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EXPERIENCES OF CONTINUOUS ON-SUN PERFORMANCE MEASUREMENTS OF PEROVSKITE MINI-MODULES

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ABSTRACT: A set of Perovskite-based mini-modules have been distributed between testing partners in Cyprus and Germany in order to acquire performance measurements of the devices under long-term outdoor exposure. The devices were tested indoors prior to mounting outdoors where their current-voltage characteristics were recorded at regular intervals over several months using various loading and voltage sweeping strategies. All modules tested showed a decrease in power conversion efficiency over time, though subsequent discoveries have shown that this arose from some recoverable process and is not an irreversible form of degradation. A basic theory is expounded that attributes both long-term performance decline and recovery to the migration of slow-moving ionic species within the Perovskite cells. Furthermore, the same process, with faster ion migration, can explain the observed behaviour of the modules under different voltage sweep and loading strategies. This work has reaffirmed the importance of considering the movement of ions in any I-V tracing strategy and provides a set of recommendations to deal with this. While MPP loading facilitates the measurement of more representative instantaneous device efficiencies, it has not been possible to conclude that real degradation is enhanced when keeping modules at open circuit between scans.

Keywords: Perovskite, Module, Characterisation, Monitoring, Experimental Methods

1 BACKGROUND & RELEVANCE

Perovskite-based photovoltaic devices are currently the focus of intense worldwide research, as they have demonstrated impressive power conversion efficiencies (PCEs) of over 21% [1] and are suitable for mass production using very simple processes. The technology is still in relative infancy, mainly due to the limited size of record efficiency devices and uncertainties regarding the long-term stability of the devices produced to date. The commercialisation of this technology has also been hampered by the lack of a consensus amongst the perovskite research community on what stability assessment protocols to apply, which has only recently been addressed [2].

Only limited experience of long-term outdoor testing of Perovskite-based PV devices is available in the literature, due to the relative novelty of this technology. For this technology to grow and achieve its commercial potential, a consensus on the methods to characterise the output of these devices needs to be established, with the aim to incorporate these into standardised test procedures. For this reason, there is a strong need for experiences of testing these devices to be published amongst the scientific community in order to build up the body of experience needed for such an undertaking. In particular, there is very limited data on long-term outdoor studies of Perovskite modules as most research currently focuses on the characterisation of cells indoors under controlled test conditions.

As part of the EU-funded Espresso project, a measurement campaign was undertaken to characterise the output of several prototype Perovskite mini-modules under real operational conditions. For this, two similar batches of encapsulated mini modules were produced within the Espresso consortium and were distributed to the two outdoor test partners: Fraunhofer ISE in Freiburg, Germany, and the FOSS group of the University of Cyprus, Nicosia, Cyprus. The campaign was designed to both gain insight into the long-term stability of these modules, as well as to build up experience of the most appropriate test procedures to apply to these novel devices.

2 METHODOLOGY

Two batches of 6 Perovskite mini-modules were distributed to the two test sites, located in Freiburg, Germany, and Nicosia, Cyprus. Control devices were selected from each batch and kept in dark, uncontrolled conditions. The aim of this was to determine whether any observed degradation in the samples under test was occurring due to outdoor exposure, or whether it arose from an inherent aging process occurring within the devices.

The test modules were mounted outdoors (see Figure 1) over a period of several months, from November 2019 to September 2020. Performance measurements of the devices were obtained using outdoor test benches equipped with an extensive array of environmental sensors to record solar irradiance in the plane of array, ambient and device temperatures, wind velocity, and humidity/ precipitation levels. The electrical characterisations in both locations are performed using almost identical setups that both employ a single current-voltage source-meter multiplexed to take sequential measurements from an array of devices under test.

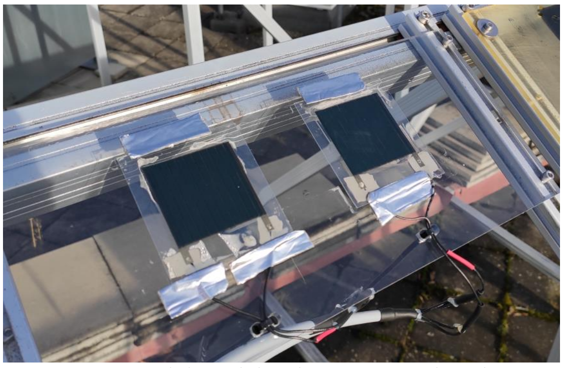

Figure 1: Two mini-modules shown mounted outdoors on a test bench at Fraunhofer ISE, Freiburg.

At both locations I-V traces are recorded automatically by LabVIEW software. Voltage sweeps across the device terminals were programmed in both the forward (< 0V to > open circuit voltage) and reverse directions (> open circuit voltage to < 0V). The software also allows for the dwell time and step size of each voltage increment to be altered. By default, this approach leaves the devices at open-circuit between I-V scans.

Initially, the dwell time and step size of the voltage sweeps at both locations were set to 1.2 seconds and 0.1 V respectively. With these measurement parameters, a single forward and reverse sweep measurement set would take between 3-4 minutes. Therefore, depending on how many modules were being tested outdoors simultaneously, measurement intervals were set to between 5 and 15 minutes.

Maximum power point (MPP) loading of the modules between I-V scans was introduced into the FOSS outdoor test bench approximately 3 months after the commencement of the experiments. The MPP load did not employ active tracking, rather the system was designed to hold the terminal voltage of the device under test at the average maximum power point voltage of both the forwards and reverse I-V sweeps. Thus, the MPP voltage would be updated immediately after an I-V sweep and held constant until the next I-V sweep occurred.

With this new capability, different approaches to device performance measurement were investigated, including holding the devices at open-circuit and maximum power point (MPP) between measurement traces. Forward and reverse voltage sweeps were also applied to the devices during each I-V characterisation. Changes were also made to the voltage sweep rates and ordering, to look for possible impacts on the recorded PCEs.

3 RESULTS

3.1 General Observations

Control modules kept indoors were found to exhibit no signs of degradation either in appearance or performance. In fact, a performance increase was noted over time for these modules, which suggests that some ongoing process within the cells was improving the device performance over the values initially measured by the manufacturer. This was also evident initially in several outdoor test modules (see Figure 2, Modules G02, C01, C02).

There was no indication that the modules were affected by humidity, rainfall or frost, leading to the conclusion that the modules were very well protected from the environment by their encapsulation. However, results of the outdoor I-V traces revealed that measurable degradation in the performance of the devices occurred almost immediately as they were left outdoors (Figure 2). This suggests that the degradation is attributed to temperature and irradiation levels at the two sites.

Indeed, differences in the device aging between the two sites were revealed quickly. Initial degradation in performance was higher in the Cyprus set of modules, but over time the degree of degradation was similar in both locations. Nevertheless, it was found in both locations that the performance degradation is driven primarily by reduction of open-circuit voltage and fill factor of the modules, while the short-circuit current showed an illumination dependent fluctuation but no obvious degradation over time (Figure 3).

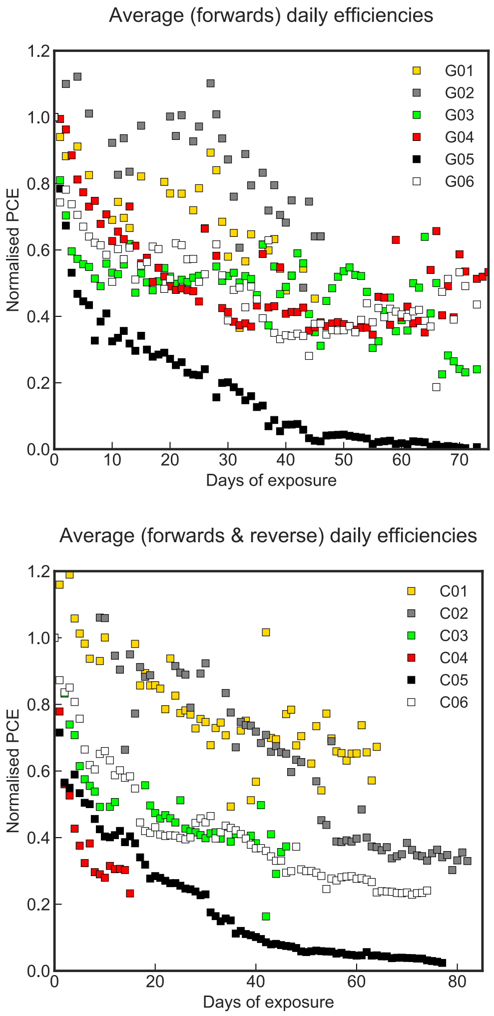

Figure 2: (Top) Normalised daily average PCE for modules measured at the test site in Freiburg, Germany. (Bottom) Normalised daily average PCE measurements for modules measured in Nicosia, Cyprus.

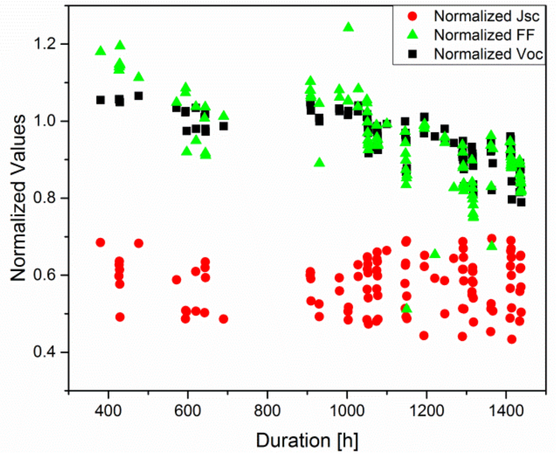

Figure 3: Evolution of short circuit current density J_{SC}, fill factor FF and open-circuit voltage V_{OC} of a test module as a function of outdoor exposure time. Values were normalized against initial measurement data obtained under protective atmosphere and AM1.5G illumination before outdoor exposure. Maximum outdoor irradiance during the observed period was 780 W/m².

3.2 Effect of interim loading

The use of MPP loading between I-V scans has been shown to reduce the apparent rate of performance degradation in Perovskite devices [3]. However, an unexpected result was obtained when a module at the FOSS test bench previously left at open-circuit between I-V scans was switched to an MPP load.

Figure 4 shows the change in normalised PCE of the test module over time. It can be seen that the performance of the module decreased to approximately 40% of the initial output after a month and a half of exposure at open circuit. After the module was transferred to the MPP loading strategy between I-V measurements on the 23/01/2020 there was an immediate improvement in the apparent performance of the device, with the output recovering to 60% of the initial efficiency. This improvement was maintained over the course of the MPP loading until it was finally disconnected on 31/1/2020. At this point the PCE dropped to a level consistent with the performance prior to the application of the MPP load.

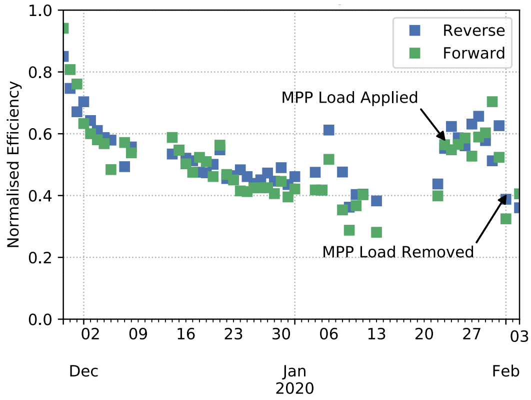

Figure 4: Change in PCE over time for one test mini-module in Cyprus.

While this result clearly shows the value of using MPP loading when attempting to obtain a representative value of instantaneous efficiency of a device, the use of MPP loading was not shown to prevent the progression of underlying performance decreases, as shown by the change in PCE over time of devices kept at MPP from the start of their outdoor testing (see Figure 2, Module C02). Instead, it appeared as though MPP loading improves I-V scan efficiencies by supressing a rapidly developing degradation mechanism that is also apparently relatively quickly reversible.

3.3 Recovery

In Cyprus, it was observed that it was common for the devices to exhibit slightly higher reverse I-V sweep power conversion efficiencies at the start of the day. This suggested that the devices were undergoing some form of 'dark recovery' overnight, that meant they would show improved performance early in the day.

To further investigate this phenomenon, a device in Cyprus was removed from the outdoor test bench after having reached 40% of the initial performance and stored in the dark in uncontrolled conditions. When it was restored to the outdoor test bench after several days, the performance of the device was recorded every few minutes after exposure at around midday. The results of this measurement can be seen in the graph in Figure 5.

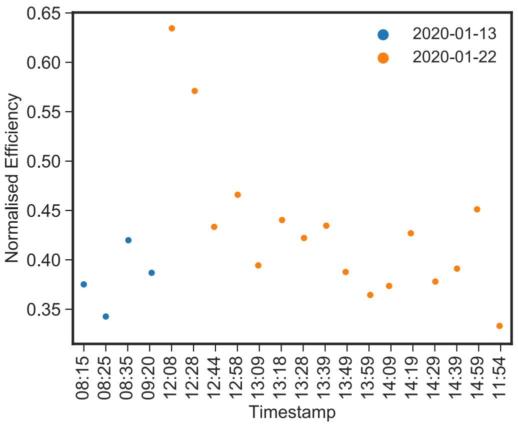

Figure 5: Change in efficiency of a test module over time. The exposed module was placed in storage on 13/1/2020. When returned to the outdoor test bench 9 days later, the device exhibited a strong initial performance recovery.

This result confirmed that the device was indeed recovering performance in the dark, and moreover that there was a rapid, apparently recoverable, degradation in the device performance over the two hours immediately following exposure.

Following several months of outdoor exposure, the reverse sweep efficiencies of module C01, C02 and C03 tested in Cyprus were shown to have dropped to 32%, 35%, and 50% of initial output respectively, and it seemed that the modules had permanently degraded. The modules were then removed and shipped to Germany for further analyses. When these devices were eventually tested, almost 2 months after removal from exposure, the indoor measured performance had recovered to 81%, 99%, and 89% respectively. These data are summarised in Table I, and the corresponding I-V curves are shown plotted in Figure 6 for each module.

Table I: Measurement data for modules measured under outdoor conditions and after recovery. Values are reported for final measurements under outdoor conditions and under simulated AM1.5G illumination after prolonged storage without illumination. The relative power conversion efficiency is calculated based on initial measurements under simulated AM1.5G illumination before outdoor exposure ($PCE_{C01,\ initial} = 4.25\%$; $PCE_{C02,\ initial} = 4.3\%$; $PCE_{C03,\ initial} = 4.3\%$).

Module	**C01**	**C02**	**C03**
Location	Outdoor / Indoor	Outdoor / Indoor	Outdoor / Indoor
Date	10.04.2020 / 15.06.2020	10.04.2020 / 15.06.2020	10.04.2020 / 15.06.2020
Illumination [W/m²]	1041 / 1000	1028 / 1000	1014 / 1000
η [%]	1.35 / 3.44	1.50 / 4.28	2.17 / 3.86
V_{OC} [V]	6.22 / 8.42	4.11 / 8.39	5.82 / 8.29
J_{SC} [mA/cm²]	0.83 / 1.24	1.27 / 1.43	1.35 / 1.43
Fill Factor [%]	26.9 / 32.9	29.7 / 35.7	27.7 / 32.5
$\eta_{relative}$	0.32 / 0.81	0.35 / 0.99	0.50 / 0.89

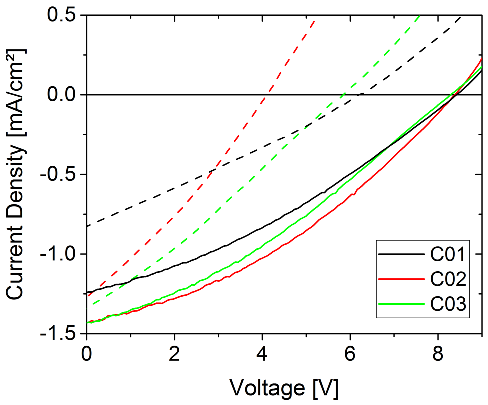

Figure 6: Comparison I-V scans (reverse sweep) for modules C01, C02 and C03 exposed outdoors in Cyprus, showing degraded performance curves (dashed lines), and performance after 2 months of dark recovery in solid lines.

This remarkable recovery – almost full recovery in one case – leads to the insight that the majority of observed decreases in performance for all the modules tested is likely to be the result of some reversible, transient process occurring within the cell, and not a consequence of a permanent degradation mechanism.

3.4 Effect of voltage sweep parameters

This finding of the previous section is also supported by with reference to the performance of modules G06 and G05 (see Figure 2). On day 35 the voltage sweep rate for these devices was slowed to 0.05 V/s, after which there is both an immediate and longer-term uptick in performance. This result provides a strong hint that the drop in measured performance is at least partially due to the choice of I-V sweep method and is recoverable with a change in sweep parameters.

To further investigate how the manner in which I-V curves are measured affects the results obtained, various parameters that control the voltage sweep were changed. Essentially, the sweep rate is controlled by varying the voltage step size and the dwell time at each step. In addition to that, the direction of the sweep is known to affect the I-V curve of Perovskite devices. Therefore, over a period of two months, two selected mini-modules were subjected to identical changes in I-V sweep parameters, the only difference between the two being that one was kept at MPP between sweeps, and the other at open-circuit.

The results of this experiment are shown in Figure 7. Looking at the centre of the plot, where there was a roughly 10-fold increase in the voltage sweep rate of the modules, interesting effects can be seen in the two cases. In the case of the device held at open circuit, the reverse sweep efficiencies remained almost constant, whereas there was a significant drop in the forward sweep efficiencies. Curiously, the reverse effect was seen in the device held at MPP, where in that case it was the forward sweep efficiencies that remained constant.

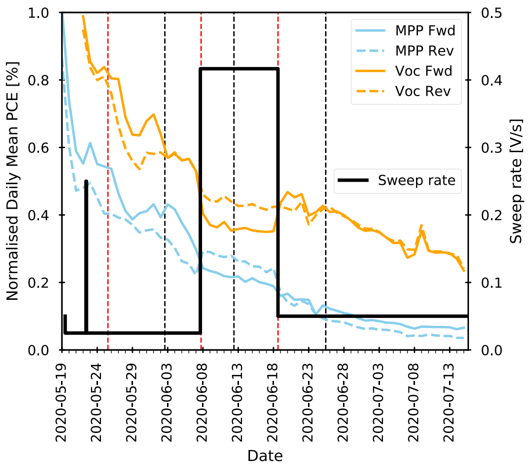

Figure 7: Forward and reverse I-V sweep efficiencies over time for two mini-modules under different loading regimes. The red vertical dashed lines indicate a switch to reverse voltage sweeps first, the black dashed lines denote a swich to forward-first voltage sweeps.

4 ANALYSIS & DISCUSSION

4.1 Theoretical Model

A detailed dissection and understanding of the physical processes taking place inside these modules is beyond the scope of this work. However, at a higher level the observed behaviour of the modules is broadly consistent with ion migration models that have already been proposed in the literature [6]. These propose that the expansion and contraction of the depletion region within a Perovskite cell with voltage bias results in the migration of ions within the absorber.

To summarise the implications of this model, under illumination and left at open circuit conditions, the depletion region of the cell will shrink, and mobile ions will diffuse into the bulk region of the cell. In the case of these particular modules, this appears to result in a reduction of open circuit voltage, fill factor, and short circuit current of the cell. Thus, the cell could be labelled as being in a ‘reduced’ state.

On the other hand, if the cell is kept at a bias voltage between 0 V and V_{MPP}, this diffusion is inhibited and ions remain in the preferred, or ‘normal’ position in the depletion region, leading to higher open-circuit voltages, short-circuit currents and fill factors.

Moreover, it can be speculated that there is a distribution of speeds at which these ions migrate, perhaps in relation to their particular species. The presence of slow-moving ions could account for the long-term changes in module performance, whilst the faster moving variants could account for the shorter-term changes seen over minutes or hours.

4.2 Relating I-V Trace Results to Real Performance

If we apply the model described in the section 4.1 to the results shown in Figure 7, we arrive at a reasonable fit for the observed behaviour. Taking the case of the device held at open circuit, we see that increasing the sweep rate only reduced the forward sweep efficiency. This is because the module is normally held in the 'reduced' state. Sweeping the module voltage quickly does not allow ions time to return to the depletion regions by the time the maximum power point voltage is reached. Therefore, the apparent efficiency is lower than when the voltage is swept slowly, providing the ions time to migrate. There is no change in the reverse sweep since the MPP voltage is approached from open-circuit, and the module will be in the 'reduced' state regardless of the speed at which the MPP is reached.

Conversely, looking at the case of the device held at MPP, we find the reverse effect. Here the ions are normally mostly in their preferred position inside the depletion region. Sweeping the voltage forwards from 0 V either slowly or quickly does not change their position, and therefore the forward sweep efficiency is unaffected. However, sweeping the voltage quickly prevents ions from migrating from their normal position during the reverse sweep. Thus, the measured efficiencies are increased in comparison to the slow reverse sweeps, where ions are given time to migrate into the absorber bulk.

Since the aim of these outdoor test campaigns is to measure the power output that can be expected under actual operating conditions, the protocol used must condition the module under test to deliver the same performance as if it were being constantly operated at maximum power point. The results discussed here show that it is therefore imperative to take into account the phenomenon of ion migration if this is to be achieved. For example, the use of an MPP load between I-V scans is an ideal way to bias the modules, but if subsequent I-V scans are taken too slowly, this can give a falsely low efficiency result if a reverse scan is used. Similarly, it may be possible to obtain a sufficiently representative I-V scan using an appropriately slow forwards scan, even if the device has been held at open circuit prior to the measurement.

4.3 Implications for Testing Protocols

The observations obtained through this measurement campaign to date have provided several hints at the most appropriate testing techniques for outdoor characterisation of Perovskite devices. Foremost, it is strongly recommended to hold the devices at, or near, MPP when on-sun in order to arrive at more representative current-voltage characterisations. The observed degradation under operating conditions is apparently at least partially reversible, as can be observed when MPP loading is applied to a device operated at open circuit and the performance of the device recovers over time. While it is suggested that the accelerated loss in performance under open-circuit arises due to a high concentration of radicals caused by unextracted photogenerated charge carriers [3], another possible origin of the observed phenomena is the interplay of mobile ions with trap-mediated and surface recombination, respectively [4,5].

Additionally, it is important to evaluate on a case-by-case basis the hysteresis caused by the voltage sweep parameters when performing current-voltage characterisations.

5 CONCLUSIONS

This campaign has provided several important lessons for the measurement of Perovskite modules outdoors. It has become apparent that the determination of degradation rates is complicated by the difficulty in detecting real, irreversible degradation, since the modules tested showed the ability to recover their performance levels almost completely after extended periods in the dark. Moreover, the measurement of power conversion efficiencies of the devices using I-V traces has been shown to be affected by the voltage sweep rate and direction, as well as the loading condition of the cells. We have shown that these choices change the apparent efficiency of the modules in a manner consistent with ion migration models.

6 ACKNOWLEDGEMENTS

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