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Light cycling as a key to understanding the outdoor behaviour of perovskite solar cells†

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Forecasting the real-world stability of perovskite solar cells (PSCs) using indoor accelerated tests is a significant challenge on the way to commercialising this highly anticipated PV technology. The lack of outdoor data and considerable magnitude of meta-stability effects (or reversible changes) in PSCs' performance over the day–night cycle makes it particularly challenging to correlate results of the commonly utilised light-soaking ageing test with outdoor experiments. Here we show the variety of short-term and long-term ageing behaviours by testing PSCs of various architectures under constant and intermitted light indoors and exposing them to natural conditions outdoors. We demonstrate that it is impossible to predict the results of a light cycling test from a continuous light test without prior knowledge of the ageing patterns for a particular device architecture. Cycling the light does not necessarily lead to an increased lifetime as expected due to dark time recovery. Instead, it sometimes reveals a different degradation behaviour resulting in a drastic lifetime reduction. The presence of various degradation patterns for different PSCs implies that an accelerated ageing with constant light experiment is no "worst-case scenario" and thus cannot replace the light cycling test nor can it reproduce the real-world scenarios. Furthermore, we show unique sets of weeks-to-years-long outdoor series on different PSCs highlighting the monumental importance of accounting for the meta-stability effects when analysing PSC outdoor data as opposed to simply following evaluation routines developed for silicon-based devices. In particular, meta-stability complicates the decoupling of the effects of environmental conditions from the cell's ageing behaviour and can result in large artefacts. A varying degree of saturation of reversible processes also results in unusual strong seasonality documented for PSCs, with summer representing favourable conditions for some PSCs' energy generation compared to winter, despite higher temperatures. For the first time, the decisive impact of meta-stable processes on the outdoor performance and stability of perovskite solar cells is demonstrated, with data from over two years in the field, which is the longest outdoor exposure of PSCs reported so far to the best of our knowledge. The correlation between the outdoor results and those from the light cycled experiments is evident.

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Broader context

Perovskite Solar Cells (PSCs) are the emerging type of photovoltaic devices that is expected to bring a breakthrough in this area. This rapidly developing technology attracts attention due to its record efficiencies, versatility in manufacturing and prospects of upscaling with competitive cost. Device stability, especially under real-world outdoor conditions, remains the main milestone to achieve before commercialization. Here, we discuss, to our knowledge, the longest dataset acquired for PSCs under outdoor operation (more than two years in Berlin) and the lessons learned from it. We found that even the impressively stable PSCs show pronounced effects of reversible (meta-stable) processes, leading to its efficiency variation over the day. Such processes not only affect the overall energy yield, but also may result in artefacts when using conventional data evaluation methods, bring pronounced (and unexpected!) seasonal variations in performance from summer to winter, and affect their long-term stability. The most popular accelerated aging tests in the laboratories study PSC stability under constant illumination stress. Such approach completely ignores meta-stability processes and, therefore, this test is missing the mark on real-world scenarios. We find indoor accelerated aging experiments with cycled light instrumental to understand and eventually foresee the PSCs real-world behavior.

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Introduction

Perovskite solar cells (PSCs) are a rapidly developing photovoltaic technology.[1] The next step on the path towards commercialisation is surmounting the challenge of stability under working conditions. Despite significant improvement of PSC stability towards light, heat, and humidity achieved over recent years,[2,3] this class of solar cells' stability in outdoor operation remains almost unexplored. Only a few studies have been published reporting on maximum power point (MPP)-tracked outdoor installed PSCs samples.[4–6] Yet, understanding real-world device operation and stability is an essential element in technology maturing and fosters trust among investors. That trust in the reliability of a device is especially important in photovoltaics, as the expected service time is in the range of 25–30 years. The investment is almost completely required initially, and commercial viability depends crucially on minimal and predictable technical degradation of the photovoltaic installation. We claim that outdoor data is also key to guiding the development of accelerated ageing tests in the lab, which would eventually allow predicting PSCs lifetime within a reasonable experimental timeframe.

Recently, the influence of transient behaviour in PSCs was found relevant in studying the long-term stability of perovskite solar cells[7,8] and modules.[9] The reason is the coexistence of several dynamics with characteristic times spanning from timescales of seconds to hours.[10] Such slow dynamics are relevant in the day–night cycling of devices in operational conditions as they occur on similar timescales. They need to be considered to estimate PSCs' energy yield over the lifespan of the specific application. Although a consensus on the particular tests to assess PSCs' stability in the research environment has been agreed upon,[11] there is no clear understanding of the strategy to predict the PSCs' outdoor lifetime from accelerated ageing under controlled conditions. Design qualification and type approval tests for conventional solar panels include series of tests featuring various stress factors.[12] There are no standards defined for perovskite devices yet, but they are likely to be based on the same concept with technology-specific extensions.

Among the other stress factors that affect device lifetime (such as humidity, temperature and its cycling, electric bias), light remains one of the main drivers for PSCs degradation. It is very unlikely that a single accelerated aging test will be capable of predicting the outdoor lifetime of PSCs. However, when such a prediction has been discussed, the applied strategy included MPP tracking under constant light and elevated temperature.[13] The vast majority of published stability data today was recorded under static ageing conditions (see Note S2 and Fig. S2, ESI†). However, in the scarce studies trying to correlate such experiments with actual outdoor behaviour, available data suggest that natural cycling of the light and temperature may significantly alter the results.[8,10,14,15] The diversity of the diurnal behaviours of perovskite cells, depending on the type and magnitude of slow transient processes affecting cell performance over the day–night cycle, poses an additional challenge. Finally, we also want to highlight that much caution should be taken when trying to extend conclusions about the applicability of certain stress tests to the whole class of halide perovskite solar cells.

Approaching outdoor stability is still a new challenge for the PSC community. When performing outdoor experiments, typically, the evolution of a performance metric (efficiency, for example) is measured under natural conditions. However, those conditions vary from day to day, between seasons or in different locations. For example, an observed decrease in efficiency (measured outdoors) can reflect device degradation or the reaction of the cell to a changing environment. Notes S3 and S4 (ESI†) pose a detailed discussion of the influence of solar irradiance and spectrum and cell temperature on the PSCs' outdoor performance. The above-mentioned transient processes over the day–night cycle further complicate the picture. In particular, they make the extraction of cell parameters (*e.g.* temperature coefficients) from outdoor data unreliable (see Note S4, ESI†) and put the evaluation methods that were working well for silicon PV under question for PSCs. Additionally, it is important to mention that the transient processes themselves change with the device ageing.[16] Decoupling "pure" outdoor stability data from seasonal weather variations remains largely unexplored by the community and will likely require adapted figures of merit (see Note S5, ESI†) and the comparison of measured PCE with that predicted/simulated for the particular combination of weather parameters.[17]

In this contribution, we analyse in-house data on PSCs' outdoor and indoor ageing behaviour and outline challenges in predicting operational lifetime through accelerated ageing. All the aging tests were performed under MPP tracking with sizable statistics, which are both critical requirements stated by the community.[11] We use four types of PSCs with p–i–n structure to highlight the spectacular variety of possible ageing behaviours, including those not reported previously. The devices have significant differences in architecture (see Note S1, ESI†) and were not selected to study the structure-stability relationship or the details of particular degradation mechanisms. These 4 types of devices were selected due to the large differences in their ageing behaviours in terms of stability, meta-stability and the difference between the results of constant and cycled light illumination. This gave us a rich base for the interpretation of the features observed during their outdoor ageing. For simplicity, we distinguish them in the following text by the number of A-site cations in the perovskite layer ($FAPbI_3$, $FACsPb(I/Br)_3$ or $MAFACsPb(I/Br)_3$ – "1cat", "2cat" and "3cat" accordingly) and the hole transporting layer (see Table S1, ESI†). Note that different self-assembled monolayers (SAMs) were used in different device types as indicated in Note S1 (ESI†). First, we will show the relationship between the cycled and constant light behaviours depending on the cell architecture. We will then share our experience with outdoor data on the same types of devices highlighting the connection to indoor stability. Although light cycling tests do not include all the stressors relevant for outdoor deployment (for example, simultaneous cycling of temperature) we find the light cycling tests at constant temperature striking the balance between simplicity

of execution in lab conditions and missing the mark on the phenomena observed outdoor (which sometimes is the case with constant light experiments).

Constant and cycled light indoor experiments

Among many tests used to characterize the stability of emerging solar cells in the lab, the constant illumination test under MPP tracking in inert atmosphere at 25 °C (ISOS-L-1I) or elevated temperature (ISOS-L-2I) are the most used proxy for operational device stability.[18] It was already argued in literature that this test is less representative for a device's outdoor behaviour than the cycled light testing (ISOS-LC), where the PSC periodically rests in the dark allowing for the meta-stability processes to reset.[8,14,19,20] However, very little research is performed under light cycling conditions (see Fig. S2, ESI† based on the Perovskite Database Project[21]) and no systematic comparison to long-term outdoor measurements was provided previously. Fig. 1 shows the results of both indoor constant light soaking and indoor cycled light tests (12 h dark/12 h light) for four different types of PSCs, chosen to demonstrate the wide range of possible PSC ageing behaviours.

In the constant light test, the four types of devices under study show 4 different ageing curve types (see also Fig. S13 and S14, ESI†). At the onset of the ageing curve a sharp increase (1cat_SAM), a sharp decrease/"burn-in" (2cat_SAM, 3cat_SAM) or a fairly constant behaviour (3cat_NiO) were observed. After the initial transient, different long-term trends are observed: an increasing trend (2cat_SAM), a moderately decreasing (3cat_NiO) or a fast-decreasing trend (1cat_SAM, 3cat_SAM). We note that the large variety of curve shapes complicates defining one metric for stability (such as T_{80} or T_{S80}[22]) without favouring some architectures other the others. In particular, 2cat_SAM devices, which show the improvement over many hundreds of hours, set a challenge to even see the degradation within a reasonable experimental timeframe. Meanwhile significant changes in the device PCE over time prevent one from claiming them being "stable".

The traces of the PCE as function of time in Fig. 1 are averaged over multiple cells prepared in different batches. In the case of 2cat_SAM devices, we observed large batch-to-batch variation with two distinctly different ageing patterns (see Fig. S15, ESI†), only one of which is shown in the main text for clarity. After studying data collected from thousands of cells, we learned that a thorough analysis of the cell-to-cell and batch-to-batch variation is fundamental to obtain conclusive results about stability. See a detailed discussion on the statistics of this work in Note S6 (ESI†).

As shown in Fig. 1, the results of light cycling (LC) ageing do not necessarily match the results from constant light (neither short-term nor long-term). First, one can see repeatable patterns of PCE changes within each 24 h-long cycle. Every time the light is turned off and then switched on, the cell undergoes some reversible changes with a magnitude reaching several

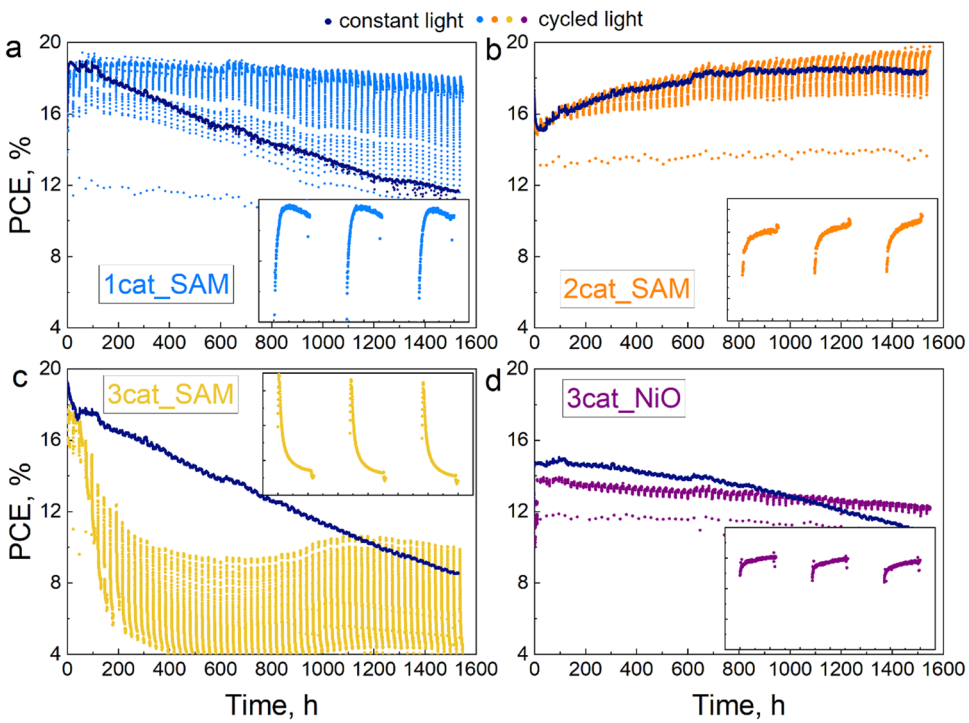

Fig. 1 Indoor photo-stability under MPP tracking of four types of PSCs upon exposure to constant (dark blue symbols) and cycled light (ISOS-LC-1I). The insets are zooming in to 3 consecutive cycles after 240 h. Every curve represents an average over 4 to 12 devices, error bars are omitted for clarity. Individual tracks and zoomed in figure for cycle shapes with scales are shown in Note S6 (Fig. S12 and S13, ESI†).

absolute percent in PCE. We would like to highlight that the four types of chosen devices show a range of different short-term (during one cycle) and long-term behaviours. The insets of Fig. 1 and Fig. S14 (ESI†) resolve 3 subsequent cycles in each case, recorded after 240 h of the experiment which is after initial changes are saturated. It varies from an increasing trend in PCE over the cycle (2cat_SAM) to a strongly decreasing one (3cat_SAM), a combination of both (1cat_SAM) or relatively stable PCE values with only ~0.2% absolute change during the cycle (3cat_NiO). Although reversible, these changes during one cycle do translate into losses of energy generation over a day in the outdoor environment. Note that the magnitude of intra-cycle PCE changes amount to up to stunning 7% absolute in some cases (3cat_SAM) while being almost fully reversed during the dark phase. Additionally, the shape of the PCE curve within a cycle is slowly changing with ageing time. Even if the peak performance per cycle remains relatively unaffected, the evolution of the cycle shape signifies device degradation and should be accounted for and reported. For example, in the case of 2cat_SAM devices that did not show any decrease in PCE during 1500 h of exposure, we clearly see an increased magnitude of meta-stability with ageing (see Note S7 and Fig. S17, ESI†). Interestingly, we did not observe a correlation between an increased magnitude of meta-stability and the extent of hysteresis in our devices, which was marginal to begin with. Strong reversible changes complicate the energy yield forecasts, as the energy yield models typically do not take meta-stability (or reversible changes) into account.

There are multiple phenomena that were shown to result in short-term reversible changes of PSCs' efficiency (both increase and decrease have been reported). This may include beneficial[23] or detrimental[19] ionic re-distribution within the perovskite layer, perovskite lattice expansion/strain relaxation,[24] defect formation[25] and healing,[26] and trapping of photo-excited electrons in HTM materials resulting in favourable band bending.[27] The diversity of possible mechanisms in PSCs rationalises the observed variety in cycle shapes and their evolution upon cell ageing.

We propose that reporting at least the extent of reversibility of the degradation (if not the fully cycled experiments) should become a standard approach in PSCs stability research. Even more importantly, there is no unambiguous correspondence between the long-term changes in the constant light and the cycled light ageing curves (see Note S8 (ESI†) for a comparison of performance ratios (PRs)). For example, by comparing 1cat_SAM and 3cat_SAM (blue and yellow in Fig. 1c) devices, we can conclude that cells with similar long-term trends in the constant light experiment can still have a tremendously different lifetime once the light is cycled. In some cases, however (2cat_SAM; 3cat_NiO), the results of cycled and not-cycled light exposures are qualitatively similar in terms of the long-term trends. Yet, for 1cat_SAM devices, the dark phase reverses the PCE loss during the light cycle which results in a dramatic increase in lifetime. Similar behaviour was previously observed for several different types of PSCs in literature.[20,28] In contrast to this, in some PSCs the situation is opposite (3cat_SAM) with light cycling revealing (not necessarily *creating*) detrimental PCE loss not visible under constant illumination. It is often argued that constant light is a harsher test and the results under outdoor conditions with the day–night cycling could only result in longer lifetimes. The results in Fig. 1c (3cat_SAM) show that this is not necessarily true for all the PSCs and must be checked for each specific device architecture.

Outdoor stability

Outdoor data is still relatively scarce for PSCs, and only few works demonstrate MPP tracking data in contrast to experiments in which periodic JV scanning or periodic indoor measurements are performed with the devices held disconnected between the measurements.[4] Ageing at open circuit condition is, however, known to significantly affect PSCs lifetime measured indoors[29] or outdoors.[30] In this section, we will show outdoor data recorded on a rooftop test field in Berlin, Germany (see Fig. S4, ESI†) under MPP tracking for the same 4 types of devices discussed in the previous section. As a figure of merit for device outdoor stability we use here performance ratio (PR), which is the ratio between the produced and expected power over one day or cycle (see Note S5, ESI† for details). Since there is no established practice for evaluation of the outdoor data in PSCs, in Fig. S12 (ESI†) we show two other possible metrics for comparison: the power at specific irradiance (here 500 W m^{-2}) and average midday PCE as metrics for stability. Chosen metrics show a slight discrepancy in the magnitude of the observed changes, however, all the figures of merit show qualitatively similar results in our experiments. It is important to acknowledge that each of these metrics not only represents the change in the status of the device (*i.e.*, the stability itself) but also reflects the dependence of PSC power output on the changing environmental factors. This includes deviations from linear behaviour with light intensity, effects of temperature and solar spectrum, as well as the metastable changes within the day–night or annual cycle that were discussed in the previous section. Disentangling these effects is mandatory for advancing perovskite-based PV for outdoor applications and to enable reliable prediction of the device energy yield.

Fig. S6 (ESI†) shows an example of PSC power output during one day of outdoor exposure, giving an idea of how the external parameters contribute to it. In the first approximation cell power output follows the irradiance (see Fig. 2c and d). In the Notes S3 and S4 (ESI†) the effects of sun spectrum and cell temperature on outdoor power output are discussed in detail. In a nutshell, they contribute to the seasonal changes of cell PR and therefore contribute to the curves discussed below, but the magnitude of the effect is not enough to completely explain the PR trend. Once again, we want to draw attention to the transient behaviour illustrated in Fig. 1 and Fig. S14 (ESI†) which affects parameter extraction (especially temperature coefficients) from the outdoor data resulting in possible large artefacts/miscorrelations (see Fig. S9 and S10 and Note S4, ESI†).

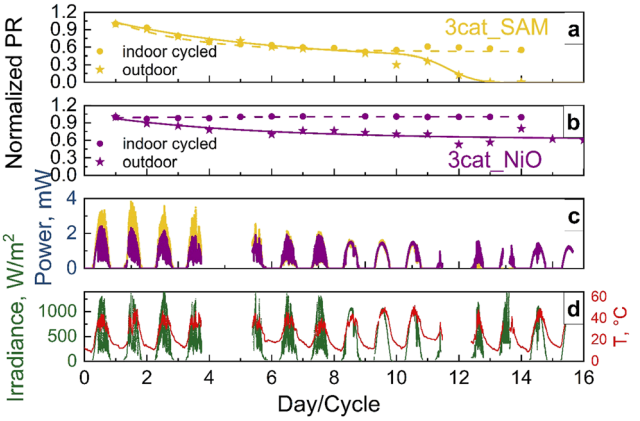

Fig. 2 Outdoor stability of PSCs with triple cation perovskite and different transport layers encapsulated with a glue-based procedure. Normalized performance ratio of 3cat_SAM (a) and 3cat_NiO cells (b) from the outdoor and cycled indoor experiments; lines are fits to guide the eye. Power output of the representative cells outdoor (c) and the corresponding irradiance and temperature conditions (d). See Fig. S16 (ESI†) for statistics.

Fig. 2 compares the outdoor stability of triple cation perovskite-based solar cells with different transport layers (3cat_SAM and 3cat_NiO devices), encapsulated with a simple glass-glue-glass procedure (see the schematics in Fig. S1, ESI†).[5] We performed two runs of this experiment (3–6 cells of each type per run) during a high irradiance summer period (see Fig. S16, ESI†). For 3cat_SAM cells, outdoor behaviour shows a rapid drop in performance very similar to that observed in the LC experiment (Fig. 2a). In this case LC and outdoor data are not only in qualitative but also in quantitative agreement. However, the outdoor results do not match the constant light experiment, where the observed degradation rate is much slower. Thus, cycling the light is essential to correlate indoor and outdoor degradation of these cells. In accordance with the indoor results, cells with NiO (3cat_NiO) are more stable outdoor compared to those with SAM transport layer. However, we observed notable degradation for these cells contradicting the indoor results. This may be due to additional stress factors that are present under outdoor conditions and not present during the indoor ageing, for example higher temperatures and temperature changes in the diurnal cycle. Most noticeable of these factors is possible water vapor/oxygen penetration through the encapsulation materials. Moisture-induced degradation results in a rapid decrease in PCE and change in the device colour due to perovskite decomposition, we discuss this in more details in Note S9 (ESI†). We note on this example, that it is unlikely that any single ageing test would be indicative for all possible degradation modes in a PSC, and therefore would not be a satisfying predictor of their realistic outdoor lifetime. However, with a good encapsulation, light remains the most important stress factor to the device degradation. Other stress tests to probe, *e.g.*, encapsulation quality or mechanical robustness would require different tests, similar to existing IEC standards.[12]

To limit the impact of humidity and oxygen, we employed an encapsulation technique based on a vacuum lamination procedure described in literature.[31,32] We followed the so called "three glass" encapsulation approach in which the substrate glass with the PSCs and contact ribbons is sealed between two larger glasses and the butyl frame to prevent ingress from the sides (see Fig. S1, ESI†). In previous research, we showed that this type of encapsulation is suitable to pass the IEC damp heat test (85 °C, 85% RH, >1000 h) and, more importantly, that passing such test results in the outdoor lifetime exceeding 1 year in Berlin, Germany.[5] In literature as well, a similar lamination approach was shown to improve photostability of some PSCs even under inert conditions.[32] Therefore, we tested whether the effect is present in PSCs studied in this work (Note S10, ESI†). In our case, the presence of encapsulation does not affect the ageing trends in indoor experiments (Fig. S21, ESI†), which justifies the comparison of unencapsulated cells in N_2 atmosphere indoor and encapsulated cells under ambient conditions outdoor.

The results of a full year of outdoor exposure in Berlin for 1cat_SAM, 2cat_SAM, and 3cat_NiO cells laminated with this procedure are shown in Fig. 3. A small-area reference silicon heterojunction solar cell (encapsulated similar to studied PSCs) was tracked with the same MPP tracking equipment outdoors for comparison. As can be seen, 1cat_SAM (Fig. 3a) devices maintain a fairly constant performance for the first 9 months of exposure (October to June), which is in clear contradiction to the results of the constant illumination test showing steady decline from the start (Fig. 1b). As revealed by the cycled light test on these type of cells, night-time recovery helps keeping these cells stable until summertime when they start losing efficiency relatively quickly. One can speculate that higher temperature in summer results in an increase in the daily degradation so that the recovery over one night is insufficient to fully restore the device performance, leading to more damage than can be recovered and an "accumulation" of the degradation during this season.[10] Note that both indoor constant and cycled light tests are performed at constant temperature of 25 °C. We will show later that even the pronounced decline in performance observed towards the end of the first year of exposure for these cells can be reversed towards the next summer.

In June, a second batch of nominally identical 1cat_SAM devices was placed on the test field in addition to the devices that were already tracked for ~ 9 months. This second batch is shown in red in Fig. 3a. It shows a remarkably similar degradation rate to that of the older batch. In this case the previous exposure history to the relatively low stress fall–winter–spring seasons did not affect the devices. If we applied the lifetime estimation based on standard T_{80} approach to this case (*i.e.* the lifetime is defined by the time it takes for the solar cell to lose 20% of its initial efficiency, see the two bold lines in Fig. 3 to guide the eye), the two batches would show a dramatic difference in the lifetime while actually being the same devices with the same stability. This example clearly demonstrates that T_{80} might be a questionable proxy to compare the outdoor stability of different PSCs. It also shows that the frequently applied practice of presenting outdoor results with a relative time count starting from "0 hours" might hide the information on which

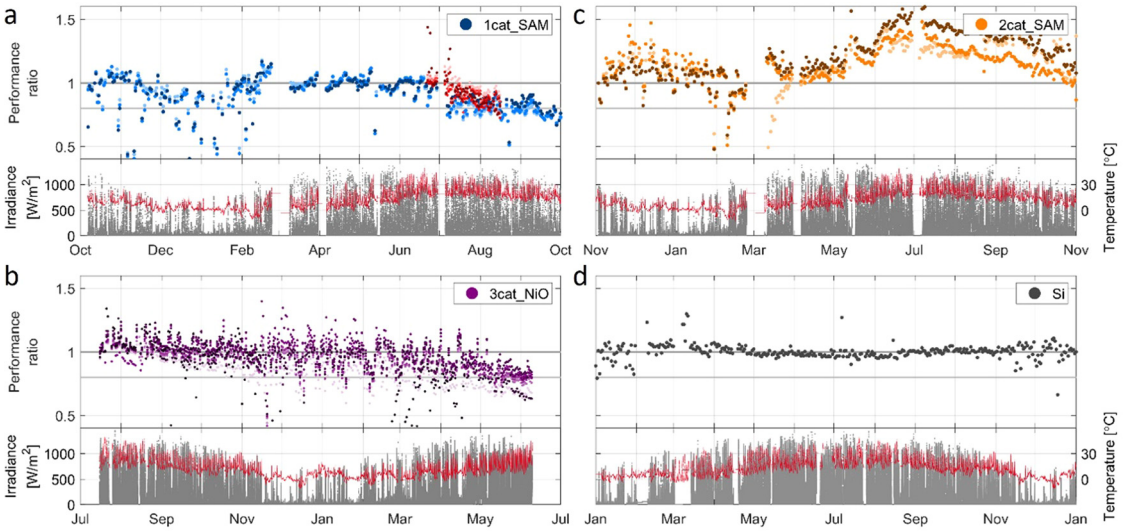

Fig. 3 Long-term outdoor stability: Normalized performance ratio of 1cat_SAM (a), 2cat_SAM (b) and 3cat_NiO (c) PSCs as well as silicon reference cell (d) covering the period of approximately one year in each case. All devices were encapsulated by vacuum lamination. Red symbols in (a) show the tracks from a second similar batch with a different exposure starting date. Horizontal grey lines show 100% and 80% of the initial level. Part of the data is adapted and extended from ref. 5,33. The bottom panels on each graph show the irradiance (gray) and cells' temperature (red) conditions during the corresponding outdoor experiments.

season the starting date was and obscures fair comparability of the outcome. Similarly, the question of fair comparability will unavoidably arise when exposing cells at different locations. Therefore, accumulating outdoor data from multiple climates is a mandatory step in PSC technology maturing that cannot be skipped. Such experiments may shine the light on the connection between PSC stability and environmental factors (such as average temperatures and humidity levels). If nothing else, outdoor experiments with the same PSCs distributed across multiple locations will provide a basis for adequate levels of stresses in the accelerated indoor tests required to emulate realistic ageing scenarios.

Comparing the long-term data for 1cat_SAM, 2cat_SAM and 3cat_NiO PSCs from Fig. 3 with the results of LC experiments (Fig. 1a, b and d) is less straight forward than in the case of the shorter-living 3cat_SAM cells shown in Fig. 2. Similar to the indoor tests, 3cat_NiO cells show a steady trend for slow decrease in PR. The best stability among studied cells, as it was predicted from the LC test, is indeed observed with 2cat_SAM cells in the outdoor conditions. For these cells, PR values in November 2020 and November 2021 are approximately the same, confirming the cells demonstrate high stability (at least, in the sense of no PR decrease compared to the same month a year ago). Note that the annual dose of irradiation in Berlin over first year of these cells exposure was only ~1100 Sun × hours, with summer months accounting for ~40% of it, comparable to that in the indoor tests shown in Fig. 1 (see Fig. S5, ESI†). Even for 2cat_SAM cells with an impressive stability, the magnitude of changes over the year is very high as compared to the silicon cell (Fig. 3d). The observed PR increase in 2cat_SAM cells in summer followed by the decrease in fall may originate from both: (1) the steady improvement in device PCE (as in the indoor tests) followed by a decrease reflecting the device degradation, or (2) the change in weather conditions themselves thus reflecting seasonal fluctuations (see the Note S3, ESI†). Likely both factors contribute, and it is challenging to accurately decouple one from the other without extensive simulations of outdoor behaviour and analysis of their meta-stability.

The extent of seasonal changes can be seen on the outdoor series going beyond a single year. Fig. 4 shows the evolution of the PR over ~2.5 years outdoors for 2cat_SAM and 1cat_SAM cells on the test field. To the best of our knowledge, this is the longest outdoor series of perovskite solar cells reported so far. 1cat_SAM cells show a steady decrease in performance from *e.g.* summer-to-summer or winter-to-winter performance. For 2cat_SAM, outdoor metrics do not show a similar decrease from season to season. However, the device cannot be considered unchanged during the exposure period (see Note S11, ESI†). Still, impressive outdoor stability and relatively mild weather conditions in Berlin allow us to demonstrate that the summer improvement has periodic nature, thus (at least, to a large extent) representing unusual seasonal changes in PSC. Seasonality is typical for any photovoltaic device; however, summer is expected to have lower PR due to the dominating effect of higher temperatures and negative temperature coefficients in a classic solar cell.[34] These expectations are well matched by the behaviour of the silicon reference cell placed next to the studied PSCs (see Fig. 3d): It demonstrates very moderate seasonal changes with a PR decrease in summer mostly due to higher temperatures, but also with a contribution of seasonal changes in the solar spectrum. In contrast to silicon and other low bandgap PV, a blue shift in the solar spectrum present in summer in Berlin is favourable for PSCs. Seasonal change in

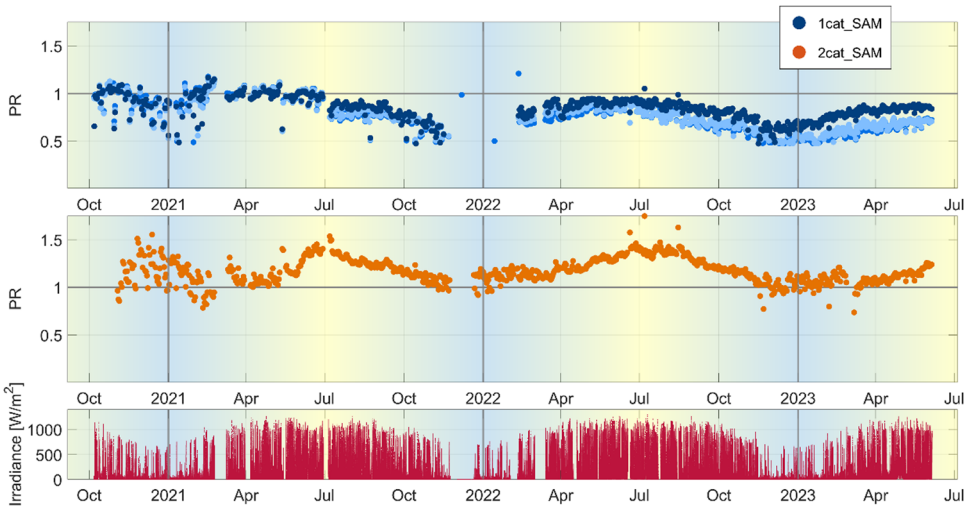

Fig. 4 Long-term outdoor data for ~2.5 years of continuous operation of laminated PSCs under MPP tracking in Berlin. The changes in the normalized performance show a periodic pattern with higher PR during the summer period. The bottom panel shows the irradiance during the corresponding outdoor experiments.

the solar spectrum, therefore, contributes to the PR increase in summer shown in Fig. 3 (see Note S3, ESI†). However, the impact of this effect can account for only up to ~10% of the increase which is only a fraction of the overall observed changes (see Fig. S8, ESI†).

As shown in Fig. S14 (ESI†), the day–night cycle for both 1cat_SAM and 2cat_SAM cells results in a light-soaking improvement when the light is on, which is reversed in the dark. In the real-world situation such an improvement will occur every day but with a varying rate depending on weather conditions, making the meta-stability an additional factor affecting measured performance ratio. On a sunny summer day with high irradiance in the morning, the light-soaking effect can be saturated much quicker, thus the device performs with higher efficiency during a longer time period. During a cloudy day, the cell might not be fully light-soaked throughout the whole day. Winters in Berlin (see Fig. S5, ESI†) are mostly characterized by low irradiances and have a much shorter light day compared to summer. This will result in a PR higher in summer relative to winter if the device requires light soaking to be efficient. It should also be noted that the light-soaking effect becomes more pronounced on the aged cells (see Fig. 1 and Fig. S17, ESI†) (fatigue effect) and when the dark part of the cycle is extended. Since light-soaking is mostly affecting device voltage, we illustrate this logic by showing V_{MPP} changes during a year in: (i) highly meta-stable 1cat_SAM devices, (ii) marginally meta-stable 3cat_NiO devices and (iii) the reference silicon cell (see Note S12, ESI†). The latter only shows slight voltage decrease in summer due to higher temperatures. On the contrary, PSCs show lower voltage values in winter, likely due to an unsaturated light soaking, with a dramatically higher magnitude of the reversible seasonal changes observed for cells with a high magnitude of meta-stability in the LC indoor experiments. The devices' meta-stability, therefore, is a key contributing factor to the unusual seasonal fluctuations shown in Fig. 4.

To summarize, we have highlighted that meta-stable (or reversible within the day–night cycle) processes have numerous consequences for PSCs outdoor data. They affect the overall energy yield, have consequences for the long-term stability, result in artefacts in parameter extraction from outdoor data and contribute to the seasonal variations observed. This may not necessarily be the case for all PSCs but taking into account the large variety of the observed meta-stable behaviours, we strongly advocate not to neglect transient processes and instead to treat them as one of the parameters of newly developed PSC architectures. The most direct way to account for them is to cycle the light in the typical indoor stability experiments, which in our experience has much better correlation with real-world stability.

Conclusions and outlook

Being able to predict the outdoor lifetime is crucial to speeding up the commercialisation of PSCs. Accelerated indoor tests, as standard (and standardized) as for other solar cell technologies, are obviously needed. Yet, those standards are not directly applicable to PSCs due to their transient behaviour that is not accounted for in common constant illumination testing. Here, we have shown a remarkable difference in PSCs ageing behaviours, depending on the device architecture. This not only manifests itself in different shapes of the ageing tracks, but also in differences in cells' transient behaviour and ability to recover. It does not seem possible to predict the results of the light cycled tests from the standard constant light experiment, in which the transient behaviour is triggered only once. PSCs could be more stable or less stable under cycled light in comparison to the constant illumination test. Importantly, the results of light cycling are found to show much better agreement to the outdoor observations, at least qualitative

(and even quantitative in some cases). Constant light tests will remain useful for studying possible mechanisms of degradation but have to be augmented with cycled light tests to gain predictive power towards real-world lifetimes.

Developing devices with minimal transient behaviour is an important milestone for current PSCs research. Such devices would enable researchers to use existing lifetime tests. However, the pace of development may slow down commercialization. Finding indoor accelerated ageing protocols that emulate outdoor degradation patterns without overcomplicating the tests is necessary to come up with adequately accurate lifetime and energy yield estimates. This goes hand in hand with attempting to unravel the degradation mechanisms present under the real-world combination of stresses. We believe that measurements of the long-term MPP tracked outdoor stability in addition to indoor accelerated aging should become a more common practice in PSCs field to bridge the gap between them.

Data availability

The key raw data for indoor and outdoor tests (including weather conditions) shown in the paper and its ESI† are available from authors upon request.

Conflicts of interest

There are no conflicts of interest to declare.

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