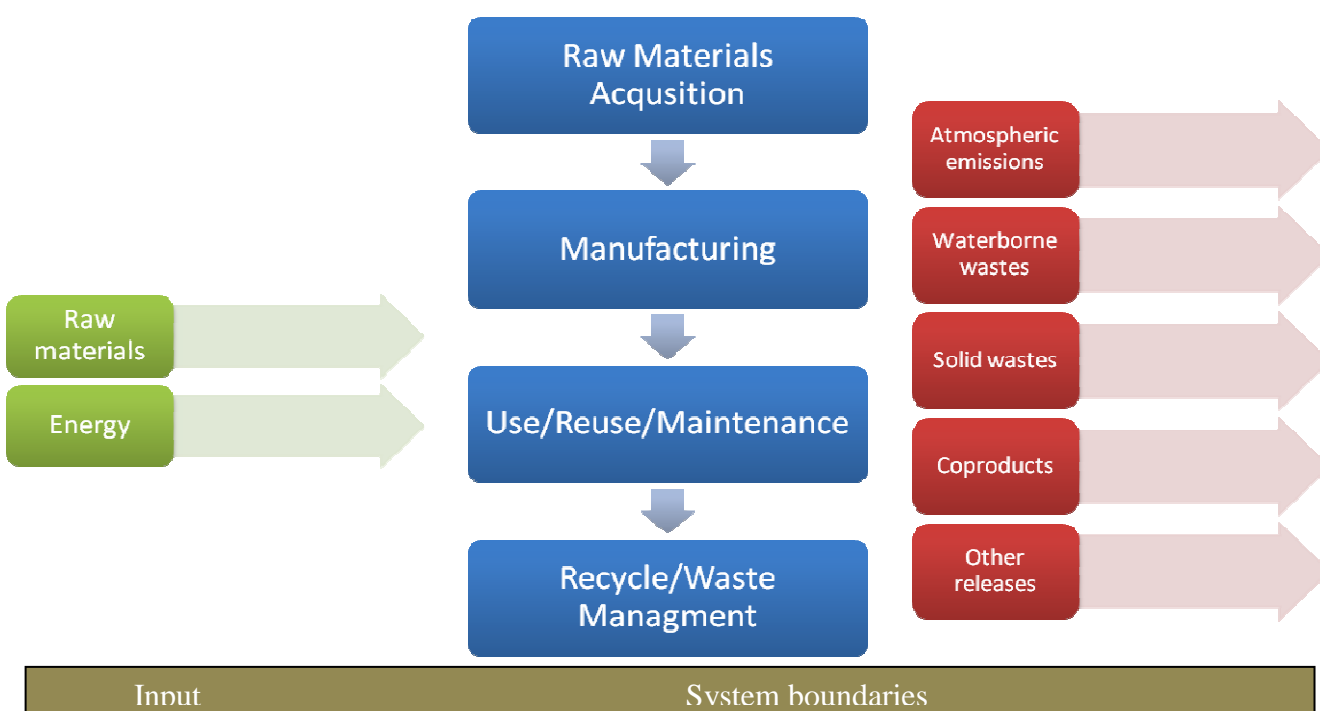
Payback time of the investment, which is a point in time where all the inflows balance the outflows is a) 1.5 years for €0.86/W cost;

- b) 1.1 years for €0.7/W cost;
- c) 1 year for €0.63/W cost.

Life Cycle Analysis

Awareness of natural resource depletion and health and nature damage leads to investing effort to analyze and change production processes. LCA is a tool that allows investigation and helps to decrease the effect on the environment by analyzing ecological footprint of the product over its lifetime. The input of this analysis is consumption of energy and materials; the boundaries are acquisition of the raw materials, manufacturing, use and disposal; the output is the calculated emission into air, water or soil (Figure). The outcome of LCA can be, for instance, recommendations to reduce a number of materials or to use materials and processes that cause least impact to the environment.

Figure 7.1: Life cycle structure



The International Organization for Standardization (ISO) defined four major stages of LCA: goal definition and scoping, inventory analysis, impact assessment, and interpretation (1).

1. *Goal and scope* – presentation of the product and the questions that should be answered, definition of system boundaries and functional units.
2. *Inventory analysis*- presentation of the energy and materials flow and emissions to the environment.
3. *Impact assessment* – characterization of human and ecological problems due to the material usage and emissions described in the inventory analysis.
4. *Interpretation* – drawing final conclusions based on the impact assessment result. Choice of materials, technology and production processes that create least impact to the environment.

As part of RobustDSC, Life Cycle Analysis of the Dye-Sensitized Solar Cell was performed on the basis of the various designs of the consortium partners. This includes designs from 3GSolar, Fraunhofer, ECN, Swerea and G24i.

Greenhouse gas emission was calculated for the 3GSolar, Fraunhofer, ECN, Swerea and G24i DSC panels and showed that the average Carbon footprint of the DSC panels with 7% efficiency and 7 year life is lower than the Carbon footprint of the crystalline Si technologies, but higher than that of CdTe. The greenhouse gas

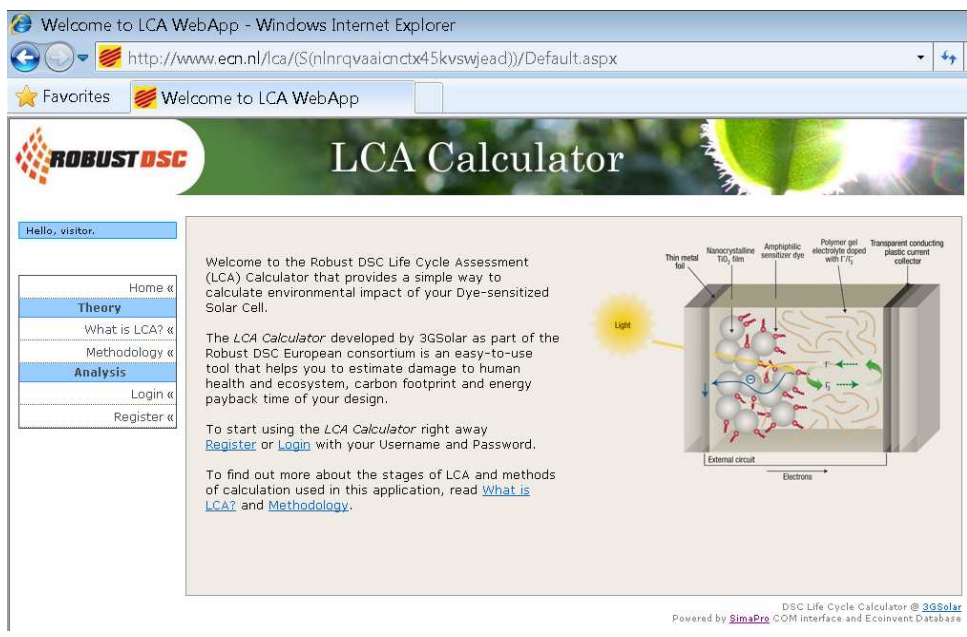
emission of dye cell panels can be reduced by increasing efficiency and/or lifetime and therefore also achieve better results than the thin-film CdTe.

Environmental damage calculations were made for Human Health, Ecosystem Quality and Resource Depletion and compared with environmental damage of mc-Si panel. We showed that overall damage of the Fraunhofer, 3GSolar and ECN designs is higher (especially in the Human Health category) than damage of the ms-Si if assumed efficiency of the DSC module is only 7% and lifetime is only 7 years. Overall environmental damage will be lower than environmental damage of mc-Si panels if the DSC panels have lifetime of at least 11-16 years (depending on the particular DSC design).

We calculated energy payback time and found that a DSC panel with 7% efficiency has energy payback time which is four to five times shorter than EPBT of all the crystalline Si panels and 1.5 time shorter than CdTe panel. The use of thinner glass will significantly reduce primary energy consumption during manufacture, thus further decreasing energy payback time of the DSC panels.

Energy payback time of different PV applications was calculated taking into account three locations: roof-top, stand-alone and façade. We showed that stand alone application has highest EPBT due to use of battery. BIPV (façade) installation has a potential to have lowest energy payback time when it replaces building materials. However, electricity production of the panel integrated in the building envelope strongly depends on the orientation of the panel towards the sun. When orientation is optimal, the EPBT is only 0.3 year.

As part of the data collection and analysis process, a web based tool was developed by 3GSolar and deployed in a dedicated ECN webpage. The web tool interface is shown in the figure.



Potential Impact

A Vision for Photovoltaic Technology

In 2005 the European Photovoltaic Technology Research Advisory Council (PV-TRAC), has prepared the report “A Vision for Photovoltaic Technology” with the purpose of contributing to the rapid development of world-class, cost-competitive European photovoltaics (PV) for sustainable electricity production. The report identified the major technical and non-technical barriers to the uptake of the technology and outlines a strategic research agenda designed to ensure a breakthrough of PV and an increase in deployment in the Union and worldwide. This Strategic Research agenda appeared in June 2007 under the auspice of the EU PV technology platform and quite recently followed by an Implementation Plan describing how to put into practice the SRA’s findings and recommendations.

The SRA stated that the end-user but they rather focus primarily on the following parameters, irrespective of the nature of the PV technology:

- the price per watt-peak of module
- the energy yield per watt-peak under field conditions
- the module’s efficiency and reliability
- size and weight of the module
- flexibility or rigidity
- appearance
- recycling scenario’s

There is a large portfolio of different PV technologies, each with their own specific advantages and disadvantages but they will all be evaluated in terms of the parameters mentioned above. For the R&D community, it is crucial to get a sound understanding of all the different cell and module technologies resulting in the work programs to achieve the required cost reduction, performance enhancement and improved environmental profiles.

It is clear that different technologies require their own research and development activities, although they have a number of issues in common. The categories of technology chosen for the SRA are:

1. Wafer-based crystalline silicon;
2. Existing thin-film technologies;
3. Emerging and novel technologies (including “boosters” to technologies in the first and second category)

While the common R&D issues can be generalized as:

- Efficiency, energy yield, stability and lifetime
- High productivity manufacturing, including in-process monitoring & control
- Environmental sustainability
- Integration

The PV market is currently dominated by wafer-based crystalline Silicon with >80 % market share in 2010. The market share of existing thin-film PV technologies like CdTe, CI(G)S is presently increasing. Thin-film PV are made by coating and patterning entire sheets of substrate, generally glass, stainless steel or even plastics, with micron-thin layers of conducting and semiconductor materials, followed by encapsulation. This leads to a process that can be highly efficient in materials utilisation, has relatively low labour requirements, and uses comparatively little energy in the total manufacturing process. It has been recognized that there is a strong potential for a low cost and high-volume production of thin-film PV modules enabling costs to reach 0.5 €/Wp in the long term if intensive R&D work is carried out. This will automatically to an increased share which is expected to grow beyond 30 % on the longer term.

In the last category of emerging and novel technologies, the focus is on realizing very low cost approaches at moderate efficiencies and/or high efficiency approaches at moderate costs. It is the first category where

organic based solar cells could play an important role. In these type of cells, the photoactive layer consists completely or partly on organic molecules or polymers. They offer the prospect of achieving very low materials and substrate costs, low energy input by high throughput atmospheric production methods and easy up-scaling. This should finally lead to costs significantly lower than 0.5 Euro/Wp.

The dye sensitized solar cell technology is one of the organic based approaches consisting of a hybrid of organic and inorganic nano-components. The main challenges for the organic based approaches relate to the increase of efficiency, stability improvement and the development of an adapted manufacturing technology. The SRA indicated that efficiency of these devices must be raised to 10% with a target of 15% for laboratory cells by 2015 and ensuring module operation for 20 to 30 years with less than 10% efficiency decrease. if they are to be deemed to hold potential in the long-term for the power generating market. These items were exactly the focus of the EU-FP7 project Robust DSC

Although currently about 80% of the modules produced are based on crystalline silicon (c-Si), the report argues that thin-film modules will become increasingly important. DSCs are thin-film cells and PV-TRAC indicated in its report that this technology is gradually moving out of the laboratory phase. In the tentative list of research areas for thin-film PV the report indicated specifically that R&D should focus at increasing efficiency to > 15% and ensuring module operation for 20 to 30 years with less than 10% efficiency decrease. Improvement of module efficiency and stability was exactly the focus of the ROBUST DSC project.

Market potential of DSC

To enable long term use of Organic based PV (including Fully OPV and DSC) to replace conventional electricity generation, e.g. in grid-connected or stand-alone roof top applications, and significant progress in efficiency and especially lifetime is needed. For this reason it is projected that large-area, high-efficiency applications will not become feasible before around 2015 as seen in the table below. Nevertheless, due to a continuous progress in device performance, OPV/DSC market will grow continuously in size over the next years and will follow a “stepping stone approach” via different product generations first entering into (niche) markets for mobile electronics applications. The table below provides a tentative timeframe for applications of OPV/DSC in short, medium and long term that can be expected from successful R&D and knowledge exploitation in this field.

Time frame	Short-term 2010-2012	Short-term 2011-2013	Medium-term >2013-	Long-term > 2018
Application Area	Mobile Electronics	Outdoor recreational remote	Off grid power and Building Integrated PV	Roof top grid-connected, bulk power generation
Product generation	Gen1: Flexible, low weight modules, product lifetime 1-2 years Lower efficiency	Gen2: Flexible, low weight PV, product lifetime 3-5 years Moderate Efficiency	Gen3: Flexible/rigid low weight modules, product lifetime 5-10 years Moderate Efficiency	Gen4: Flexible/rigid low weight modules, product lifetime >10 years
Typical applications	Low-power applications for indoor electronic devices and portable consumer products (e.g. PDAs, laptops, navigation systems, mobile phones, MP3 players, toys, remote controls)	Shading elements (“powerbrellas”, awnings, parking lots), tents, sails, bags and backpacks	Stand-alone outdoor applications, e.g. solar-homes, rural electrification; building structures such as windows, skylights, facades, roof's, and walls.	Established competitive solar technique for 4 out of 5 PV market segments
Scientific /	• New European	• New European	• Exploitation of	• Establishment of

technological prospects	base patents <ul style="list-style-type: none"> • Improved efficiency • Proven power output stability • Improved robustness • Enhanced industry understanding and awareness 	base patents <ul style="list-style-type: none"> • Improved efficiency • Verified indoor and outdoor stability 	patents <ul style="list-style-type: none"> • Birth of new European organic-PV industrial sector 	European OPV/DSC industry for large area power application <ul style="list-style-type: none"> • Molecular Design PV
--------------------------------	---	---	--	--

Pre-commercialization activities of DSC in Europe and worldwide

The prospect of unique selling points like lightweight, flexibility, full transparency, color variation and/or low cost processing technology as well as the wider applicability of DSC in areas that are inaccessible to conventional inorganic PV technologies have triggered a number of companies to start R&D on DSC.

The following lists up some of the leading companies with commercial ambitions and activities on glass-based DSC prototype development: Sharp Solar (Japan), Sony (Japan), Fujikura (Japan), TIMO (Korea), 3GSolar, (Israel), Pilkington (US). Further, flexible type DSC module prototypes are developed e.g. by DAI Nippon Printing (Japan), Solarprint (Ireland), Panasonic (Japan), Peccel (Japan), G24i (UK) and Tata Steel/Dyesol (UK). Robust DSC partners G24i being the first company in setting-up a production line for flexible DSC. Additionally, several companies are involved in producing and selling specific DSC materials and production equipment for DSC like Solaronix (Switzerland), Dyesol (Australia), Iolitec (Germany), Merck and BASF (Germany).

The short-term targets of these companies are to launch first stepping stone applications most likely in the low and mid power market segment of consumer products portables, which have a relatively small, but nevertheless substantial share in the total market for PV. The restrictions on performance in terms of efficiency, lifetime and costs for these segments are more relaxed compared to the performance profile needed to enter the on-grid market, making them more suitable for DSC at this stage of development.

Dissemination and/or exploitation of project results

The consortium followed a policy of active dissemination of knowledge and results which was realised by the following actions:

- Exchange of scientific staff took place with the aim of increasing the scientific output, propagation of “best practices”, side-by-side comparisons of different technologies and preparation of integration;
- Scientific publications in relevant journals
- Contributions to conferences (orals, posters, exhibitions)
- Cross fertilization with related EU projects in other frames or thematic areas like NMP.

In addition, we can say that a number of achievements obtained by the partners in Robust DSC are of crucial importance for further dissemination and exploitation to accelerate the uptake of the DSC technology as a viable PV technology for several application areas.

These can be highlighted as follows:

- The portfolio of available sensitizing dyes and electrolyte compositions able to achieve > 10 % efficiencies for small cells have been extended tremendously, since the start of the project. Over 13 % efficiencies are obtained for single junction DSC at 0.6 sun illumination conditions for selected materials combinations. The Robust DSC project has achieved unprecedented efficiency records and set new performance benchmarks, which will be of great benefit to the practical implementation and commercial development of this promising new PV technology.

- Development of a characterisation tool set and a whole cell model for predictive evaluation of device performance. The model and tool set have been completed to conditions where it can be disseminated to a wider public. The developing partners Imperial is considering commercialization of a generic transient experimental system based on the designs developed in this project.
- It has been proven by Corning that hole-closure can be done by glass-frits using laser assisted sealing methods with the aim to demonstrate hermetic packaging of the DSC under all possible operating conditions
- Large Area demonstrators up to 6000 cm² have been manufactured by Fraunhofer ISE showing the potential of large scale manufacturability of DSC
- The research institutes responsible for the manufacturing of large area modules have all made significant progress in the development of the processing technology, device stability and performance, resulting in two different device technologies (monolithic serial-connected modules and glass-frit sealed sandwich modules) that will be further developed towards commercialisation after ROBUST DSC.
- It has been shown that it is not straightforward to compare the results between different module manufacturers since the processing significantly affects the results.
- It has been shown that there are difficulties involved in defining the degradation of DSC devices due to the dynamic (and module-specific) behaviour of the performance. This has led to the formulation of a pre-normative standard test protocol for DSC taking into account the specific properties of the DSC concepts
- An extensive report has been written including cost of materials, evaluation of large scale manufacturability, and life cycle analysis. Additionally, calculations on the Return on Investment (ROI) are provided. Detailed life cycle analysis and energy payback calculations were completed on the module designs of all Robust DSC partners. As a result, a web tool accessible by all partners was created to assist in the analysis. The web-tool will be disseminated for continued use of the partners and others in the dye cell field.
- Outdoor tests have been made by especially ECN and 3GSolar. The latter has achieved one year operation under Israeli outdoor conditions without any degradation of the device performance.
- Modules from different partners have passed the temperature cycling and damp-heat tests with < 10 % degradation of the performance, as defined by IEC 61215, the International Standard for crystalline PV devices.

List of beneficiaries and contact persons

1. ECN Solar Energy	Dr. J. Kroon (j.kroon@ecn.nl)
2. Swerea/IVF	H. Pettersson (henrik.c.pettersson@swerea.se)
3. Fraunhofer ISE	Dr. A. Hirsch (andreas.hirsch@ise.fraunhofer)
4. EPFL	Prof. Dr. M. Graetzel (michael.graetzel@epfl.ch)
5. Imperial	Dr. B. O'Regan (b.oregan@imperial.ac.uk)
6. ICIQ	Prof. Dr. E. Palomares (epalomares@iciq.es)
7. 3GSolar	Dr. B. Breen (bbreen@3gsolar.com)
8. Corning	Dr. S. Vallon (VallonS@Corning.com)
9. G24i	Dr. Silvia Villarroya-Lidon ('silvia.villarroya-lidon@g24i.com)
10. UAM	Prof. Dr. T. Torres (tomas.torres@uam.es)

Public website
www.robust.dsc

4.2 Use and dissemination of foreground

A plan for use and dissemination of foreground (including socio-economic impact and target groups for the results of the research) shall be established at the end of the project. It should, where appropriate, be an update of the initial plan in Annex I for use and dissemination of foreground and be consistent with the report on societal implications on the use and dissemination of foreground (section 4.3 – H).

The plan should consist of:

- Section A

This section should describe the dissemination measures, including any scientific publications relating to foreground. **Its content will be made available in the public domain** thus demonstrating the added-value and positive impact of the project on the European Union.

- Section B

This section should specify the exploitable foreground and provide the plans for exploitation. All these data can be public or confidential; the report must clearly mark non-publishable (confidential) parts that will be treated as such by the Commission. Information under Section B that is not marked as confidential **will be made available in the public domain** thus demonstrating the added-value and positive impact of the project on the European Union.

Section A (public)

This section includes two templates

- Template A1: List of all scientific (peer reviewed) publications relating to the foreground of the project.
- Template A2: List of all dissemination activities (publications, conferences, workshops, web sites/applications, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters).

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES										
NO.	Title	Main authors	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages	Permanent identifiers ² (if available)	Is/Will open access ³ provided to this publication?
1	Dye-Sensitized Solar Cells Employing a Single Film of Mesoporous TiO ₂ Beads Achieve Power Conversion Efficiencies Over 10%	F.Sauvage/M. Graetzel	ACS Nano	4(8), 4420, 2010	The American Chemical Society		2010	4420-4425		No
2	Doping a TiO ₂ Photoanode with Nb ⁵⁺ to enhance Transparency and Charge Collection Efficiency in Dye-sensitized Solar Cells	A. Chandiran/M. Graetzel	J. Phys. Chem. C	114, 15849, 2010	The American Chemical Society		2010	15849-15856		No
3	Utilization of Direct and Diffuse Sunlight in a Dye-Sensitized Solar Cell-Silicon Photovoltaic Hybrid Concentrator System	G.D. Barber//M. Graetzel	J. Phys. Chem. Lett.	2, 581, 2011	The American Chemical Society		2011			No
4	Hierarchical TiO ₂ Photoanode for Dye-Sensitized Solar Cells	F. Sauvage//M. Graetzel	Nano Letters	10, 2562, 2010	The American		2010	2562-2567		No

² A permanent identifier should be a persistent link to the published version full text if open access or abstract if article is pay per view) or to the final manuscript accepted for publication (link to article in repository).

³ Open Access is defined as free of charge access for anyone via Internet. Please answer "yes" if the open access to the publication is already established and also if the embargo period for open access is not yet over but you intend to establish open access afterwards.

					Chemical Society					
5	Panchromatic ruthenium sensitizer based on electron-rich heteroarylvinylene p-conjugated quaterpyridine for dye-sensitized solar cells	A. Abboto/M. Graetzel	Dalton Transaction	40, 234, 2011	The Royal Society of Chemistry		2011	234-242		No
6	A Dendritic Oligothiophene Ruthenium Sensitizer for Stable Dye-Sensitized Solar Cells	F.Sauvage/ M. Graetzel	ChemSusChem	2, 761, 2009	Wiley-VCH Verlag GMBH.KGa	Weinheim	2009	761-768		No
7	Pulsed Laser Deposition of hierarchical anatase TiO ₂ for Dye Sensitized Solar Cell	F. Sauvage/ M. Graetzel	Nano Letters	10(7), 2010	The American Chemical Society		2010	2562-2567		No
8	Ga ³⁺ and Y ³⁺ cationic substitution in mesoporous TiO ₂ photo-anodes for photovoltaic applications	A.K. Chandiran/ M. Graetzel	J. Phys. Chem C	In press	The American Chemical Society		2011			No
9	Effect of anchoring groups in zinc phthalocyanine on the dye-sensitized solar cell performance and stability	M.Iglesias/ M. Graetzel/T.Torres	Chemical Science	In press	The Royal Society of Chemistry		2011	DOI: 10.1039/C0SC00602E		No
10	Incorporating Multiple Energy Relay Dyes in Liquid Dye-Sensitized Solar Cells	J. Yum/ M. Graetzel/T.Torres	ChemPhysChem	11, 1-6, 2010	Wiley-VCH Verlag GMBH.KGa	Weinheim	2010			No
11	Lowering the sensitization adsorption temperature improves the performance of Dye-sensitized Solar Cells	F. Sauvage/ M. Graetzel	J.Am. Chem. Soc	accepted	The American Chemical Society		2011			No
12	Doping TiO ₂ photo-anode by Nb ⁵⁺ to enhance transparency and charge collection efficiency in dye-sensitized solar cells	F. Sauvage/ M. Graetzel	J. Phys. Chem. C	114(37) (2010) 15849-15856	The American Chemical Society		2010			No
13	Increasing the efficiency of zinc-phthalocyanine based solar cells through modification of the anchoring ligand.	T. Torres	Energy Environ. Sci	4, 189-194			2011			
14	Co-sensitized DSCs: Dye selection criteria for optimized device V _{oc} and efficiency	E. Palomares/T.Torres	J. Mat. Chem.	In press			2011			
15	On the Significance of Phthalocyanines in Solar Cells	T.Torres	Handbook Porphy. Sci.	45, 142-181			2011			

16	Structure-Function Relationships in Unsymmetrical Zinc Phthalocyanines for Dye-Sensitized Solar Cells.	T.Torres/M.Graetzel	Chem. Eur. J	15, 5130-5137			2009			
17	Carboxy-1,4-phenylenevinylene- and carboxy-2, 6-naphthylenevinylene unsymmetrical substituted zinc phthalocyanines for dye-sensitized solar cells.	T.Torres/M.Graetzel	J. Porphyrins Phthalocyanines	13, 369-375.			2009			
18	Ru(II)-phthalocyanine sensitized solar cells: the influence of co-adsorbants upon interfacial electron transfer kinetics.	T. Torres/ E.Palomares/ B.O'Regan	J. Mater. Chem	19, 5016-5026.			2009			
19	Kinetic and energetic paradigms for dye-sensitized solar cells: Moving from the ideal to the real.	<i>Brian C. O'Regan</i>	<i>Acc. Chem. Res.</i>	42	<i>American Chemical Society (ACS)</i>		2009	1799-1808		
20	Water based electrolytes for dye sensitized solar cells.	<i>Brian C. O'Regan</i>	Advanced Materials	22	Wiley	Germany	2010	4505-4509		
21	Re-evaluation of recombination losses in dye-sensitized cells: The failure of dynamic relaxation methods to correctly predict diffusion length in nanoporous photoelectrodes	<i>Piers Barnes/ Brian O'Regan</i>	Nano Letters	9	ACS	USA	2009	3532-3538		
22	Factors controlling charge recombination under dark and light conditions in dye sensitised solar cells.	<i>Piers Barnes/ Brian O'Regan</i>	Phys. Chem. Chem. Phys.	13	Royal Chemical Society (RCS)	UK	2011	3547-3558	10.1039/c0cp01855d/	
23	Simulation and measurement of complete dye sensitised solar cells: Including the influence of trapping, electrolyte, oxidised dyes and light intensity on steady state and transient device behaviour.	<i>Piers Barnes/ Brian O'Regan</i>	Phys. Chem. Chem. Phys.	Article Online January 2011	RCS	UK	2011		DOI:	
24	Parameters influencing the efficiency of electron injection in dye-sensitized solar cells.	<i>James Durrant</i>	Journal of the American Chemical Society	131	American Chemical Society	USA	2009	4808-4818		
25	Structure/function relationships in dyes for solar energy conversion. A two atom change in dye structure and the mechanism for it's effect on cell voltage	<i>Brian C. O'Regan,</i>	Journal of the American Chemical Society	131	American Chemical Society	USA	2009	3541-3548		
26	Quantifying regeneration in dye sensitized solar cells.	<i>Brian C. O'Regan,</i>	Journal of Physical	115	American Chemical	USA	2011	2439-2447		

			Chemistry C		Society					
27	Simultaneous transient absorption and transient electrical measurements on operating dye-sensitized solar cells: Elucidating the intermediates in iodide oxidation.	Brian C. O'Regan,	Journal of Physical Chemistry C	114	American Chemical Society	USA	2010	1953-1958		
28	Kinetic competition in a coumarin dye-sensitized solar cell: Injection and recombination limitations upon device performance.	James Durrant	Journal of Physical Chemistry C	114	American Chemical Society	USA	2010	8054-8061		
29	Electron recombination kinetics and the analysis of collection efficiency and diffusion length measurements in dye sensitized solar cells.	Piers Barnes/ Brian O'Regan	Journal of Physical Chemistry C	114	American Chemical Society	USA	2010	19134-19140		
30	Electron injection efficiency and diffusion length in dye-sensitized solar cells derived from incident photon conversion efficiency measurements.	Piers Barnes/ Brian O'Regan	Journal of Physical Chemistry C	113	American Chemical Society	USA	2009	1126-1136		
31	Ru(ii)-phthalocyanine sensitized solar cells: The influence of co-adsorbents upon interfacial electron transfer kinetics.	James Durrant/T.Torres	Journal of Materials Chemistry	19	Royal Chemical Society	UK	2010	5016-5026		
32	Zn(ii) versus ru(ii) phthalocyanine-sensitised solar cells. A comparison between singlet and triplet electron injectors.	James Durrant/T.Torres	Energy and Environmental Science	3	Royal Chemical Society	UK	2010	1573-1579		
33	A new ruthenium polypyridyl dye, tg6, whose performance in dye-sensitized solar cells is surprisingly close to that of n719, the 'dye to beat' for 17 years.	Brian O'Regan	Journal of Materials Chemistry	18	Royal Chemical Society	UK	2010	4246-4253	10.1039/b808255c	
34	Development of large area photovoltaic dye cells at 3GSolar	J. Goldstein	Solar Energy Materials and Solar Cells	94	Elsevier	UK	2010	638-641		
35	Panchromatic response composed of hybrid visible-light absorbing polymers and near-IR absorbing dyes for nanocrystalline TiO ₂ -based solid-state solar cells	S. A. Haque, T. Torres, Michael Grätzel	J. Power Sources	196	Elsevier	UK	2011	596-599.		
36	High Excitation Transfer Efficiency from Energy Relay Dyes in Dye-Sensitized Solar Cells.	T. Torres, M. Grätzel	Nano Lett	10	American Chemical Society	USA	2010	3077-3083.		

37	Increased light harvesting in dye-sensitized solar cells with energy relay dyes.	M. Grätzel, T. Torres,	Nature Photonics	3	Nature publishing group	UK	2009	406-411		
38	PbS and CdS Quantum Dot-Sensitized Solid-State Solar Cells: "Old Concepts, New Results"	S. A. Haque, T. Torres, Michael Grätzel	Adv. Funct. Mater.	19	Wiley	GE	2009	2735–2742		

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES

NO.	Type of activities ⁴	Main leader	Title	Date	Place	Type of audience ⁵	Size of audience	Countries addressed
1	Conference presentation and proceedings	Jan Kroon (ECN)	European Photovoltaic Solar Energy Conference	September 9, 2010	Valencia	PV specialists from Scientific Comm., industry	300	International
2	Workshop presentation	Jan Kroon (ECN)	PV and nanotechnology: from innovation to industry	September 30, 2010	Aix-les-Bains, France	PV specialists from Scientific Comm., industry	50	International
3	Conference presentation	J. Goldstein (3GSolar)	3 rd DSC Industrialization Conference	April, 2009	Nara, Japan	DSC specialists	300	International
4	Conference presentation	J. Goldstein (3GSolar)	24 th European PVSEC	September, 2010	Hamburg, Germany	PV specialists	300	International
5	Workshop presentation	J. Goldstein (3GSolar)	6 th Workshop on Future directions of PV	March 2010	Tokyo, Japan	PV specialists	300	Mainly Japanese
6	Conference presentation	J. Goldstein (3GSolar)	IPS-18	July 2010	Seoul, Korea	Specialists in photoconversion	300	Mainly Japanese

⁴ A drop down list allows choosing the dissemination activity: publications, conferences, workshops, web, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters, Other.

⁵ A drop down list allows choosing the type of public: Scientific Community (higher education, Research), Industry, Civil Society, Policy makers, Medias ('multiple choices' is possible).

						of energy		
7	Conference presentation	J. Goldstein (3GSolar)	DSC-IC 4 th DSC Industrialization Conference	October, 2011	Colorado Springs, USA	DSC specialists	300	International
8	Conference	B. O'Regan (Imperial)	17 th International Conference on Photochemical Conversion and Storage of Solar Energy	July 2008	Sydney, Australia	Scientific Community	150	International
9	Conference	B. O'Regan (Imperial)	Excitonic Solar Cell Conference	Sept. 2008	Warwick UK	Scientific Community	75	International European
10	Workshop	B. O'Regan (Imperial)	Nanoscience for Solar Energy Conversion	Oct 2008	Trieste, Italy	Scientific Community	25	European
11	Presentation	B. O'Regan (Imperial)	at: Lawrence Berkeley Laboratory,	Jan. 2009	Berkeley Calif. USA	Scientific Community	40	USA
12	Presentation	B. O'Regan (Imperial)	at: Portland State University	Jan. 2009	Portland, OR, USA	Scientific Community	25	USA
13	Presentation	B. O'Regan (Imperial)	at: University of CA Santa Cruz	Jan. 2009	Calif. USA	Scientific Community	20	USA
14	Conference	B. O'Regan (Imperial)	European Materials Research Society	May 2009	Strasbourg France	Scientific Community	100	European
15	Conference	B. O'Regan (Imperial)	SPIE	Aug. 2009	San Diego, Calif, USA	Scientific Community	70	International
16	Conference	B. O'Regan (Imperial)	Electrochem09	Sept. 2009	Manchester UK	Scientific Community	75	European
17	Conference	B. O'Regan (Imperial)	Materials Research Society	Nov 2009	Boston USA	Scientific Community	50	International
18	Conference	B. O'Regan (Imperial)	International Conference & Korea-Japan Symposium on Frontier Photoscience and Functional Materials	April 2009	Seoul Korea	Scientific Community	50	Korea, Japan
19	Workshop	B. O'Regan (Imperial)	International Simulation Workshop,	June 2010	Zurich Switzerland	Scientific Community	25	European
20	Conference	B. O'Regan (Imperial)	Semiconductor Photochemistry 3	April 2010	Glasgow UK	Scientific Community	100	International, European

21	Conference	B. O'Regan (Imperial)	Hybrid and Organic PV 2	May 2010	Assisi Italy	Scientific Community	100	International, European
22	Conference	B. O'Regan (Imperial)	18 th International Conference on Photochemical Conversion and Storage of Solar Energy	July 2010	Seoul, Korea	Scientific Community	200	International
23	Conference	B. O'Regan (Imperial)	American Chemical Society	August 2010	Boston, USA	Scientific Community	70	International
24	Conference	B. O'Regan (Imperial)	Materials Research Society	Nov 2010	Boston, USA	Scientific Community	50	International
25	Conference poster	W. Veurman (ISE)	EU PV conference	September 2009	Hamburg, Germany	PV specialists	150	International
26	Conference poster	W. Veurman (ISE)	EU PV conference	September 2010	Valencia (Spain)	PV specialists	150	International
27	Conference presentation	F. Sauvage (EPFL)	PVSEC19 conference,) –	November 2009	Jeju (South Korea)	PV specialists	300	International
28	Conference presentation	F. Sauvage (EPFL)	EMRS	May 2009	Strassbourg, France	Scientific community	200	International
29	Conference poster	J. Kroon (ECN)	EUPVSEC	September 2009	Hamburg, Germany	PV specialists	150	International
30	Conference presentation	T. Torres	4th International Symposium of Macrocyclic and Supramolecular Chemistry (ISMCS),	June 2009	Maastricht, The Netherlands.	Scientific community	200	International
31	Conference presentation	T. Torres	13th Congress of the European Society for Photobiology,	September 2009	Wroclaw, Poland.	Scientific community	150	International
32	Conference presentation	T. Torres	The International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC-11)	November 2009	Kyoto, Japon	Scientific community	500	International
33	Conference presentation	T. Torres	6th International Conference on Porphyrins and	Julio 2010	Santa Ana Pueblo,	Scientific community	200	International

			Phthalocyanines (ICPP-6),		New Mexico, USA			
34	Conference presentation	T. Torres	3rd European School on Molecular Nanoscience	October 2010	Miraflores de la Sierra, Madrid, Spain	Scientific community	100	International
35	Conference presentation	T. Torres	International Symposium: The Chemistry of Synthetic Carbon Allotropes,	November 2010	Erlangen, Germany	Scientific community	150	International

- *It should be noted that Prof. M. Graetzel from EPFL gave > 50 invited presentations all over the world partly presenting Robust DSC results during the project period. Prof. Graetzel received in 2010 the very prestigious Millennium Technology Prize for all his scientific achievements in the field of DSC from 1990 onwards.*

