STATUS OF THE DYE SOLAR CELL TECHNOLOGY (DSC) AS A GUIDELINE FOR FURTHER RESEARCH

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ABSTRACT: Recently first commercial dye solar cell (DSC) products based on the mesoscopic principle have successfully been launched. The market introduction is accompanied by a strong increase in patent applications in the field during the last 4 years which is a good indication that further commercialization activities are undertaken. Materials and cell concepts have been developed to such extend that an easy uptake by industrial manufacturers is possible. The critical phase for a broad market acceptance is therefore reached which implies to focus on standardization related research topics. In parallel the amount of scientific publications on DSC is growing further (larger 3500 since 2012) and the range of new or renewed more fundamental topics is broadening. One most recent example is the introduction of the perovskite mesoscopic cell concept where an efficiency of 14.1 % has been certified. In this sense a growing divergence between market introduction and research could be the consequence. In this paper an attempt is undertaken to show, that such an unwanted divergence can be prevented e.g. by developing suitable reference type cell and module concepts as well as manufacturing routes. We propose an in-situ cell manufacturing concept which can be applied to mesoscopic based solar cells in a broader sense. As a guideline for future module concepts, our recent results from large area glass frit sealed DSC modules for efficiency studies (6.6% active area efficiency) and for outdoor analyses are explained. Another important point addressed is the issue of sustainability both affecting market introduction as well as the direction of fundamental research.

Keywords: Building Integrated PV (BIPV), Dye-Sensitised, Electroluminescence, Module, Perovskite, Thin Film Solar Cell, Efficiencies, Stability

1 INTRODUCTION

1.1 Dye Solar Cell technology

Since 20 years, the DSC technology has undergone a lot of research and development and received constant funding through international, European and national research programs. The basic idea of DSC being printable solar cells in which an organic based dye is used as the photoactive compound has been very successfully verified. A highly interdisciplinary research has been necessary which also reflects back in the huge numbers of publications and patents (figure 1).
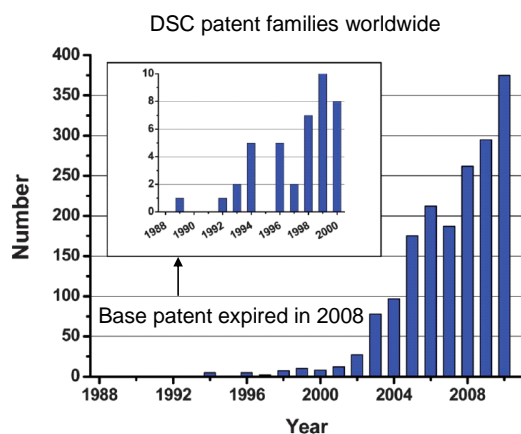

Figure 1: Yearly increase in DSC patent families world-wide, adopted from [1]

Solar cell efficiencies of 12 % for single cells [2] and 9.9% for smaller modules [3] have been reached in several laboratories and further enhancement is predicted with progress in materials development. This has been shown with new material concepts in which the dye molecules have been replaced by perovskite nano-crystals and 14.1% has been demonstrated recently [4]. Important benefits from the commercialization point of view are the low investment costs which allows for decentralized production, the high sustainability and the large variety of product designs. A direct market competition with silicon solar cells is not seen at this stage.

1.2 DSC technology activities

Basic research on DSC is continuously carried out for materials optimization. The morphology of the nano-colloidal electrode layers is controlled, metal organic and highly absorbing organic dyes are developed, and various routes are followed for the transport of the photo-oxidized charges like molten salt based redox electrolytes, solid-state organic or hybrid hole conductors. In addition, various concepts for the cell set-up are studied like glass-glass and glass-monolithic based concepts as well as flexible DSC on metal and plastic foils. A lot of know-how has been built up in the characterization and understanding of both material and photo-electrochemical properties of DSC. A constant further development and the integration of new concepts for materials and cells are foreseen.

Applied research addresses the design and development of DSC modules; several interconnection concepts are followed and sealing methods like glass frit sealing, polymer sealing and laser sealing have been implemented. Depending on the application, durability and accelerated ageing tests like light soaking, temperature cycling and mechanical testing are successfully established but still not performed to the level of standardization [5].

Prototyping of DSC, which is done at institutes and companies, addresses and proves the up-scalability of DSC modules, as well as the flexibility in customized and decorative module design. Also first approaches towards system integration are undertaken.

For the commercial production of DSC, several pilot-lines have been installed or are under construction. A first full production line is under operation since 2012 for flexible DSC.

Figure 3: Dye solar module showroom for BIPV applications using large area glass frit sealed DSC modules (meander type) as developed at Fraunhofer ISE 2012

Specific production equipment is under constant development and automation and quality control are addressed. Triggered by this development, for the key components of DSC, several companies increasingly work on the up-scaling and quality control of materials.

1.3 Market related DSC activities

Due to the beneficial low-light performance of DSC (up-to 23 % have been shown under indoor light conditions) the first attractive market for DSC products is the consumer electronic market, which goes together with the development of suitable electronics. The recent example is the successful introduction of flexible DSC in the global lifestyle product market and a DSC powered mobile phone charger (figure 2).

Figure 2: Two recent examples of commercially available DSC powered products; a flexible keyboard from Logitech, DSC module produced by G24i, UK (above) and a battery charger for cell phones from MKE Technology, Taiwan (below).

A particular aspect of DSC is the possibility for a decentralized local production which is realized by the early stage market introduction of DSC modules for solar home systems and also for custom made decorative DSC products. The recent success in up-scaling of DSC modules on glass and foils demonstrates the suitability of DSC for the potentially very large building integrated PV market, although a certification step is still required. In particular the combination with decorative architectural glass seems attractive (figure 3) since it can exploit the large flexibility in transparency and colors of DSC

devices for facade application. In this case, beyond the initial electrical characteristics of the device in terms of energy production, the reliability of the facade throughout the device lifetime is mandatory. Electrical production and, more importantly, uniformity in the aesthetics over single cells and arrays of modules are pivotal for this kind of application where an expected lifetime of 20-25 years should be achieved.

For certain types of roof elements a potential advantage of DSC is seen in the design flexibility. Because of the demand from first real DSC productions, the market for DSC specific materials is growing which increases the engagement of fine chemical companies for the synthesis of nano-materials, dyes, electrolytes and organic hole conductors. In parallel to the setting up of DSC production equipment also a growing interest from machine manufactures is seen. There will be a demand for system integration for DSC from the electronic industry and the building construction sector.

1.4 Reviews on DSC research

Several detailed review papers have been written on DSC research in the past and the most recent are cited in the following. A broad thematic review is given in [6]. A review paper focusing on the dye molecules and optimization of high efficient DSC is given in [7]. In a further review [8] novel generation materials and cell concepts are presented.

1.5 Results from scientific literature survey

For this paper a literature survey has been performed using the Scopus database for peer-reviewed scientific literature about DSCs and perovskite solar cells as a new mesoscopic concept [9]. In the data range 1985 to present more than 11000 documents (i.e. articles, conference papers, reviews) have been published on the topic of dye solar cells with a remarkable increasing trend in the very recent years (7000 papers in the past 3 years); see figure 4a.

Institutes and research groups that contributed most, beyond EPFL (388 publications, almost 3.5% of the total), Uppsala University and KTH from Sweden (333 publications), are Asian groups from Taiwan, Japan, Korea as well as from China (table 1). An impressive exponential behavior is also seen for publications on perovskite solar cells (figure 4b) reflecting the growing importance this field is acquiring in the last two years.

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By focusing on the 20 most-cited papers of the years 2012 to 2013 it is possible to gain an insight in the latest most relevant research topics in the DSC field.
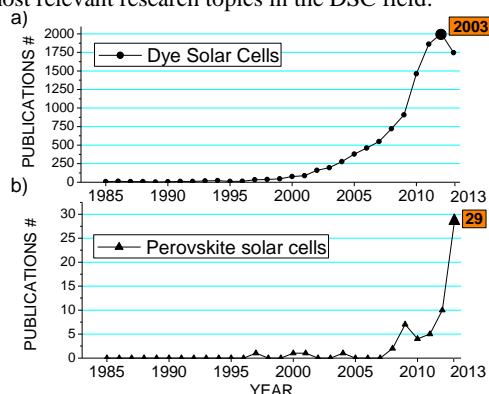

Figure 4: Number of scientific publications published per year in the field of dye solar cell (a) and perovskite solar cell (b). The values shown in the boxes represent the maximum value reached in the 2012 for DSC and in 2013 for perovskite solar cells. Note that the data from 2013 is not conclusive. The literature search was performed by using the keyword "dye solar cell" and "perovskite solar cell" in the scopus database.

	AFFILIATION NAME	COUNTRY	PUBLICATIONS	
1	Ecole Polytechnique Federale de Lausanne (EPFL)	Switzerland	388	3,484%
2	National Taiwan University	Taiwan	229	2,056%
3	National Institute of Advanced Industrial Science and Technology (AIST)	Japan	188	1,688%
4	Korea University	Korea	170	1,526%
5	Uppsala Universitet	Sweden	168	1,508%
6	The Royal Institute of Technology (KTH)	Sweden	165	1,481%
7	Korea Institute of Science and Technology (KIST)	Korea	163	1,463%
8	Dalian University of Technology (DUT)	China	160	1,437%
9	National University of Singapore	Singapore	156	1,401%
10	Imperial College London (ICL)	UK	139	1,248%
11	Seoul National University	Korea	138	1,239%
12	Pusan National University	Korea	135	1,212%
13	Huaqiao University	China	132	1,185%
14	Tsinghua University	China	132	1,185%
15	Institute of Plasma Physics Chinese Academy of Sciences	China	131	1,176%
16	Chinese Academy of Sciences	China	127	1,140%
17	Kyoto University	Japan	121	1,086%
18	Hanyang University	Korea	117	1,050%
19	Wuhan University	China	116	1,041%
20	Monash University	Australia	115	1,033%
72	Fraunhofer Institute for Solar Energy systems	Germany	51	0,464%

Table 1: Number of scientific publications published and relative percentage to the whole DSC literature from 1985 (approx. 11000) produced by the first 20 research institutes in the field. The literature search was performed by using the keyword "dye solar cell" in the scopus database.

It emerges that the investigation of the optical and electrochemical characteristics of dyes for broadband absorption, electron lifetime increase and anti-aggregation dye molecules properties occupies a relevant position [2, 10-13]. In this context several studies are particularly focusing on porphyrine sensitizers. Secondly, it can be observed that TiO_2 with various morphologies from 1D nanostructures (nanowires and nanorods arrays) to 3D spheres (spherical aggregates, hollow spheres, core–shell particles) for photoanodes fabrication are extensively explored. A third area involves the research about iodine free redox couples (i.e. cobalt complexes, disulfide/thiolate) for achieving transparent and non-

corrosive properties. Among these, new hole transport materials for solid state DSCs are also relevantly investigated. Finally, different catalytic materials are analyzed for better charge transport mechanisms, higher performance and economic benefits.

1.4 Development of dyes

A large variety of different classes of dyes have been tested and thoroughly optimized for DSC. In table 2 a selection is given. It can be expected, that further modification of the molecular dye structure in combination with DFT calculations of the HOMO and LUMO electronic states will lead to a further increase in efficiency [14].

Color appearance in DSC	Type of dye	Laboratory	$\eta^{*)}$
Red to dark brown	Standard type ruthenium metal organic dye	EPFL	10.7%
Green to black	Wide band ruthenium metal organic dye	Fujifilm, Sharp	11.9% [15]
Green to dark green	Organic zinc porphyrin dye	EPFL	12.3% [16]
Blue to dark blue	Organic donor acceptor dye (donor-chromophore-anchor strategy)	Dongjin Semichem, EPFL	9.8 % [17]

Table 2: Examples of state-of-the-art efficiencies achieved for different classes of dye molecules in DSC laboratory cells. ($^{*)}$ measured with solvent based electrolytes, containing either I^-/I_3^- or $[Co(bpy)_3]^{2+/3+}$ as the redox pair).

1.5 Development of redox electrolytes

Electrolytes using the I^-/I_3^- redox couple have been established as a standard since many years and good stability data [18, 19] has been reported for solvent-based and solvent-free, i.e. molten salt based electrolytes, in particular in combination with ruthenium bipyridine dyes [5]. In addition to that, the combination with e.g. metal-free organic dyes like the MK-type dyes has led to long-term stable cells in this case [20]. In 1st generation type DSC the distance between photo- and counterelectrode is rather large (typically 20 µm). This means that diffusion limitation of the $[I_3^-]$ can occur for operation under full sun illumination. Therefore the electrolyte has to be highly doped with $[I_3^-]$ in particular when more viscous molten salt electrolytes are used. A typical "dark concentration" in this case is 0.1 M, which enhances the electron recombination at the photoelectrode at high illumination levels. At low light illuminations this is not critical because electrons trapped in states below the conduction band of TiO_2 are only slowly recombining. Furthermore, an important point is the UV-stability of these electrolytes where unwanted side reactions with photocatalytically formed OH-radicals occur. Therefore the water in the electrolyte has to be minimized [21].

More recently, a lot of work has focused on the optimization of highly soluble cobalt bi-pyridine and

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related redox complexes with the aim to lower the oxidation potential towards the oxidized state of the dyes. This has led to DSC with photovoltages up to 1 V which is 250 mV higher than in the case of the I^-/I_3^- redox couple. The cobalt based electrolytes are not compatible with ruthenium bi-pyridine dyes as a slow ligand exchange can be expected over time, but very suitable in combination with organic dyes.

1.6 Development of solid organic hole conductors

With the aim to replace the electrolyte in DSC by a an easy to oxidize solid hole conductor, several transparent organic p-conductors have been studied. The most successful example is spiro-OMeTAD which is commercially available. This concept works best in combination with highly absorbing organic dyes of the donor-acceptor type as the distance for the diffusion of the electron hole to the back contact can be minimized to below 5 µm in this case. Recently also the p-doping with Co^{III} complexes has been shown and a maximum efficiency of 7.2% has been reached [22].

1.7 Development of organic-inorganic perovskites as new types of absorbers

Since the recent discovery [23] that the dye in DSC can be replaced efficiently with organo-metal halide crystals in the perovskite structure in a volume ratio of 50:50, it became obvious, that these soluble materials have very interesting properties for the realization of low-cost solar cells. A certified cell efficiency of 14.1% has been reached in 2013 [24] which has triggered a large research interest and started discussions about the underlying principles and the potential for improvement of efficiency. An important finding is that, as the perovskite currently under study is a strong light absorber with an energy gap of 1.5 eV, the electrode spacing can be smaller than 0.5 µm and the p-selective contact at the backside can be achieved with an even thinner layer of < 50 nm (s. table 3). The energy difference between the conduction band of the perovskite and that of TiO_2 is very narrow which should favor unwanted back reactions which seemingly are not crucial at all. It is therefore not obvious if a high inner surface contact to an electron selective material like TiO_2 is beneficial.

Cell performance	I_{sc} [mA/cm^2]	V_{oc} [V]	FF	η
	20.0	1.0	0.73	15 %
Perovskite $CH_3NH_3PbI_3$	E_{gap} [eV]	VB [eV]	CB [eV]	Layer[1]
	1.5	- 5.4	- 3.9	0.4 µm
mesoporous TiO_2	3.2	- 7.2	- 4.0	0.4 µm
Dense TiO_2 "n-contact"	3.2	"	"	< 30 nm
Spiro-MeOTAD "p-contact"	-	-	- 5.2	< 50 nm

Table 3: Summary of parameters for a most recent mesoscopic perovskite cell made from the material $CH_3NH_3PbI_3$ as taken from [24] ([1] TiO_2 as a 50:50 host for the perovskite)

Classical type thin film concepts for perovskite solar

cells will increase in research interest, although the mesoscopic concept of filling a porous metal oxide layer with the perovskites from solution has without doubt practical advantages.

2 EXPERIMENTAL

2.1 Details on module manufacturing at Fraunhofer ISE

The Fraunhofer ISE 60 x 100 cm² modules and the small 10 x 10 cm^2 modules are manufactured with industry-relevant procedures and machines. 3.2 mm float glass coated with fluorine doped tin oxide (FTO) is used (TEC-8, Pilkington) as a substrate for the front as well as for the back electrode. The glass substrates are cut mechanically to the proper size and the filling holes (at the back electrodes) are drilled by laser, as well as the structure in the TCO layer in order to electrically insulate the cells. After these preparation steps, the substrates are washed mechanically using demineralized water. Then all the layers, including the glass frit sealant and the ultra-thin platinum back electrode layer, are screen printed. Between every printing step, the layers are dried in a low pressure step followed by convection drying.

The glass frit sealant is a lead- and bismuth free paste which is based on a $ZnO-SiO_2-Al_2O_3$ composition. For the catalytic back electrode a nano-colloidal platinum paste is used (3D-nano / Poland). Furthermore, for the TiO_2 layer and the silver contacts commercially available pastes were purchased (Dyesol DSL 18 NR-T, Ferro lead free silver paste). To burn out the organics from the printed pastes, the front and back electrodes are then sintered in an oven. After the sintering step, the front and back electrodes are carefully positioned on top of each other and sealed tightly in a second furnace step at around 600°C. For both steps common glass fusing ovens were used, heating the substrates by IR radiation from the top along with thin graphite foil as an under layer.

When the oven steps are completed, the modules are colored through the filling holes. For applying the dye and the electrolyte, a customized, in-house development is used [25]. The filling device (figure 5) consists of chemical inert tubing and valves made from Teflon.
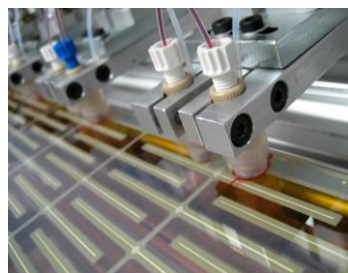

Figure 5: Customized, in-house developed filling device to apply dye and electrolyte inside an inert system into up-scaled dye solar modules.

During the coloration process, the dye solution is pressed through the module by applying a constant gas pressure with 3 bars. For the drying process nitrogen gas is purged through at a similar pressure. The electrolyte is first degassed by ultrasonification and then pressed into the module. After filling, the holes are cleaned and sealed with a small 0.3 mm thick glass. A high power UV-LED is used to cure the glue (Threebond) between the glasses.

As a last step the electrical connections are soldered to the silver grid of the front and back electrode using an ultra-sonic soldering device.

2.2 Preparing the specialized 60 x 100 cm² modules

A batch of TCO 60 glasses (30 front and 30 back electrodes) was prepared and screen printed in an application laboratory. Afterwards all glasses were sintered and the front and back electrodes were melted to each other in an IR oven. The fused modules have a plate distance of approximately 50 μm. Two modules out of this batch were then prepared, one for high efficiency experiments *(A)* with a TiO_2 layer thickness of 12 μm and one for outdoor long-term-measurements *(B)* with a TiO_2 layer thickness of 8 μm.

Module *A* was colored with 2.0 mM C101 dye dissolved in pure DMSO. After the dying process acetonitrile was rinsed through the cells to get rid of the remains of the dye solution. Then electrolyte was pumped into the module (0.6 M PMII, 25 mM I_2, 60 mM GuSCN, 0.3 M NBB in acetonitrile).

For module *B* a pure solution of 0.3 mM N719 dye in ethanol was used. After coloring, the module has been dried by purging nitrogen and then filled with a high viscous, solvent free electrolyte, based on ionic liquids (Merck). With these materials a lower efficiency of approx. 2.5 % on the active area resulted. The module was heated up to 65°C during the hole sealing process to prevent later thermal expansion problems. Afterwards the finished module was glued on a hardened glass with a UV blocking 2-compound silicon epoxy (Wacker). Using a standard spacer frame the module was then totally encapsulated with a back glass, only leaving out the electrical contacts. The module was finally mounted on the roof of Fraunhofer ISE, equipped with a thermocouple for module temperature monitoring.

2.3 Outdoor tests

Outdoor tests on 60 cm x 100 cm DSC modules have been performed at Fraunhofer ISE this summer (2013). The tilt angle of the module (45°) was set as the optimum for the summer season and for the latitude of Freiburg. The azimuth of the outdoor stand where the module was mounted was south. The module operated continuously at the maximum power point through a suited MPP tracker. Electrical and meteorological data were collected every 5 minutes.

2.4 Measuring of electroluminescence

Electroluminescence imaging was performed on a 100 cm² module. The module was forward biased in the dark till a current equivalent to the I_{sc} under 1 sun illumination was reached. The current in this case was 0.42 A, the applied voltage was 1.59 V, 0.8 V per cell. The exposure time was 60 seconds. A Silicon CCD detector was used to detect the signal. The photoanode was directed towards the camera.

3   RESULTS AND DISCUSSION

3.1 Glass frit sealed DSC modules

In a recently published paper [25] we were able to show the up-scaling of dye-sensitized solar cells to large area DSC modules prepared by glass frit technology. The modules were developed using a meander and integrated series connection and reached the dimension of 6000 cm². For this paper, prototypes were now reproduced in a more stable industrial environment. A batch of 60 substrates has been screen printed. Optimised screen printing and drying processes were applied as well as improved handling of the chemistry. With the aim to demonstrate high efficiency a combination between C 101 dye and an acetonitrile based electrolyte has been applied. An active area efficiency of 6.6 % and a total area efficiency of 3.2 % under 1 sun illumination (class B constant-illumination at a module temperature of 45 °C) has been reached (module *A*). Figure (6) shows the performance for such a module. These values could relatively easy be improved in the near future. The non-active area of 46 % in these module prototypes is still too high. In a next step, to achieve 20 % non-active area by printing of thinner glass frit lines is a realistic goal. Also, the series resistance caused by the contacts and the catalytic function of the back electrode limits the fillfactor. Assuming a fillfactor of 70 %, the active area efficiency would then be 8.8 %. When this can be combined with a non-active area of 20 % a module efficiency of 7 % is within reach.
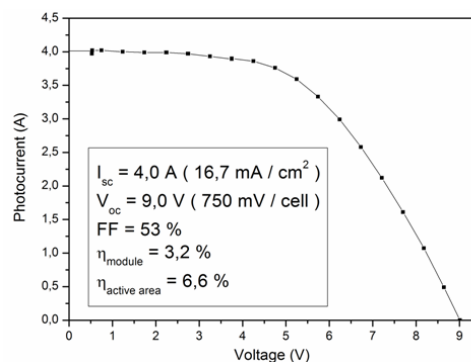

Figure 6: Photocurrent characteristics for a large 6000 cm² module.

3.2 Results on module outdoor stability

A continuous outdoor monitoring activity was performed on the 100 cm x 60 cm module B. The trend of the maximum power point P_{max} at 1000 W/m² of irradiation on the module plane is shown in figure 7 over the first 100 days of exposure.
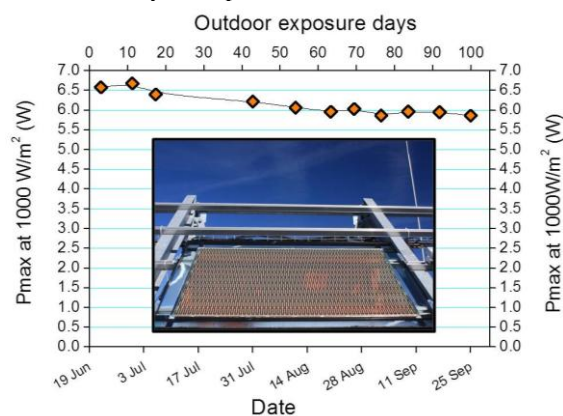

Figure 7: Trend of the maximum power point P_{max} at 1000 W/m² of irradiation on the module plane over 100 outdoor exposure days (summer season). The line connecting the P_{max} points is a guide to the eye. The inset shows the 100x60 cm module mounted on the ISE rooftop stand (tilt=45°C, azimuth south).

The P_{max} values are obtained through polynomial fitting the P_{max} vs. irradiance curve for sunny days extracting the value at 1000 W/m^2. The influence of meteorological parameters such as module temperature T_{mod}, wind speed and the angle of incidence of the sun rays is not taken into account. However, only a small deviation in these parameters can be expected since the measurements were performed during the same season, and thus the module behaviour can be considered reliable and close to the reality. After a small 1.5% P_{max} increase over the first outdoor exposure days, a small constant decrease is observed in the trend till reaching an apparent stabilization in the last period. The P_{max} decay after 100 days is less than 11%.

To better analyze the outdoor behaviour of the module, figure 8a shows the P_{max} plotted vs. the irradiation on the module plane after 5 days of module exposure (22 Jun) and after 100 days (25 Sep). Interestingly it can be observed that the P_{max} deviation between the two trends up to 400 W/m^2 remains rather small. The reasons for the 11% P_{max} decrease at 1000 W/m^2 after 100 days can be analysed through figure 8b where voltage (V_{max}) and current (I_{max}) at the maximum power point are plotted. After 100 days V_{max} decreases by 9% while I_{max} suffers only a 3% reduction denoting an irrelevant J_{SC} drop. Hence the decrease of the V_{OC} with time, along with a possible increase of the series resistances, plays the main role in the loss of the module performance.
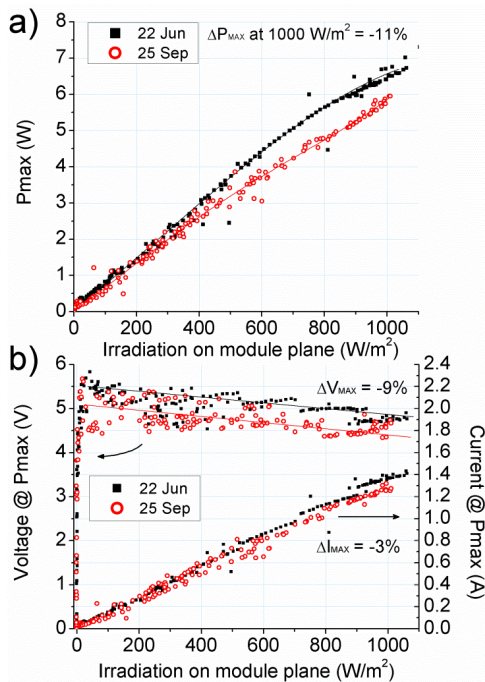

Figure 8: P_{max} (a), voltage and current at the maximum power point (V_{max} and I_{max}) (b) plotted vs. irradiation on the module plane after 5 days of outdoor module exposure (22 June) and after 100 days (25th September). The variations reported in the graph for P_{max}, V_{max} and I_{max} show the decrease in the electrical performance occurred in 100 days. Solid lines in (a) and (b) show polynomial and linear fittings performed for P_{max} and V_{max} respectively.

3.3 Electroluminescence as a new quality tool for DSC

Electroluminescence is a well-known tool for silicon PV technologies to study shunts and effects of serial resistances. Lately, also DSC cells and modules are studied using this technique [26]. It is hypothesized that the intensity of the electroluminescent signal is a function of the amount of active dye molecules, local current density and a measure for the quasi Fermi level splitting. Figure 8 shows the image of the electroluminescent radiation for a 100 cm^2 module. The homogeneity of the luminescence indicates that the TiO$_2$ layer does not show manufacturing irregularities or poor adhesion to the TCO electrode. Some areas show a gradual decrease in signal intensity caused by an inhomogeneous coloring process. Also, areas not covered by the electrolyte caused by in-sufficient filling with electrolyte can be seen clearly.
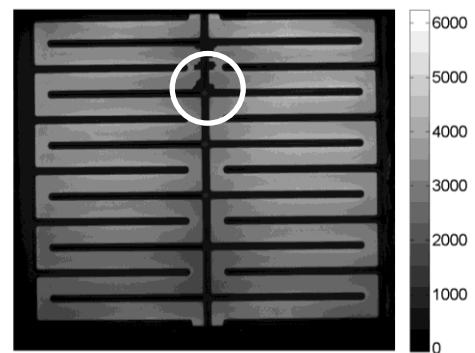

Figure 8: Two electroluminescence image of a 100 cm^2 module measured at Fraunhofer ISE showing a mostly homogenous coloration. The circle indicates non-active areas due to in-sufficient electrolyte filling.

3.4 Homogenous minimization of electrode distance in glass frit sealed modules

Since the interest in the perovskite cell technique is strongly growing, it is a necessary research how to upscale the cell in an economically way. At Fraunhofer ISE it is investigated to use the standard dye solar cell glass frit setup for this purpose. Due to the ultra-thin carrier layers of the active materials in the perovskite cell it is a necessary first step to lower the electrode distance of the glass frit setup down to a minimum and to equip it with a range of process supporting optimizations.
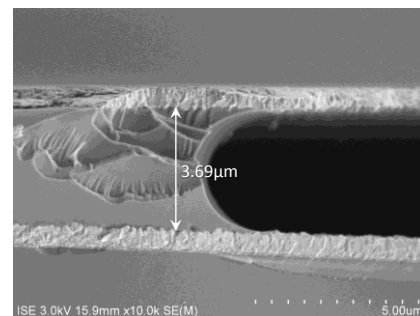

Figure 9: SEM cross section of a glass frit sealed cell without active layer showing the homogenous

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A batch of experimental plates (7.5 x 10 cm²) was screen printed, sintered and fused to investigate the possible minimization of the distance between the counter und the working electrode. Therefore the glass frit paste (Fraunhofer ISE recipe) was diluted and the oven curves of the IR oven were varied and optimized, so that the distance was minimized reproducible to 4 µm. The distance was checked via scanning electron microscope measurements, as to be seen in the cross section (figure 9)

4 CONCLUSIONS

4.1 DSC research and technology

Recently first commercial dye solar cell (DSC) products based on the mesoscopic principle have successfully been launched. The market introduction is accompanied by a strong increase in patent applications in the field during the last 4 years which is a good indication that further commercialization activities are undertaken. Materials and cell concepts have been developed to such extend that an easy uptake by industrial manufacturers is possible. The critical phase for a broad market acceptance is therefore reached which implies to focus on standardization related research topics. In parallel the amount of scientific publications on DSC is growing further (larger 3500 since 2012) and the range of new or renewed more fundamental topics is broadening. One most recent example is the introduction of the perovskite mesoscopic cell concept where an efficiency of 14.1 % has been certified. In this sense a growing divergence between market introduction and research could be the consequence.

4.2 In-situ manufacturing concept for mesoscopic solar cells

With the aim to prevent a growing divergence between market introduction and broadening of scientific concepts we propose an in-situ cell manufacturing concept which can be applied to mesoscopic based solar cells in a broader sense.
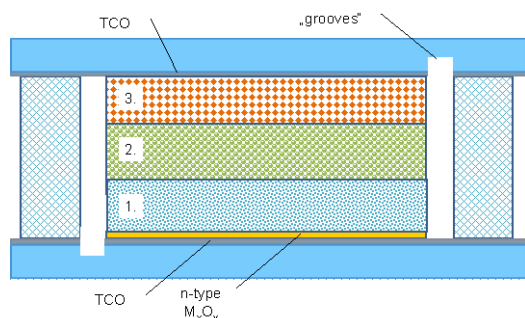

Figure 10: Generalized in-situ cell concept for the up-scaling of sealed mesoscopic solar cells as proposed by Fraunhofer ISE in 2013. The mesoscopic in-organic layers 1 – 3 have different porosity and particle size; this allows in-situ the sequential wet chemical deposition of the active materials through capillary forces. Filling and drying is facilitated through grooves in the glass.

A procedure is proposed, wherein the screen printed mesoscopic carrier layers are sequential flushed with dissolved active materials, through a specific arranged groove, into the glass frit sealed cell. Through varying porosities and particle sizes in the layer structure the dissolved active materials are guided to their destinations in a self-organized process (see figure 10 for the in-situ cell concept). Thermal treatment and pressure/vacuum operations support this procedure. The encapsulation and the in-situ formation of the PV active materials are in this case combined in a cost-effective and sustainable process (figure 11).
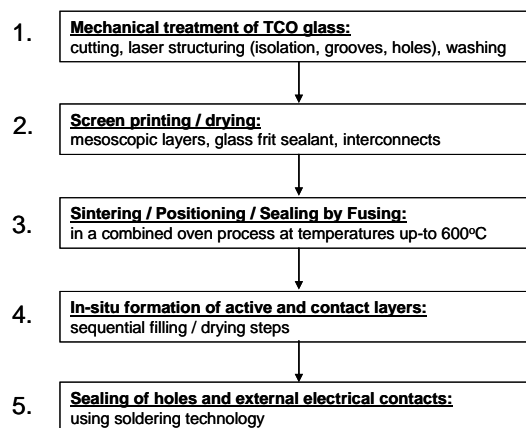

Figure 11: Basic production steps, developed by Fraunhofer ISE, which are related to the manufacturing of glass frit sealed DSC or mesoscopic solar cell modules in the thematically broader sense. The encapsulation and the in-situ formation of the PV active layers are combined in a cost-effective and sustainable process.

4.3 Sustainability

Important factors to judge the sustainability of photovoltaic modules are the carbon foot print and the availability of materials. A detailed LCA analysis requires in-depth investigation and has to be accounted for in further optimization. In the frame of this paper only a brief calculation for the carbon foot print could be drawn. Following the above described manufacturing concept more than 99.5% of the module material consists of recyclable glass and no additional lamination foils are required. By assuming a factor of 1.5 of additional energy consumption for the sintering and fusing steps, the energy balance is comparable to that consumed in the production of flat glass. This means, that a very low carbon footprint number of 16 g CO_2 per photovoltaic generated kWh is resulting [27]; assuming a PV module efficiency of 12% which is a realistic mid-term target after the recent progress in dye and in particular perovskite development as well as an operational time for 25 years.

The amount of active materials in DSC is low, although for the first generation type materials (0.1 g Ru/m², 0.02 g Pt/m² and 1 - 3 g I_2 /m²) there might be limitations in larger GW_p production volumes. For the next generation materials like metal-free organic dyes, cobalt complex redox electrolytes (0.5 g Co/m²), organic hole conductors and none-precious metal organo-halide perovskites (< 0.2 g/m² of Pb, Sn, Bi, Fe etc. and 0.3 g/m² I_2) there will be virtually no limitations of availability. For cobalt and lead also the environmental effect (critical concentration in soils is approximately 0.1 g/kg soil for both metals) has to be taken into concern if

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modules are broken and eventually leached out by rain. In comparison, the values for these metals are still a factor of 100 less critical than that of cadmium.

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REFERENCES

[1] H. Pettersson, K. Nonomura, L. Kloo, A. Hagfeldt, Trends in patent applications for dye-sensitized solar cells, Energy & Environmental Science, 5 (2012) 7376-7380.
[2] L.-L. Li, E.W.-G. Diau, Porphyrin-sensitized solar cells, Chemical Society Reviews, 42 (2013) 291-304.
[3] M. Morooka, R. Ogura, M. Orihashi, M. Takenaka, Development of dye-sensitized solar cells for practical applications, Electrochemistry, 77 (2009) 960-965.
[4] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, Solar cell efficiency tables (version 42), Progress in Photovoltaics: Research and Applications, 21 (2013) 827-837.
[5] J.M. Kroon, N.J. Bakker, H.J.P. Smit, P. Liska, K.R. Thampi, P. Wang, S.M. Zakeeruddin, M. Grätzel, A. Hinsch, S. Hore, U. Würfe, R. Sastrawan, J.R. Durrant, E. Palomares, H. Pettersson, T. Gruszecki, J. Walter, K. Skupien, G.E. Tulloch, Nanocrystalline dye-sensitized solar cells having maximum performance, Progress in Photovoltaics: Research and Applications, 15 (2007) 1-18.
[6] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-Sensitized Solar Cells, Chemical reviews, 110 (2010) 6595-6663.
[7] S. Zhang, X. Yang, Y. Numata, L. Han, Highly efficient dye-sensitized solar cells: progress and future challenges, Energy & Environmental Science, 6 (2013) 1443-1464.
[8] B.E. Hardin, H.J. Snaith, M.D. McGehee, The renaissance of dye-sensitized solar cells, Nat Photon, 6 (2012) 162-169.
[9] http://www.scopus.com/, in.
[10] L. Han, A. Islam, H. Chen, C. Malapaka, B. Chiranjeevi, S. Zhang, X. Yang, M. Yanagida, High-efficiency dye-sensitized solar cell with a novel co-adsorbent, Energy & Environmental Science, 5 (2012) 6057-6060.
[11] S. Haid, M. Marszalek, A. Mishra, M. Wielopolski, J. Teuscher, J.-E. Moser, R. Humphry-Baker, S.M. Zakeeruddin, M. Grätzel, P. Bäuerle, Significant Improvement of Dye-Sensitized Solar Cell Performance by Small Structural Modification in π-Conjugated Donor–Acceptor Dyes, Advanced Functional Materials, 22 (2012) 1291-1302.
[12] Y.-S. Yen, H.-H. Chou, Y.-C. Chen, C.-Y. Hsu, J.T. Lin, Recent developments in molecule-based organic materials for dye-sensitized solar cells, Journal of Materials Chemistry, 22 (2012) 8734-8747.

[13] W. Zou, C. Visser, J.A. Maduro, M.S. Pshenichnikov, J.C. Hummelen, Broadband dye-sensitized upconversion of near-infrared light, Nat Photon, 6 (2012) 560-564.
[14] M. Pastore, E. Mosconi, F. De Angelis, M. Grätzel, A Computational Investigation of Organic Dyes for Dye-Sensitized Solar Cells: Benchmark, Strategies, and Open Issues, The Journal of Physical Chemistry C, 114 (2010) 7205-7212.
[15] Source Sharp cooperation certified by AIST in 2013, designed area 1.00 cm^2.
[16] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diau, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel, Porphyrin-Sensitized Solar Cells with Cobalt (II/III)–Based Redox Electrolyte Exceed 12 Percent Efficiency, Science, 334 (2011) 629-634.
[17] J.-H. Yum, T.W. Holcombe, Y. Kim, K. Rakstys, T. Moehl, J. Teuscher, J.H. Delcamp, M.K. Nazeeruddin, M. Grätzel, Blue-Coloured Highly Efficient Dye-Sensitized Solar Cells by Implementing the Diketopyrrolopyrrole Chromophore, Sci. Rep., 3 (2013).
[18] N. Jiang, T. Sumitomo, T. Lee, A. Pellaroque, O. Bellon, D. Milliken, H. Desilvestro, High temperature stability of dye solar cells, Solar Energy Materials and Solar Cells, 119 (2013) 36-50.
[19] A. Hinsch, J.M. Kroon, R. Kern, I. Uhlendorf, J. Holzbock, A. Meyer, J. Ferber, Long-term stability of dye-sensitised solar cells, Progress in Photovoltaics: Research and Applications, 9 (2001) 425-438.
[20] K. Hara, Z.-S. Wang, Y. Cui, A. Furube, N. Koumura, Long-term stability of organic-dye-sensitized solar cells based on an alkyl-functionalized carbazole dye, Energy & Environmental Science, 2 (2009) 1109-1114.
[21] H.B. Katrine Flarup Jensen, Chan Im, Jürgen Wilde, Andreas Hinsch, Stability of UV illuminated Dye Sensitized Solar Cells (DSC) studied by Photoinduced Absorption in the second range, PVSEC proceeding, Paris 2013, (2013).
[22] J. Burschka, A. Dualeh, F. Kessler, E. Baranoff, N.-L. Cevey-Ha, C. Yi, M.K. Nazeeruddin, M. Grätzel, Tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) as p-Type Dopant for Organic Semiconductors and Its Application in Highly Efficient Solid-State Dye-Sensitized Solar Cells, Journal of the American Chemical Society, 133 (2011) 18042-18045.
[23] M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami, H.J. Snaith, Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites, Science, 338 (2012) 643-647.
[24] J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin, M. Gratzel, Sequential deposition as a route to high-performance perovskite-sensitized solar cells, Nature, 499 (2013) 316-319.
[25] A. Hinsch, W. Veurman, H. Brandt, R. Loayza Aguirre, K. Bialecka, K. Flarup Jensen, Worldwide first fully up-scaled fabrication of 60×100 cm2 dye solar module prototypes, Progress in Photovoltaics: Research and Applications, 20 (2012) 698-710.
[26] M. Bokalic, U. Opara Krasovec, M. Hocevar, M. Topic, Spatial characterization techniques for dye-sensitized solar cells, in: Photovoltaic Specialists Conference (PVSC), 2012 38th IEEE, 2012, pp. 001507-001511.

[27] Data for glass production (31 kg CO2 / m2 of double glazing isolation window pane) was taken from press release of company Saint Gobain, Januar 2013 for the calculation. The fluorine doped tin oxide which is used as TCO is commercially spray-coated onto the hot glass in the float glass line with little additional energy input. Also an integrated photovoltaic generation of 3000 kWh/m2 of module area over 25 years has been assumed., in.