



Cite this: *Energy Environ. Sci.*, 2018, 11, 739

## Reconsidering figures of merit for performance and stability of perovskite photovoltaics†

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The development of hybrid organic–inorganic halide perovskite solar cells (PSCs) that combine high performance and operational stability is vital for implementing this technology. Recently, reversible improvement and degradation of PSC efficiency have been reported under illumination–darkness cycling. Quantifying the performance and stability of cells exhibiting significant diurnal performance variations is challenging. We report the outdoor stability measurements of two types of devices showing either reversible photo-degradation or reversible efficiency improvement under sunlight. Instead of the initial (or stabilized) efficiency and  $T_{80}$  as the figures of merit for the performance and stability of such devices, we propose using the value of the energy output generated during the first day of exposure and the time needed to reach its 20% drop, respectively. The latter accounts for both the long-term irreversible degradation and the reversible diurnal efficiency variation and does not depend on the type of process prevailing in a given perovskite cell.

Received 14th October 2017,  
Accepted 5th February 2018

DOI: 10.1039/c7ee02956j

rsc.li/ees

### Broader context

The quality of solar cells is commonly quantified by their power conversion efficiency (PCE) and by their lifetime, defined as the time when the PCE drops to 80% of its initial value. Metal-halide perovskites are semiconductors exhibiting physical properties highly beneficial for the photovoltaic conversion of solar energy. Perovskite solar cells (PSCs) have already reached PCEs above 22%. Particular interest is in the realization of tandem PSC/silicon cells. Tandem devices with PCEs over 30% could be realized with a low additional cost to current silicon technology. However, the poor operational stability of PSCs has been the main limiting factor. Moreover, unlike conventional photovoltaic devices, PSCs often exhibit reversible degradation processes, leading to significant PCE variation during a day–night cycle. This makes quantifying the performance and stability challenging: if the PCE drops during the day but recovers during the night (or *vice versa*), what is the cell's lifetime? How can the performances of different device architectures, with various diurnal dynamics, be compared? We propose using the energy output generated during the first day of operation and the time needed to reach its 20% drop as the figures of merit for the performance and stability of such devices, respectively.

The commercialization of hybrid organic–inorganic halide perovskite solar cells (PSCs) requires the development of devices combining high Power Conversion Efficiency (PCE) and extended

operational stability. The latter has been the Achilles heel of PSCs. Moreover, testing protocols for assessing the PCE<sup>1,2</sup> and operational lifetime<sup>3,4</sup> of PSCs need to be developed.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ee02956j





dynamics of the diurnal degradation, and therefore, it can lead to a misleading conclusion in terms of the total energy generated by the cell during its lifetime:<sup>13–15</sup>

$$E_{T_{80}^{\max}} = \int_0^{T_{80}^{\max}} \text{PCE}(t) \times P_{\text{in}}(t) \times dt, \quad (1)$$

where  $P_{\text{in}}$  is the incoming sunlight power (for simplicity,  $P_{\text{in}} = 1 \text{ Sun} = 100 \text{ mW cm}^{-2}$ ).

It is worth noting that the  $E_{T_{80}^{\max}}$  calculated using only the maximal diurnal PCE values (the dashed upper curve in Fig. 1a) during  $T_{80}^{\max} = 4 \text{ d}$  gave an almost 20% overestimation as compared to that calculated using the measured diurnal dynamics of the PCE during these first four days of exposure (see Fig. S2 and related discussion in the ESI†).

Fig. 1b depicts the evolution of the daily energy output generated by the type 1 cell,  $E_{\text{day}}$ :

$$E_{\text{day}} = \int_0^{t_{\text{day}}} \text{PCE}(t) \times P_{\text{in}}(t) \times dt, \quad (2)$$

where  $t_{\text{day}}$  is the illumination time during one day.

Now, we can estimate  $T_{80}' \approx 9 \text{ d}$  as the time when  $E_{\text{day}}$  drops to 80% of its value on the first day of exposure. We suggest that this  $T_{80}'$  is a reliable figure of merit for PCE stability, taking into account both the reversible and irreversible degradation of the cell performance.

Accordingly, the total energy generated by the cell during its lifetime can be properly calculated as:

$$E_{T_{80}'} = \int_0^{T_{80}'} \text{PCE}(t) \times P_{\text{in}}(t) \times dt. \quad (3)$$

This value may serve as the figure of merit for the interplay between the cell performance and its stability whose overall improvement is the ultimate purpose of any photovoltaic technology. A similar parameter has already been employed for other photovoltaic technologies.<sup>14</sup> An important advantage of our approach is that it does not depend on a certain type of PCE change during the day/night (light/dark) cycle. In particular, the type II modules demonstrated fatigue-like behavior: a pronounced performance enhancement during the day followed by “degradation at night” (Fig. 2a). In both device types, we observed (a) the superposition of reversible and irreversible degradation mechanisms, and (b) a dramatic difference compared to the results from the continuous illumination experiment. The use of  $T_{80}'$  and  $E_{T_{80}'}$  (Fig. 1b and 2b) as figures of merit for the cell lifetime and performance is appropriate for both cell types, and allows the comparison of the overall performance of different cells and devices.

Finally, we discuss the reliability of the initial PCE as a representation of PSC performance. As a rule, PCE is measured after the short preconditioning time needed for the stabilization of cell parameters.<sup>16</sup> An appropriate preconditioning time should be chosen for each cell separately depending on its transient characteristics and it might take hours in some cases.<sup>2</sup> Christians *et al.*<sup>17</sup> showed that the improvement of PCE under illumination might take even hundreds of hours

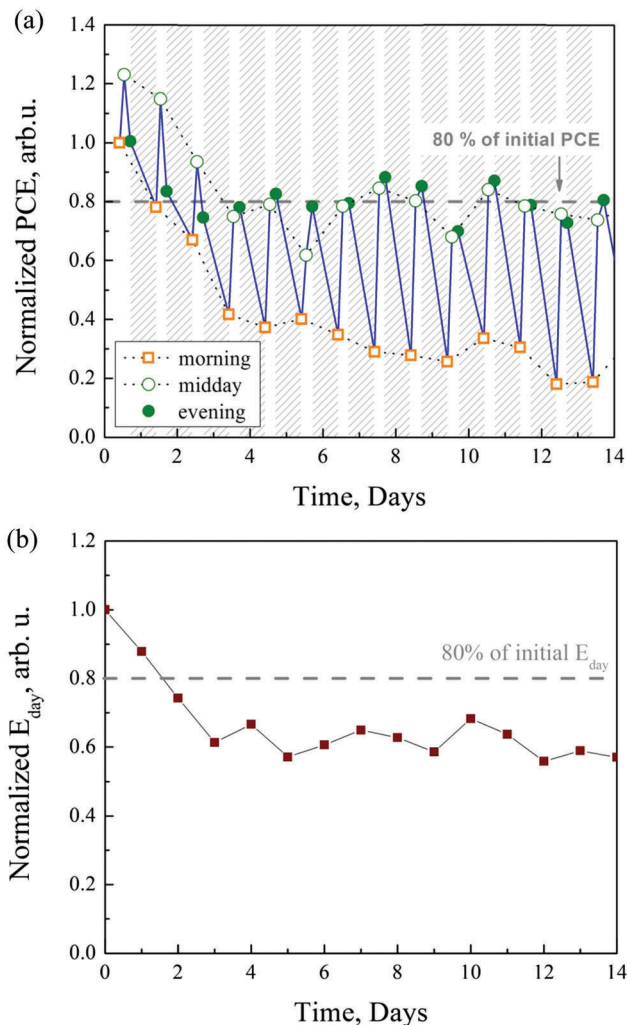


Fig. 2 (a) PCE evolution of type II mini-modules (glass/ITO/TiO<sub>2</sub>/MAPbI<sub>3</sub>/Spiro-OMeTAD/Au) during their outdoor sunlight exposure. (b) Evolution of the daily energy output generated by this cell. For simplicity, we used a constant  $P_{\text{in}} = 1 \text{ Sun}$  for the  $E_{\text{day}}$  calculation. All lines are guides for the eye.

(see Fig. S18 in ref. 17). The choice of the preconditioning time might determine the reported efficiency value and mask the real picture in terms of energy production. Obviously, such a protocol is not suited for determining the cell performance in stability assessing experiments, especially for solar cells with reversible degradation, where pre-measurement conditioning can superimpose on continuing degradation. Furthermore, this value is not representative of the actual cell performance under operational conditions, where long preconditioning is impractical. Instead, we suggest that the energy output ( $E_{\text{day}}$ ) during the first day of exposure (which automatically accounts for the naturally occurring preconditioning history) can serve as a universal figure of merit for the initial cell performance.

In our work, we use the ISOS-O-1 protocol<sup>5</sup> for outdoor aging. This allows the degradation effect to be separated from the non-trivial variations of the PSC's PCE throughout the day,<sup>18</sup> reflecting the effects of the diurnal variations in ambient temperature and the intensity and spectrum of natural sunlight.<sup>19</sup>





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