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Title: Performance and Stability of Mixed FAPbI₃(0.85)MAPbBr₃(0.15) Halide Perovskite Solar Cells Under Outdoor Conditions and the Effect of Low Light Irradiation

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Abstract: We demonstrate for the first time, the real lifetime response of mixed halide perovskite solar cells (PSCs) for >1000 h under outdoor conditions and the exceptional photoresponse observed at low-light intensities attributed to the ionic-electronic nature of the halide perovskite. The investigated devices were fabricated by utilizing mixed perovskites containing formamidinium (FA) and methylammonium (MA) cations, in a one step solution-process method through a solvent engineering approach. The devices' architecture was a FTO/TiO₂ (blocking layer) TiO₂ (mesoporous)/FAPbI₃(0.85)MAPbBr₃(0.15)/Spiro-OMeTAD/Au. Notably the outdoor stability analysis of the solar cells at T50 and T0 (50% and 100% degradation of the initial power conversion efficiency, PCE) revealed the presence of iodine in the Spiro-OMeTAD layer suggesting ion migration to the hole transport layer, and possible cause for the decay in performance and degradation of devices. Although a very low short circuit current (J_{sc}) was observed at low light intensities (< 50 W/m²), a high open circuit potential build-up was observed, which resulted in high PCEs. This is in agreement with a "double-current" model of a mixed ionic-electronic material where the ionic component is dominant at low light intensities and the electronic component dictates at high irradiances. Our results highlight the exceptional stability of mixed MA/FA mesoscopic PSCs when operated for >1000 h under real outdoor conditions and the strong ionic component observed at low light irradiation.

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Dear Editor,

July 7, 2016

We are submitting our manuscript "Performance and Stability of mixed $\text{FAPbI}_{3(0.85)}\text{MAPbBr}_{3(0.15)}$ halide perovskite solar cells under outdoor conditions and the effect of low light irradiation" which reports for the first time > 1000 h stability analyses of Perovskite Solar Cells (PSCs) under real conditions.

The excellent performance of PSCs, right now at 22 % efficiency, requires more than ever the understanding of its working mechanism under real conditions taking into account multiple and correlated environments. Most of the stability studies reported for PSCs are made under dark conditions or under indoor artificial light where specific variable conditions and testing environments are predetermined. Additionally, the ionic-electronic nature of the halide perovskites results in device response just recently observed for a photovoltaic technology, thus its understanding is a key factor for the advancement of the research area.

Our results demonstrate the exceptional stability response of PSCs, and highlight the importance of the mixed ionic-electronic conductivity for both, stability and device response. The delicate interplay of the ionic component and low light irradiation is in agreement with a 'double current' model representing a mixed conductivity mechanism. These results could pave the way to the understanding of the PSCs behavior and the issues observed in these devices linked to ionic drift and ionic migration or to the hysteresis effects. All of the later is in line with the objectives of Nano Energy for the publication of significant, innovative and excellent science. For all these reasons, we believe the work is worthy of the high exposure granted by your journal and we kindly request your consideration for publication.

Sincerely yours,



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Highlights

- Above 1000 h outdoor stability of Mixed $\text{FAPb}_{3(0.85)}\text{MAPbBr}_{3(0.15)}$ Halide Perovskite Solar Cells.
- Modelling of the ionic-electronic conductivity of the perovskite solar cell.
- Observed high V_{oc} and efficiency under low light irradiation.
- Strong effect of the ionic component at low irradiations.

Performance and Stability of Mixed $\text{FAPbI}_{3(0.85)}\text{MAPbBr}_{3(0.15)}$ Halide Perovskite Solar Cells Under Outdoor Conditions and the Effect of Low Light Irradiation

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Keywords: halide perovskite solar cells, hybrid solar cells, stability, ISOS protocols, outdoor analyses

We demonstrate for the first time, the real lifetime response of mixed halide perovskite solar cells (PSCs) for >1000 h under outdoor conditions and the exceptional photoresponse observed at low-light intensities attributed to the ionic-electronic nature of the halide perovskite. The investigated devices were fabricated by utilizing mixed perovskites containing formamidinium (FA) and methylammonium (MA) cations, in a one step solution-process method through a solvent engineering approach. The devices' architecture was a FTO/TiO₂ (blocking layer) TiO₂ (mesoporous)/FAPbI_{3(0.85)}MAPbBr_{3(0.15)}/Spiro-OMeTAD/Au. Notably the outdoor stability analysis of the solar cells at T₅₀ and T₀ (50% and 100% degradation of the initial power conversion efficiency, PCE) revealed the presence of iodine in the Spiro-OMeTAD layer suggesting ion migration to the hole transport layer, and possible cause for the decay in performance and degradation of devices. Although a very low short circuit current (J_{sc}) was observed at low light intensities (< 50 W/m²), a high open circuit potential build-up was observed, which resulted in high PCEs. This is in agreement with a “double-current” model of a mixed ionic-electronic material where the ionic component is dominant at low light intensities and the electronic component dictates at high irradiances. Our results highlight the exceptional stability of mixed MA/FA mesoscopic PSCs when operated for >1000 h under real outdoor conditions and the strong ionic component observed at low light irradiation.

1. Introduction

The application of organic-inorganic metal halide perovskite as a semiconducting pigment has stunned the thin film photovoltaic community. Perovskites shows strong light absorption, as well as generating electron and hole pairs under light illumination. From a mere 3.8% power conversion efficiency (PCE) reported by Miyasaka *et al.*, in 2009,^[1] currently certified PCE of 22% is reported.^[2] The ease of device fabrication in various architectures, such as planar, mesoscopic and inverted, has triggered its swift development. Scientist and technologist across the globe are working to increase its stability as well as PCE. Its high absorption coefficient up to 800 nm, makes it suitable also for tandem device configuration together with other thin film or silicon technologies. In spite of its PCE reaching 22.1%,^[2] its operational stability is of foremost concern. PSCs suffer from intrinsic and extrinsic degradation issues such as the effect of moisture, oxygen, UV light and temperature.^[3] The additives used as a dopant in the hole transport materials (HTM), also affect device lifetime.^[3] Furthermore, mobile ions are an important issue,^[4] ion defects are known to act as deep traps for charge carriers,^[5] while also modifying the perovskite crystal structure^[6, 7] or the iodization of the metal electrodes, especially in the case of scalable Ag cathode.^[8] Stability of the perovskite structure can be increased by identifying proper stoichiometry in a mixed perovskite environment. For example, methylammonium lead trihalide (MAPbX₃) perovskite shows phase instability at low temperature^[9] and is relatively more sensitive to temperature, moisture^[10] and light^[11] than the formamidinium cation thus resulting in the segregation of the halide component.^[11] More importantly formamidinium lead halide (FAPbX₃) perovskite, has a reduced band gap (1.47 eV), shows red shift in the absorption in comparison with MAPbX₃, (1.53 eV),^[12] but it is unstable at room temperature^[13] and sensitive to solvents and moisture.^[14] While in the case of inorganic CsPbX₃, higher annealing temperature, >300 °C, is required to make it photoactive, which is a high energy consuming process and trade off.^[15] The use of mixed perovskites along with a solvent engineering approach is identified as an

approach to overcome stability issues, and also allows the fabrication of state-of-the-art certified devices so far.^[14, 16-18] The use of mixed cations/halides in perovskites increases device stability by decreasing ion movement^[19] and strengthens the resistance to solvents and thermal stress.^[14, 17, 18] Other methods which have been adopted to increase the stability are the use of inverted-planar PSC configuration,^[20] or the use of novel barrier layers^[8, 21, 22]

Despite the tremendous advances in device optimization, long-term stability analyses under realistic conditions are still rare. Recently some of the reported studies were carried out following the ISOS-D protocol (storage in the dark)^[22, 23, 24, 25] or in the laboratory weathering conditions by varying temperature / humidity / light irradiation,^{[26],[27],[28],[29]} for a few hours only (<100 h), under artificial illumination using a mild LED as a light source.^[24, 29, 30] Li, *et al.*, performed outdoor stability analyses of MAPbI₃-based PSCs with PCE of c.a 13 %. The devices were kept outdoor for 168 h (7 days), and were probed only once a day at high light intensities.^[26] Other stability analyses performed by the authors, encompassed the ISOS-L-2 protocol^[31] (encapsulated sample, 80-85°C, 1 sun LED white light) for 2160 h (90 days). The device showed a final PCE of around 10%.^[26] Recently, Saliba, *et al.*, reported the application of 21.1 % efficient "triple cation" based (Cs/MA/FA) PSCs with good device lifetimes of 250 h under LED light illumination.^[16] Here, we report >1000 h stability studies under real outdoor conditions carried out with mixed MA/FA halide PSCs. The fabricated devices have a configuration of FTO/TiO₂/(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}/Spiro-OMeTAD/Au and showed good stability under outdoor conditions. Analysis of the PSCs response in different conditions suggests a strong ionic-electronic character of the perovskite material, with a large ionic component observed under low light irradiation.

2. Results and Discussion

Mesoporous TiO_2 and Spiro-OMeTAD were used as electron- and hole- selective contacts respectively (**Figure 1a**) and a perovskite layer was deposited using a one-step method utilizing solvent engineering approach. The average device photovoltaic performance was as follows: short-circuit density (J_{sc}) = 20.74 mA cm^{-2} , open-circuit voltage (V_{oc}) = 0.97 V, fill factor (FF) = 0.71 and the represented J - V curve is shown in **Figure 1**. The incident photon to electron conversion efficiencies (IPCE) of the devices were over 85% in the visible region (**Figure 1d**). The integrated J_{sc} values obtained from the IPCE spectrum (20.50 mA/cm^2) are in well agreement with the J - V curves (21.04 mA/cm^2) recorded at AM 1.5. **Figure 1b**, illustrates the cross sectional scanning electron microscopy (SEM) image of the device where the mesoporous TiO_2 thickness was limited to <150 nm infiltrated by perovskite and also forms a capping layer of around 400 nm, while the HTM thickness is of ~150 nm.

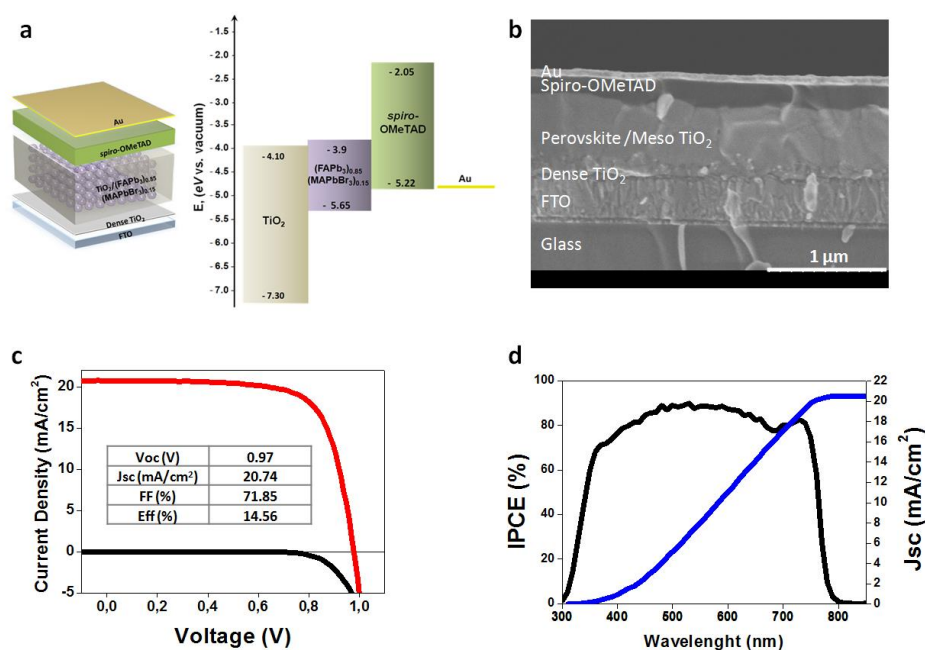


Figure. 1. a) Schematic representation and the energy level diagram for a mesoscopic perovskite solar cell. b) cross sectional SEM image of a representative cell. c) J - V curves for a representative cell under AM 1.5G illumination measured in reverse direction from V_{oc} to J_{sc} at a scan rate of 100 mV/s. d) IPCE spectrum of a typical device.

The devices showed an almost negligible degree of hysteresis (**Figure 2a-b**). A histogram of the devices (**Figure 2c-f**) points towards an average PCE of 14.5 %, though quite reproducible. It is to be noted that the histogram represented here correspond to individual devices (one solar cell per device), and not an array of solar cells in a single device. During our initial outdoor stability tests, it was found that the use of a UV filter and the nature of sealant are paramount to influence the device lifetime. During the initial 72 h outdoor testing of PSCs with and without UV filter (**Figure S1**), it was found that UV light was detrimental to the devices.^[25] The dimension of the devices was such that the sealant covered the active area and degradation of the PSCs components can also occur by the interaction with the sealant. We have observed that using the sealant 1 (Threbond), the devices could degrade easily and more abruptly after the first 300-500 h, representing a degradation in the color of the perovskite with time (it is to be noted, that this is complete color degradation and not changes from dark to yellow as reported due to perovskite degradation). The application of sealant 2 (Ossila) allowed us to obtain the results presented in this work for more than 1000 h. Nevertheless, no evidence of any interaction between the sealant and the PSC components was evaluated beyond the visual stability of the color with time.

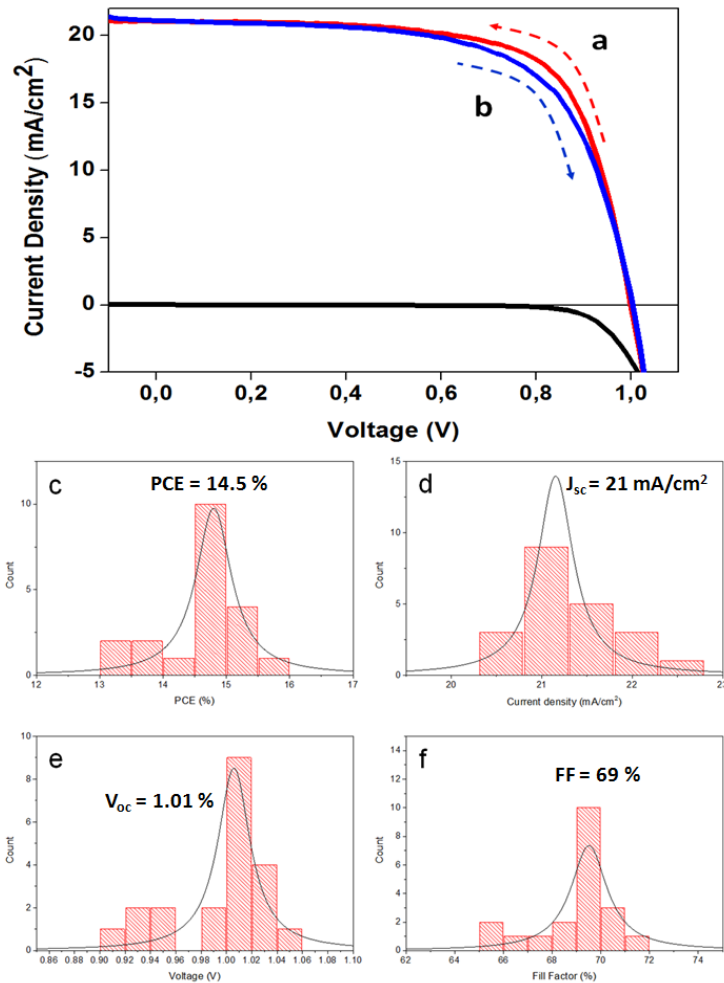


Figure 2. Representative example of the J - V curves of the champion cell, showing the hysteresis in our samples. a) Reverse mode, b) Forward mode. A histogram of our PSC samples. Efficiency of 21 devices indicating good performance reproducibility, with an average PCE of 14.5 %.

To analyze the long term performance of the PSCs we followed the ISOS-O-2 protocol:^[31] outdoor analyses under ambient temperature and ambient relative humidity (RH). The analyses took place from November 20, 2015 to January 27, 2016 at the ICN2 outdoor suntracker testing facility in Barcelona, Spain (41.30 °N, 2.09 °W).^[32] Outdoor stability analyses were made by measuring J - V curves *in-situ* under real outdoor conditions under sunlight irradiation and also during night. The J - V curves were recorded every 5 min, at a scan rate of 20 mV/s in a forward direction (J_{sc} - V_{oc}). Considering the outdoor season for the analyses (winter), the maximum outdoor temperature was always below 25 °C during daytime and above 3 °C at night, while light irradiation at 1000 W/m² was achieved around mid-day

(noon time). We discard any effect on device performance from relative humidity (RH) due to encapsulation and sealing. The photovoltaic parameters of the PSC analyzed samples are shown in **Table 1**. **Figure 3** shows the outdoor stability analysis for first 1000 h for one of the devices (Sample 5), with all the photovoltaic values plotted as a function of time. The photovoltaic response in **Figure 3** was obtained from the *J-V* curves made under light irradiances above 850 W/m². Initial PCE (11%) increased slightly during the initial ~500 h, after which a steady decrease to 8.5% PCE was observed at ~700 h. This drop in PCE can be due to changes in atmospheric condition (slight increase in light irradiation, or decrease in temperature, or the combination of these or other factors). Overall, outdoor analyses revealed very competitive long-term stability of the device with T₈₀ reached after 846 h of testing. At the end of the analysis at ~1080 h, the solar cell showed a stability corresponding to T₆₀, the highest ever reported outdoor stability for PSCs. The outdoor analyses of the PSCs were also very reproducible. **Figure S2** depicts the first 300 h of two other samples, demonstrating the reproducibility of the stability analysis for the PSC.

Table 1. Photovoltaic data of the mesoscopic Perovskite Solar Cells FTO/TiO₂d/TiO₂/FAPbI_{3(0.85)}MAPbBr_{3(0.15)}/Spiro-MeOTAD/Au. Active area = 0.36 cm². Stability analyses following ISOS-O-2 protocol.

Sample No	Voc (V)	J _{sc} (mA/cm ²)	FF (%)	Eff (%) HOME	Starting Date	Filter	Outdoor Time (h)
Batch 1							
7	1.02	18.9	55.5	10.5	21/11/15	UV Filter	300
11	1.04	18.62	61.64	11.94	21/11/15	UV Filter	502
13	1.05	19.92	63.2	13.2	20/11/15	No Filter	300
17	1.05	18.84	61.9	12.2	20/11/15	No Filter	300
18	1.03	19.97	57.9	11.38	20/11/15	No Filter	300
Batch2							
4	0.91	22.41	65.13	13.28	18/12/15	UV Filter	1008
5	0.92	22.64	66.14	13.4	18/12/15	UV Filter	1008
7	0.97	20.74	71.85	14.56	18/12/15	UV Filter	1008
20	0.94	22.17	65.48	13.71	18/12/15	UV Filter	1008
25	0.98	21.19	66.99	13.91	18/12/15	UV Filter	360
26	1.01	20.6	67.6	14.1	18/12/15	UV Filter	360

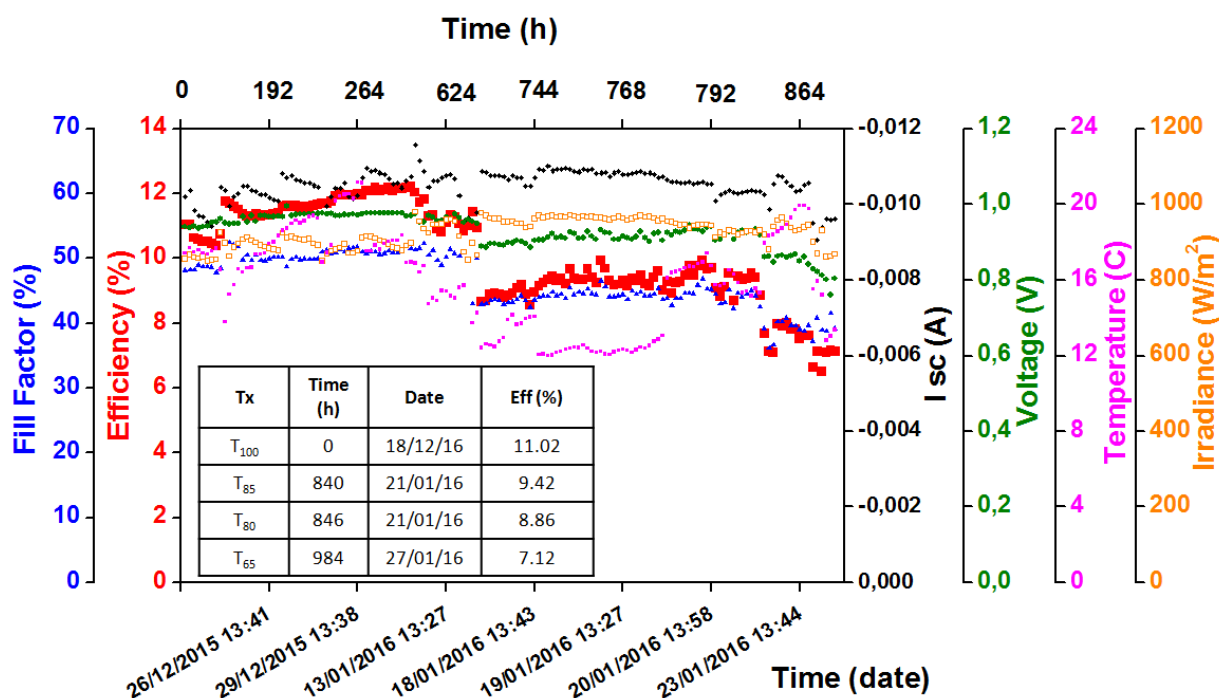


Figure. 3. 1000 h outdoor stability test following ISOS-O-2 protocol for mesoscopic perovskite solar cells of the type FTO/TiO₂-bl/TiO₂/Perovskites/Spiro-OMeTAD/Au. Values correspond to light intensity levels between 900W/m² and 1000 W/m². (■) Efficiency, (- -) Voc, (-) Irradiance, (-) FF, (-) Current, (*) Temp.

To elucidate the possible causes of performance degradation in the devices during analyses, we carried out scanning electron microscopy and energy dispersive spectroscopy analyses (SEM/EDAX) to identify the possible migration of ions during tests. Ion migration is of concern in organo-halide perovskites due to their ionic-electronic nature.^{[33],[34],[35],[36],[37],[38],[39],[4],[7]} Any of the constituting ions (i.e., I⁻, Pb²⁺ and MA⁺) may migrate in the examined MAPbI₃ films. Additional species resulting from material decomposition or contamination, such as H⁺ can also migrate. Taking the well-studied ABO₃ structure oxide perovskites as an analogy, I⁻ may be the migrating species in MAPbI₃, analogous to the O²⁻ ion conduction in the oxide perovskites or in simple binary oxides already reported for hybrid solar cells.^[40] Yuan *et al.*^[6] evidenced that both the MA⁺ and I⁻ migrate in the MAPbI₃ films at relative small fields while the Pb²⁺ remains immobile within the resolution of the EDX equipment. In a MAPbI₃ structure, the I⁻ ions on the edge of the

PbI_6^{4-} octahedron have a shorter distance with the nearest Γ vacancy ($\sim 4.46 \text{ \AA}$) than MA^+ and Pb^{2+} ions ($\sim 6.28 \text{ \AA}$). Therefore it is reasonable to speculate that Γ ions are the most likely mobile ions in the $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ perovskite and the possible cause of device degradation. Thus, SEM/EDAX analyses were carried out to PSCs devices after stability tests at T_{50} and T_{100} (**Figure 4**). For all analyzed samples, we observed the deterioration in the microstructure of the perovskite layer, and the presence of iodine (I) in the hole transport layer i.e. Spiro-OMeTAD. These observations are an indication of ion migration during device stability analyses, in well agreement with the ionic-electronic nature of the halide perovskites. This can also be one of the different possible causes of the slight device decay observed with time.

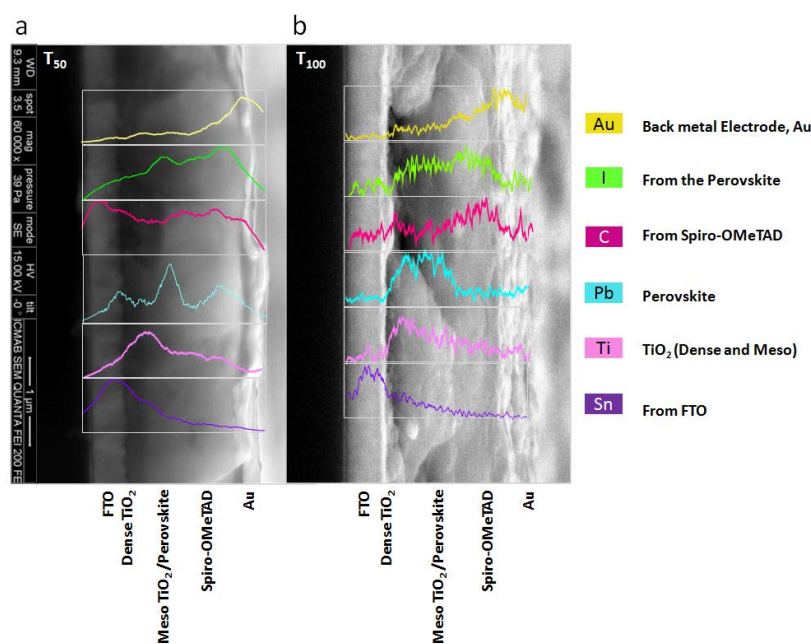


Figure 4. Ion migration after outdoor stability analyses. SEM/EDAX Analyses of two solar different PSC analyzed after reaching T_{50} (a) and T_{100} (b) outdoor analyses. In both cases, the presence of Iodine is observed at the Spiro-OMeTAD hole transport layer, an indication of ion migration and one of the possible causes of device failure.

To study the PSCs response under different outdoor conditions, single-day analyses of a PSC (sample 5) on different days are presented in **Figure 5**. The outdoor analysis of the devices is represented for three different days: during a sunny day (**Figure 5a**, irradiation up to ~ 800

W/m²); in a cloudy day (**Figure 5b**, irradiation up to ~50 W/m²) and in a mixed sunny/cloudy day (**Figure 5c**, irradiation between ~50 W/m² and ~650 W/m²). These days are the first 3 days of the outdoor testing for a single sampl. During all the analyzed days, the photovoltaic response of the device was characterized by large V_{oc} values at very low light irradiation. The response was observed during early morning hours (8:00 h - 9:00 h), or during late afternoon and in the evening (after 17:00 h), when sunlight shines on the device at very low light intensities (<50 W/m²). For **Figure 5b** (cloudy day) where light irradiation was very low for the whole day, high V_{oc} values were observed almost constant around 0.8 V for the entire day. Despite the unexpected large voltage values, the J_{sc} shows very low current density values, following the linear response with the light intensity. Consequently, the corresponding PCE increases up to 14 % with FF around 60 %. Analyzing the device response in outdoor condition at higher light irradiation, above 600 W/m², the device PCE was lower, around ~11 % (**Figure 5a** or **Figure 5c**), with a slight increase in V_{oc} up to 0.95 V. To mimic this, we have also measured PSC in a laboratory conditions, under variable light intensity. Similar observation as of outdoor condition was observed showing linear response of J_{sc} while V_{oc} was slightly lower at low light intensities if compared to higher irradiances. At very low irradiances the V_{oc} is already 0.8 V (**Figure 6**) in agreement with outdoor analyses.

Thus, in general, we observe two photovoltaic regimes, one at low light intensities where the PCE is about 14% and V_{oc} is about 0.78 V; and a second regimen at high light intensities where the PCE is around 11 % and the V_{oc} value was 0.95 V. This effect is reproducible and observed in all analyzed PSCs devices, independently of the use of with/without UV filter (**Figure S2**). We have also found that the effect is observable only during the initial days of the outdoor stability test, and gradually disappears after several days (**Figure S2**).

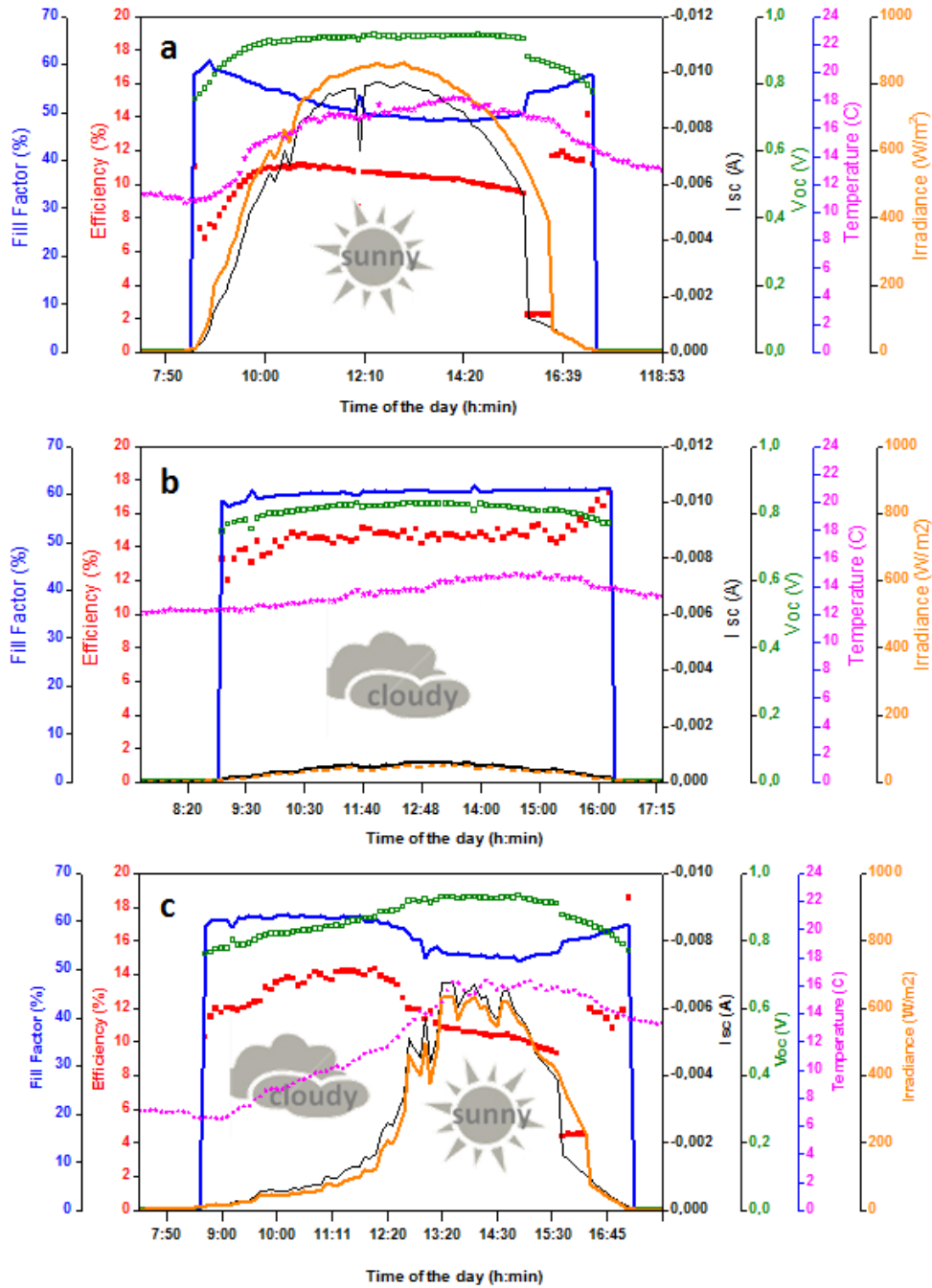


Figure 5. Single-day outdoor analysis of PSC carried out in Barcelona (Spain) during a (a) high irradiation day between 0 and 850W/m², (b) low irradiation day between 0 and 50 W/m² and a day with mixed irradiation levels (c). (■) Efficiency, (- -) Voc, (-) Irradiance, (-) FF, (-) Current, (*) Temp.

To investigate this response, a modeling scheme was made taking into account several properties of organo-halide perovskites: their exceptional ionic-electronic conductivity,^[4, 7, 17, 33-37, 39, 41, 42] and their ion-migration, a phenomena linked to the hysteresis response^[33, 42] observed in *J-V* curves.^{[39],[4],[7]} Other characteristics linked to ion movement are giant

switchable photovoltaic properties,^[35] field-effect mobility enhancement due to ion freeze out^[43] and/or an apparent giant static dielectric constant.^[44] The smaller activation energy of iodide has been verified by using ab-initio simulations by Eames *et al.*^[5] and Azpiroz *et al.*^[45] Dong *et al.*,^[46] also describe the effect of diffusion lengths and device performance (long diffusion length means less recombination) in CH₃NH₃PbI₃ single crystals exceeding 175 μm under 1 sun (100 mW cm⁻²) illumination, and 3 mm under weak light for both electrons and holes. Thus, we constructed a "double-current" model in order to understand and reproduce these results (**Figure 7**). To determine the parameters of the model, the main PV properties of the film have been presented as a function of the irradiance, i.e., V_{oc} , J_{sc} , FF and Eff vs I_c (**Figure S4** and **S5**). We have observed that the dependence of the electronic component of the PV current dependence on the irradiance is linear with a PV coefficient of 0.22 A/W. We assume that this is the most important contribution under normal circumstances after the initial burn-out. The open circuit voltage also depends on the irradiance but in this case on a logarithmic basis. The higher the irradiance the higher the V_{oc} will be, for both the ionic and electronic contribution. V_{oc} build up from dark condition to 1 Sun. It was observed that the FF significantly decreases (linearly vs I) for moderate irradiances (i.e. ~100 W/m²) and therefore for the electronic component.

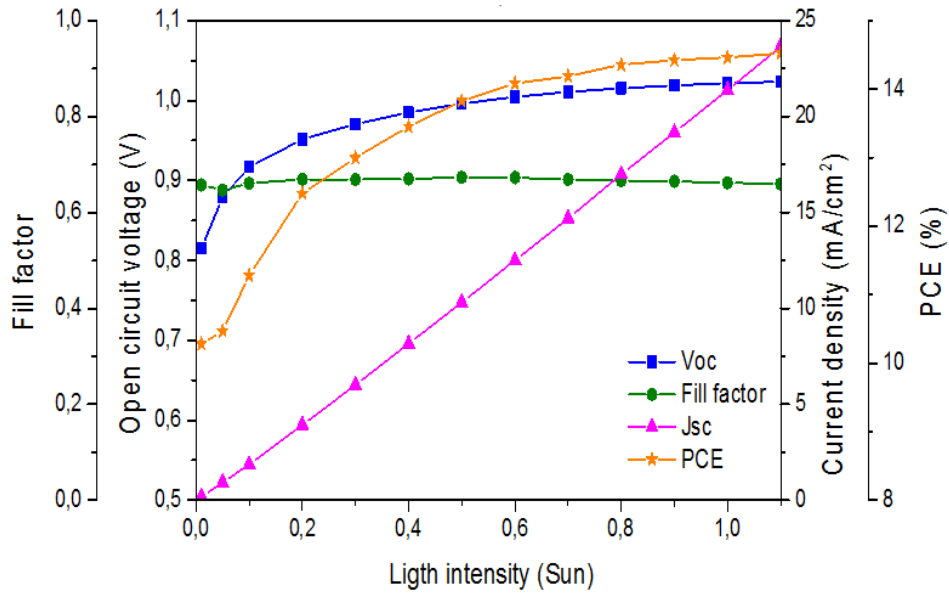


Figure 6. Photovoltaic parameters of a representative device as a function of light irradiation.

Our model replicates the observed PSC response and attributes it to the mixed ionic-electronic behavior that characterizes the halide perovskite material, which is known for migration of one or several ionic species (I^- , MA^+ or Pb^{2+}). These ionic defects in perovskites are known to drift under internal electric field producing accumulation of charges.^{[6],[47]} This charge accumulation mechanism can also take place under dark conditions.^[48] In our samples, the PSCs were analyzed by *I-V* curves made at 20 mV/s every 5 minutes both during daylight but also in dark conditions at night (under temperatures between 3°C and 8°C). Thus, the accumulation of charges can take place during the entire night, and upon illumination, large photovoltages and capacitances are observed.^[49] The response is associated with the accumulation zone at the electron^[48-50] or hole^[51] extraction interfaces. This mechanism is in accordance with the observed high V_{oc} response of PSCs under low light irradiation and indicates the huge effect that the experimental history of the devices can have on the response under light irradiation. Moreover, this "pretreatment" in the dark can also be behind the extraordinary long-term stability observed for our devices, since a self-healing and recovery effect can also occur in PSCs when treated in the dark at low temperatures.^[52]

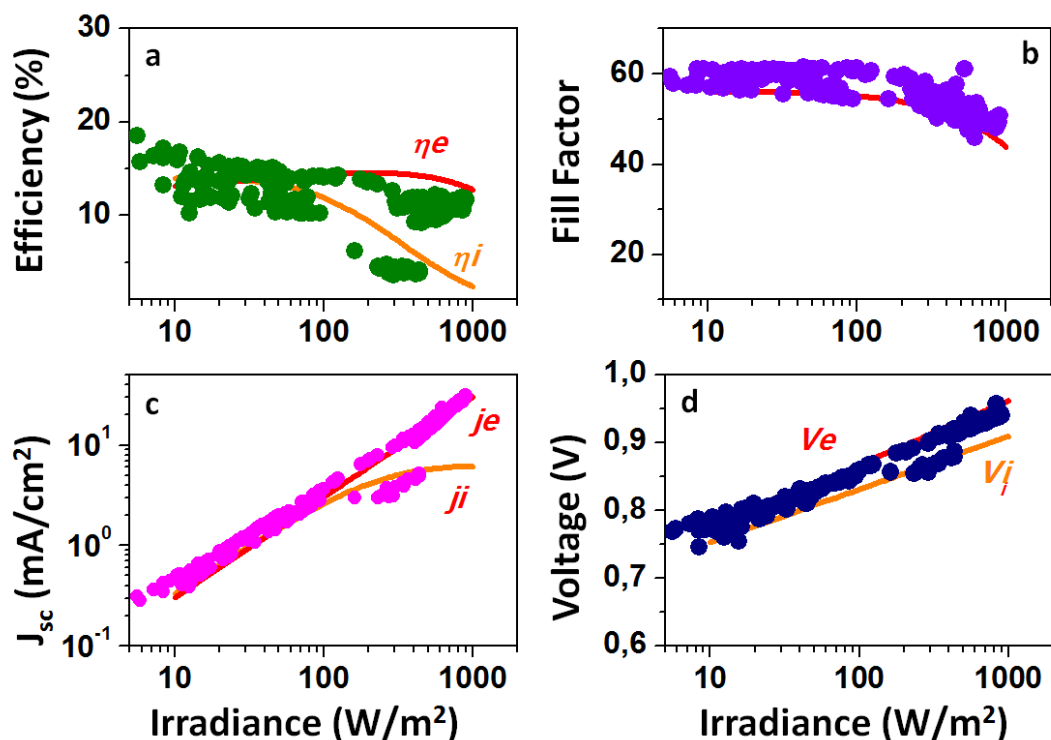


Figure 7. Dependence of the main solar cell parameters as a function of the irradiance; (a) power conversion efficiency (μ), (b) fill factor, (c) short-circuit current (j) and (d) open-circuit voltage (V) vs irradiance (in the range $1-10^3$ W/m^2). Dots are experimental data (outdoor operation during several days) and solid lines are the model prediction (see supplemental). Sub-indexes e and i refers to the electronic and ionic components respectively.

4. Conclusions

To conclude, we have demonstrated >1000 h outdoor stability of mixed halide perovskite solar cells in the configuration $\text{FTO}/\text{TiO}_2/(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}/\text{Spiro-OMeTAD}/\text{Au}$. The PSCs maintained 80 % of the initial photovoltaic properties after 846 h of continuous real atmospheric analyses. High open circuit voltage was obtained at very low light irradiation, a response attributed to the ionic-electronic properties that characterize halide perovskites. A "double current model" made to reproduce the real outdoor operation conditions of the devices, demonstrated that the ionic component dominates at low intensities, but is annihilated at high irradiances where the electronic component is dominant. The response is affected by the "pretreatment" of the PSCs in the dark (during the night), where charge

accumulation triggers the formation of high V_{oc} values once the sample is irradiated at low light intensities, demonstrating the importance of device pretreatment and the history of the device. Our results represents real world stability of PSCs for >1000 h for the first time. The extraordinary effect of ion migration observed at low irradiation can contribute to the understanding of the working mechanisms of perovskite solar cells under real conditions and will encourage the perovskite solar cells community to fabricate more stable and efficient devices.

4. Experimental Section

Materials. FAI, MABr were bought from Dyesol and PbI_2 , and $PbBr_2$ were bought from Sigma-Aldrich. Chlorobenzene, Anhydrous DMF and DMSO were obtained from Sigma – Aldrich. Sealants such as UV curing Resin 3035B (sealant 1) obtained from Three Bond Europe SAS. The product contains isobornyl Acrylate, Acrylic Acid, 3-(trimethoxysilyl)propyl ester. Sealant 2 was brought from Ossila, Encapsulation Epoxy E131. It contains proprietary substances called epoxy resin 96%, photoinitiators >3%, photostabilisers>3%, with a curing wavelength of up to 600nm.

Solar Cells Fabrication Procedure. TEC15 Ω /sq was used as substrate and was cleaned by ultrasonication in 2% Hellmanex water solution for 30 min. followed by rinsing with deionized water and ethanol. Then, ~40nm TiO_2 compact layer was deposited on FTO substrate via spray pyrolysis at 450 °C from a precursor solution of titanium diisopropoxide bis-(acetylacetonate) in anhydrous ethanol. After the spraying, the substrates were left at 450 °C for 45 min and allowed to cool down till room temperature. Mesoporous layer was deposited using spin coating for 30 s at 4000 rpm, using 30 nm particle paste (Dyesol 30 NR-D) diluted in ethanol (1:5) to achieve 150–200 nm thick layer. After the spin coating, the substrates were dried at 100 °C for 10 min and then sintered again at 450 °C for 30 min under dry air flow. After cooling down to 150 °C, the substrates were transferred to a atmospheric

glovebox for depositing the perovskite films. The perovskite films were deposited from a precursor solution containing FAI (1 M), PbI_2 (1.2 M), MABr (0.2 M), and PbBr_2 (0.2 M) in anhydrous DMF:DMSO 4:1 (v:v). The perovskite solution was spin coated in a two-step program at 1000 and 4000 rpm for 10 and 30 s, respectively. During the second step, 100 μL of chlorobenzene was used as an antisolvent and poured on the substrate 15 s prior the end of the program. The substrates were then annealed at 100 °C for 1 h in a glovebox. Followed by the perovskite annealing and cooling, the hole transport layer was deposited using Spiro-OMeTAD (70 mM in chlorobenzene) was spun coated at 4000 rpm for 30 s. Spiro-OMeTAD was doped with bis- (trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, from Aldrich), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III)-tris(bis- (trifluoromethylsulfonyl)imide) (FK209, from Dynamo), and 4-tert-Butylpyridine (t-BP, from Aldrich). The molar ratio of additives for HTMs was: 0.5, 0.03, and 3.3 for Li-TFSI, FK209, and t-BP, respectively. To finish the devices, 70–80 nm of gold was thermally evaporated under low vacuum (10^{-5} - 10^{-6}) as cathode.

Characterization. Characterization of devices were carried out following best practices for PSC^[53] and ISOS-protocols.^[31]

Indoor PV characterization. Current density–voltage (J – V) curves were recorded with a Keithley 2400 source-measurement-unit under AM 1.5 G, 100 mW cm^2 illumination from a certified Class AAA, 450 W solar simulator (ORIEL, 94023 A). Light output power was calibrated using a NREL certified calibrated mono-crystalline silicon solar cell. A black metal mask (0.16 cm^2) was used over the square solar cell active area (0.5 cm^2) to reduce the influence of scattered light. The scan rate and the active area used for measuring the devices were optimized as such to calculate the real value for efficiencies without having hysteresis effect. (Active area: 0.16 cm^2 , Scan rate: 10 mV/s, Pre sweep delay: 30s). The IPCE measurements were performed using a Newport 150 W xenon lamp coupled to an Oriel Cornerstone 260 motorized $\frac{1}{4}$ m monochromator as the light source, and a 2936-R power

meter to measure the short circuit current. The cross-sectional SEM image of mixed cation perovskite was captured to see the different layer thickness and interfaces using a Hitachi S5200 field-emission microscope operating at 5.0 keV.

Outdoor Stability Analyses. The outdoor stability analyses were carried out following the ISOS-1 procedures⁶³ at the Catalan Institute of Nanoscience and Nanotechnology (ICN2-CSIC), located in Barcelona, Spain (41.30 °N, 2.09 °W), using a home-made solar tracking positioning system. The system comprises a large dual axis-controlled platform with fully automated motors, which enables turning of the tracker hour angle up to 100° (which translates to nearly 7 hours of perpendicular solar tracking) and turning of the tracker elevation angle from 15° to 90° (which enables full tracking of solar elevation). We developed in-house software to control the photovoltaic response of sixteen solar cells at the same time and to continuously monitor light irradiation, temperature and relative humidity over time. I-V curves were measured using a 2602A dual-channel SMU multimeter and a 3700 series switch/ multimeter (both from Keithley). PCE values were calculated using the maximum daily irradiance level. The light irradiation was measured with a Zipp&Konen CM-4 pyranometer. The temperature and relative humidity were monitored with a combined sensor (Theodor Friedrichs). The voltage scan rate was 20 mV s⁻¹, and no device preconditioning (such as light soaking or similar) was applied before starting the measurement. The starting voltage was -0.1 V in forward bias, no equilibration time was used. The devices were analyzed by measuring I-V curves every 5 min during the 24h of the day (day and night). For the stability results irradiance values above 900 W/m were used, for single-day analyses all data points collected during a 24 h period were used.

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