25th European Photovoltaic Solar Energy Conference and Exhibition
5th World Conference on Photovoltaic Energy Conversion
Valencia, Spain, 6-10 September 2010

EFFICIENT AND ROBUST DYE SENSITIZED SOLAR CELLS AND MODULES

[1]Kroon, J.M*., [1]Sommeling, P.M., [1]Bakker, N.J., [1]Mansom H. van, [2]Hinsch, A., [2]Veurman, W., [3]Pettersson, H. [3]Gruszecki, T., [4]O'Regan, B.C., [5]Sauvage, F., [5]Zakeeruddin, S.M., [5]Graetzel, M., [6]Palomares, E., [6]Clifford, J., [6]Martinez,E., [7]Torres, T., [8]Feigenson, M., [8]Breen, B., [9]Vallon, S., [10]Logunov, S., [11]Spratt, M.,

*[1]Energy research Centre of the Netherlands (ECN Solar Energy), P.O. Box 1, 1755 ZG Petten, The Netherlands, E-mail. j.kroon@ecn.nl; [2]Fraunhofer Institut für Solare Energiesysteme, FhG ISE (Germany); [3]Swerea/IVF AB, (Sweden); [4]The Imperial College of Science, Technology and Medicine, ICL (United Kingdom); [5]Ecole Polytechnique Fédérale de Lausanne, EPFL (Switzerland); [6]Institute of Chemical Research of Catalonia, ICIQ (Spain); [7]Universidad Autonoma de Madrid, UAM (Spain); [8]3GSolar, Israel; [9]Corning SAS (France); [10]Corning Inc. (USA); [11]G24i, United Kingdom

ABSTRACT: This paper describes the progress of the research and development that is carried out by a consortium in the frame of the European project ROBUST DSC. The project spans a wide range of activities 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. The combined efforts have led to maximum power conversion efficiencies under full sunlight of >12.0 % for single cells with active areas < 0.2 cm^2 and total area module efficiencies between 4 and 5 % for aperture areas of up to 225 cm^2. Accelerated life time testing at elevated temperatures and continuous illumination reveals dynamic ageing patterns with negligible degradation after 1000 hours of ageing for all investigated cell and module designs up to temperatures of 60 °C, storage up to 85 °C resulted in typically 5-20 % decrease of performance, depending on design and materials.

Keywords: Dye-sensitized Solar Cell – Module fabrication - Durability

1 INTRODUCTION

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[1].
Since 2008, 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) cooperate in the frame of the European project ROBUST DSC.
The project has followed a research strategy that covers 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 is 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 will be fed into the module development line immediately.
In this contribution, we will report on the progress in the ROBUST DSC project towards achievement of the targeted objectives.

2 EXPERIMENTAL

2.1 Measuring objects, single cells, masterplates and modules

Exploratory research in the research line is carried out on laboratory cells with active areas ranging from 0.1 to 1 cm^2. The detailed fabrication procedure for the nanocrystalline TiO_2 photoanodes and the assembly of complete, hot-melt sealed cells is described in previous work of EPFL [2].
As an intermediate step from small cell fabrication in the research line towards fabrication of larger sized cells and modules in the development line via semi-automated manufacturing procedures, single cells on so called "masterplates" have been manufactured following procedures described earlier [3]. New components (dyes, electrolytes, metal oxides) have been pre-screened for their performance in these masterplates to make a proper selection of components for module fabrication.
In the development line, modules of different designs and sizes have been manufactured by the different partners using proprietary fabrication methodologies. Examples of three different large area module prototypes are shown in Figure 1.

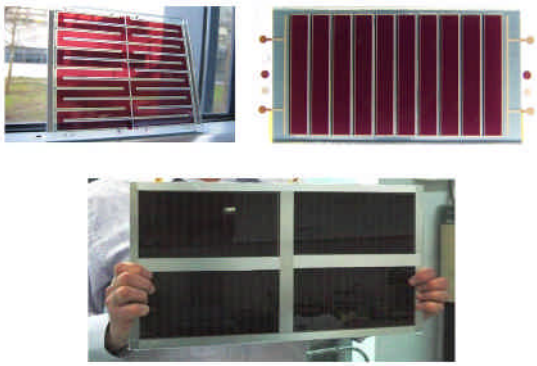

Figure 1. Upper left: a 100 cm^2 current collecting 2-cell interconnected double glass based sandwich module (ECN, ISE). Upper right: A 50 cm^2 single glass-substrate monolithic serial-connected module (Swerea/IVF AB). Below: A 4 cell (cell area 225 cm^2) externally interconnected double glass-substrate module (3GSolar).

2.2 Advanced characterisation and modelling

In support of all the technical activities in the research and development line, an extended set of characterisation and modelling tools is developed to investigate all the functional elements in DSC and to identify new component interactions in fresh and aged devices. The experimental toolset includes transient absorption, luminescence and electrical measurements (charge extraction, current and voltage decay), impedance spectroscopy, electron microscopy (TEM, SEM). A numerical model for complete DSC is developed, which allows the performance of different device compositions and architectures to be predicted.

3 RESULTS AND DISCUSSION

3.1 Materials development

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

Transparent Conducting Oxides

The transparent front electrode is a thin coating of SnO_2:F on glass. In the development line, LOF:TEC8 from Pilkington is often used as the standard material. In the research line, Nippon Sheet Glass (NSG10) is often used since it shows an improved transmission , leading to 10 % higher currents compared to LOF:TEC8.

Nanocrystalline metal oxide materials

Nanocrystalline TiO_2

Screenprintable TiO_2 pastes are used for the manufacturing of the cells and modules. For the preparation of the base transparant TiO_2 layer, the consortium has chosen for commercially available colloidal pastes from Dyesol (DSL 18NR-T and DSL 30NRD-T) after an extensive comparative study with home made pastes.

Scattering layers

On top of the transparent base layer, a (white) light scattering layer is commonly applied to enhance the light harvesting properties of the sensitizer in the red part of the spectrum. As a standard scattering paste, a commercial paste from Dyesol has been used (DSL 18NR AO). This paste consists of DSL 18NR-T paste intermixed with spherical particles of 200nm.

Second generation metal oxides

To further improve the optoelectronic properties of the photo-anode, the following approaches have been followed:

- The nano-crystalline TiO_2 particles have been modified by inclusion of n-type or p-type aliovalent dopants. In particular, we have focused on the pentavalent niobium element [4], and also on the trivalent gallium and yttrium elements that come in substitution of the titanium site in the anatase lattice. As a result of fine tuning of the dopant concentration, in the case of the niobium we have been able to improve cell transparency and all dopant cases enhanced the charge collection efficiency in the transparent layer.
- Core-shell structures are being prepared by using Atomic Layer Deposition (ALD) and wet chemical techniques. Thin layers of wide band-gap materials are deposited on TiO_2. Recent progress shows an advantage of using a shell of Ga_2O_3 covering TiO_2 particle using the ALD technique. Surprisingly, it was found that the Ga_2O_3 shell results in a faster electron collection time while the rate constant for the electron recombination is not affected. Thin MgO layers have been coated on the surface of the Titania nanoparticles after adding magnesium acetate to the TiO_2 dispersion and subsequent sintering of the printed electrodes. For specific ratios of Ti:Mg beneficial effects have been observed compared to pure TiO_2 films.
- Beads of anatase TiO_2 were synthesized using solvo-thermal approach. The advantage of those beads is niche in their dual functionality. High dye loading achieved owing to their high surface area (ca. 87 m^2/g) and light scattering property accordingly to Mie-theory. The SEM micrographs in Figure 2 show the film morphology containing 800 nm diameter beads of TiO_2 forming very beneficial macropores while the inner part of the particles is found to be entirely mesoporous with 23 nm pore size. The latter being possibly controlled from 12 to 23 nm depending on the synthesis conditions [5].

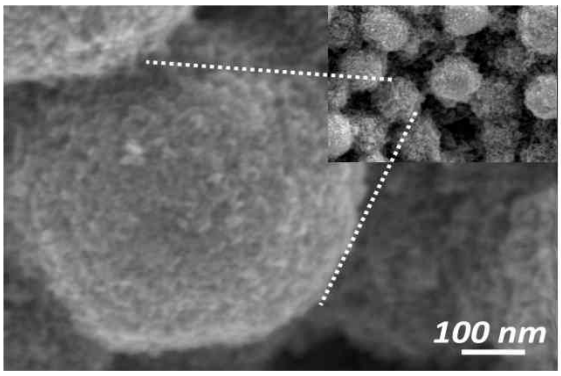

Figure 2. SEM pictures of TiO_2 beads

Dye

Ruthenium(Ru)-based sensitizers are commonly used DSC to achieve the highest efficiencies. EPFL introduced new types of Ru-heteroleptic dyes in the consortium with improved extinction coefficients of the MLCT absorption bands in the Visible absorptionspectrum compared to the "standard" red dye N719. This improvement was realized by the incorporation of one or two thiophene units between the hydrophobic alkyl chain and the bipyridyl rings complex. Two chemical structures of these dyes, coded as C101 and Z991, are displayed in Figure 3[6].
The C101 dye was subsequently selected as the standard dye for the module fabrication and could be obtained in larger amounts.

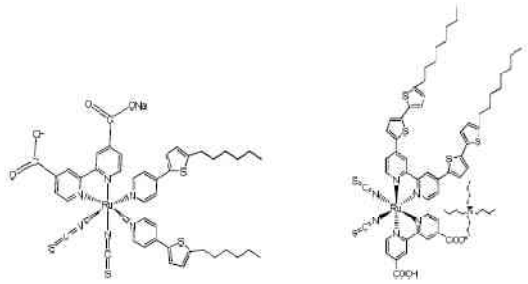

Figure 3. Chemical structure of the C101 dye (on left) and Z991 dye (on right)

In addition, phthalocyanine sensiziters have been synthesized to cover the NIR part of the spectrum and might be useful in combination with complementary absorber materials in co-sensitized DSC using molecular cocktails.

Electrolytes

During the project, a significant number of commercial and home made electrolyte compositions have been used for the optimization of the efficiency and stability of the DSC. The components that are typically used in these mixtures are alkylimidazolium iodides, LiI, I_2 and additives such as *tert*-butylpyridine (TBP), benzimidazole derivatives (benzimidazole, N-Alkylbenzimidazole), guanidinium thiocyanate, carboxylic and phosphonic acids in solvents such as acetonitrile, propionitrile and methoxyproprionitrile.

Counterelectrodes

Depending on the cell or module design, different counter electrodes have been used. In the standard double glass sandwich based cells, SnO_2:F substrates coated with a catalytic amount of platinum are used. The simplest way is to apply the Pt-layer by solvent casting of an organic platinum containing solution and subsequent heat treatment leading to a very efficient tri-iodide electrocatalyst with charge transfer resistances lower than 1 $\Omega.cm^2$. The standard counterelectrodes of the masterplates and modules are obtained by screen-printing a platinum based paste (home-made or commercial), after which a heat treatment is applied to obtain homogeneous layers of Pt on SnO_2:F.

For the monolithic cells and modules, a carbon/graphite electrode is screen-printed on top of a double layer consisting of a base TiO_2 and an insulating ZrO_2 spacer layer.

Sealing materials

For the small cells in the research line, hot melt polymers like Surlyn and Bynel are used. For the modules, ECN and ISE use lead free glass frits while Swerea and 3GSolar are using hot melt polymer sealants. Corning's task in the project to prove the feasibility of a laser assisted sealing of glass frits.

3.2 I-V characteristics for single cells

A large number of small test cells (< 1 cm^2) have been prepared to test the materials described in section 3.1 and to apply improved fabrication protocols.
After optimization of the photoanode configuration and the dye staining process, a non-certified AM1.5 power conversion efficiency of 11.5 % (V_{oc} = 765 mV, J_{sc} = 20.2 mA/cm², FF = 0.73) in full sunlight for cells prepared at EPFL with an active area < 0.2 cm^2 could be achieved using C101 as the sensitizing dye.
Z991 exhibits a higher molar extinction coefficient and displays a red-shifted response in the IPCE spectrum as compared to C101 (Figure 4).
Champion cells (active area <0.2 cm^2) using Z991 as the sensitizer show 12.0 % conversion efficiency (J_{sc} = 22.1 mA/cm², V_{oc} = 746 mV, FF = 0.74) at full sun illumination and even 12.4 % at half sun equivalent illumination.
Recently, we have demonstrated double digit efficiency using a single photo-anode film based on TiO_2 beads, i.e. 10.7 % at 1 equivalent sunlight using an equivalent of the C101 dye, i.e. C106 (chemical structure not shown) and 11.2 % using a double layer geometry consisting of a transparent layer of layer sheltered by beads.

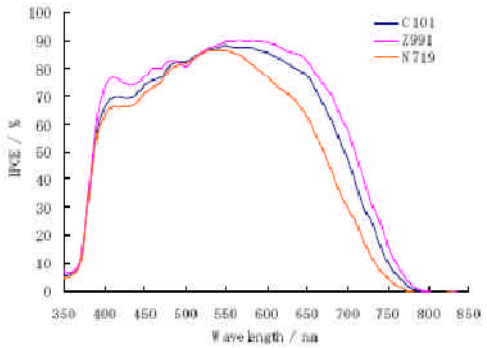

Figure 4. Comparison between the IPCE spectra of the N719, C101 and the new Z991 dye.

3.3 IV characteristics of the modules

As mentioned under section 2.1 three different types of large area cells and modules are manufactured in the frame of the project. The strategy has been 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 manufacturing partners. It should be mentioned here that the dye-electrolyte combination in the modules is selected for its anticipated robustness, and does not necessarily lead to the highest possible initial module efficiencies. It turned out that it is not straightforward to compare the results and experiences from the different module manufacturers with each other, since the specific device designs require different and adapted processing methods. In the table below, a summary is given of the highest initial efficiencies of the different module designs.

Table I: Total aperture area efficiencies measured at 1000 W/m^2, AM1.5 conditions for the different module design and the fraction of active area coverage (FrAA)

Design	η(%)	Area (cm^2)	FrAA(%)
ECN/ISE	3.8(4.2*)	100	74
Swerea IVF	4.0	50	?
3GSolar	4.5(5.4**)	225	100

* After 24 hour pre-conditioning at 80 °C
** Champion efficiency using a N719/High efficiency electrolyte

3.4 Accelerated lifetime testing

Extensive accelerated lifetime testing has been carried out for masterplate cells and modules at elevated temperatures: 60°C and 80°C in the dark and under continuous illumination at open circuit. It is important to note that the stability of the DSC modules may depend on the design itself and the different materials and processing protocols, implying that a specific dye/electrolyte combination will not necessarily lead to identical ageing patterns for the different cell and module designs.
Hereunder we will present some typical examples of lifetime experiments that have been performed for the different device structures.

Double glass based sandwich cells and modules

A typical ageing pattern for double glass based DSC under the applied stress conditions appears to be quite dynamic and is often expressed by an initial rise in efficiency, followed by a gradual decrease in the course of testing [7]. The initial rise in efficiency at the given stress conditions is often caused by a strong initial increase of the J_{sc} and FF overcompensating the continuous loss of V_{oc} over time. The initial increase of the FF is related to a pre conditioning of the Pt-catalyst on the counter electrode at elevated temperatures leading to a decrease of the Charge Transfer resistance. The magnitude of this preconditioning effect depends strongly on the initial quality of the Pt catalyst in combination with the electrolytes used in the experiments. After the initial rise, a slow decrease of the efficiency appears, mainly caused by the continuous loss of V_{oc} over time which becomes stronger at increased temperatures.

This typical pattern as described above is also observed for small cells (<0.2 cm^2) and described in a number of papers from the EPFL group using somewhat different dye-electrolyte combinations from the standard components used in this project [6]. Initial efficiencies of 8-9 % were reported and excellent stabilities were demonstrated during 1000 hours of ageing up to 80 °C retaining more than >95 % of its initial photovoltaic performance prior to testing.

A representative example of a lifetime experiment carried out for a double glass based ECN module at 60 and 80 °C in the dark is shown in Figure 5.

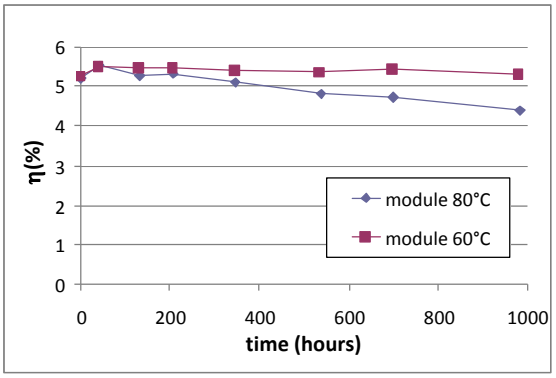

Figure 5. Temporal evolution of the active area efficiency of ECN modules upon exposure to 60 and 80 °C in the dark. Dye: C101; Electrolyte: 0.6 M Propyl-Methyl-Imidazolium Iodide, 0.1 M I_2, 0.5 M N-methyl-Benzimidazole in Propionitrile.

It is shown that the modules, when aged at 60 and 80 °C, show a fast initial rise in efficiency from 5.3 to 5,5 % followed by a subsequent decrease of the efficiency, retaining 100 % and 85 % of the initial efficiency respectively. If one takes the peak efficiency as the starting point, the degradation is 4 and 20 % respectively after 1000 hours of ageing. To compare this result to earlier work done by EPFL [8], the decrease of performance relative to the peak efficiency ranges from 7 to 15 % in that case after 1000 hours of dark ageing at 80°C.

The acceleration of the degradation from 60 to 80 °C is solely due to an accelerated decrease of the V_{oc}, resulting in a concomitant loss of the FF, while J_{sc} remains constant after an initial rise at both temperatures. The voltage loss over time is a general observation for many investigated DSC and could be explained by an accumulation of small cations during the ageing process, like protons, at the TiO_2 surface, leading to a shift of the TiO_2 conduction band in the positive direction. The magnitude of the voltage loss may differ and depends on the material combination, purity and way of processing (avoid ingress of water). The mechanistic origin is not known and to minimize this effect, further engineering of the titania/dye/electrolyte interface and adaptation of production protocols may be required

Monolithic serial connected modules

A typical evolution of the module performance over time for illuminated monolithic modules(1000 W/m^2, appr. 50°C) is shown in Figure 6, i.e. an initial rapid increase followed by a stable period and a slow degradation. Storage of modules in dark at 60°C leads to no degradation, while increasing the temperature to 80 °C leads to a strong continuous degradation This indicates that the 80°C test is not merely an acceleration test for the monolithic devices, but that a threshold temperature has been reached that opens new reaction pathways. This seems to be quite specifc for this design.

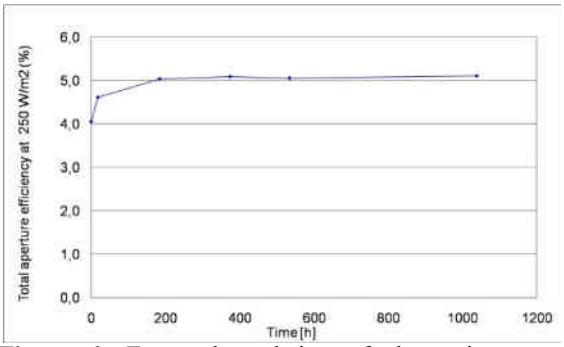

Figure 6. Temporal evolution of the active area efficiency measured at 250 W/m^2 of Swerea modules upon continuous exposure to 1000 W/m^2 light at approx. 50 ^{o}C. Dye: C101; Electrolyte: 1 M 1,3-dimethyl Imidazolium iodide, 0.5 M N-butylbenzimidazole, 0,15 M I_2, 0.1 M Guanidinumthiocyanate in Methoxypropionitrile

3GSolar cells

3GSolar has fabricated large area cells of 225 cm^2 size using N719 dye and C101 dye for comparison in a 3300 hour 85°C endurance testing, both under 1-sun and in the dark. The used electrolyte is a commercial composition from Dyesol (Dyesol EL-HSE). The lifetime data for the 85^{o}C dark test are shown in Figure 7. It is shown that the two dyes show similar performance over time with a continuous slow decrease of the performance in the first 1000 hours followed by a stable period until 3000 hours.

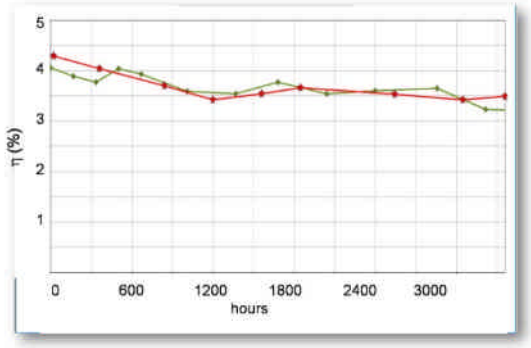

Figure 7. Temporal evolution of the efficiency measured at 1000 W/m^2 of a 3Gsolar cell upon continuous exposure to 85°C Dye: C101(red line), N719 (green line); Electrolyte: Dyesol HSE (high stable electrolyte).

As a general observation for the cells on masterplates and modules after conducting many experiments we can state that the cell and module stability under illumination have been proven good up to 60 °C as long as all the components are chosen carefully. Increasing the temperature up to 85 °C, 1000 hours ALT gives rise to an acceleration of the degradation of 10-20 % in the best cases, given the set of materials that have been used in the project up to now. It is of utmost importance to guarantee the quality (purity) of the dye and electrolyte materials to prevent a vast range of undesired processes at these temperatures like the loss of iodine, Pt dissolution, corrosion and unidentified side reactions. Moreover, hermeticity of the seals should prevent loss of electrolyte and ingress of water which can lead to dye desorption and accumulation of positive charge at the interface. Further analysis will be required to get a better understanding of the dynamic behaviour of the DSC upon ageing and the specific mechanistic functions of the various additives that stabilizes the long term performance.

3.5 Analysis of large scale commercialization

The technical activities in this project are supported by an assessment of the DSC technology in terms of a cost and environmental analyses. This includes:

- An evaluation of the large scale manufacturing scalability and costs of materials including Return on Investment calculations and analysis of in-line production processes.
- A life cycle analysis and calculation of energy payback times.

4 CONCLUSIONS

The R and D in the project Robust DSC span 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 combined efforts have led to maximum power conversion efficiencies under full sunlight of >12 % for single cells with active areas < 0.2 cm^2 and module efficiencies between 4 and 5 % for aperture area's up to 225 cm^2.

Accelerated lifetime testing carried out at elevated temperatures in dark and under illumination reveals encouraging stabilities up to 60 °C (<10 % degradation after 1000 hours), for most of the investigated module designs. Continuous exposure of DSC to temperatures up to 85 °C leads to a logical acceleration of potential degradation processes and appears to be an important stress factor for a number of module designs. Hence, improvement of the quality (purity) of the active materials (dyes, electrolytes), hermeticity of the non-active materials (sealants), further tailoring of the dye and electrolyte chemistry, frozen fabrication protocols and improved understanding of the mechanistic function of all the components used in different DSC designs should pave the way for a Robust DSC that will pass the critical IEC test protocols and survive outdoor conditions in various climate zones.

5 ACKNOWLEDGEMENT

The work in this paper has been made possible by the European Commission under grant agreement number 212792, ROBUST DSC

6 REFERENCES

[1] NREL has recently certified 2.9 % for a 300 cm^2 flexible, production DSC module from G24i. See for further information www.g24i.com
[2] Ito,S. *et al.,* Thin Solid films, 2007
[3] Späth,M. *et al*. Progress in Photovoltaics: Res. and Appl. 11(2003) 207
[4] Chandiram, A.K. *et al.*, J. Phys. Chem. C, in press
[5] Sauvage, F. *et al.,* ACS nano, 4(2010) 4420
[6] Gao et al., J.Am.Chem.Soc., 130(2008) 10720
[7] Sommeling, P.M. *et al.,* Proceedings EUPVSEC 2009, Hamburg

[8] a. Kuang,S.*et al.,* Advanced Materials, 19 (2007) 1133
b. Kuang,S. *et al.,* Advanced Functional Materials 17(2007) 154