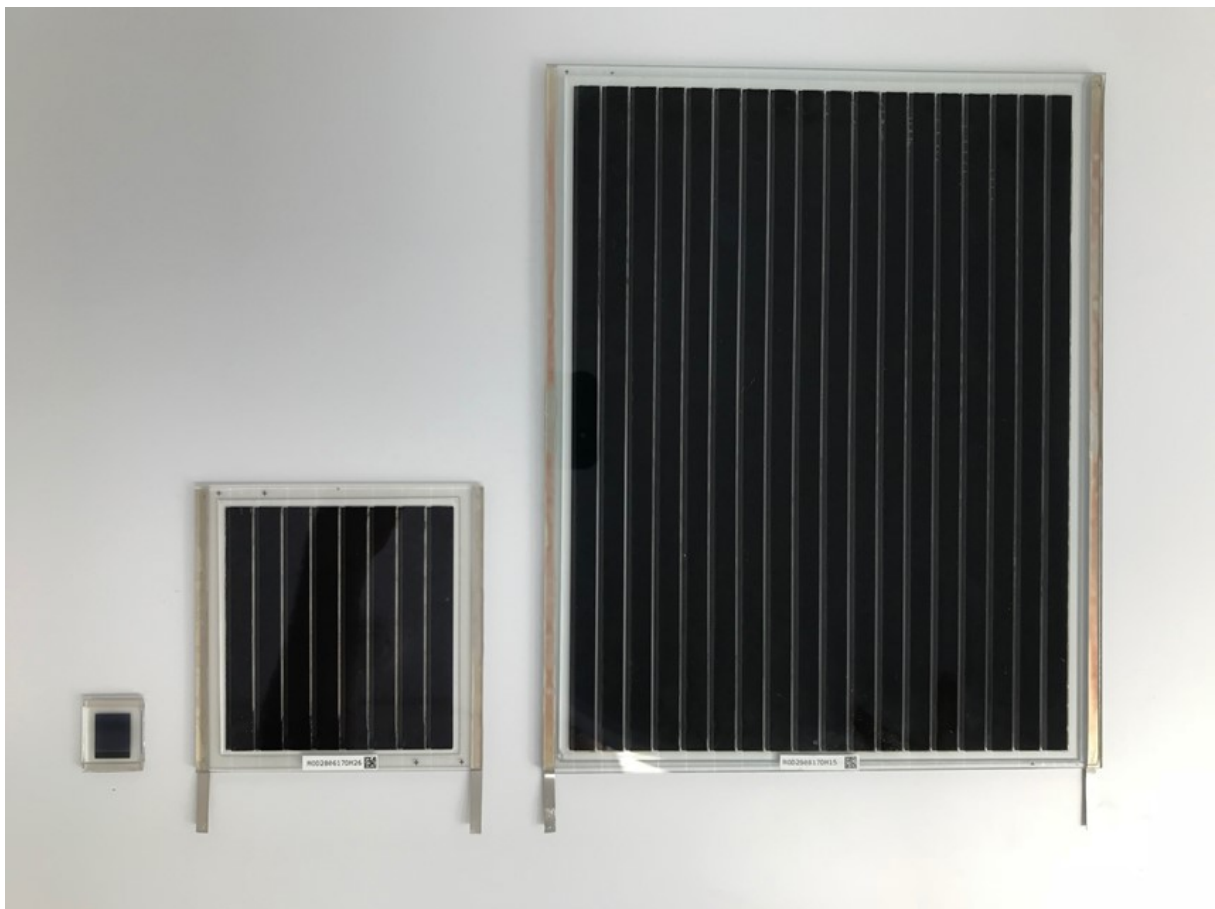




Final report

PEROPRINT

Large Area Perovskite Solar Cells



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Summary

The PeroPrint project is exploring alternative methods to produce multilayer monolithic stacks composed of metal-oxide layers and carbon black and to test perovskite solar cells and modules made thereof. The conventional screen-printing technique used by Solaronix was replaced by the much faster slot-die coating process yielding solar cells with comparable power conversion efficiency of 12%. Slot-die coating furthermore allowed to drastically reduce the thermal input required in the fabrication process by co-firing all layers in a single high temperature step.

Zusammenfassung

Das Projekt PeroPrint untersucht alternative Methoden zur Herstellung von monolithischen Multischicht-Bauteilen aus Metalloxiden und leitfähigem Kohlenstoff für die Anwendung in Perovskit Solarzellen und Modulen. Das von Solaronix verwendete, herkömmliche Siebdruckverfahren wurde dabei durch das schnellere Schlitzdüsenverfahren ersetzt unter Beibehaltung des Solarzellen-Wirkungsgrades von 12%. Zudem erlaubte das Schlitzdüsenverfahren eine beachtliche Reduktion des für den Zellbau notwendigen Wärmeeintrags, indem lediglich ein einziger Brennschritt bei hoher Temperatur für das gesamte Schichtsystem benötigt wird.

Résumé

Le projet PeroPrint explore différentes méthodes alternatives pour la fabrication de composants multicouches à base d'oxydes métalliques et de carbone conducteur pour l'application dans les cellules et modules à base de pérovskite. Ainsi, la fabrication par sérigraphie, couramment utilisé par Solaronix, a été remplacée par le revêtement par filière à fente plus rapide tout en conservant le rendement des cellules solaires de 12%. De plus, la fabrication par filière à fente a permis de réduire l'apport énergétique requis dans la fabrication des cellules, n'employant qu'une seule étape de recuit pour l'ensemble des multi-couches.





Contents

Summary	3
Zusammenfassung.....	3
Résumé.....	3
Contents	5
List of abbreviations	7
1 Introduction.....	8
2 Context	9
2.1 Background.....	9
2.2 Motivation of the project	9
2.3 Goals	10
3 Approach and methodology.....	10
3.1 Initial process.....	10
3.2 Limitations and Challenges	10
3.3 PeroPrint.....	10
4 Results and Discussion	12
4.1 Slot-die Coating of Full MPSC.....	12
4.1.1 Ink development for slot-die coating.....	12
4.1.2 Process development for slot-die coating	15
4.1.3 Co-firing	15
4.2 Layer and device characterization.....	16
4.2.1 Layer characterization	16
4.2.2 Device performance of fully slot-die coated MPSC and shelf life stability	17
4.2.3 Performance statistics	18
4.3 Module fabrication	19
4.4 Stability assessment and temperature resistance of printed MPSC	20
5 Conclusions and outlook.....	22
5.1 Next steps after end of project.....	22
6 Patents and Publications	24
7 References	24
8 Appendix	26
8.1 Appendix 1: Toxicity issues of organo-metal halide perovskite solar cells	26
8.1.1 Overview and risk assessment.....	26
8.1.2 Possible remediation	27
8.1.3 Considerations regarding perovskite solar cell technology at Solaronix	27
8.1.4 References:	28





List of abbreviations

SFOE	Swiss Federal Office of Energy
MPSC	Monolithic Perovskite Solar Cell
PCE	Power Conversion Efficiency
FTO	Fluorine Doped Tin Oxide
cTiO ₂	Dense Titania
mTiO ₂	Mesoporous Titania
mZrO ₂	Mesoporous Zirconia
MAPbI ₃	Methylammonium Lead Iodide Perovskite
OLED	Organic Light Emitting Diode
OPV	Organic Photovoltaic
AFM	Atomic Force Microscope
XRD	X-ray Diffraction
OMHP	Organo-metal Halide Perovskites
ITO	Indium Tin Oxide



1 Introduction

Thin film solar cells based on hybrid organic-inorganic salts with perovskite structure are considered to be the most promising technology for low cost, large-scale photovoltaic energy conversion. Perovskite Solar Cells are the fastest growing photovoltaic technology till time and have reached certified efficiencies of above 22% in laboratory cells.^[1,2] It became therefore an exciting new photovoltaic technology, raising hope to answer the ever-growing energy needs of an increasing human population. Especially thicknesses of only a few 100 nanometers and the use of economical starting materials make this technology very attractive. Being a rather new solar cell technology, a huge number of research groups work on pushing the cell efficiency and gain a better understanding of the working principle. Also, obstacles that may prevent the technology to enter the market are researched heavily. Examples are the danger of lead entry into the environment, so is the life-time under real operation conditions,^[3, 4] researchers from Switzerland,^[5] Great Britain^[6] and Korea^[7] being front at the top.

Different film architectures of Perovskite solar cells are explored (Figure 1), each of them having advantages and disadvantages in terms of performance, stability, or freedom of processing. The Monolithic Perovskite Solar Cell (MPSC) is a specific device architecture that showed reasonable performances and long term stability^[8, 9, 10] in laboratory devices. This architecture was therefore identified as the most suitable for industrial manufacturing. The MPSC architecture had been introduced by H. Han et al. in 2013^[11] and since then investigated by a couple of research laboratories.^[12] In this architecture, the solar cell is built atop a fluorine-doped tin oxide (FTO) substrate. On the anode area, the dense titania (cTiO₂, 50 nm thick) and mesoporous titania (mTiO₂, 500 nm) layers form the electron selective anode. These layers are covered by an insulating layer of mesoporous zirconia (mZrO₂ 1000 nm), followed by a carbon layer (10 μ m) composed of a graphite and carbon-black blend, which constitutes the hole-selective cathode (see also Figure 5). The solar cell is completed by the introduction of methylammonium lead iodide perovskite (MAPbI₃) precursor solution infiltrated into the porous structure with an annealing step to form the perovskite crystals.

Modules using this architecture are then made by connecting adjacent cells, where the carbon layer of one cell interconnects with the FTO layer of the adjacent cell.

Perovskite Solar Cells are also considered as top-cell in tandem devices with silicon, thin films and organic solar cells,^[13] due to the thick and non-transparent carbon charge collection layer, the MPSC architecture is not suitable for this purpose.

In the PeroPrint project, we successfully demonstrated the fabrication of fully screen-printed 250 x 200 mm MPSC modules, as well as the slot-die coating of individual solar cells on 100 x 100 mm large substrates using this more industrially favorable fabrication technique. We also demonstrated that such

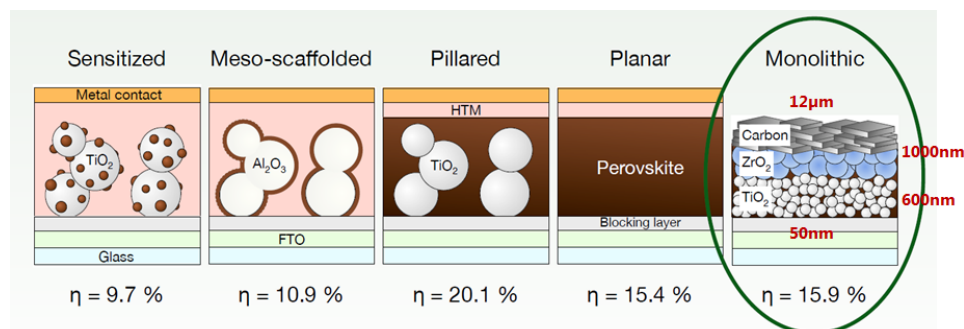


Figure 1: Different Perovskite Solar Cell architectures.



an efficient device can be stable for over 10'000 hours, witnessing a robust device architecture at a competitive efficiency, paving the way forward to industrialization. Screen-printing of the full electrode stack was developed and was used as a reference for the slot-die coating development. Individual layers of the MPSC were coated and tested for their performances, sequentially replacing each reference screen-printed layer, starting from the bottom up.

Slot-die coating of the individual layers of compact titania, mesoporous titania, mesoporous zirconia, and porous carbon as well as the entire stack was optimized to reach a power conversion efficiency (PCE) of 12%, hereby reaching the milestone to utilize only one same industrial wet coating process. On that account, we are reporting for the first time a highly efficient and stable slot-die coated MPSC with efficiency exceeding 12%, having a shelf life stability of more than 12 months when stored under ambient conditions without any encapsulation. Two EU patents were filed to protect the invention of fully slot-die coated MPSC and the inventive co-firing step where only one high temperature step is involved, hereby significantly reducing manufacturing time and the heat signature of the production process.

The accomplishments of PeroPrint are highly promising, and pave the way towards module manufacturing using slot-die coating. The making of a complete MPSC with this technique has not been reported yet to the best of our knowledge. Slot-die coating is a proven competitive industrial fabrication technique in the fields of organic solar cells and lithium ion batteries. In this report, we will provide the summary of the ink and process development of each layer of the MPSC, as well as the characterization of individual layers and devices.

2 Context

2.1 Background

The success of commercializing Perovskite Solar Cells relies on the existence of key advantages over established solar technologies to be able to compete. These advantages may be low processing and materials' costs, and smaller capital expenditure at relatively high efficiencies. The focus of attention is here shifting increasingly to printing and coating processes.^[14] The suitability of different coating techniques such as slot-die coating,^[15] screen-printing,^[16] spray-pyrolysis^[17] or ink-jet printing^[18] is explored for different specific layers. Differently, reports on fully printed cells are rather rare. Fully screen-printed MPSCs have been manufactured by NTU Singapore but employing manual infiltration of the perovskite precursor ink (efficiencies of their cells reached maximum values of 10.74%)^[19] and Swansea University with screen printed modules showing efficiencies of 6.6%.^[20] Worth mentioning are the printing and coating efforts of Hanergy, Swansea/Specific, IMEC, Holst Center, Choshu Industry Co, Ltd., and a number of partners united in the Soliance Alliance. The project partner Solaronix SA contributed significantly to the advancement of the technology by developing screen-printing inks.

2.2 Motivation of the project

Despite huge scientific research efforts, only few attempts are made to develop printing and deposition techniques that are truly compatible with industrial manufacturing. Even though screen-printing is suitable for manufacturing homogeneous, large-area cells, the maximally achievable throughput is limited by the relatively low printing speed and does not meet the requirements for industrial upscaling and reduction of the manufacturing costs.^[21] There was thus a need to investigate alternative processing techniques as well as to identify challenges when scaling up cells to larger areas.



2.3 Goals

The goals of the PeroPrint project can be summarized as follow:

- Investigate printing and coating processes for the industrial fabrication of perovskite solar cells.
- Characterize and monitor stability under accelerated ageing tests under laboratory conditions. Environmental effects due to the presence of lead, specifically in case of leakage or fracture shall be evaluated.
- Bring the technology from laboratory to prototyping scale.

3 Approach and methodology

3.1 Initial process

The project built upon a process that was well established at Solaronix and is based on the MPSC architecture (see Figure 5). The processing details are as follows: first, the FTO coated glass substrate is LASER scribed to separate conductive areas for anodes and cathodes. Then, the compact titania layer is formed by spray pyrolysis of an organotitanate solution onto a hot substrate at high temperature. The subsequent layers are screen-printed from the corresponding pastes prepared by Solaronix. Lastly, a perovskite precursor solution of methylammonium iodide and lead iodide is dispensed over the porous electrode stack and annealed in an oven to evaporate the solvent and let perovskite crystalize in-situ. At the starting date of PeroPrint, an array of 18 cells could be fabricated by spray pyrolysis and screen-printing on an area of 100 x 100 mm in the laboratories of Solaronix. The infiltration of the perovskite precursor was done manually; later on, a robotized computer controlled pipette was employed at Solaronix to remove that manually operated step too.

3.2 Limitations and Challenges

The bottleneck in the starting process was the spray pyrolysis step required to deposit the dense TiO_2 layer. It is much more time and energy consuming than the subsequent printing steps, and far less secure because of the spraying of a flammable solvent onto a very hot surface. While the process could be performed on a small scale, it surely isn't desirable for an industrial manufacturing. This step would be advantageously replaced by a simpler, faster, and safer method like slot-die coating.

Screen-printing the subsequent layers makes a viable route for development purposes, but it is an inherently discontinuous process that makes it cumbersome for module fabrication.

3.3 PeroPrint

On one side the project was exploring alternative methods to the production of the different electrode layers to make them either more efficient, or to leverage limitations preventing them from reaching higher module performances. On the other side, scaling up was advanced, but still utilizing conventional screen-printing. The development work was carried out in parallel at EMPA and Solaronix and is summarized in Figure 2. Module fabrication including the necessary scale-up to 200 x 250 mm and sealing steps were continued at Solaronix using screen-printing. At the same time, Solaronix supplied reference devices. There were long term visits to Solaronix spanning over a full week, for the fabrication of solar cells with slot-die coated electrodes. The close collaboration also helped to maintain the standard MAPbI_3 infiltration and annealing conditions as well as standard measurement conditions.

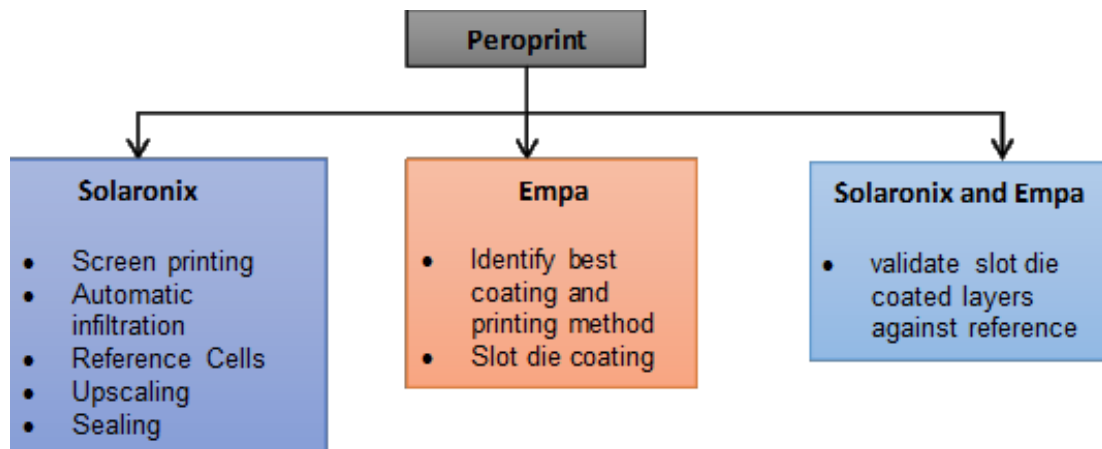


Figure 2: PeroPrint development work at Solaronix and Empa

At Empa, the C600 printing machine incorporates flexo, gravure and screen-printing, which was investigated for fabrication of MPSCs. We were successful in transferring the developed screen-printing technique from the semi-automatic screen printer at Solaronix to the automatic precision printing line C600 at Empa (Figure 3a). In parallel we investigated the tabletop slot-die coater at Empa for the fabrication of MPSC. Also here the preliminary coatings were very promising. One peculiarity of the MPSC architecture is the huge differences in thickness of the various layers. The cTiO_2 layer measures 50 nm, while the carbon layer exceeds 10 μm . As only coating technique, slot-die coating offers the possibility to cover that thickness range (Figure 3b) and had thus been identified as the most promising technique to manufacture MPSCs on a large industrial scale.

Stripe coated slot-die deposition was developed for full cells, reaching a size of 100 x 100 mm. We are reporting here the developments and results.

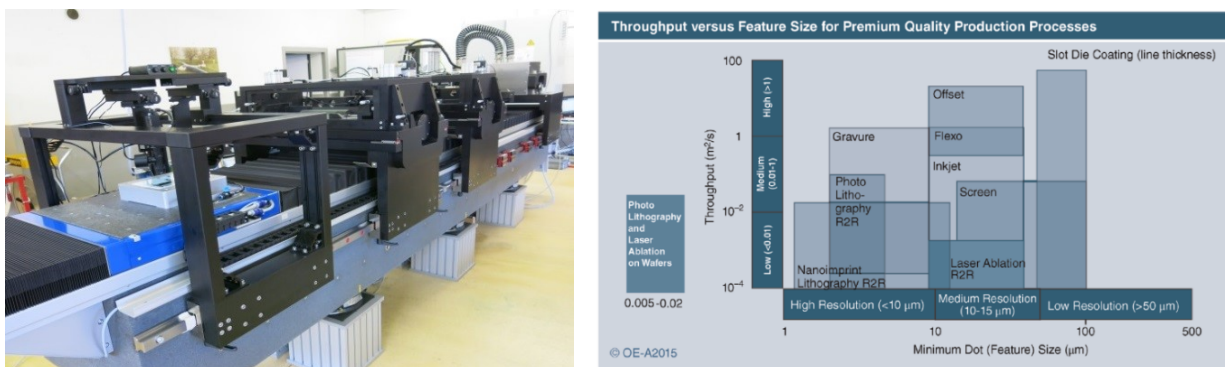


Figure 3: (a) C600 machine (b) process requirements and abilities^[22]



4 Results and Discussion

4.1 Slot-die Coating of Full MPSC

Slot-die coating is a simple pre-metered coating process to deposit a thin liquid film on a substrate. The film thickness depends on the flow rate of the fluid being pumped through the slot-die (Figure 4). Thus, the wet film thickness can be calculated theoretically. It can be easily integrated into roll-to-roll coating facilities or large area flatbed coaters. This method can deposit uniform wet films across the coating direction as well as in the direction of coating. It is a closed compact system; hence there is no possibility of solvent evaporation, which is of high advantage in functional coating involving organic solvents. A slot-die head can handle viscosities ranging from 1 mPas to more than 10,000 mPas offering a wide operating window defined by interfacial surface tension and viscosity. Owing to this, slot-die coating films with a thickness ranging from nanometers to several microns can be fabricated. Slot-die coating is not particle sensitive like ink-jet printing and can operate at speed of a few millimeters to several meters per second. Nowadays, slot-die coating is being investigated for lab-scale fabrication of thin-films to pilot-level fabrication of OLEDs, batteries, OPVs and perovskite solar cells. A disadvantage though lies in its high sensitivity to the processing parameters; thus requiring in-depth ink and process development.

Slot-die may be used in two modes, i.e. stripe coating or full area coating. Stripe coating is interesting for initial investigations of film quality and suitable for making small cells as well as to comply with the stripe based module design. The full area coating combined with laser scribing is interesting for large area modules with maximum active area. Given that at the time neither Solaronix nor Empa had the possibility to explore laser scribing, slot-die coating was developed in the stripe mode only.

The “coating window” (Figure 4, right) defines the region where a stable meniscus forms between substrate and coating head. Ink and processing parameters had to be developed and matched such that the process falls in the stable region of the diagram. This part took months of research and development work to achieve stable ink and process parameters and constituted the most time consuming part of the project.

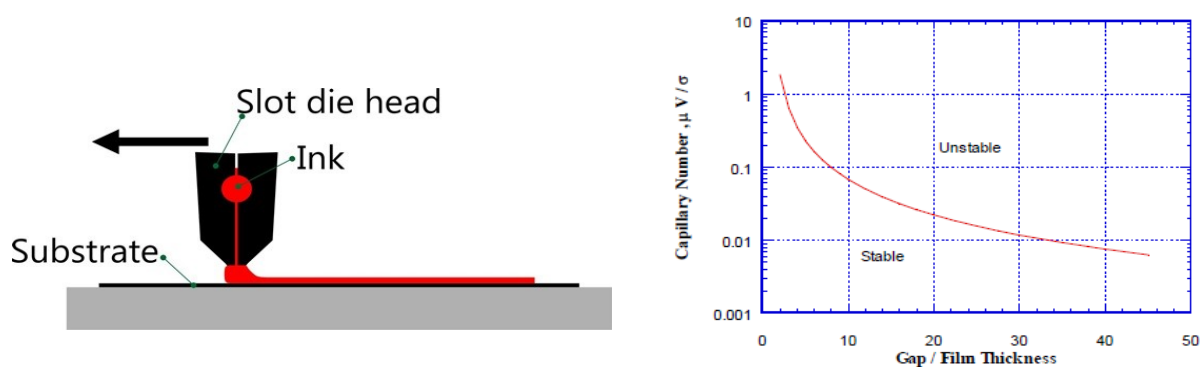


Figure 4: Slot-die coating operation and coating window defined by capillary number and gap to film thickness

4.1.1 Ink development for slot-die coating

Finding a coating solution for the very first layer of compact titania (cTiO_2) was the most challenging as the standard fabrication method for this layer was spray pyrolysis. We therefore started by developing a screen-printing ink first. From there, the deposition technique could be further advanced to slot-die coating by careful ink engineering and process development which required tuning the capillary number of the inks (Figure 4b).

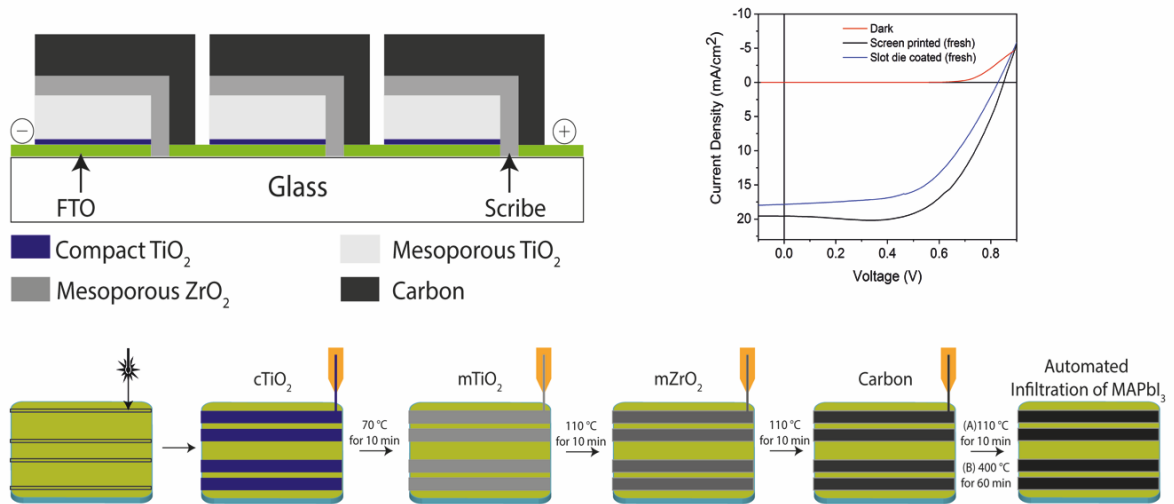


Figure 5: Schematic cross-section of a monolithic perovskite solar module (top left). In the standard process, the coating methods applied are spray pyrolysis (cTiO_2) and screen printing (all layers other than cTiO_2). In the new development, slot-die coating is used, J-V curve of a screen and slot coated device (top right) and the top-view process flow of slot-die coating (bottom).

The MPSC layers were formed by using reactive precursor inks for cTiO_2 , nanoparticle dispersions for mTiO_2 and mZrO_2 layers and a carbon and graphite dispersion forming the cathode. This diverse group of ink particle systems required careful ink development to form uniform layers and functional devices. The ink properties like viscosity, surface tension, density, boiling point, vapor pressure and surface energy of the substrate played a critical role, and thus needed to be optimized precisely. Table 1 below shows the typical stages of a generic ink development process for a nanoparticle ink and cTiO_2 as an example. Here, a multi-solvent system was used to address the wetting and drying behavior, surfactants were used for leveling the wet film leading to sharper rectangular edges. Pinning of the contact line is necessary to get a rectangular profile of the dried thin films and thus was optimized by solvent engineering of the inks. A rectangular profile reduces the dead area at the edges and thus increases usable active area. Drying temperatures were also optimized for uniform drying, solvent removal and better morphology.



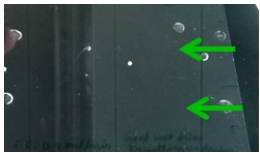
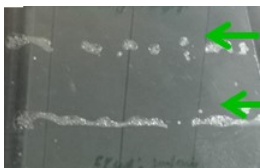
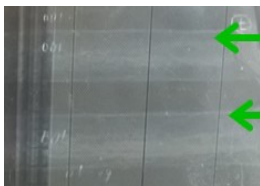
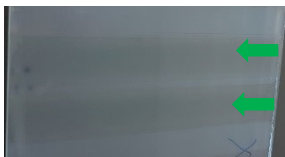
Layer Formation	Ink formulation	Observation/Comments
	Ink 1: TiO ₂ (Tetralin) (1:10)	Good wet film formation (1X- one time coating), Bad pinning.
	Ink 1: TiO ₂ (Tetralin) (1:10)	Good wet film formation (2X- two times coating), Average pinning.
	Ink 1: TiO ₂ (Tetralin) (1:10)	Substrate temperature: 69°C. De-wetting while coating
	Ink 2: TiO ₂ (Tetralin: iPrOH) 1:1 vol% + cTiO ₂ (1:10)	Homogeneous wet film formation (2X), Average pinning. Substrate at room temperature.
	Ink 3: TiO ₂ (Tetralin: iPrOH:EtOH) 15:3:2 vol% + cTiO ₂ (1:20)	Homogeneous wet film formation (2X), Good pinning. Annealing-70°C. Substrate at room temperature..
	Ink 4: TiO ₂ (Tetralin: iPrOH:EtOH) 10:7:3 vol% + cTiO ₂ (1:20)	Homogeneous wet film formation (2X), but thinner edges. Good pinning. Annealing-70°C. Substrate at room temperature.
	Ink 5: Tetralin: iPrOH:EtOH (TIE) in 10:7:3 vol% + 0.002 vol% surfactant	Homogeneous wet film formation (2X). Good pinning. Annealing-70°C. Substrate at room temperature. Average levelling.

Table 1: Influence of speed, flow rate and dilution on meniscus formation and resultant coating. 1X stands for layer deposition by a single coating step while 2X indicates that two subsequent coating steps were involved for that particular layer.



4.1.2 Process development for slot-die coating

To achieve the desired film thickness and functional properties, the processing conditions like speed, flow rate, stability of meniscus, die lip gap, and height of the die were adjusted to yield optimal results. Our target was to use the fastest coating speed on a table coater as possible, in order to get closer to industrial conditions. For this reason, all the oxide layers were coated at a minimum speed of 1 m/min, and all of the other parameters mentioned above were optimized accordingly. The optimized processes for the developed inks are summarized in the Table 2.

4.1.3 Co-firing

During the project, we developed an unprecedented and highly efficient slot-die coating process for the fabrication of MPSC that furthermore reduced processing time. Our innovative co-firing process reduced the fabrication time required from over 14 hours to less than 4 hours. The slot-die coating inks developed in this work allowed for the firing of all the layers together, which was not possible with the initial screen-printing process. Such co-firing of the full stack significantly reduces the manufacturing heat footprint, and gets rid of lengthy intermediary firing steps altogether. Slot-die coating inks and co-firing were both patented by the project partners at the occasion. The process flow of the slot-die coating process is demonstrated in Figure 5.

Layer	Ink	Speed	Flow rate	Thickness	Comments
Compact titania	1 vol% TAA in Tetralin: iPrOH:EtOH (TIE) in 10:7:3 vol% + 0.002 vol% surfactant	1 m/min	0.2 ml/min	50 nm (2x-two times coating)	Homogeneous wet film formation (2X), Good pinning. Annealing-70°C. Sub: RT. Average levelling.
Mesoporous titania	1 vol% of titania nanoparticles dispersed in 10 vol% of terpineol and 2 vol% of iPrOH	1 m/min	0.2 ml/min	500 nm (2x)	Good wet and dry film formation, Drying at 90°C @10min.
Mesoporous zirconia	4 vol%. of zirconia nanoparticles suspended in a ternary mixture of 1 vol%. terpineol, 9 vol%. of iPrOH and 2 vol% of EtOH	0.9 m/min	1.25 ml/min	1000 nm (2x)	Good wet and dry layer formation. Drying at 110°C for 10 min
Carbon	10 vol%. Carbon paste 25wt% of C in terpineol + 2 vol.% EtOH +8 vol% IPA	0.2 m/min	0.2 ml/min	10-12 micron	Good wet and dry layer formation. Drying at 110°C for 10 min

Table 2: Optimized inks and processes for fabricating a fully slot-die coated MPSC. 2X indicates that two subsequent coating steps were involved for that particular layer.



4.2 Layer and device characterization

The thickness of the layers was measured using profilometry and a laser scanning microscope. The inks were characterized on a viscometer and drop shape analyzer for viscosity and interfacial tension and contact angle, respectively.

4.2.1 Layer characterization

The AFM images below show the morphology obtained using different coating methods. With spray pyrolysis, the compact titania layer follows the profile of the FTO underneath and has a similar roughness profile of 266 nm. The slot-die coated sample shows a reduction in roughness, as the liquid ink can be imagined to fill the valleys of the FTO, reducing the roughness to around 160 nm. The XRD diffraction pattern of all three coating methods produced comparable crystallinity.

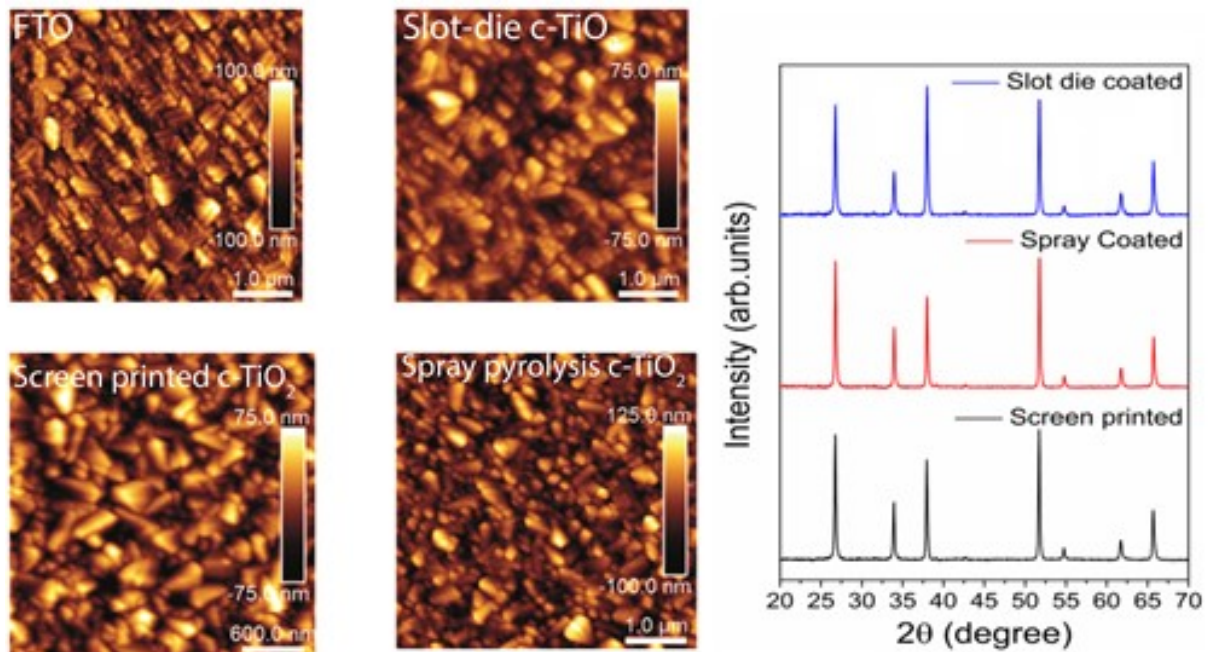


Figure 6: AFM & XRD data of c-TiO₂ layers fabricated using spray pyrolysis, screen-printing and slot-die coating methods.

We performed an XRD analysis of the complete MPSC stack as well, to investigate the perovskite formation in the device. The obtained results match the literature values, thus confirming a crystallization behavior similar to previous reports. All of the perovskite peaks are present, and are indexed as shown in Figure 7.

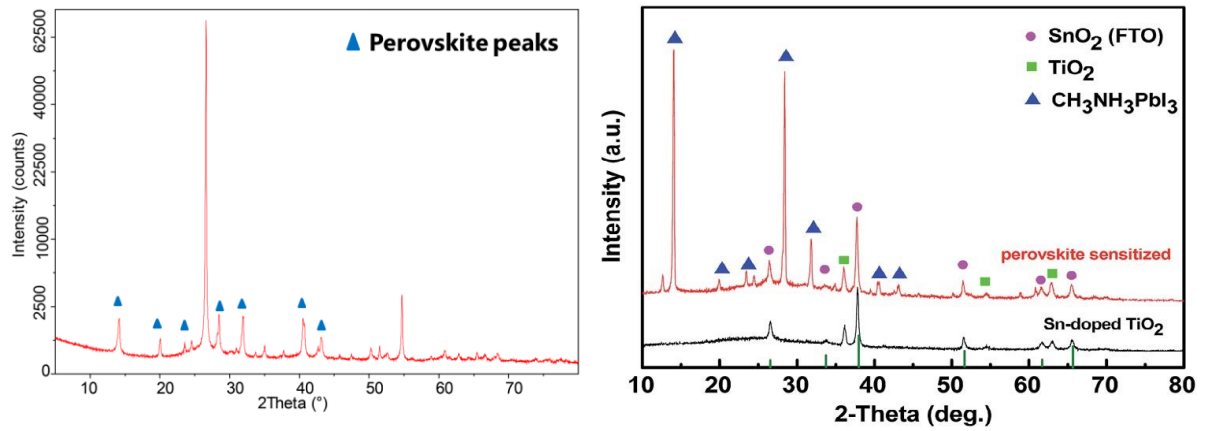


Figure 7: Perovskite formation in the MPSC slot-die coated devices compared to reported data.^[23]

4.2.2 Device performance of fully slot-die coated MPSC and shelf life stability

The solar cell samples were measured in a SolarSim 150 solar simulator from Solaronix, producing a Class B AM 1.5 simulated sunlight from dual metal halide and halogen sources. The light intensity was calibrated to 1000 W/m² with the help of a reference silicon solar cell (Ixys XOB 17). The samples were placed on a thermostated sample holder set to 20°C, and fitted with a 64 mm² aperture mask to precisely delimit the lit area. Output current was probed between 1 V and -0.3 V, by 5 mV increments, every 1200 ms.

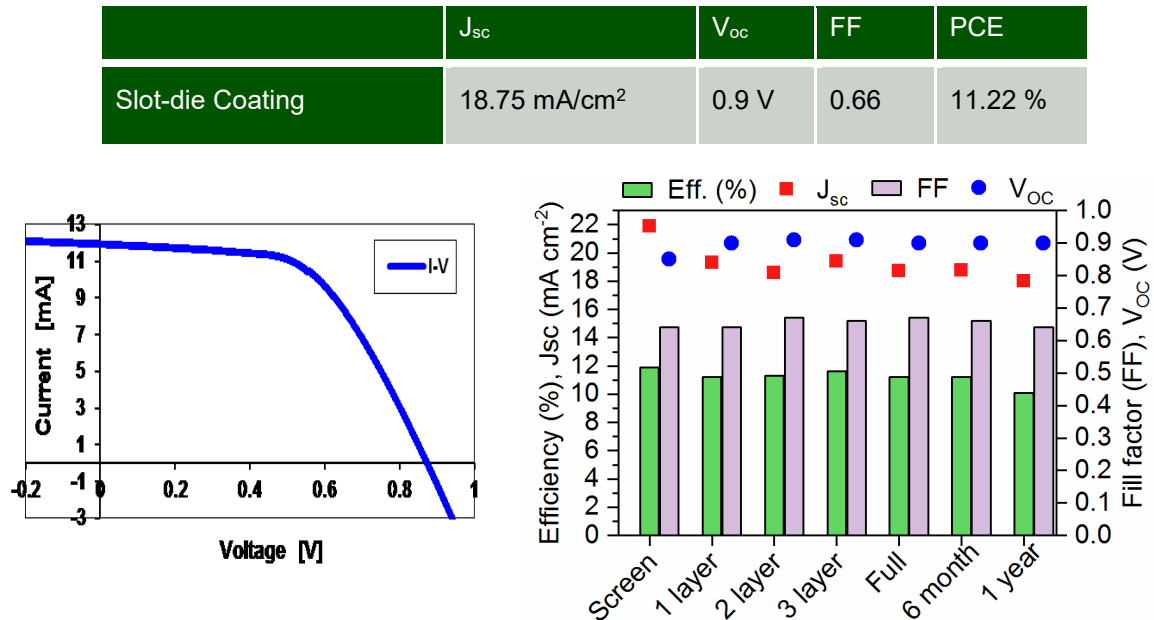


Figure 8: Power conversion efficiency of a typical slot-die coated device (top and left). Right: Performance of screen-printed reference cells, 1 layer (cTiO₂ slot-die coated, the rest completed by screen-printing), 2 layers (cTiO₂ and mTiO₂ slot-die coated), 3 layers (cTiO₂, mTiO₂ and mZrO₂ slot-die coated), Full (all oxide plus the carbon electrode slot-die coated). The values under “6 month” and “1 year” represent data of cells re-measured after 6 month and 1 year storage time, respectively.



A typical I-V curve of a fully slot-die coated MPSC is shown in Figure 8. We were able to obtain V_{oc} of 0.9 V, a fill factor of 67 %, a J_{sc} of >18 mA/cm² and an efficiency of over 11.2 % on average. As mentioned before, the full electrode stack was developed by sub-sequentially replacing a screen-printed layer by slot-die coating, starting from the bottom.

The MPSC shows incredible shelf life stability when stored under ambient conditions without any encapsulation. This finding allows for more processing freedom during the production cycle, and requires a simpler and inexpensive manufacturing environment.

4.2.3 Performance statistics

Each layer of the MPSC was screened individually, and their reproducibility turned out to be very satisfactory. Among the 36 cells fabricated, the success rate was higher than 95%. Failure of functioning cells was due to misalignment of the subsequent layers. This could be easily fixed by installing an alignment setup on the slot-die coater. A summary of the performance of MPSCs following the nomenclature of Figure 8 and including data of co-fired cells is shown in Figure 9.

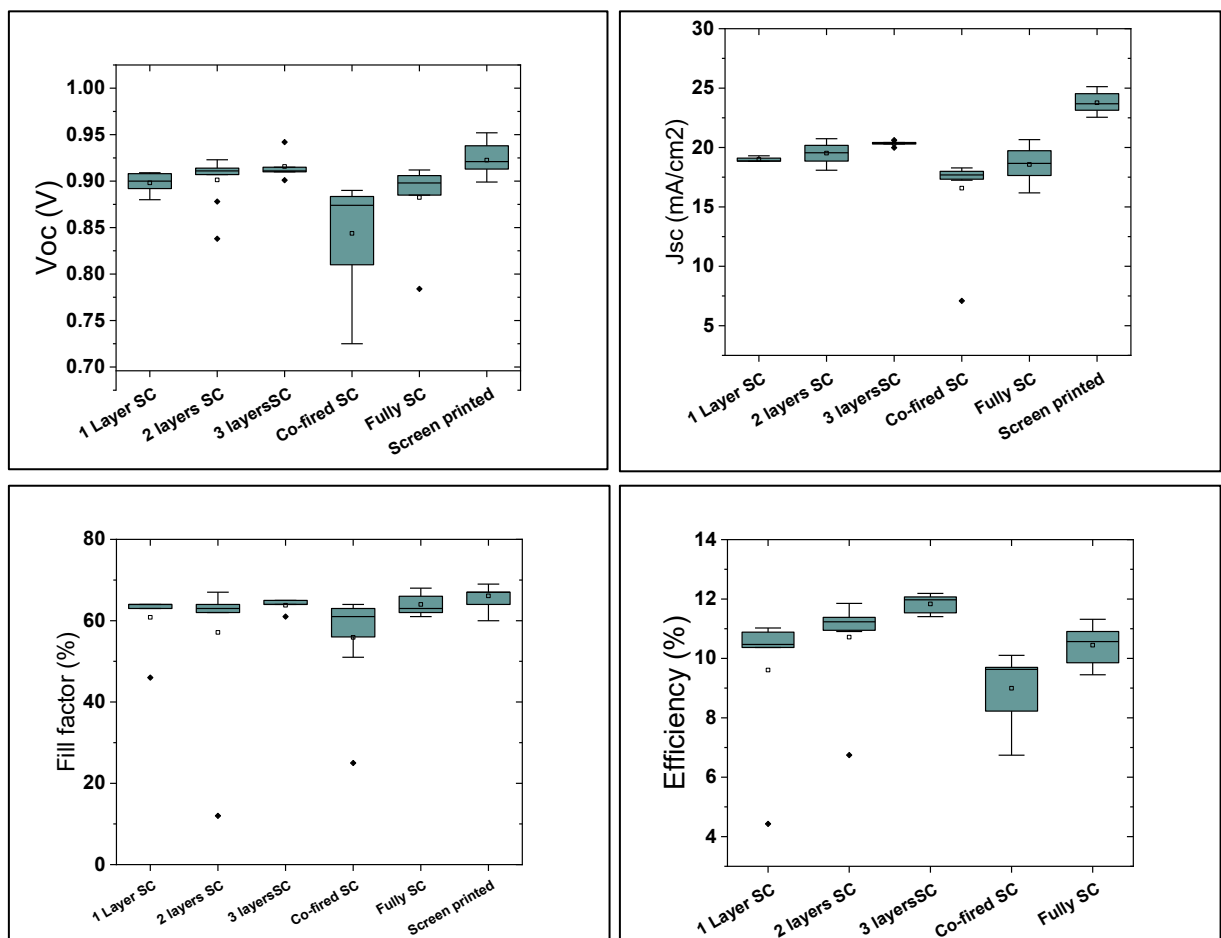


Figure 9: Reproducibility of the cells using sequential layer development of slot-die coating leading a fully slot-die coated MPSC. The V_{oc} , J_{sc} , FF and efficiencies of devices incorporating different numbers of slot-coated layers plotted in comparison to the screen printed reference devices. The total number of cells measured was 35. The boxes represent the first and third quartiles, the horizontal black line the



median, the upper whisker the data within 1.5 times the interquartile range of the upper quartile and the lower whisker 1.5 times the interquartile range of the lower quartile, black dots are outliers.

4.3 Module fabrication

The translation from a single laboratory cell to a module is accompanied by the necessity to obtain a 2D pattern forming the interconnection of adjacent cells. Screen-printing was the most accessible module fabrication technique due to its inherent 2D ability, and thanks to the intermediary cTiO_2 ink formulation mentioned above.

Although more desirable, the slot-die coating method successfully developed here couldn't have been ready early enough during the project, and would have required the development of a secondary laser treatment to obtain the 2D patterning. The combination of highly efficient slot-die coating with laser patterning will be the object of future up-scaling works. We were able to manufacture fully screen-printed, yet efficient and stable modules on the same 100 x 100 mm substrate size used to prepare 18 laboratory cells at a time. Typical I-V plots of laboratory solar cells and these modules are depicted below. Table 3 shows the reproducibility of both sample sizes. It's worth noting that average device efficiencies are increasing year over year in reflection of incremental improvements. The timespan of this project allowed the fabrication of larger modules using the same technique, on 250 x 200 mm substrates. This size was purposely adjusted to fit with existing equipment at both partners' ends, including the length of slot-die coating table for future development during a forthcoming project.

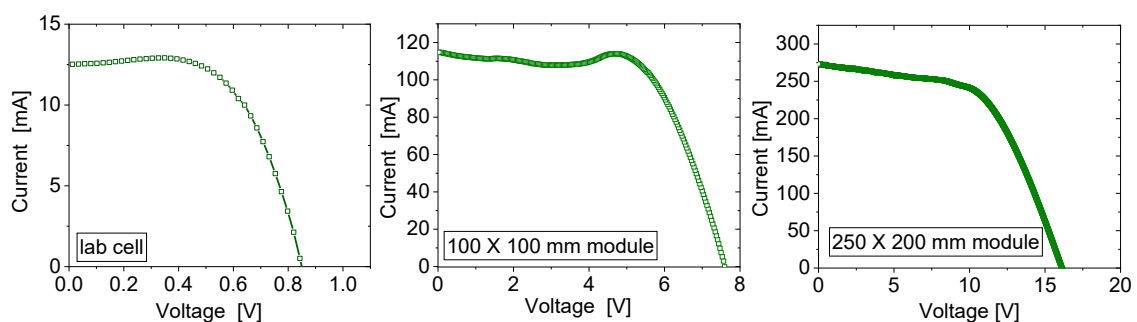
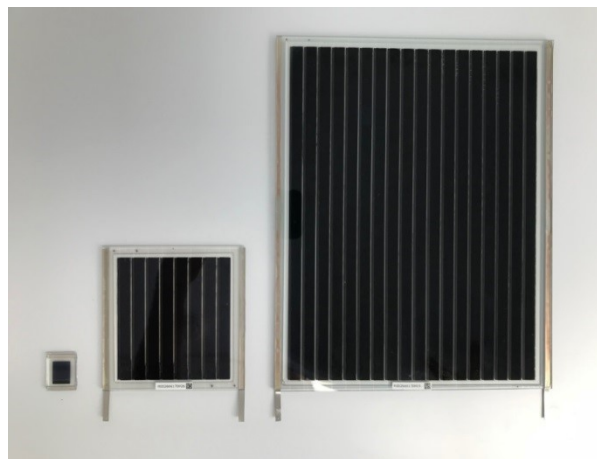


Figure 10: Laboratory solar cell (left), 100x100 mm (center) and 250 x 200 mm (right) fully screen-printed MPSC modules. The J-V curve on bottom left represents a typical laboratory cell and bottom center represents a 100x100 mm modules and bottom left a 200 x 250 mm module.



Laboratory Cell				100×100 mm Module			250×200 mm Module		
V_{oc} [V]	FF	J_{sc} [mA]	Eff.[V]	V_{oc} [V]	J_{sc} [mA]	Eff.[%]	V_{oc} [V]	J_{sc} [mA]	Eff.[%]
0.85	0.64	21.9	11.9	6.8	130	10.2	16.2	273	10.3
0.85	0.60	23.2	11.8	6.8	94.3	10.4	16.2	257	10.2
0.85	0.57	26.3	12.9	7.2	96.2	10.8	15.7	217	8.8
0.84	0.63	24.0	12.7	7.1	91.7	11.2	16.1	242	8.8

Table 3: Reproducibility of laboratory and module monolithic perovskite solar cells fabricated by screen-printing

4.4 Stability assessment and temperature resistance of printed MPSC

Long-term stability tests were also carried out with module prototypes. For that purpose, a basic encapsulation was performed on the samples by sealing a rear glass sheet with the help of a hot-melt Surlyn gasket. The samples received an epoxy rim as a secondary sealing for extra precaution. Figure 11(a) shows the evolution of module efficiency over more than a year of continuous light-soaking under AM 1.5 Class A simulated sunlight. Under these conditions, the samples' temperature stabilizes at about 55°C. After an initial wear-in period, the module reaches a performance that stays relatively constant with no drastic degradation. The simulated irradiation duration of 10'000 h is approximately equivalent to 10 years of natural sunlight exposure, given the sunrise and sunset cycle.

Such results suggest that the carbon-based monolithic perovskite solar cell technology can be inherently stable for several years. Further stability tests will now imply the search for a true photovoltaic encapsulant, which would allow maintaining a similar stability under damp-heat stress tests.

The early achievement with module prototypes allowed us to immediately assess the stability of these monolithic perovskite solar cell devices fabricated by screen-printing. Module samples were placed on a thermostated holder in a solar simulator at Solaronix, and exposed to a 0.9 sun illumination (nominal power output of the equipment used). The temperature of the modules was gradually adjusted from 30°C to 90°C, back and forth, with a 30 min plateau between each step. Figure 11(b) depicts of the module efficiency upon temperature.

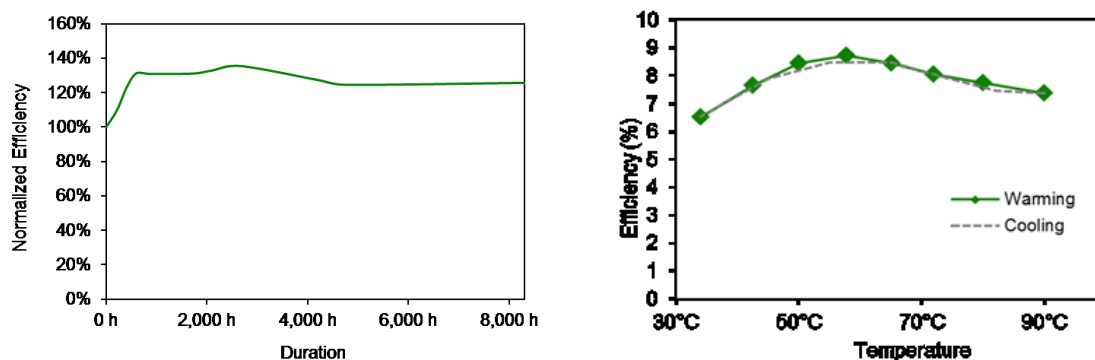


Figure 11: (a) Stability plot of a monolithic perovskite solar module under continuous AM 1.5 illumination. (b) Module efficiency under light-soaking upon temperature cycling.



After such a temperature cycle up to 90°C, the devices nonetheless regain their initial performance measured at 30°C. Interestingly, the power conversion efficiency rises to an optimum situated in the 50–60°C range, temperatures naturally met under sunlight exposure outdoors.

An accelerated lifetime test was also performed on 50 x 50 mm sized screen-printed modules having 5 interconnected cells and it shows little apparent degradation as shown in Figure 12.

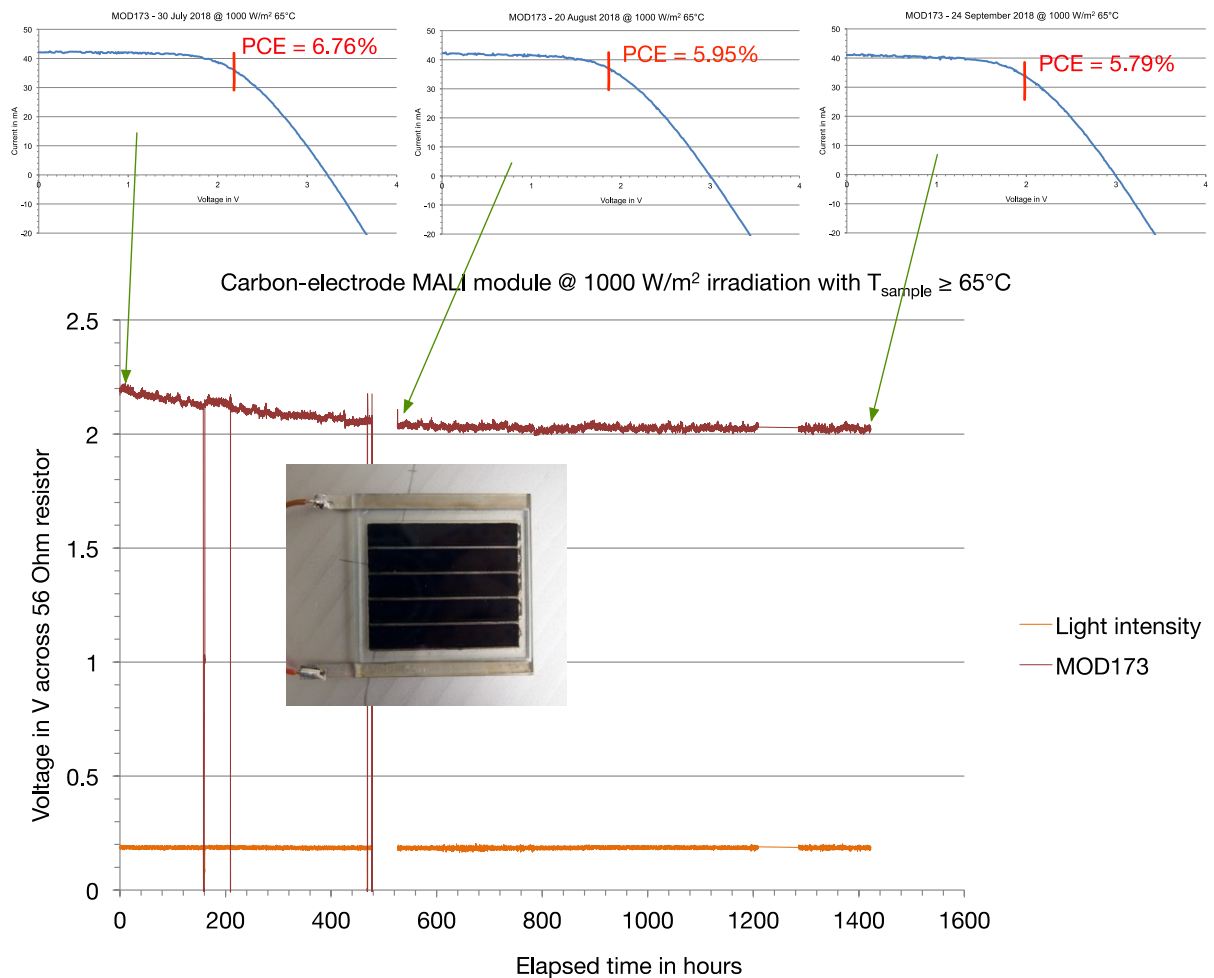


Figure 12: Accelerated life time test plot at 65°C of a 50 x 50 mm sized all printed MPSC mini-module.

In this experiment, the samples were continuously under load across a resistor of 56 Ohm to be close to the working point, while being illuminated with artificial sunlight (Class A), the sample temperature was at least 65°C. This first aging experiment showed a performance drop of ca. 15% after 1'400 hours light soaking at elevated temperature.

During a preliminary test, a 200 x 250 mm sized monolithic perovskite module with 24 interconnected cells, having an apparent edge contact strip problem, was exposed for 1176 hours at a temperature of 90°C (or more) in an oven set to 100°C. After that thermal exposure, the power conversion efficiency (PCE) had still a value of 3.7% when measured at 1000 W/m² artificial sunlight (Class A), despite that



that module has only a 2 mm narrow Surlyn hot-melt based edge sealing with glass transition temperature of $\sim 85^{\circ}\text{C}$.

Visually, that module seemed not to be manifestly damaged by this harsh temperature exposure, opening the hope that these MPSC solar modules may survive a thermal cycling or a thermal soaking test according to the IEC61646 standard adopted for thin film solar cells.

5 Conclusions and outlook

We have successfully demonstrated for the first time that industry compatible slot-die coating can be used for the fabrication of each electrode layer in MPSC applications. What's more, slot-die coating enabled co-firing of all layers together, hereby reducing drastically the number of fabrication steps and the associated energy consumption. Those breakthroughs got translated in two joint patent fil-ings.

The development of a wet deposition ink for screen-printing, as a preamble to the same for slot-die coating, offered the ability to produce 100 x 100 mm modules at first, followed by larger area 200 x 250 mm modules with efficiencies exceeding 11%. Such module prototypes have demonstrated high stability of MPSC for more than 10'000 hours under continuous AM1.5 illumination, and an excellent resistance to thermal cycling between $+30^{\circ}\text{C}$ to $+90^{\circ}\text{C}$. Besides, non-encapsulated laboratory samples revealed a shelf-life stability of over a year.

The achievements obtained during the PeroPrint project open up immense possibilities to further develop MPSC technology to an industrially relevant level.

On the one hand, slot-die coating should be now scaled up to larger area for module fabrication, concomitantly to the development of a Laser patterning process for the creation of solar cell inter-connections. Prior art demonstrated the sequential slot-die coating of lead iodide and methylammonium iodide. However, the slot-die coating of a single precursor ink would allow more control and higher throughput than the coarse pipetting method currently employed.

On the other hand, ink formulations developed in this work opened up the door to inkjet formulations. This method can help to screen MPSC layer configurations more easily at higher pace. Thanks to digital stencils and printing accuracy, inkjet allows for the fine tuning of layer patterns and thicknesses. Inkjet printing may also be used to simplify module fabrication by avoiding layer post-patterning normally used to create solar cell interconnections after each layer deposition.

Here too, inkjet has proven to be a viable technique for perovskite deposition,^[15] with the advantage of manipulating minimal volumes of perovskite precursor solution ink.

5.1 Next steps after end of project

The success of the PeroPrint project should be carried further in a continuing joint development over a 2-3 year period where the focus will be on developing large area perovskite solar panels of 300 times 600 mm. The next project will demonstrate the slot-die coating of large area modules, including laser patterning steps to maximize active area and simplify manufacturing.

This scale-up implicates several challenges. First of all, the homogeneity of the coatings have to be guaranteed on a large surface with minor deviations at the edges of the active area. Laser scribing parameters have to be optimized to be selective to the different layers of the monolithic structure targeted in the project. Other structuring methods will be explored if the aperture area of the modules can match the results obtained by laser scribing.



Finally, the devices need to be encapsulated, and there is still no established approach for this young photovoltaic technology. It is however a necessary step before panels can be tested under standard conditions.

The resulting perovskite prototype panels will be good examples of a marketable photovoltaic technology. Empa has already shown their interest in mounting those perovskite panels on their exploratory NEST building for real-life evaluation.



6 Patents and Publications

EMPA_2018	EP18180245.5 Novel Electronic Device and Method for Slot-Die Depositing Layers of the Same
EMPA_2018	EP18180243.0 Novel Electronic Device and Method for Producing Layers of the Same
EMPA_2018	Publication 2018, fully slot-die coated stable perovskite solar cells (in pipeline)

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8 Appendix

8.1 Appendix 1: Toxicity issues of organo-metal halide perovskite solar cells

8.1.1 Overview and risk assessment

Toxicity of lead salts is of high concern. It is well known that intake of lead by the human body affects the liver, kidney and nervous tissues leading to various forms of intoxication^[1], which represent a major risk especially for infants.^[2] Lead has a relatively short half-life in the latter soft tissues, but is eventually deposited in the skeleton where it fixates as lead phosphate.^[3] Health issues with lead are known since Roman times, where lead water pipes were used particularly for urban plumbing.^[4] In modern times the use of lead in soldering, batteries, ammunition, electronic devices gasoline and plumbing has been of great concern and has now to obey strong regulations.

Free exposure leads to release of lead into the environment due to the considerable solubility of organic lead-halide salts used in high efficiency perovskite technology.^[5] This high solubility is inherent to the rather weakly bound perovskite structure incorporating organic cations. Conversely, the latter property is also one of the major selling arguments for this promising technology, since it allows low temperature deposition of the absorber layer.

A comprehensive approach of the hazard risks incurred by this young technology implies a proper analysis of the full lifecycle, including raw materials extraction, synthesis of starting products, device fabrication, use and eventually disposal.^[6] While the first two points can be considered as controlled at an industrial level, the latter three points require particular attention, since they are specifically related to the thin film technology.

As a matter of fact, organo-metal halide perovskites (OMHP) are rather soluble in water at environmental pH values and it has been established that the hybrid lead halide structure first transforms to PbI_2 under direct contact with water or humidity.^[5] With a solubility product of 10^{-8} , the solubility of lead is 14 orders of magnitude higher than cadmium in CdTe which has been a debated argument for many years before the latter thin film technology was commercialized on a large scale. It is therefore not appropriate to treat this young thin film technology the same way as CdTe. Indeed, if a non-encapsulated OMHP film is exposed to running water, it can be considered that all the lead will be washed away, even if the perovskite was embedded in a nonporous scaffold. Given the optimum OMHP thickness of 300 nm, a typical lead amount of 0.4 g/m² would be released in the soil, looking at a worst case scenario. Assuming that the lead would first accumulate in the first few cm of the soil, a concentration increase of about 70 ppm can be calculated, which is slightly higher than in uncontaminated soil (> 30 ppm) and comparable to slightly contaminated soil in urban areas (>100 ppm).^[7] In this perspective, the ecological footprint may not seem severe. This becomes even more so, if one considers that between 5900 t/year and 93 000 t/year of lead are generated by the electric power sector in the U.S. during coal processing and combustion in the form of coal ash and blackwater. In comparison to this considerable load, 160 tons/year of lead would be enough to supply all of the U.S with electricity solely using efficient perovskite technology (the assumption adopted here is a 25% power conversion efficiency and a lifetime of 25 years).^[8]

From a life cycle perspective the ecological impact is not just given by the specific toxicity aspects related to the use of heavy metals in OMHP. On the contrary, the particular multilayer architecture used for the thin film solar cell and the associated electricity burden may dominate the big picture.^[9] The analysis is highly sensitive on the electricity mix being used, which in many countries is dominated by coal based production. Further ecological hotspots come from the use of gold (and to a lesser extent silver), ITO glass and the use of organic solvents.^[10] It is clear that the ecological impact highlighted by life cycle



assessment can be straightforwardly lowered if low impact materials and energy efficient processes are being used.

All these promising aspects may tempt us to think that organo-lead halide based thin film photovoltaic technologies may be unscrupulously deployed on a large scale. This however means neglecting its severe toxicity caused to human and animal organisms by substantial intake via ingestion or inhalation.^[6] Severe hazards may occur in the case of local toxicant accumulation, which may occur if solar modules break or disintegrated. In such a case, the exposed perovskite layer is degraded by rain water and may then contaminate the ground water. Also if such OMHP cells with exposed perovskite layers would get into direct touch with humans, the risk of intoxication would be very high. Related to such a risk is the use of lead in any electronic components, which was banned by the European Union as of July 2006.^[11] It therefore appears that the lead content in OMHP is an issue to be taken seriously, should such modules be deployed on the market.

8.1.2 Possible remediation

There are two principle possibilities to contain or surmount the risk of lead contamination. The first approach is to replace lead by another atom with high photovoltaic efficiency in perovskite solar cells. Sn^{2+} is a homovalent substituent that has been most successfully investigated with resulting power conversion efficiencies of 7.6%^[12] to 14.1 %.^[13] However, tin also has a known toxicity^[14] and therefore is not the ideal candidate to replace lead. Among the various substitution possibilities there are a number of monovalent and heterovalent substituents, which still need to be studied in depth.^[15,16] The second approach would be to live with the highly efficient OMHP absorber layer and to apply a robust encapsulation, which then avoids ingress of water and possible lead leakage even in the case that a module should break. This second approach very likely will be bound to a highly regulated recycling program at the end of life disposal. Such a scheme has also been applied to the commercialization of CdTe solar cells.^[17]

8.1.3 Considerations regarding perovskite solar cell technology at Solaronix

The particular cell architecture of perovskite solar cells at Solaronix has a number of highly advantageous attributes with respect to the toxicity issue of lead, which are closely related to the fabrication process and the materials being used.

First of all, the cell is constituted of various oxide layers as well as a carbon top electrode, which are deposited from solution at low temperature and fired at 400°C to 500°C. No ecologically critical metals such as gold or silver are used. Furthermore, a multilayer co-firing process was recently developed and patented, drastically reducing the thermal energy input during fabrication. Both of above aspects would considerably lower the ecological impact and it would indeed be interesting to confirm this by carrying out a life cycle assessment.

Second, the potentially hazardous organo-metal halide perovskite layer is applied only at the very end of the solar cell production, i.e. the lead containing step can be fully isolated from all other layer deposition processes and thus limit the risk of contamination during fabrication. This is not the case for all other OMHP device architectures.

Third, the carbon top electrode constitutes a hydrophobic repulsion layer which can considerably slow down and perhaps even inhibit water ingress. While this layer is porous in the currently used device architecture in order to allow impregnation of the multilayer stack with organo-metal halide solution, it is possible to apply a dense graphite capping layer in order to seal these cells completely. Such a strategy could indeed be deployed in the future.



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