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The Effect of Electrode Metal and Shadow Masking on Perovskite Solar Cell Outdoor Stability

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One of the greatest challenges facing the commercialization of perovskite solar cells (PSCs) is their long-term stability. A better understanding of device responses to long-term outdoor stresses is necessary for ensuring the success of PSCs. This project is focused on investigating the effects of shadow-masking and electrode metal on the outdoor stability of single-junction perovskite devices. The devices studied here (fabricated at NREL by Dr Fengjiu Yang) are based on perovskite with a bandgap of 1.53eV and have the architecture: indium tin oxide (ITO)/ self-assembled monolayer (SAM)/ perovskite/ passivation/ C_{60}/ SnO_x/ Metallization, half with gold and half with silver contacts. We encapsulated devices then installed them outdoors in Berlin, Germany under maximum power point tracking (MPPt). We accompanied outdoor tracking with a set of characterization techniques to clarify the degradation mechanisms. This included current density-voltage (JV) curves, electroluminescence (EL), photoluminescence (PL), fast-hysteresis measurements, Intensity-Modulated Photocurrent Spectroscopy (IMPS), and JV curves with varied light intensity. We observed an onset of degradation under outdoor exposure already in the first week of exposure. Although degradation rate varied between cells, cells with gold electrodes consistently showed faster degradation. Preliminary results point to increased ionic movement with ageing. The outdoor experiment will continue beyond the duration of the program.

Introduction

Despite high efficiencies, perovskite solar cells face a variety of stability problems, which limit their commercial viability. Thorough outdoor testing of PSCs is necessary to better understand the combined effects of stressors relevant to operating conditions such as variable light intensity(1).

Device architecture and ageing conditions both affect the mechanisms and extent of degradation in PSCs. This project focused on the effects of shadow masking and back electrode metal on PSC stability outdoors. Shadow masks are primarily used to obtain accurate efficiency values for cells by ensuring a known active area. While the effect of mask design on performance characteristics and indoor stability has been investigated, (2,3) the effect of masking on ageing during outdoor operation is unknown.

Metal electrode choice has implications for both device performance and stability. The gold and silver electrodes we tested are widely used for high efficiency devices, and have been shown to impact the degradation of PSCs in varying ways dependent upon device architecture. (4,5,6)

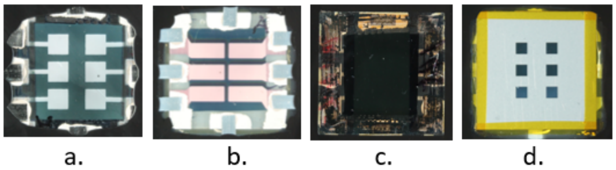


Fig 1. Photograph of substrates with silver (a) and gold (b), back electrodes (rear side). Photograph of the front side of unmasked (c) and masked (d) substrate.

The PSCs studied here were p-i-n cells based on perovskite absorber with a bandgap of 1.53eV, fabricated at NREL (Dr Fengjiu Yang). Each one inch by one inch substrate had 6 individual small area solar cells (see photos on Figure 1). Cells measured before encapsulation had initial power conversion efficiencies (PCEs) around 20%.

In preparation for outdoor testing, devices were encapsulated at HZB with glass on either side, butyl edge-sealants, and for some cells a polyolefin encapsulant, using a vacuum lamination procedure. This packaging has been shown to provide sufficient long-term protection against moisture and other factors influencing perovskite degradation outdoors. (7,8) Using the encapsulant polymer between the glasses required higher lamination temperature of 130°C (versus 100°C for lamination without encapsulant). To determine if these methods damaged cells, we took JV measurements before and after encapsulation and found marginal efficiency losses that were similar with or without the encapsulant.

Post-encapsulation, devices were wired and installed on a rooftop testing array in Berlin, Germany. Around half of the total devices were connected to MPPt tracking, and the rest were connected to a constant resistance. This meant that the ageing conditions were slightly different between these groups, which seems to have resulted in differences in degradation in some samples (see Figure 4).

To study the PSCs degradation mechanisms, the cells were characterised before outdoor exposure using a variety of techniques and periodically taken indoors to repeat the characterisation. When samples were taken indoors, JV measurements were taken using a simulated AM1.5G spectrum. JV curves were additionally taken under varying light intensity from an LED source, providing insight into the low-light response of cells. Spatial characteristics of cell degradation were measured using EL and PL imaging. As mobile ions are one of the main causes of electrode-related degradation, (4,5) we took more detailed measurements focused on ionic movement. Fast-hysteresis measurements, which rely on a series of J-V scans at varying sweep rates, allows comparisons of ionic losses during degradation. (9) IMPS measurements provide further insights into charge carrier dynamics. Ionic movement, which takes place on longer timescales than electron-hole dynamics, can be observed through low-frequency IMPS peaks. (10)

Results

After 1 week of outdoor exposure, cells already showed a significant decrease in performance. Cells with gold contacts showed more severe degradation, showing average absolute PCE losses of 8.5%. The degradation was apparent across the range of measurements taken on these devices. Efficiency losses seem to originate from an increased non-radiative recombination rate and enhanced ionic movement. Cells with silver electrodes also showed degradation, but less consistently. Some cells experienced complete performance losses, likely due to contacts disconnection, while most cells with Ag contact showed only moderate losses.

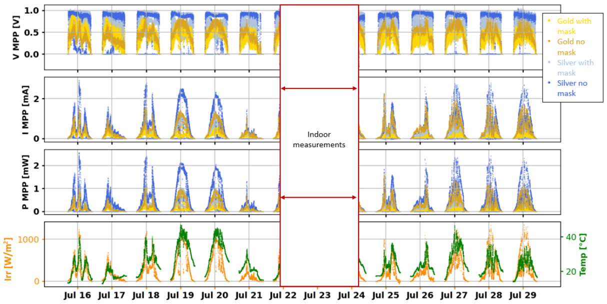
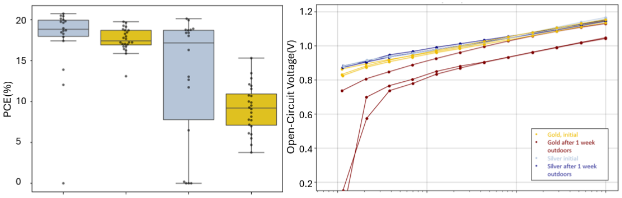


Fig 2. Outdoor performance parameters (V_{mpp}, I_{mpp}, P_{mpp}), displayed with irradiance and temperature data from around 2 weeks of outdoor exposure.

As shown by the outdoor data in Figure 2, the shape of daily V_{mpp} curves are "rounded" in the mornings/evenings, which could arise for multiple reasons, including light-soaking effects and low shunt resistances, which can result in performance losses at low irradiances.



a. b.

Fig 3. Indoor efficiencies before and after 1 week of outdoor exposure, sorted by electrode material. Unmasked silver pixels are excluded due to contacting issues with that substrate (a). Open-circuit voltage (V_{oc}) vs. normalized light intensity (b).

Indoor JV measurements confirm losses observed in outdoor performance tracking, showing losses mostly in fill factor and short-circuit current. JV curves at low light intensities additionally show V_{oc} drops for cells with gold contacts after 1 week of outdoor exposure, similar to what is suggested by the shape of diurnal voltage curves in Figure 2.

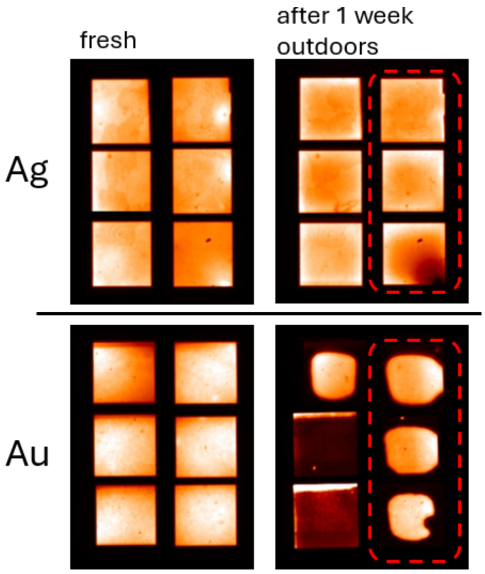


Fig 4. EL images of masked silver(top) and gold(bottom) substrates before (left) and after (right) 1 week of outdoor exposure. Cells boxed in red were connected to constant resistance instead of MPP tracking.

The spatial extent of this degradation is visible through EL and PL imaging. As shown in Fig. 3, this includes degradation around local defects as seen for example on the bottom right silver cell, as well as brightening and darkening at the edges of cells. Several gold cells, mostly those connected to fixed resistance instead of MPP tracking, show significant area reduction with dark regions progressing from the edges. The growth of dark areas, whether around point defects or at the edges of cells can be due to an increase in non-radiative recombination.(11)

More detailed investigations of the relation of ionic losses to cell degradation were accomplished through fast-hysteresis measurements. For the select cells measured after outdoor exposure, fast-hysteresis measurements not only reflect performance losses, but also show increased ionic losses as well. The difference between efficiencies at fast and slow scan rates is attributed to mobile ion-induced losses. After outdoor exposure, this efficiency difference increases for two of the gold cells measured, although for cell 3, ionic losses did not increase (Figure 5). Cells 2 and 3 on Figure 5 are also imaged in Figure 4 as the middle left and right gold cells, respectively, where they show clearly different degradation patterns.

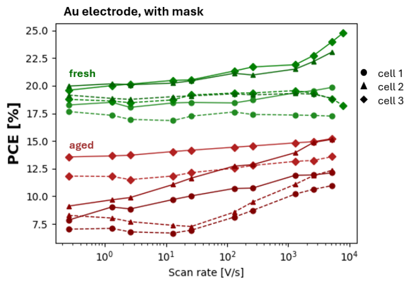


Fig 5. Fast-hysteresis before(green) and after 1 week outdoors(red).

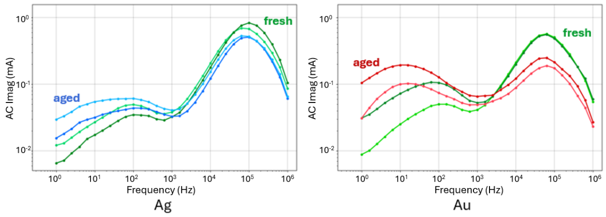


Fig 6. IMPS measurements of silver cells(left) and gold cells(right) before and after 1 week of outdoor exposure.

IMPS measurements further corroborate the changes in ion movement. Not only are there initial differences between cells with different electrodes, but after aging outdoors, the low-frequency peak, associated with ionic movement, increased. This change at low frequencies is particularly noticeable in cells with gold electrodes.

Discussion

While cells with gold electrodes consistently displayed faster degradation, the reasons for this are not yet apparent. The speed and severity of this degradation, especially in relation to that of the silver cells, is surprising and not in accordance with prior understandings of contact-related degradation in perovskites. (6) It is important to note that additional factors such as contact shape, area, or unknown processing differences could have also contributed to the behaviour observed in the two groups of cells. Variations in the mechanism of degradation for cells with gold contacts, and a possible correlation with aging conditions (MPP tracking vs. constant resistance) further complicates our understanding of degradation in these cells.

For degraded devices, the increased impact of ion movement is apparent in fast-hysteresis and IMPS measurements, in which ionic responses increased after outdoor exposure. The effects of shadow masking are not immediately apparent, as cells that were aged unmasked showed similar outdoor degradation patterns and performance losses as masked cells. However, the analysis and measurements of these cells during outdoor exposure is ongoing.

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