

Perovskite solar cells with carbon-based electrodes monitored under different operating modes, in real outdoor and controlled conditions

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SUMMARY - The best-performing devices all use gold or silver as the back contact which limits perovskite solar cells large-scale application. However, the use of such noble metals is a source of instability in these devices. Performance and stability of triple mesoscopic perovskite solar cells with a carbon electrode, a promising architecture for the next generation of photovoltaics will be disclosed. Comparative study between indoor and outdoor tests is motivated by the lack of data on real conditions of use. This communication describes the manufacture of the PSCs and the indoor (under constant illumination and regulated temperature) and outdoor (on the SIRTa observatory, with monitoring and measurements of environmental conditions) test platforms. The initial results, collected between July and November 2024, have shown differences in performance and lifetime according to the operating mode.

Key words – Perovskite solar cells, carbon-based electrode, operating conditions, outdoor and controlled characterizations, degradation.

1. INTRODUCTION

To enter the photovoltaic (PV) market successfully, perovskite solar cells (PSCs) are still facing several tough challenges. Scalability of the processes and long-term stability of the devices need to be ensured. The latter especially has been one of the main causes of scepticism for a long time and is still underestimated in most studies.

The best-performing devices all use gold or silver as the back contact in conjunction with hole-transporting materials acting as electron-blocking layers. The use of such noble metals limits PSC's large-scale application. In 2017, we published [1] a structure proven to be stable for more than 10000 h, measured under controlled standard conditions, by engineering an ultra-stable 2D/3D perovskite junction. This structure is based on a fully printable architecture made of three mesoporous layers in which the perovskite is embedded. Triple mesoscopic devices use a carbon counter electrode that has proven to be an effective method to significantly enhance the device's lifetime, which has nowadays become one of the most prevailing scaffolds for constructing stable PSCs. Since then, carbon electrode-based

PSCs have established themselves as highly promising device architectures for the next generation of PV with efficiencies of over 21% and unprecedented stabilities.[2, 3] The most common carbon-based materials used in the PSCs field are graphite/amorphous carbon, graphene, and carbon nanotubes. They represent a suitable solution to substitute noble metals, due to their low cost, high conductivity, eventual low-temperature processing and work function close to that of gold. Nonetheless, carbon-based materials also present many drawbacks, associated especially with their processability on a large scale. For example, graphene, the 2D layer of graphite, is a very versatile material with metal-like properties; however, it is difficult to be obtained by mechanical or chemical exfoliation on a large scale. The dispersion of graphene layers from graphite requires a large amount of organic solvents, such as dimethylformamide for example.

The main trend in the literature scenario highlights that the power conversion efficiency (PCE) values of carbon electrode-based PSCs are lower than those of their gold-based counterparts, and the main reason lies in the poor contact at the perovskite/electrode interface; as secondary issues, resistance of carbon electrodes and charge recombination phenomena also contribute to lower Jsc and FF values. [4]

A further challenge in the path towards gold-free PSCs will be the investigation behind the markedly improved stability of carbon-based devices. Indeed, even though many groups have carried out long-term stability experiments, not much is understood on the relationship between the singular aging of internal interfaces and components, and to what extent they affect the overall device stability against different external stress sources.

Outdoor characterizations of photovoltaic technologies, particularly PSC, have often been underappreciated in the research community, as evidenced by the limited number of studies focusing on such evaluations [5, 6]. The primary concern highlighted by the few existing reports on this topic is the performance of these devices under real operating conditions [7, 8]. These studies consistently demonstrate that, over extended periods of testing, the devices experience significant degradations. These degradations are both reversible and, more crucially, irreversible, potentially affecting the long-term performance and reliability of the solar cells. Notably, these

degradation phenomena are not easily detected under standard laboratory testing conditions, such as those involving constant temperature and one-sun irradiance Maximum Power Point (MPP) tracking (MPPT) procedures [9-12]. Such procedures, while useful for initial assessments, fail to replicate the complex and variable environmental conditions that solar cells are subjected to in actual outdoor settings. For perovskite technologies to achieve the level of consistent outdoor reliability currently demonstrated by silicon-based solar cells, and thereby reach a state of commercial viability, a more robust and extensive program of outdoor testing and operational evaluations must be instituted. This would not only help in understanding the various potential failure modes that could occur in real-world settings but also guide improvements in material and device design to address these issues. Therefore, the expansion of research efforts to include comprehensive outdoor testing protocols is critical for advancing the commercial prospects and reliability of perovskite photovoltaic technologies, ensuring they meet and potentially exceed the performance standards set by silicon counterparts.

In this communication, we will first present the structure and performance of the studied PSCs, then the indoor and outdoor test benches, and finally some results.

2. TRIPLE MESOSCOPIC DEVICES DESCRIPTION

Several triple-mesoscopic PSCs (Figure 1) were prepared according to the following procedure. The FTO glass was first etched to form two separated electrodes before being cleaned ultrasonically with soap water, DI water, acetone and finally isopropanol. Then, the patterned substrates were coated by a compact TiO₂ layer by aerosol spray pyrolysis, and a 500 nm mesoporous TiO₂ layer was deposited by screen-printing of a TiO₂ slurry, (commercially available Solaronix T165 SP). After being sintered at 450 °C for 30 min, a 1200 nm ZrO₂ spacer layer was printed on the top of the mesoporous TiO₂ layer using a ZrO₂ slurry, which acts as an insulating layer to prevent electrons from reaching the back contact. Finally, a carbon black/graphite counter electrode with a thickness of about 10 nm was coated on top of the ZrO₂ layer by printing a carbon black/graphite composite slurry, (Solaronix G/SP) and sintering at 400 °C for 30 min. After cooling down to room temperature, the perovskite precursor solution was infiltrated through a semi-continuous printing process from the top of the carbon counter electrode by inkjet printing.

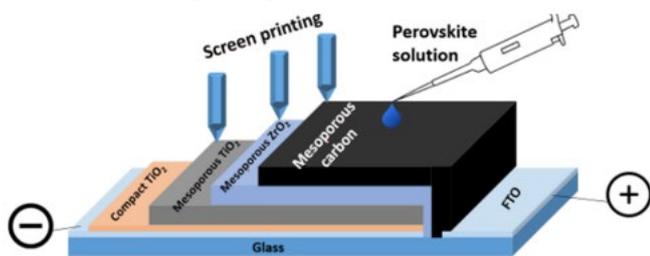


Figure 1. Schematic diagram of a triple mesoscopic structure

The complete printing process was carried out in air conditions. After drying at 50 °C for 30 min, the mesoscopic solar cells containing perovskite was obtained. The perovskite precursor solution was prepared as follows: 1.2M of MAI and 1.2M of PbI₂ with 3 vol% of AVAI were dissolved in gamma-butyrolactone, and then stirred at 80 °C overnight. All the cells were subjected to a humidity assisted thermal treatment [13] during 120h to mature them and allow them to reach their nominal efficiency. They were then encapsulated in ambient atmosphere to protect the cell from mechanical damage, with no special control on the humidity and oxygen content. The

encapsulation was performed by covering the cells with a thin glass and sealing the edges using DuPont Surlyn polymer.

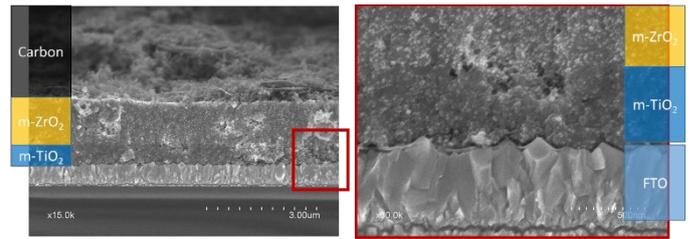


Figure 2. SEM image of a PSC cross section

PSC were initially characterized under controlled standard conditions (Figure 3). I-V curves provide valuable information about solar cells, including their efficiency. The shape of the curve indicates how the cell behaves under illumination. Performing I-V measurements under a solar simulator (AM1.5G) at regular intervals on cells deployed outdoors allows for more effective monitoring of their degradation over time.

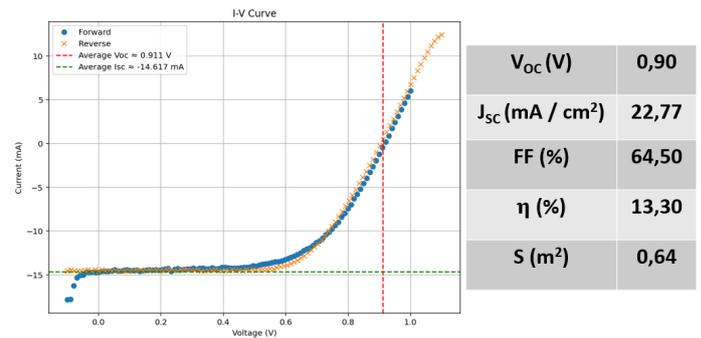


Figure 3. I-V curve and results table

Electroluminescence and photoluminescence measurements play a crucial role beyond simple monitoring. As depicted in Figure 4, these techniques are employed initially and will be consistently repeated in upcoming campaigns to ensure comprehensive evaluation. Electroluminescence is particularly valuable for identifying areas within solar cells where carrier recombination is inefficient, thus highlighting potential problem zones. In contrast, photoluminescence provides detailed insights into the intrinsic quality of the material, revealing any underlying defects or impurities. Together, these techniques form an indispensable toolkit for maintaining the efficiency and longevity of solar cells by proactively identifying signs of degradation.

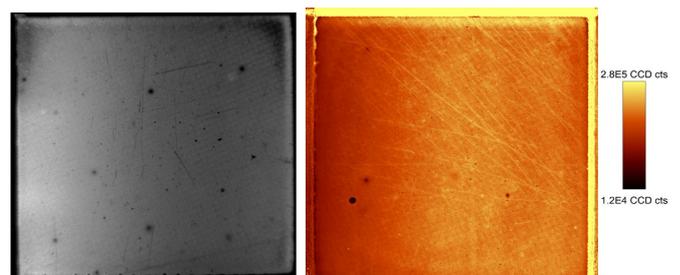


Figure 3. Schematic diagram of a triple mesoscopic structure and EL and PL images of this PSC.

3. EXPERIMENTAL TEST BENCHES

This section presents the experimental set-ups for outdoor and laboratory characterization.

3.1. Outdoor monitoring platform

The measurement capabilities of the SIRTAs [14] PV test bench at Ecole Polytechnique in Palaiseau were expanded and coupled with existing equipment at CEA Saclay. Encapsulated cells were installed on a dedicated test bench (Figure 5) to monitor their performance under outdoor conditions while the experiment was duplicated in an indoor controlled environment (Figure 6). Global plan of array irradiance (photodiode from SOLEMS) and cell temperature (Class A Pt100 sensor encapsulated in perovskite materials) are also monitored.

The experimental test bench is installed facing south and tilted at 27°, which maximizes the irradiance received in the plane of the cells over a full year. Acquisitions are made from sunrise to sunset, whenever irradiance exceeds 50 W/m².

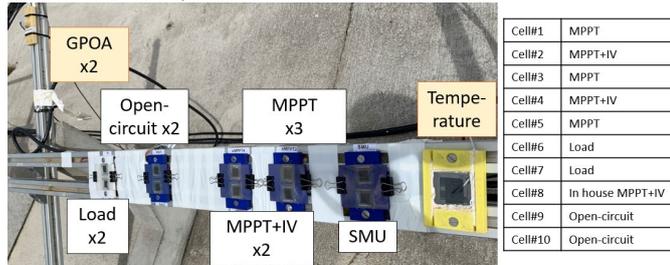


Figure 4. Outdoor PSC characterization test bench

Some cells (Cell#1 to Cell#5) are connected to an MPP tracking card [12], with (Cell#2 and Cell#4) or without (Cell#1, Cell#3 and Cell#5) regular IV curve (one per hour). Cell#8 is connected to a Tektronix Source Measure Unit with regular IV curves and tracking of the MPP using an in-house algorithm. For both, MPPT algorithm is Perturb and Observe with a tracking period of 200 ms, a voltage step of 10 mV and an acquisition frequency of 50 Hz. IV curves are measured by a Tektronix Source Measure Unit. There are 110 points per IV curve measured each hour, with a time step of 100 ms. The IV measurement starts in reverse, then forward, this allows us to observe potential hysteresis.

Other cells (Cell#6 and Cell#7) are connected to a fixed resistive load, which is the softest monitoring system, which is supposed to cause the least disturbance to the cells and is also the closest to the actual operation of PV modules connected to the grid. Cell#9 and Cell#10 are left open circuit to simulate non connected PV modules.

We keep some cells close to their MPP, just like PV systems do in residential and commercial applications. This lets us study how variable outdoor conditions – like diurnal cycles, fast-changing irradiance, temperature variation, and rain – affect performance and stability. We also test the market readiness of new cell technologies. Regular IV curve measurements also monitor the evolution of other key properties, such as short-circuit current, open-circuit voltage, and fill factor, and identify both reversible and irreversible degradation phenomena.

3.2. Indoor monitoring platform

The same characterization bench was installed under controlled conditions. The PSCs were subjected to continuous 1-sun illumination, with a UV cut-off filter and a regulated temperature of 25°C using a Solixion A20 solar simulator. The light source is based on a plasma lamp technology that allows long-term ageing experiments while keeping the same solar spectrum quality. (Figure 6)

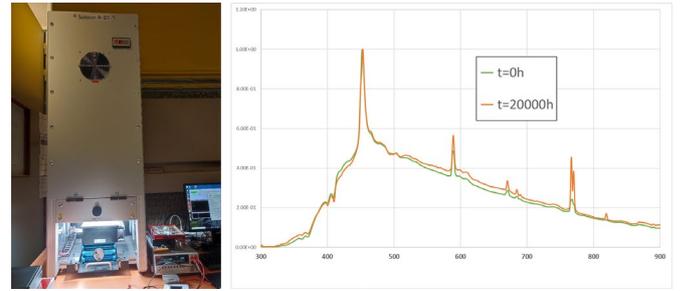


Figure 5. Indoor PSC characterization test bench and AM1.5G solar spectrum after 20000h of constant illumination.

In a first experiment (Figure 7) some cells were left open circuit and others were kept under resistive load for around 8000 hours (11 months) showing their extreme stability for PSCs. Then in a second experiment, the MPPT card [15] was used to constantly track the MPP coupled with regular IV characterizations.

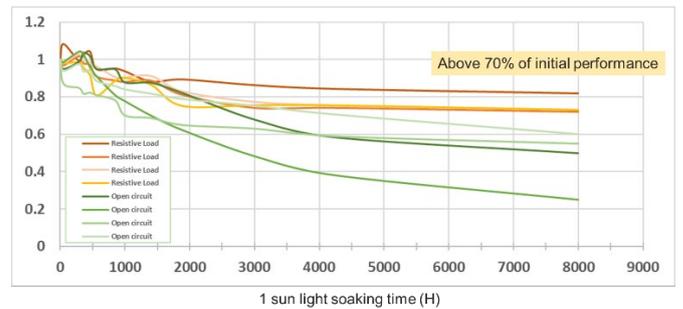


Figure 7. Indoor PSC stability assessment under constant illumination AM1.5G

4. RESULTS

The data have collected during four months from July to October 2024. It has allowed us to optimize the measurement process (MPPT algorithm, type of measurements, and frequency...) and define performance indicators and figures of merit that can help us analysing the indoor/outdoor performance and degradation of the installed cells.

Figure 8 shows that the performance of these cells initially increases for few days, before stabilizing for several months and then deteriorating. During the stable period, Cell#7 (pink), on a resistive load, performs better than those under MPPT (blue, green). The one using in-house protocol (Cell#8 in yellow) is better than those using the commercial MPPT card. Cells with periodic IV measurements (Cell#2 in green) have a shorter lifetime.

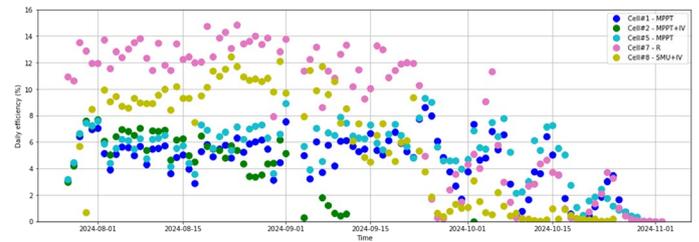


Figure 6. Evolution of outdoor efficiency over time.

We can plot the daily profiles for the power conversion efficiency, output power, voltage and current (Figure 9). This figure shows the severe degradation of all cells after 4 months of operation, following a long period of stability. Voltage remained very stable. We can also see that MPP cells tend to show diurnal recovery. No-load voltage decreases over the course of the day, certainly due to the rising ambient temperature.

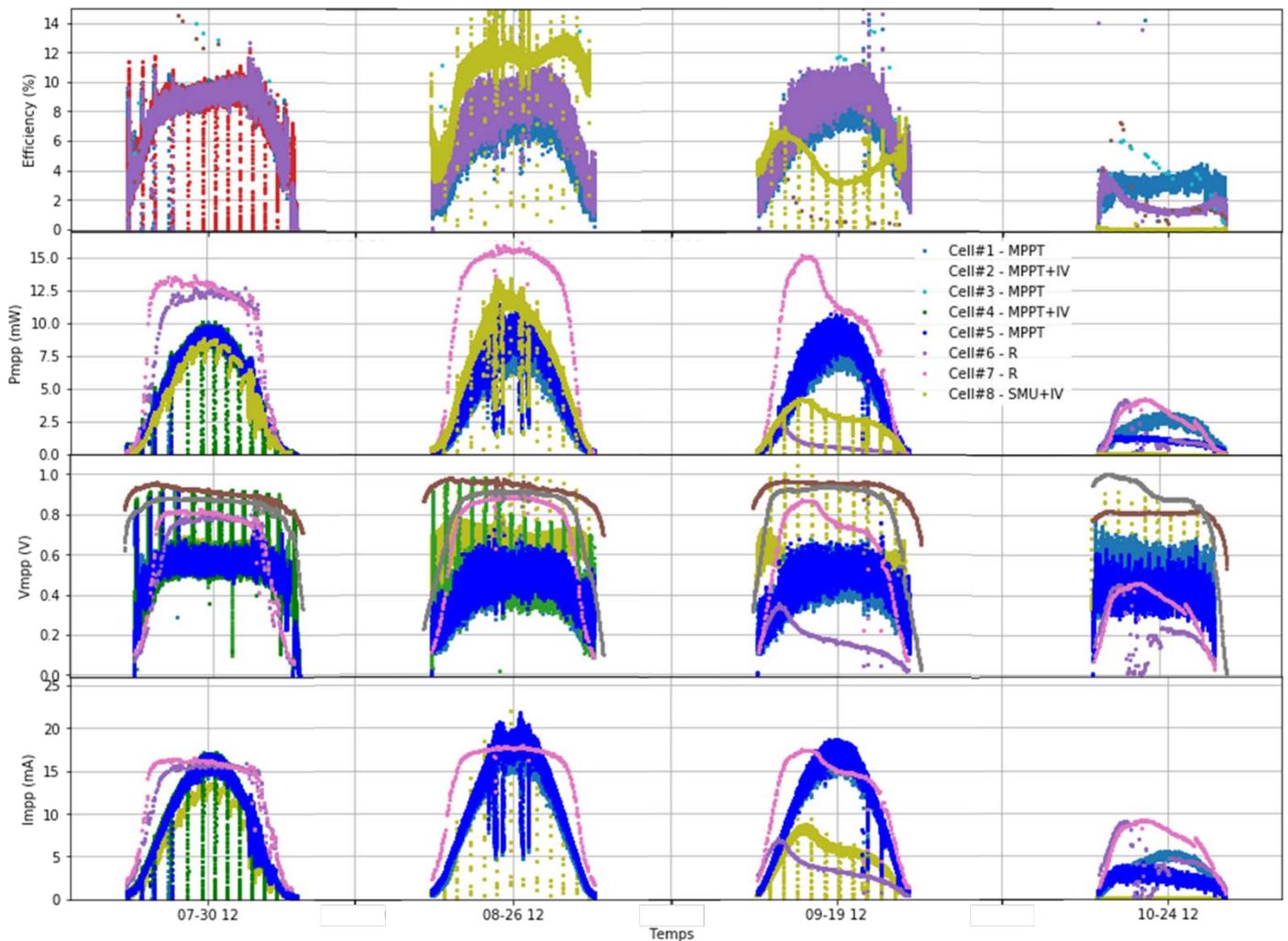


Figure 9. Example of daily profiles of power conversion efficiency (top), output power (2nd ligne), voltage (3rd line) and current (bottom) for all PSCs, in July, August, September and October.

IV curve measurements taken at different dates with similar irradiance levels (Figure 10) confirm that the current increases in the first few days before stabilizing for a fairly long time and then deteriorating. It also shows a fading hysteresis. Open-circuit voltages and fill factors also fall slightly.

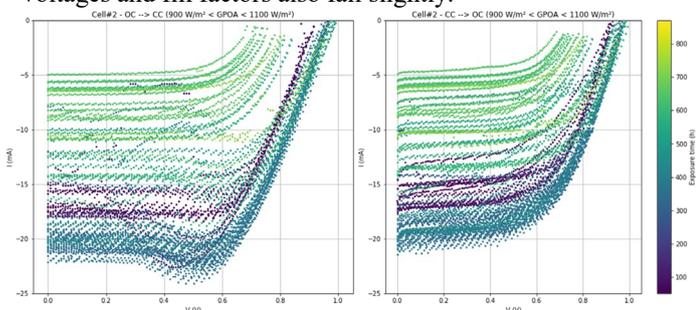


Figure 10. Evolution of outdoor measured IV curves, reverse and forward for cell#2 for selected irradiance between 900 and 1100 W/m²

5. CONCLUSIONS

This communication highlights significant advancements in the development and testing of triple mesoscopic perovskite solar cells with carbon-based electrodes. This architecture offers promising alternatives to traditional noble metal contacts, addressing issues of cost and scalability while maintaining competitive performance and stability. Through comprehensive outdoor and controlled indoor testing, we identified marked differences in cell performance based on operating modes, with

superior results observed in cells functioning under resistive load conditions. Despite a generally promising stable period, the findings also underscored the cells' susceptibility to performance degradation over time, particularly under outdoor conditions that approximate real-world environments more closely than traditional laboratory settings. The indoor results have not yet been analysed but these insights lay groundwork for future material and design optimizations aimed at extending the lifespan and commercial application of perovskite-based photovoltaics.

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