

# The effect of current density–voltage measurement conditions on the operational stability of hybrid perovskite solar cells

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## ABSTRACT

Organic–inorganic lead halide perovskites have attracted great attention for use in solar cells, because of their efficient solar power conversion, along with compatibility with simple solution processing. To evaluate the operational stability of perovskite solar cells (PSCs), measurements on their current density–voltage ( $J$ – $V$ ) curves are periodically repeated in most literature studies. However, how the periodic  $J$ – $V$  measurements affect the operational stability of PSCs has not been well understood to date. In this study, we found that repeating the  $J$ – $V$  measurements, especially applying a voltage higher than the open-circuit voltage of PSCs, under continuous illumination, causes serious ion migration, which lowers the operational stability of PSCs. On the other hand, we observed no decrease in operational stability when the applied voltage is close to or lower than the open-circuit voltage of PSCs during the periodic  $J$ – $V$  measurements because of the suppressed ion migration. These findings are important in evaluating the intrinsic operational stability of PSCs.

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Organic–inorganic lead halide perovskite solar cells (PSCs) have attracted great attention because of their efficient solar energy conversion.<sup>1–4</sup> By optimizing perovskite fabrication conditions and PSC architectures, the performance of PSCs has dramatically been improved, with the highest certified power conversion efficiency (PCE) having reached 25.2%.<sup>5,6</sup> However, a hysteresis phenomenon is frequently observed when the current density–voltage ( $J$ – $V$ ) curves of PSCs are measured in consecutive forward and reverse scans. One of the origins of this  $J$ – $V$  hysteresis is attributed to ion migration.<sup>7,8</sup> Ions and ionic vacancies migrate through the perovskite layer and accumulate at interfaces during the  $J$ – $V$  measurements.<sup>9,10</sup> For example, it is known that the accumulation of positive ions at an interface between the electron transport layer and the perovskite layer and the accumulation of negative ions at an interface between the hole transport layer and the perovskite layer lead to nonradiative recombination of holes and electrons,<sup>9–17</sup> thereby inducing the  $J$ – $V$  hysteresis.<sup>14,17</sup>

The ion migration also makes the operational stability of PSCs lower; PCEs of PSCs gradually decrease over time under illumination

because of the ion migration, which is another serious issue that needs to be solved for future commercialization.<sup>18</sup> This ion-induced PCE decrease is sometimes recoverable by keeping PSCs in the dark condition because the ions return to the original position.<sup>19,20</sup> The operational stability of PSCs has frequently been evaluated by periodically measuring  $J$ – $V$  curves with different time intervals. For example, the reported time intervals were 15 (Ref. 4), 30 (Refs. 21 and 22), and 360 (Ref. 23) min. However, the  $J$ – $V$  curve measurements are not carried out during solar cell operation implemented in final commercial products. Therefore, it is necessary to clarify the effect of the periodic  $J$ – $V$  measurements on the operational stability of PSCs.

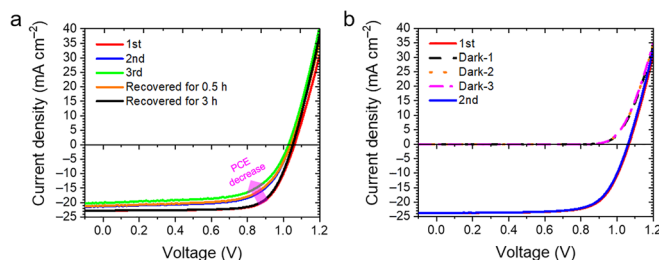
To understand how the  $J$ – $V$  measurements affect the operational stability clearly, in this study, we measured the  $J$ – $V$  curves of PSCs with different voltage scan ranges or time intervals. As a result, we found that applying a voltage higher than the open-circuit voltage ( $V_{OC}$ ) many times during the stability test accelerates the ion migration and, therefore, causes the PCEs of PSCs to significantly decrease. We were able to suppress the decrease in PCEs by applying a voltage

lower than the  $V_{OC}$  or increasing the time intervals of the  $J-V$  measurements. Therefore, this work suggests the importance of choosing a suitable  $J-V$  measurement condition to know the intrinsic operational stability of PSCs.

The PSC structure used in this study was glass substrate/indium tin oxide (ITO) electrode (100 nm)/tin oxide ( $\text{SnO}_2$ ) electron transport layer (ETL) ( $\sim 30$  nm)/perovskite light absorber ( $\sim 650$  nm)/chemically doped spiro-OMeTAD hole transport layer (HTL) ( $\sim 150$  nm)/Au electrode (100 nm). The composition of the perovskite layer was  $\text{Cs}_{0.05}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.95}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$  (hereafter abbreviated as CsFAMA). Spiro-OMeTAD, FA, and MA stand for 2,2',7,7'-tetrakis[ $N,N$ -di(4-methoxyphenyl)amino]-9,9'-spirobifluorene, formamidinium, and methylammonium, respectively. See the [supplementary material](#) for details of the PSC fabrication and measurement conditions.

Figure 1(a) shows the  $J-V$  characteristics of PSCs measured three times subsequently with a voltage bias range from 1.2 to  $-0.1$  V under the AM 1.5 G (1 sun) condition. Table S1 summarizes the short-circuit current density ( $J_{SC}$ ),  $V_{OC}$ , fill factor (FF), and PCE values extracted from Fig. 1(a). The first  $J-V$  measurement led to a PCE value of 17.5% as indicated by the red line of Fig. 1(a). The PCEs decreased to 14.73% and 13.17% when the  $J-V$  measurements were further repeated [the blue and green lines in Fig. 1(a)]. As we will discuss later, applying a voltage higher than the  $V_{OC}$  ( $\sim 1.06$  V) to PSCs is one source of the PSC performance degradation. After the  $J-V$  measurements three times under the illumination, PSCs were placed in the dark, and their performance was recovered with time [the orange and black lines in Fig. 1(a)]. Nearly 100% recovery was obtained after 3 h of storage in the dark. A similar reversible behavior of PSC performance was observed in a previous report,<sup>19</sup> which was attributed to the ion migration effect.

The ion migration is unlikely in the dark because the activation energy for the ion migration is very high in the dark compared with under the illumination.<sup>24</sup> To check if the ion migration occurs in our PSCs in the dark, we carried out a couple of  $J-V$  measurements as



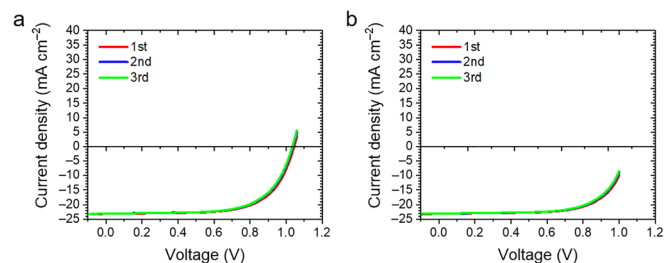
**FIG. 1.** (a) and (b)  $J-V$  curves of PSCs. (a) We subsequently measured the  $J-V$  curves three times under the illumination. The red, blue, and green curves correspond to the  $J-V$  curves measured with first, second, and third scans, respectively. After the aforementioned three-times  $J-V$  measurements, we placed PSCs in the dark for 0.5 or 3 h. Then, we measured  $J-V$  curves again under the illumination. The orange and black curves correspond to the  $J-V$  curves measured after placing PSCs in the dark for 0.5 and 3 h, respectively. (b) We first measured a  $J-V$  curve under the illumination (the red curve). After we placed PSCs in the dark for 3 h, we measured  $J-V$  curves three times under the dark (the black, orange, and pink curves). Just after the dark measurements, we measured a  $J-V$  curve under the illumination (the blue curve). The  $J-V$  measurement condition used here was a voltage scan from 1.2 V (above the  $V_{OC}$ ) to  $-0.1$  V.

follows. A  $J-V$  curve was first measured under the illumination as indicated by a red line of Fig. 1(b) and Table S2. After PSCs were kept in the dark for at least 3 h, dark  $J-V$  curves were measured three times as shown by the black, orange, and pink dashed lines of Fig. 1(b) and Table S2. Right after these dark measurements, a  $J-V$  curve was measured under the illumination [the blue line in Fig. 1(b) and Table S2]. The PCEs were almost similar before and after the dark  $J-V$  measurements three-times, indicating the negligible effect of the dark  $J-V$  measurements on the ion migration.

To obtain insight into the observed PCE decrease shown in Fig. 1(a), we repeated  $J-V$  measurements on fresh PSCs three times with different voltage scan ranges under the illumination (Fig. 2). The voltage scan ranges used here were from 1.06 (close to the  $V_{OC}$ ) to  $-0.1$  V and from 1.0 (below the  $V_{OC}$ ) to  $-0.1$  V. Interestingly, compared with the previous voltage scan range from 1.2 V (above the  $V_{OC}$ ) to  $-0.1$  V, these voltage scan ranges did not decrease the PSC performance. This indicates that applying a voltage higher than the  $V_{OC}$  to PSCs induces the PSC performance degradation.

Based on the aforementioned results, we illustrate the ion migration dynamics when a voltage above the  $V_{OC}$ , close to the  $V_{OC}$ , or below the  $V_{OC}$  is applied to PSCs (Fig. 3). When the applied voltage is higher than the  $V_{OC}$ , the ion migration occurs under the illumination with a driving force of the electric field; positively charged ions move to the  $\text{SnO}_2$  side and negatively charged ions move to the spiro-OMeTAD side as shown in Fig. 3(a). Since these ions accumulating at the interfaces impede the charge extraction to the electrodes,<sup>14,17</sup> it is reasonable that PCEs of PSCs decrease. In contrast, there is no significant ion migration occurring in PSCs when the applied voltage is close to or lower than the  $V_{OC}$ , because the electric field gradient is flat [Fig. 3(b)] or its direction is opposite [Fig. 3(c)].

Next, we checked how  $J-V$  measurements affect the operational stability of PSCs under the illumination. For this purpose, we measured  $J-V$  curves every 10 min with the three different voltage scan ranges used earlier. In between  $J-V$  scans, the PSCs were put at a maximum power point (MPP) condition under the continuous illumination from a white LED with a light intensity of  $100 \text{ mW cm}^{-2}$ . As shown in Fig. 4(a), it was clear that the PSC degradation happened only when a voltage above the  $V_{OC}$  was applied. This is consistent with the earlier discussion on the ion migration caused by the application of the high voltage. Furthermore, this PSC degradation was  $\sim 100\%$  recoverable by keeping the PSCs in the dark for 3 h, which is similar to the  $J-V$  curves returning to the original position in the dark as we discussed earlier.



**FIG. 2.**  $J-V$  curves of PSCs measured three times with voltage scan ranges (a) from 1.06 V (close to the  $V_{OC}$ ) to  $-0.1$  V and (b) from 1.0 V (below the  $V_{OC}$ ) to  $-0.1$  V under the illumination.

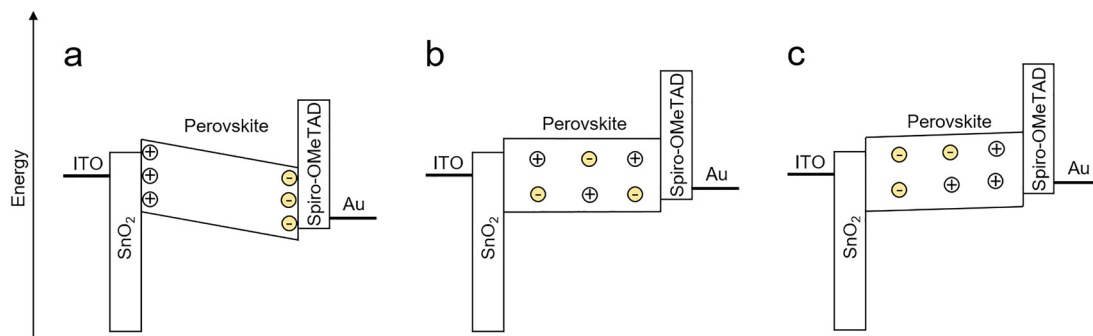


FIG. 3. Energy-level diagrams of PSCs with an applied voltage, which is (a) higher than, (b) close to, or (c) lower than the  $V_{OC}$ .

Before and after the operational stability measurement for 1440 min (24 h), we removed the Au and spiro-OMeTAD layers from PSCs using a method we previously reported (Ref. 25) and measured the x-ray diffraction (XRD) patterns and top-view scanning electron microscope (SEM) images of the CsFAMA perovskite layer surfaces. As results, we observed no appreciable degradation of the CsFAMA perovskite layers after the operation (Fig. S1).

Next, we repeated the operational stability measurements under the illumination for  $\sim 24$  h and under dark storage for  $\sim 3$  h (Fig. S2). The  $\sim 100\%$  PCE recovery was difficult to obtain after the third dark storage, which could be related to destabilization of ions in the perovskite lattice, leading to permanent degradation.<sup>19</sup>

Furthermore, we tested if a similar PCE recovery behavior can be seen from other methylammonium lead triiodide (MAPbI<sub>3</sub>)-based PSCs. However, no PCE recovery was observed in MAPbI<sub>3</sub>-based PSCs (Fig. S3).

We conducted an additional stability test with the voltage scan range from 1.2 V (over the  $V_{OC}$ ) to  $-0.1$  V and different time intervals of 5, 10, 15, 20, 60, and 1440 (only two times at the start and end points) min for  $J-V$  measurements. The operational stability decreased as the measurement time intervals were decreased [Fig. 4(b)]. When

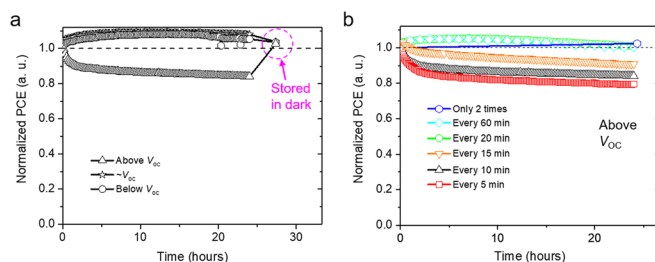


FIG. 4. Evolution of PCEs when PSCs were operated under the continuous illumination at the MPP condition. The triangle, star, and circle symbols in (a) indicate the PCEs calculated from  $J-V$  curves measured with the voltage scan ranges from 1.2 V (above the  $V_{OC}$ ) to  $-0.1$  V, from 1.06 V (close to the  $V_{OC}$ ) to  $-0.1$  V, and from 1.0 V (below the  $V_{OC}$ ) to  $-0.1$  V, respectively. The measurement time interval was 10 min. (b) indicates the evolution of PCEs calculated from  $J-V$  curves measured with the voltage scan range from 1.2 V (above the  $V_{OC}$ ) to  $-0.1$  V and the different time intervals of 5 (red), 10 (black), 15 (orange), 20 (green), 60 (light blue), and 1440 (blue; the measurements at the initial and end points only) min, respectively. The black triangle symbols in (b) are taken from (a) for comparison.

the intervals were 20 min or longer, the PSC degradation was not observed. This indicates that the measurement interval of at least 20 min is required to cause the ions to return in the CsFAMA-based PSCs we used in this study. To check reproducibility, we carried out the same stability test on nine individual PSCs with different two intervals of 10 and 1440 min. We obtained the similar degradation behaviors (Fig. S4). Furthermore, we tested the stability of PSCs at an elevated temperature of  $40^\circ\text{C}$  by measuring the  $J-V$  curves twice at the start and end points with a long interval of 1440 min. Although the negligible change of the PCE was observed at room temperature ( $\sim 25^\circ\text{C}$ ), the PCE significantly decreased at  $40^\circ\text{C}$  (Fig. S5), probably because of the ion migration being accelerated at the high temperature.

In this Letter, we studied the effect of the  $J-V$  measurements on the operational stability of PSCs during the continuous illumination. We found that repeating  $J-V$  curve measurements decreased the operational stability of PSCs, because of the ion migration. Especially, applying a voltage higher than the  $V_{OC}$  markedly accelerated the ion migration. Since typical solar cell products are usually operated below  $V_{OC}$ , this type of device degradation associated with the ion migration would be negligible in products. Thus, we need to pay attention to a stability measurement condition to know the intrinsic degradation behaviors of PSCs.

See the [supplementary material](#) for the experimental details, SEM and XRD results, operational stability of PSCs under operation with other conditions, and summary of solar cell parameters.

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## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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