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CHEOPS – Production technology to achieve low Cost and Highly Efficient phOtovoltaic Perovskite Solar cells

Deliverable D2.1

Report on measurement and stability testing protocols

WP2 – Upscaling and stability

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Revision History

Author Name, Partner short name	Description	Date
Matthias Bräuninger (EPFL)	Draft deliverable	07/07/2017
Sylvain Nicolay (CSEM)	Revision 1	07/24/2017
Matthias Bräuninger (EPFL)	Final version	07/24/2017

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Acronyms

CHOSE	Università di Roma Tor Vergata
CSEM	Centre Suisse d'Electronique et de Microtechnique
EPFL	École polytechnique fédérale de Lausanne
Fraunhofer	Fraunhofer Institute for Applied Polymer Research
H2020	Horizon 2020
WP	Work Package
LIV	Light I-V
MPP	Maximum power point

Executive Summary

In this deliverable we describe the development and consolidation of protocols for measuring the characteristics and testing the stability of the perovskite photovoltaic cells fabricated in the project.

Need for the Deliverable

A large number of CHEOPS partners are fabricating and measuring photovoltaic cells. Often, samples are sent to another laboratory and characterised by both sender and recipient. This creates the need for a well-defined testing procedure, since measurement practices can differ widely between individual research groups. Furthermore, many parameters such as measurement speed, light soaking duration or pre-biasing, as well as the order in which the tests are performed, can have an influence on the cell performance. The project partners thus need to agree on a standardised set of cell performance tests, so as to ensure maximum comparability of the results on exchanged samples.

Objectives of the Deliverable

With the help of this Deliverable, we aim to standardise the following cell performance tests:

- I-V measurements
- Maximum power point (MPP) tracking
- Light soaking
- Thermal cycling
- Damp-heat testing

Outcomes

The consolidated tests mentioned in Section 2.4 below were mutually agreed on between the project partners and implemented in their measurement schemes. They constitute the project milestone MS3.

Next steps

The project partners will follow the consolidated protocols described below when characterising their samples in order to compare their data upon exchanging samples.

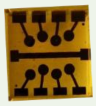
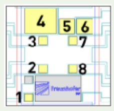
1 I-V measurements

Table 1 and Table 2 provide an overview on the standards of the different groups.

Table 1 – Status of the measurement protocols of the different groups.

	Fraunhofer	CSEM	UOXF	EPFL	MERCK
Current-voltage (JV) regime	Forward and Backward	Forward and Backward	Backward and forward	Forward and Backward	Forward and Backward
Scan rate of JV measurement	100 mV/s	20 to 100 mV/s	0.38 V/s (adjustable)	20 to 100 mV/s	ca. 0.1V/s
Number of scan cycles per JV measurement	2	>2	1	>2	1
Voltage region of JV measurement	-0.5 to 1.2 Volts	-0.5 to 1.2 Volts	0 - 1.4 V (adjustable)	-0.5 to 1.2 Volts PK single, -0.5 to 2 V tandem	-0.2 to 1.2 Volts
JV measurement performed in air/glovebox	N2-Glovebox	air	air	air	air
Temperature of JV measurement	20-25 C	25 C room temperature, not active cooling	20-25˚C	25 C room temperature, active cooling for tandems	25 C
Other measurements					
Measurement of IPCE	Yes	Yes	Yes	Yes	No
Sun illumination intensity	Up to 90% of 1 sun	> 1 sun possible, white, blue, red, NIR possible	100 ± 0.6 mW/cm2	> 1 sun possible, white, blue, red, NIR possible	
Reference cell	Si with KG filter	Si cell with beam splitter, regularly calibrated	Si with KG5 filter	Si cell with beam splitter, regularly calibrated	
Calibration of reference cell	Yes	calibration	File from supplier	calibration	
Factor of spectral mismatch calculation	No	No	Yes	No	
Dimensions of cells tested	4, 16 and 60 mm²	0.25, 1 and 12 cm²	0.0919 cm2	0.25 and 1.4 cm²	variable (0.1-0.4 cm²)
Are masks being used?	Yes	Yes	Yes	Yes	yes
Type of mask used	Metal mask for 16 and 60 mm² cell	Metal masks	Black anodised aluminium	Metal masks	black metal mask
Percentage of cell covered by mask	0,09	depends on design	0,227	0.25 cm² cells: 30%, 1.44 cm² cells: 15%	variable
Cell size being covered	16 and 60 mm²	depends on design	all	typically 0.5 mm each edge	variable
Hysteresis measurement	Yes	Yes	Yes	Yes	yes
Number of samples measured	8 substrates per batch	Typically ~15 substrates per batch	~ 16 samples per batch	Typically ~15 substrates per batch	
Total solar cells measured	8 cells per substrate → 64 cells	1-3 cells per substrate -> 15-45 cells	8 pixels per sample → 128 pixels per batch	1-3 cells per substrate -> 15-45 cells	
Time from PK deposition to JV measurement	1-2 days	1-2 days	2-24 hrs	1-2 days	<24h
Pre-condition of solar cells (e.g. light, bias)	No	no	Pre-bias at starting voltage (e.g. 1.4V for 5s under illumination)	no	optional
Stability test conditions	Climate chamber: ambient, tropical, 60/90, 85/85	Climate chamber: 85/85	Light soaking w/wo applied voltage in air (w/o temperature control and UV-filter)	Climate chamber: 85/85	light soaking (20-60°C) thermal ageing (60-85°C), open circuit
	Under UV	1 sun illumination 60°C	Heat in N2/air at open circuit	1 sun illumination 60°C	
	Outdoor measurement	thermal cycling		thermal cycling	
	Measurements performed under open circuit conditions (ISOS 1)				
Thickness measurement	Profilometer	Profilometer, x-section SEM	Yes (Dektak) and closs section SEM	Profilometer, x-section SEM	Profilometer, SEM

Table 2 – Status of the preparation protocols of the different groups

	CSEM	UOXF	MERCK	EPFL	Fraunhofer
Layer information	FTO (400nm) cp-TiOx (20nm) mp-TiO2 (150nm) Perovskite (300nm) S-OMeTAD (150nm) Au (60 nm)	FTO cp-TiO2 (50 nm) C60 (20 nm) Perovskite (300 nm) S-OMeTAD (200 nm) Ag (80 nm)	FTO (500 nm) cp-TiO2 (50 nm) mp-TiO2 (300 nm) PK (300 nm) S-OMeTAD (100 nm) Au (80 nm)	ITO (80 nm) PEIE (~ 1 nm) PCBM (20 nm) PK (300 nm) S-OMeTAD (150 nm) Au (60 nm)	ITO (200 nm) PEDOT:PSS (30 nm) PK (250 nm) PCBM (90 nm) Ca/Ag (30/150nm)
Cell shape	101 mm^2 	12 mm^2 	10 – 40 mm^2	25 mm^2 	4, 11, 16, 60, 88mm^2 
JV Chars	Voc = 1.09 (V) Jsc = 21 (mA/cm²) FF = 72.3 (%) PCE = 16,6 (%)	Voc = 1.07 Jsc = 22.17 FF = 71.8 PCE = 16.9	Voc = - Jsc = - FF = - PCE = -	Voc = 1.06 Jsc = 19.9 FF = 77.3 PCE = 16.3	Voc = 1.05 Jsc = 17.9 FF = 78.8 PCE = 13.12

Since the strongly differing nature of the group-internal standards are very different, the following requirements to sample fabrication and measurement conditions and protocols were agreed on during the WP1/WP2 technical meeting in Munich (June 2016) and the first annual meeting in Rome (January 2017):

Sample requirements:

- Sample geometry 1 cm^2, defined by shadow mask, shape is chosen by the project partners
- 1-sun illumination and, if possible, low illumination.
- No dedicated pre-conditioning or light soaking.
- Measurement speed is 50 mV/s.

Measurement conditions:

- No UV filters: Spectrum should be as close to AM1.5g as possible
- Temperature during MPP tracking/light soaking: room temperature

Measurement protocol:

1. Dark-IV scans in reverse (from V_{oc} to J_{sc}) and forward (from J_{sc} to V_{oc}) direction
2. Light-IV scans in reverse and forward direction
3. MPP tracking for 5 minutes
4. Light-IV scans in reverse and forward direction

Data to be communicated to other groups:

- V_{oc}, J_{sc}, FF and PCE for both scan directions
- Ratio between best scanned forward and reverse PCE and stabilised MPP efficiency
- Results from four co-deposited substrates with 1 cm^2 aperture

2 Encapsulation and stability

2.1 CSEM

CSEM encapsulated single-junction perovskite cells made in collaboration between EPFL and CSEM using glass front and back sheets combined with a butyl rubber edge sealant. A schematic of the encapsulation process is shown in Figure 1.

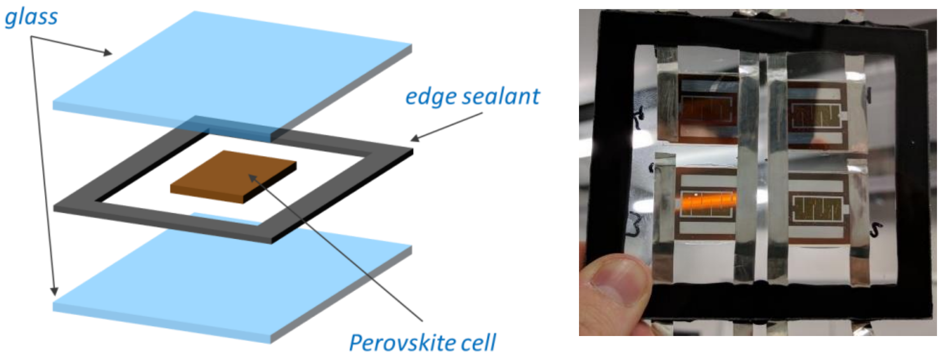


Figure 1 – Sketch of the sealing procedure (left) used by CSEM and photograph of the encapsulated cells (right).

The encapsulated 1 cm^2 cells were based on a planar multi-cation, mixed-halide perovskite layer and featured transparent front and rear electrodes for high near-infrared transparency required in tandem cells. The cell performance during and after damp-heat testing according to the IEC 61646 protocol (85% relative humidity, 85°C) for 1000 h is shown in Figure 2. An overall efficiency drop of less than 10% was observed after 1000 h.

Following current developments in CHEOPS WP1 and WP4, CSEM is migrating towards a p-i-n solar cell structure with all-inorganic charge transport materials that will support the development of more intrinsically stable single-junction and tandem devices. The encapsulation technique described in this section is compatible with this cell type as well.

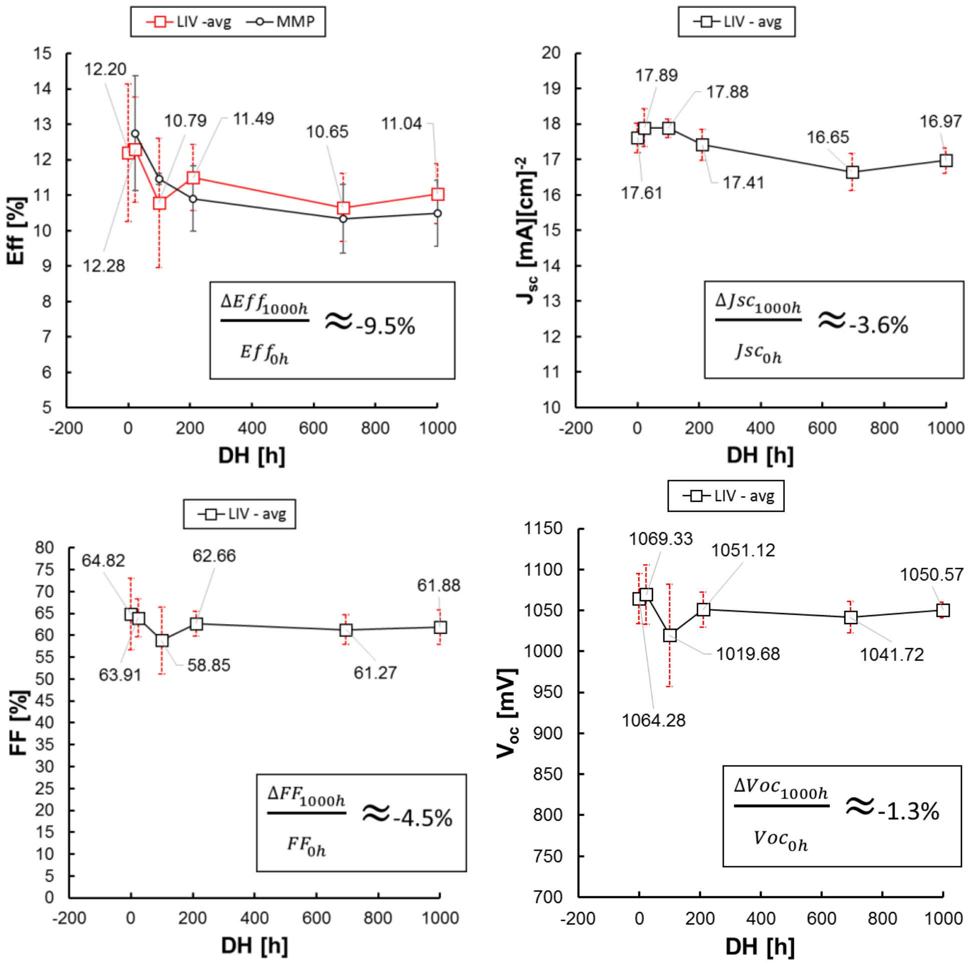


Figure 2 – Cell data for a perovskite cell aged for 1000 h and encapsulated with CSEM's butyl rubber edge sealant.

2.2 Fraunhofer IAP

Fraunhofer IAP is responsible for the development and optimisation of the encapsulation process in perovskite solar cells.

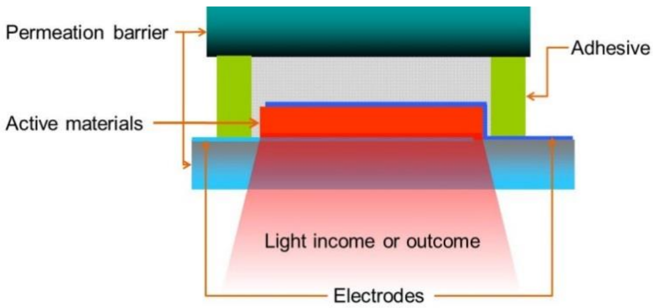


Figure 3 – General set-up of an encapsulated device.

The degradation mechanisms are determined by different processes on each one of the device layers:

Active Layer - Perovskite Materials:
These layers are known to react with oxygen and/or water. Additionally, the stability is influenced by temperature and light.

Electrodes:
In these cells, gold and silver are mostly used as contacts and they are mostly stable under environmental conditions. Calcium is also used as a low work function electrode and it is known to react with water and oxygen in the following manner:

$$2\,Ca + O_2 \rightarrow 2\,CaO$$
$$Ca + 2\,H_2O \rightarrow Ca(OH)_2 + H_2$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$

In order to prolong the lifetime of the solar cells, the stacking layers need to be protected mainly from oxygen and water. We discuss the most important mechanisms below.

Permeation through the adhesive

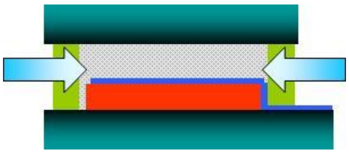


Figure 4 – Important pathways for degradation of sealed Perovskite device (adhesive).

- With the assumption that the encapsulation adhesives have a thickness of about 10 µm and a width of 1 mm, the adhesive-specific permeation rates are:
    - $7*10^{-5}$ g m/ (m^2 d) for H_2O
    - 0.2 cm^3 m/ (m^2 bar) for O_2

These properties can be determined through Calcium mirror tests. In this way, it is possible to:

- Evaluate the permeation through substrates, caps and adhesives
- Test if sample is completely sealed by the degradation of calcium
- Control the diffusion of water through the barrier layer and/or adhesive by restricting the filtering path
- Measure degradation of metallic calcium and the rate via light transmission when it forms $Ca(OH_2)$
- Optical transmission is correlated to layer thickness via calibration
- Transmission rate as function of time, temperature and humidity
- Lower test limit $5*10^{-6}$ g/(m²d)
- Test conditions depending on demands:
    - 23 °C @ 50% RH
    - 38 °C @ 90% RH
    - 60 °C @ 90% RH
    - 85 °C @ 85% RH

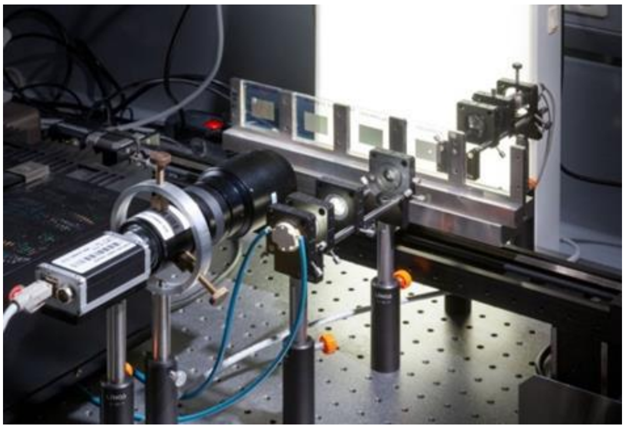


Figure 5 – Calcium mirror set-up @ Fraunhofer IAP.

A typical investigation shows the reduction of the Calcium mirror thickness.

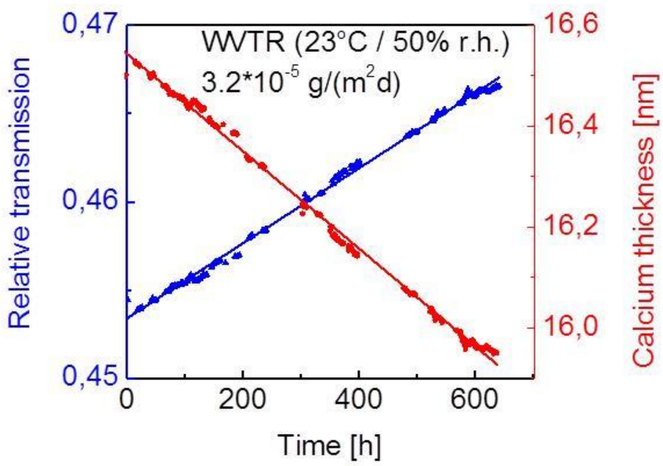


Figure 6 – Determination of the water vapour transmission rate.

Encapsulation adhesives need to have good barrier properties, optimise with respect to thickness and layer width. For this purpose, various adhesives were examined by Fraunhofer IAP and examined for their suitability.

- Araldite Araldite® 2011, thermal curing for full encapsulation
    - only stable up to 65 °C / 50 % RH
- ACW Glue AC A 1430, http://www.addisoncw.com/assets/Product-Data-Sheets/aca1430b.pdf
    - for edge encapsulation; stable up 85 °C / 85 % RH
- DELO Katiobond LP 651, http://www.syneo.net/pdf/Colle/KB/colle-uv-resine-epoxy-DELO-KATIOBOND_LP651_(TIDB-GB).pdf
    - for edge encapsulation; stable up 85 °C / 85 % RH
- Double adhesive tape from 3M (Fraunhofer provides it for EPFL)
    - for full encapsulation; stability is under investigation

Permeation through interfaces

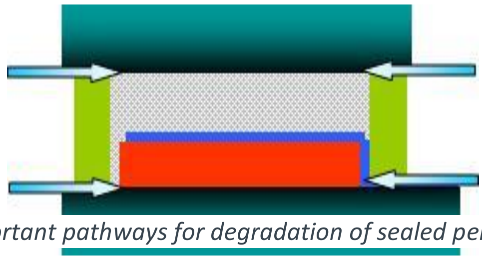


Figure 7 – Important pathways for degradation of sealed perovskite device (interface).

High-energy surfaces, metals or oxides, in contact with the resin tend to bind, thus forming adsorbates and working as permeation channels. To prevent this from happening, the contact surfaces need to be cleaned before encapsulation.

Reverse permeation

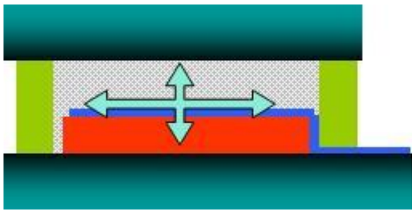


Figure 8 – Degradation of sealed perovskite devices (capsulated oxygen and moisture).

Different materials contain different amounts of water, e.g. PET (0.5 %), PC (0.35%), PI (2.9 %). Reducing the water contained within the space of the perovskite layers via the encapsulation materials is critical for the long-term lifetime of an encapsulated device.

Additionally, in the search for highly stable devices, Fraunhofer has experimented with a perovskite mix that contains rubidium and cesium, in addition to the more common methylammonium and formamidinium cations. Long-term testing of these devices has shown that they maintain more than 80% of their initial performance after 70 days. These devices were kept in the dark, at open-circuit condition, room temperature and inert conditions. The decline of performance over time is shown in Figure 9.

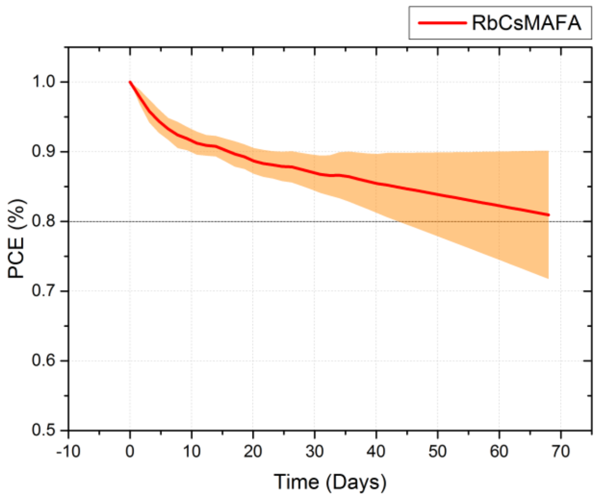


Figure 9 – Degradation of perovskite solar cells made of RbCsMAFA.

It should be noted that these devices were built in a p-i-n structure containing PEDOT:PSS as hole transport layer (HTL). It is known that this material does not possess long-term stability due to its water retention.

2.3 CHOSE

The realisation procedures used for CHOSE's encapsulation technique are resumed in the following:

- Lamination of the PK module using the Kapton adhesive tape deposited on the active area of the device
- Deposition of a light curable glue on the whole active area of the PK module
- Positioning of a protective glass
- Curing of the light-curable glue under Class A Simulator at 1-sun illumination for 30 seconds
- Deposition of a UV-curable glue on the edge of the protective glass
- Curing of the UV glue under UV irradiation for 40 s, masking the active area of the PK module using a black adhesive.

2.4 Oxford PV

Oxford PV performed stability measurements on their perovskite/silicon tandem cells. Measurements according to the IEC61646 standard protocol were conducted:

- Thermal cycling between -40°C and 85°C: Less than 10% efficiency loss after 200 cycles
- Light soaking at 60°C: Less than 10% efficiency drop after 1000 h
- Damp-heat test at 85% rel. hum. and 85°C: Less than 10% efficiency drop after 1000 h

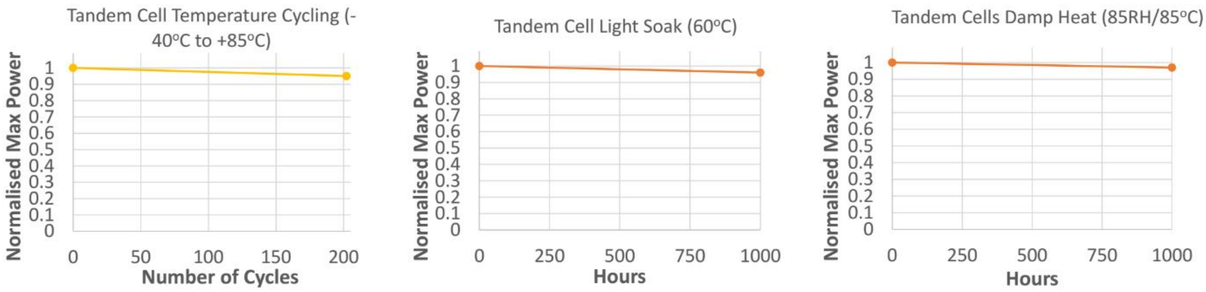


Figure 10 – Stability testing performed by OxfordPV (presented at Genoa meeting, September 2016)

3 Consolidated protocols

All tests requiring irradiation of the solar cell must be performed in a steady-state sun simulator with the AM1.5 spectrum.

3.1 Cell performance measurements

1. Dark-IV scans in reverse (from V_{oc} to J_{sc}) and forward (from J_{sc} to V_{oc}) direction
2. Light-IV scans at 1-sun illumination in reverse and forward direction
3. MPP tracking for 5 minutes
4. Light-IV scans at 1-sun illumination in reverse and forward direction
5. External quantum efficiency measurement

3.2 Stability testing for encapsulated cells

- Test cells at 85°C in the dark in inert atmosphere or air (only encapsulated samples)
- Thermal cycling between -40°C and 85°C for 200 cycles
- Light soaking at 60°C for 1000 h at the MPP if a suitable setup is available
- Damp-heat test at 85% rel. hum. and 85°C for 1000 h