Novel test scenarios needed to validate outdoor stability of perovskite solar cells

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Abstract
Perovskite solar cells (PSCs) will eventually operate outdoors, subjected to diurnal cycles with varying irradiance and cell temperature throughout 24 h periods. Hereby, we show the PSC stability results from laboratory accelerated stress tests can not obviously suggest their stability in outdoor-like situations. Thus, to validate PSC outdoor stability, it is necessary to emulate outdoor conditions, for which we propose possible test scenarios.

Halide perovskites, due to their high absorption coefficient [1] and high tolerance on sub-bandgap defects [1, 2], have become one of the most attractive photovoltaic (PV) materials. After 10 years of development, thin film solar cells based on polycrystalline halide perovskites have evolved into one of the most efficient PV technologies, with record lab scale cell efficiency exceeding 25% [3], and mini-modules exceeding 17% [4]. Apart from its high efficiency, the low-cost material and fabrication approaches further facilitate its commercialization. Despite all these merits, the performance stability remains a question. Halide perovskites are sensitive to many factors such as moisture, illumination, temperature etc. The extrinsic factors like moisture could be sheltered by effective encapsulation [5], yet, a well encapsulated cell still faces the impact from intrinsic stress factors: light and temperature. Often researchers assess PV device stability by an accelerated stress test (AST), for instance, by tracking cell efficiency under continuous illumination at elevated temperatures for hundreds or thousands of hours. However, a terrestrial solar cell naturally undergoes diurnal cycles, with varying sun irradiance and environmental temperature through the 24 h period. Keeping in mind that eventually perovskite solar cells (PSCs) will operate outdoors, hence on top of AST, it is necessary to understand the stability of PSCs under diurnal cycles, especially after various PSCs have shown reversible performance changes under light-darkness cycling (table 1).

Hereby, we propose a series of tests as shown in figure 1, which are designed to complement stability results from AST with outdoor stability-emulation scenarios by adding changes in stresses step by step. In these scenarios, we mimic winter-like conditions assuming that the daytime is 6 h and night is 18 h. Figure 1(a) illustrates conventional AST in a lab, which is observing efficiency change under constant irradiance and elevated cell temperature. As the first step to simulate the diurnal cycle, the irradiance and cell temperature are kept the same and 18 h ‘nights’ are introduced, as shown in figure 1(b). Then on top of (b), scenario (c) further introduces variation in cell temperature, mimicking the temperature change of a terrestrial solar cell. Eventually as depicted in figure 1(d), irradiance variation is introduced, resulting in a winter-like stress profile, where the irradiance constantly varies during the day and cell temperature accordingly changes [16].

Our preliminary results indicate that different perovskites behave differently. For each scenario, at least two PSCs were tested. To present the results clearly, only one set of representative data is shown in each graph. As shown in figure 2, PSC with FAMA double cation perovskite continuously degrades in scenario (a). However, in scenario (b) when ‘nights’ are present, although degradation is observed during some days, the performance recovers after ‘nights’. Thus, although being stressed with the same irradiance and temperature for the same
amount of time, FAMA PSCs become more stable in scenario (b) than in (a). For such PSCs, it will be inappropriate to claim its instability solely from the AST results. Thus, diurnal tests are strongly recommended for such PSCs.

The unstable behavior of FAMA perovskites under illumination could result from the volatile \cite{17,18} and mobile \cite{11} nature of the MA cation. After replacing MA with Cs, the resultant FACs perovskites are stable in both scenarios (a) and (b) as shown in figure 3. However, when introducing temperature variation during ‘days’ as shown in (c), the cells start degrading after 5 days. Such degradation has been reported and attributed to temperature variation which promoted ion accumulation at the interface between perovskite and selective contacts \cite{19}. This implies stable PSCs in AST are not necessarily stable in outdoor settings with varying meteorological parameters.

In the end, aforementioned observations lead us to conclude that it is not obvious to relate the PSC stability in AST with actual, real-life outdoor stability. Real outdoor stressing of PSC requires specific emulation of those conditions for which we propose possible scenarios here.

\textbf{Table 1.} PSCs that show reversible performance change under light-darkness cycling. Only the elements in perovskite are presented for easier reading.

| Device structure | References |
|------------------|------------|
| ITO/PEDOT:PSS/MAPbI or FAPbI or MAFAPbI/PCBM/Ca/Al | [6] |
| ITO/PEDOT:PSS/MAPbI/PCBM/Al | [7] |
| FTO/TiO2/MAPbI/spiro-OMeTAD/Au | [8] |
| FTO/TiO2/MAPbI/spiro-OMeTAD/Au | [9] |
| ITO/TiO2/MAPbI/spiro-OMeTAD/Au | [10] |
| FTO/TiO2/MAFAPbIBr/spiro-OMeTAD/Au | [11] |
| FTO/TiO2/MAFAPbIBr/spiro-OMeTAD/Au | [12] |
| ITO/SnO2/MAFAPbIBr/spiro-OMeTAD/Au | [13] |
| FTO/SnO2 or TiO2/MAFAPbIBr/spiro-OMeTAD/Au | [14] |
| ITO/SnO2/MAFAPbIBr/spiro-OMeTAD/Au | [10] |
| FTO/TiO2/CsRbMAFAPbIBr/PTAA/Au | [15] |

*MA and FA represent methylammonium and formamidinium cations, respectively.*

Figure 1. Stress profiles aiming for understanding outdoor stability of PSCs.
Figure 2. ‘Eight-day’ tests performed with unencapsulated PSCs according to stress profiles shown in figure 1 (a) and (b). The device structure is ITO/SnO₂/PCBM/FAMAPbIBr/Spiro-OMeTAD/Au. Through the tests, cells are kept inside a glovebox filled with N₂. For both cases, irradiance is ∼1 sun and cells are kept at 60 °C during illumination. During ‘nights’, cells are kept at 25 °C.
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