Fatigue behavior of planar CH₃NH₃PbI₃ perovskite solar cells revealed by light on/off diurnal cycling

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ABSTRACT

Long-term stability represents a major challenge for the commercial deployment of hybrid perovskite solar cells (PSCs). The stability of solar cells is commonly tested under continuous illumination over extended periods of time, for example, 1000 hours. We have found that such a method does not adequately reflect the long-term performance of perovskite solar cells under the diurnal solar irradiation cycles experienced in real-world applications. We report a new characterization protocol of multiple 12-hour cycles of darkness and illumination, uncovering a unique ‘fatigue’ behavior of PSCs. The PSC efficiency was found to decrease to 50% or less of its maximum value after storage in the dark for 12 hours under open circuit conditions. The solar cell performance was capable of recovering to its maximum value in the subsequent 12-hour illumination period, but the recovery rate slowed significantly with successive illumination/darkness cycles. This fatigue mechanism was strongly dependent on the cell temperature. The identification of this fatigue behavior renders our proposed characterization protocol an essential component of perovskite solar cell testing.

KEYWORDS: Perovskite solar cells; stability; fatigue.

1. Introduction

Hybrid organic-inorganic perovskite solar cells (PSCs) have been intensely studied since the technology was first reported 6 years ago.[1-7] In a PSC, organic-inorganic lead halide perovskites, such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3),[3, 8] $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ ($\text{MAPbI}_{3-x}\text{Cl}_x$)[1, 9] and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr_3)[10, 11] simultaneously act as light absorbing and charge transporting materials. The beneficial properties of these perovskite materials have resulted in power conversion efficiencies (*PCEs*) exceeding 20%.[12] Such solid state devices present promising prospects for commercialization, and towards this end, significant research has been focused on developing solution based fabrication techniques[3, 13-17] and new device architectures[18-20] to further enhance device efficiencies. A number of innovative fabrication methods have been developed to produce optimized perovskite films that result in high *PCEs* including a two-step sequential method,[3] a solvent engineering method[13, 14] and a gas-assisted precipitation method.[21] Considering that the end-goal of PSC development is the commercial deployment of the technology, stability issues relating to PSC devices have raised great concerns.[22-24] Previous studies have identified the degradation of perovskite materials under UV illumination[25] and through contact with moisture,[26] which was concluded to be a main cause of device degradation.[26, 27] Various efforts have been made to improve the device stability through the introduction of new materials such as $(\text{PEA})_2(\text{MA})_2[\text{Pb}_3\text{I}_{10}]$ ($\text{PEA}=\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3^+$),[28] as well as the use of new device architectures such as the inverted structure[29, 30] and hole-transport-layer free mesoporous structure[31]. Surface coatings, such as Al_2O_3 , have also been used to enhance the chemical stability of the perovskite material.[32, 33] An alternative means of addressing the issue of moisture induced degradation is through the development of good sealing and encapsulating methods. A recent study performed by Li *et al.* has reported some encouraging results for sealed devices measured under high temperature and long-term illumination conditions.[34]

The conventional method for studying the long-term performance of solar cells is to monitor the device performance under continuous simulated **one** sun illumination for a set period of time, typically 1000 **hours**.^[31] Temperature and humidity variations and/or cycling have been employed in combination with continuous illumination as part of advanced protocols for testing the thermal and chemical stability of photovoltaic (PV) devices.^[35, 36] A plot of the normalized *PCE* measured under constant illumination as a function of time is commonly used to demonstrate the performance stability of perovskite-based solar cells. In real-world conditions, however, the solar cells are illuminated in the daytime and remain in the dark at night. Thus, they are exposed to alternative periods of illumination and darkness, i.e., diurnal cycling. To date, no differences between continuous illumination and diurnal cycling tests have been reported for PSC devices. A unique feature of PSCs, compared to other photovoltaic technologies, is the characteristically slow polarization of the light absorbing perovskite material,^[37] which has been linked to the current-voltage (*IV*) hysteresis observed during efficiency measurements.^[22] This polarization is believed to be associated with lattice displacements, ionic migration^[38-41] and/or the rotation of MA molecules.^[42] The driving force for the perovskite polarization is expected to originate from the illumination of the material, and previous studies have identified a higher-degree of perovskite polarization under illumination compared to dark conditions.^[43] In this case, the polarization is retained under constant illumination testing and is expected to diminish under dark conditions. Regardless of the actual mechanism of polarization, it is likely that the increase and decrease in polarization concomitant with on/off illumination cycling can produce differences for stability measurements performed under constant illumination in comparison to experiments simulating diurnal cycling. The latter testing protocol should be an integral component of stability characterization, as it explores an aspect of solar cell long-term performances in a real-world scenario.

In the present study, we report a new testing method to examine the performance of PSC devices under diurnal cycling conditions. This characterization protocol entails the *IV*-testing of sealed devices under cycles of a continuous illumination (light on) for 12 hours followed by a dark period (light off) for 12 hours. Under these conditions, the perovskite-based devices exhibit a novel behavior, not witnessed in other photovoltaic technologies. After only 2 to 3 cycles of illumination/darkness, significant ‘fatigue’ degradation was observed in the device performance, and efficiencies measured immediately after the 12 hours dark period were about 50% or less of their initial values. It was possible for the device performance to recover during the subsequent 12 hours illumination period, but it was increasingly difficult to achieve full recovery with each successive illumination/darkness cycle. These stability results are quite different from those obtained using constant illumination tests. The fatigue degradation uncovered by this work reveals an endemic characteristic of PSC performance, and must be taken into consideration in future stability tests of perovskite solar cells.

2. Material and Methods

Solar cell fabrication: The MAPbI₃ perovskite solar cells were prepared via a one-step gas assisted method.[21] In brief, 40 μ L of a 45 wt% MAPbI₃ DMF solution made by mixing equimolar ratios of methylammonium iodide (MAI) and PbI₂ was spread over a cleaned and patterned FTO glass slide (2 cm x 2 cm) that was placed on a spin coater. The FTO glass was then spun at 6500 rpm and, after 2 s, dry argon gas (40 psi) was blown over the film for 10 s. After spinning for 30 s, the film was heated on a hotplate at 100 °C for 10 min. It was then cooled quickly on a steel substrate. A 40 μ L spiro-MeOTAD solution, which was prepared by dissolving 41.6 mg spiro-MeOTAD, 7.81 μ L of a stock solution of lithium bis(trifluoromethylsulphonyl)imide (500 mgmL⁻¹) in acetonitrile and 16.88 μ L of 4-tert-butylpyridine in 0.5 mL chlorobenzene, was coated on the perovskite film by spin-coating at

3000 rpm for 30 s. An 80 nm Au layer was deposited by thermal evaporation to form the complete device. Finally, the device was sealed with a glass cover and a UV-curable epoxy sealant.[27]

Characterization: The surface of the prepared perovskite films was examined using an FEI Nova NanoSEM 450 microscope. To obtain the cross-sectional TEM image, several cycles of gentle milling were carried out to obtain a final cross-section of 150 nm in thickness. TEM images were obtained on a FEI Tecnai G2 F20 microscope. *IV* curves of the solar cells were measured by using a Keithley 2400 Source Meter under illumination of simulated sunlight (100 mW/cm^2) provided by an Oriel solar simulator with an AM1.5 filter. A black metal mask was employed to provide an aperture area of 0.16 cm^2 . *Impedance spectroscopy (IS) characterization* and *IV* measurements were performed using an electrochemical workstation (BioLogic VSP). IS measurements were performed under illumination (white LED at $\sim$ one sun) using a 10mV perturbation in the 1 MHz to 30 mHz frequency range.. *IS* were analyzed using ZView (Scribner) software. *IV* measurements were performed in the dark at a scan-rate of 100 mV/s, and curves were analyzed using Origin Pro 8 SRO (OriginLab Corporation). Additional information of the IS equivalent circuit and *IV* calculations are shown in the supporting information. *X-ray diffraction measurements were performed by a D2 PHASER (Bruker Corporation).*

Cyclic stability testing: The stability test was carried out in an environmental chamber (Atlas 340) equipped with a solar simulator. The devices were fitted in the environmental chamber where the relative humidity was maintained at approximately 10%. The devices were illuminated for 12 hours and then kept in dark for 12 hours. This process was repeated for several cycles. *IV* curves were measured every 5 minutes regardless of whether the devices were under illumination or in the dark. The cell temperature was monitored via

thermal couples fitted on the surface of the devices. The device temperature, under illumination and in the dark, was controlled by adjusting the temperature setting of the environmental chamber.

3. Results and Discussion

3.1 Device Structure

As shown in Figure 1a, the PSC devices used in this study employed a planar configuration comprising a compact TiO_2 blocking layer (~ 30 nm), a MAPbI_3 photoactive layer (~ 300 nm) and a spiro-OMeTAD hole transporting layer (~ 200 nm). FTO and Au were used as charge collection anodes and cathodes, respectively. The dense MAPbI_3 layer was fabricated via the gas-assisted method, which we have previously reported to be capable of forming a dense, uniform perovskite film.[21] The SEM image in Figure 1b shows that the MAPbI_3 perovskite layer is composed of densely packed, large grains. The pin-hole free perovskite layer inhibits shunting between the TiO_2 and spiro-OMeTAD layers. A representative *IV* curve of the devices used in this study, scanned in the short-circuit (*SC*) to open-circuit (*OC*) direction and *OC-SC* direction, is plotted in Figure 1c. This device showed a *PCE* of $\sim 11.1\%$ (*SC-OC*) and $\sim 13.8\%$ (*OC-SC*) respectively.

Figure 1. (a) Cross-sectional TEM image of the planar PSC device, (b) SEM image of the surface morphology of the MAPbI₃ film prepared by the gas-assisted method, (c) typical *IV* curves of the prepared PSC with the scan direction from short-circuit (SC) to open-circuit (OC) and OC-SC, and (d) PSC stability under simulated continuous one sun illumination at 25°C and 10% relative humidity.

3.2 Stability tests under constant illumination

The devices were sealed with a glass cover via a UV-curable epoxy sealant to avoid contact with moisture.[27] A typical stability curve for a planar device, under continuous one sun illumination in an environment chamber, is shown in Figure 1d and Figure S1. The ATLAS Environmental Chamber (SC 340 MHG) enables tests to be carried out between -20 °C to 100 °C, between 0% to 80% relative humidity under one sun illumination. In the constant illumination test, the cell temperature was maintained at ~25 °C and relative humidity at ~10%. It is clear that there is a small (7% relative) drop in the solar cell PCE over

the 300 hour duration of the constant illumination testing. This is effect is commonly observed in perovskite-based devices, and is largely due to prominent chemical and physical degradation mechanisms. However, this result indicates that the perovskite cell was relatively stable under constant illumination at room temperature and low humidity.

3.3 Illumination/darkness cycling tests

Seven planar PSC devices (the photovoltaics performances were listed in Table S1) were loaded into the environment chamber where the simulated one sun intensity light was switched on for 12 hours and then turned off for 12 hour. This on/off process is denoted as one testing cycle. During the testing, the environmental conditions were automatically adjusted to maintain a cell temperature of 25 °C and 10% humidity, in both the illumination and dark conditions. The solar cell temperature was measured by a thermocouple which was in direct thermal contact with the solar cell. The temperature profile of a typical device over fourteen illumination/darkness cycles is presented in Figure S2. *IV* characteristics were measured every five minutes by scanning the voltage from -0.1V to 1.2 V, and the seven cells were maintained under open-circuit conditions between measurements. Due to limitations in measurement capabilities of the environmental chamber, maximum power-point tracking measurements or continuous loading at near maximum power-point conditions were not possible. Hence, the cells were maintained at open-circuit conditions between each *IV* scan. The typical photovoltaic performance parameters of the devices over fourteen cycles (i.e., 14 days) are plotted in Figure 2. The results of the all seven cells measured are presented in Figure S3, which exhibit similar behavior. The *IV* parameters were normalized with respect to the highest value recorded over the fourteen day experiment. A comparative plot of the performance of a silicon-based reference cell under the same experimental conditions is shown in Figure S4.

Figure 2. . Normalized photovoltaic performance parameters of (b) V_{oc} , (c) J_{sc} , (d) fill factor, and (e) PCE for a typical PSC device recorded during repeated (a) 12 hours light on/off cycles at 25°C and 10% relative humidity in the environment chamber.

In the first 12 hours of illumination, the short-circuit current density (J_{SC}), the open-circuit potential (V_{OC}) and the fill-factor (FF) steadily increased by less than 10% with respect to their initial values. Thus, the power conversion efficiency (PCE) showed the similar trend of the J_{SC} , V_{OC} and FF , increasing from a normalized value of ~ 0.8 to ~ 0.9 over the first 12 hour illumination period. After 12 hours resting in the dark, the device performance was significantly poorer at the start of the second illumination cycle. This was mainly accounted for by the decrease in the FF immediately after the first 12 hours period of darkness. During the second illumination cycle the normalized J_{SC} and V_{OC} exhibited a similar increase to what was observed in the first illumination cycle. This pattern was also observed for the remaining 12 illumination cycles. However, with each successive illumination/darkness cycle, there was a degradation in the recovery of the FF over the 12 hours illumination period. Due to the slowing rate of the FF recovery, the maximum value attained after each illumination cycle decreased over the course of the 14 day experiment. This languid recovery of the FF was equally reflected in the behavior of the PCE . With each successive cycle, the PCE began from a lower starting point immediately after the 12 hours of darkness, and took a longer time to recover back to its maximum value. Despite both the V_{OC} and J_{SC} reaching a normalized value of ~ 1 over the last two illumination cycles, the FF and PCE were not able to fully recover over the 12 hours period, and could only reach a maximum of ~ 0.9 . This decrease in the recovery rate with successive cycles is what we term the ‘fatigue’ of the device performance. XRD patterns of the perovskite film before and after the cycling experiments (Figure S5) indicate that the composition of perovskite layer did not change significantly after the cycling test.

It is clear from these results that the fatigue of the PCE was mainly due to the drop in the FF , which is largely governed by the series resistance (R_S) and shunt resistance (R_{Sh}). The R_S values (Figure S6), calculated from the IV characteristics, decreased when the device was

under illumination, which correlated with the increase in the FF under the same conditions. The evolution of the ‘fatigue’ response is also apparent in the slowing recovery-rate of the series resistance with each successive cycle. Some important conclusions can be drawn from this cyclic illumination/darkness testing: (1) illumination/darkness cycling caused a significant performance deterioration after only 3 to 5 cycles; (2) PCE recovery can occur under sustained illumination, but it is a process that takes place over several hours; (3) ‘fatigue’ behavior is identified, as it takes a longer time for the solar cell performance to recover with increasing illumination/darkness cycles. Fatigue is a major failure mechanism for materials under repeated cyclic stresses. In solar panels, for example, fatigue degradation can arise from thermal stresses caused by cyclic temperature changes and mechanical stresses from vibrations during transportation and use.[44] But fatigue has not been reported for solar cells tested repeatedly under cycled illumination/darkness conditions. The findings from this study have serious implications for the deployment of perovskite solar cells in real-world applications, as the solar cell devices will inevitably be subjected to light and dark periods on a daily basis.

3.4 Illumination/darkness cycling at low temperature

A further six planar perovskite solar cells were subsequently used for a similar cycling experiment, where the conditions under darkness were altered. In this modified experiment, the cell temperature during the 12 hours illumination was maintained at 25 °C, and was reduced to -10 °C during the 12 hours darkness period. This experiment is defined as the -10°C/dark condition in contrast to the previous 25°C/dark condition. Once again, the illumination/darkness cycling was performed over a duration of 14 days, and the IV parameters were recorded every 5 minutes. The V_{OC} , J_{SC} , FF and PCE data for a representative cell is presented in Figure 3. The IV parameters for all six devices are shown in Figure S7. Similar to the previous 25°C/dark conditions (Figure 2), the V_{OC} and FF measured

under the $-10^{\circ}\text{C}/\text{dark}$ condition also exhibit an initial increase at the start of the 12 hours illumination period before plateauing at a maximum value. This results in a similar recovery response of the *PCE*.

Figure 3. Normalized photovoltaic performance parameters of (b) V_{OC} , (c) J_{SC} , (d) fill factor, and (e) PCE for a typical PSC device recorded during repeated (a) 12 hours dark (-10 °C) and 12 hours light (25 °C) cycles in an environment chamber with 10% relative humidity.

What distinguishes the -10°C/dark results, however, is that the languid performance ‘fatigue’ response is significantly reduced, and all IV parameters are able to recover to their maximum values within the first 30 minutes of illumination. This performance recovery is markedly different to the sluggish performance response of the perovskite devices held continuously at 25 °C. In Figure 3, there is a similar reduction in the FF and PCE over the course of the 14 cycles under the -10°C/dark condition, which is equally observed in the 25°C/dark data presented in Figure 2. However, the near-constant performance of the V_{OC} and J_{SC} parameters under the -10°C/dark condition (Figure 3b and 3c) are in stark contrast to the fatigue-like behavior of the 25°C/dark data (Figure 2b and 2c). Interestingly, the series resistance measurements (Figure S8) performed under the -10°C/dark condition equally reflected the relatively rapid recovery of the other solar cell parameters.

3.5 Perovskite solar cell fatigue

Comparisons between the continuous 25 °C measurements and the low-temperature darkness tests reveal a correlation between the fatigue behavior and the device temperature. During the low-temperature measurements the degree of cell fatigue was significantly reduced compared to the constant 25 °C measurements. Additional experiments exploring the relationship between the performance fatigue and the cell temperature (Table S4) also highlight the reversible nature of the fatigue degradation process. Thus, it is likely that the fatigue behavior is linked to the temperature induced solid-state diffusion of species within the constituent materials. As mentioned previously, other studies have proposed the polarization and relaxation of the perovskite material under different experimental

conditions.[37] In these models, the perovskite material exhibits different polarization states between the illumination and dark conditions, owing to the alternating CH_3NH_3 rotation[42] and the cyclic migration of ions and vacancies[39]. The migrating species can be vacancies (V_{I} , V_{Pb} , V_{MA} , etc), interstitial ions sourced from impurities, and/or lattice ions (I^- and MA^+) in the perovskite film, which may induce defects and lattice strain within the perovskite structure. Defects serve as a detrimental influence on the charge-carrier extraction rate and the ensuing photovoltaic performance.[41] Xiao *et al.* observed direct evidence of ionic movement in the perovskite film under an externally applied electric field.[39] Bisquert and co-workers have also reported that excess capacitance due to the perovskite polarization can build-up at electrode interfaces when a bias is applied.[45] This accumulation of mobile ions/vacancies at the interfacial regions of the perovskite layer has been widely supported by models reported in previous literature.[40, 46]

Ion diffusion must be driven fundamentally by the electrical field within the perovskite layer. There is existing evidence to suggest that there is an electrical force driving ion diffusion under dark, short-circuit and/or open-circuit conditions.[47-49] The cycling experiments reported in the present study do not provide us with a thorough map of the electrical driving force within the perovskite layer, or the nature of the ion diffusion. However, from the repeated degradation of the performance during dark conditions and the repeated increase in the performance during illumination, it appears that ions diffuse in one direction during illumination and in the counter direction during dark conditions. Furthermore, the direction of ion diffusion during dark conditions appears to hamper the device performance, while ion diffusion in the opposite direction (under illumination) appears to aid the performance recovery. It is likely that the cyclic movement of mobile ions results in defects within the perovskite layer, caused by both ionic vacancies and lattice interstitials. The formation of these defects is analogous to the degradation of lithium-ion batteries.[50]

We speculate that the density of defects increases with each successive diffusion cycle, ultimately leading to the performance degradation of the solar cell. As defects are formed via ion diffusion during cycling, the chemical consistency of the perovskite crystal is unable to be recovered over time. This phenomenon accounts for the decreasing FF and PCE as a function of the illumination/darkness cycle number, as well as the slowing rate of performance recovery. By limiting ionic diffusion in the low-temperature experiments, it was possible to arrest the formation of further defects, and therefore preserve the device performance irrespective of the illumination/darkness cycling.

The temperature-dependent diffusion of ionic species within the perovskite layer is one possible model that may account for the fatigue behavior uncovered with this new testing protocol. We have performed some initial IS characterization (Figure S9) and IV scans (Figure S10) to probe the polarization of the perovskite film under alternating 12 hours illumination and darkness conditions. These initial results reveal a clear correlation between the illumination intensity and the measured interfacial capacitance. The IS data implies an increase in the solar cell capacitance during the 12 hours illumination period. IV scans performed immediately after this illumination period indicate that the solar cell capacitance is reduced over the subsequent 12 hours of darkness. However, further experimentation is required to fully unravel the cause of this fatigue response. An extensive investigation of the factors underpinning this unique behavior will no doubt form an interesting comparison to the results reported in the present study.

Furthermore, a planar PSC underwent the 12 hour illumination/darkness cycling test with an initial performance of 12.79% PCE and it exhibited a performance of 3.13% PCE after five cycles. The device was then heated at 75 °C while illuminated with a table lamp for 4 minutes. After cooling down to room temperature, the device showed a performance of

11.94% PCE, which is comparable to the initial value (Table S4). This experiment indicates that the fatigue behavior is temperature related and can be recoverable. However, due to other decay mechanisms present in the solar cell as well, the PCE did not return to its initial value of 12.79%. This experiment shows that even though the short-term fatigue degradation can be recoverable, the other degradation mechanisms may not be recovered through simple illumination or heat treatments.

4. Conclusion

We have developed a new testing protocol specifically designed for perovskite solar cells, which involves repeated 12 **hours** cycling under illumination and dark conditions. This cycling test has uncovered a novel behavior in perovskite-based PV devices, namely the ‘fatigue’ of the planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells. During the cycling tests, the device efficiency decreased to $< 10\%$ of its maximum value after resting in the dark for 12 hours. However, this performance may be slowly recovered after several hours of illumination, but the rate of the recovery decreased with each successive illumination/darkness cycle, which was classified as a performance fatigue. The device fatigue was strongly dependent on the cell temperature, which implies the temperature-limited diffusion of mobile species within the solar cell materials. These results raise concerns for real-world applications of perovskite solar cells where the technology is subject to the daily cycling of light and dark conditions. We propose that future long-term performance testing of perovskite solar cells should address the fatigue behavior identified by this study, and that periodic illumination/darkness cycles should form part of a stability evaluation protocol for this technology.

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Acknowledgment

The authors acknowledge the Australian Centre for Advanced Photovoltaics (ACAP), the Australian Renewable Energy Agency (ARENA) and the Victorian State Government (DBI-VSA and DPI-ETIS) for financial support. The Commonwealth Scientific and Industrial Research Organization is acknowledged for providing support through OCE Science Leader position (UB). Y.Y acknowledges the support from US DOE Next Generation Photovoltaic 3 program. We thanked Dr. Sergey Rubanov of the University of Melbourne for the help on the TEM work. Monash University Centre for Electron Microscopy (MCEM) and the Advanced Microscopy Facility at The University of Melbourne are acknowledged for electron microscopy facilities. The authors thank Wenchao Huang for his assistance with the manuscript artwork and Wenxin Mao for performing the XRD measurement.

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