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Interfacial dynamics and contact passivation in perovskite solar cells

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Charge accumulation at the electron and hole transport layers generates anomalous electrical behaviour in perovskite solar cells (PSCs). Hysteresis in the current-voltage characteristic and recombination at the interfaces are the clearest manifestations of this phenomenon, which compromises device performance and stability. Here, we investigate the underlying charge-carrier dynamics of a variety of PSCs by analysing their transient photocurrent response.

Towards shorter time scales, PSCs often show increasingly severe hysteretic responses. This phenomenon is correlated with the presence of interfacial accumulated charges that hinders the photo-generated carrier extraction process. However, introducing passivating contacts improves the carrier-injection properties and the devices become completely hysteresis free. These results underline the importance of contact passivation for PSCs and the need to further develop new

passivating interlayers that simultaneously eliminate charge-carrier recombination and provide selective transport for each carrier type at the PSC's contacts.

1. Introduction

Perovskite solar cells (PSCs) have seen their power conversion efficiency (PCEs) increase from ~4% to ~23% in less than a decade.^[1] This unprecedented surge in device performance is a testament of the extent to which PSCs upended the scientific knowledge of solution-processed photovoltaic devices. This remarkable success can largely be ascribed to a steadily improved device design, combined with optimization of the employed materials: from the first mesostructured configuration^[2] – a legacy of the evolution of PSCs from the work on dye-sensitized solar cells^[3] – to the planar thin-film design;^[4] and from the early methyl-ammonium lead iodide perovskite,^[5] to the quadruple-cation mixed-halide perovskite.^[6] However, despite excellent optoelectronic properties such as a sharp onset of its absorption coefficient combined with long free-carrier diffusion lengths,^[7] several challenges currently hinder further progress of PSCs. The presence of interfacial trap states or interfacial barriers is a particular roadblock,^[8] which compromises the open circuit voltage (V_{oc}), the PCE, and ultimately generates undesired effects such as hysteresis in current/voltage curves. Although several hysteresis-free PSCs have now been reported,^[6, 9] the underlying origin of hysteresis and its suppression is still heavily debated. The most accredited interpretations of its origin are linked either to recombination of photo-generated charge carriers at the contact interfaces,^[10] or to the presence of mobile ions inside the perovskite absorber.^[11] Such ions, which can be either positively or negatively charged,^[12] result from the presence of intrinsic defects, formed during the perovskite crystallization process.^[13] Under the influence of an electric field, these ions may then migrate

through the perovskite to accumulate either at the electron- or hole-transport layers (ETLs and HTLs), resulting in a net accumulation of charge at the contact interfaces.^[14] Several reports suggest that this migration is based on vacancy-assisted hopping, where positive and negative ions drift through their respective vacancies; recently, interstitial migration has also been proposed.^[15] Whereas several reports describe the phenomenology of such ion migration in perovskites,^[16] a consistent analysis of their role and influence on the operational mechanisms of PSCs has only partially been explored.

In this article, we elucidate the consequences of charge accumulation and recombination induced by ion displacement on the working mechanism of PSCs in a microseconds-to-seconds time window. Using transient photocurrent (TPC) measurements and device simulations, we assess the response of PSCs in short-circuit and working conditions. We find that the accumulation of interfacial charge can generate early reverse photocurrents, decrease the V_{oc} , and hamper the overall performance of the device. Finally we demonstrate that such charge accumulation is the result of two processes with different dynamics. The first process is due to ion migration on a milliseconds-to-seconds time scale. The second process is much faster and relates to charge-carrier recombination at the perovskite/transport-layer interface. In particular, we demonstrate that the presence of a passivating interlayer, inserted between the perovskite and the electron contact, can dramatically change the photocurrent dynamics in the microseconds range. This device implementation results in the suppression of the hysteretic response, combined with an improvement of V_{oc} from 1100 mV to 1175 mV, leading to a PCE increase from 18.1 % to 20.1%.

2. Results and discussion

To investigate the working dynamics of PSCs we focused on devices fabricated in the *n-i-p* configuration.^[4] For this, a compact layer of titanium dioxide (*c*-TiO₂, ~80 nm), covered by a mesoporous scaffold of TiO₂ (*m*-TiO₂, ~150 nm) was used as the ETL. For passivating-contact devices, this stack was then capped by a polymer-fullerene based layer.^[17] On this contact stack, a mixed-cation (caesium, rubidium, methyl ammonium, and formamidinium) mixed-halide perovskite Cs_{0.07}Rb_{0.03}FA_{0.765}MA_{0.135}PbI_{2.55}Br_{0.45} was then deposited as the photovoltaic absorber; the combined thickness of the *m*-TiO₂ and the perovskite absorber is ~500 nm. Finally, spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenyl-amino)-9,9'-spirobifluorene) was employed as HTL, covered by gold electrodes. More details on the device fabrication can be found in the experimental section. **Figure 1a** shows a cross-sectional scanning electron microscopy (SEM) micrograph of the device, including the schematic of the structural layers. Figure 1b gives the current-voltage characteristics of a representative device using the described structure, featuring reduced hysteresis, compared to flat-junction PSCs, thanks to the presence of the mesoporous scaffold.^[17] The averaged photovoltaic parameters of our reference device are: short circuit current (J_{sc}) 22.9 mA/cm², V_{oc} 1100 mV, fill factor (FF) 71.5%, resulting in an overall PCE of 18.1% with a hysteresis factor (defined as $1 - [PCE_{forward_scan} / PCE_{reverse_scan}] \times 100$) of 9%.

In PSCs, ions from the perovskite absorber accumulate at the interface between the perovskite and charge-transport layers, due to the presence of built-in electric fields and/or an externally applied voltage bias.^[11a, 16b] This induces an inhomogeneous distribution of electric charge.^{[8d, 11a-c], [18]} To address how this influences the operating mechanism of PSCs under different conditions, we divide the discussion between short-circuit and forward bias, below the V_{oc} . The final section of this paper discusses the beneficial role of contact passivation in PSCs.

2.1. Short-Circuit Condition

In short circuit $V_{\text{bias}} = 0\text{V}$, which corresponds to equal Fermi-level positions at both contacts. Generally, when exposing a short-circuited solar cell to light, photo-generated carriers are extracted as a negative photocurrent. In the “ideal PSC”, all the ionic species present in the perovskite are homogeneously distributed and immobile, rendering the material essentially intrinsic. However, more realistic PSCs feature mobile ions. In this case, once the ions reach their equilibrium positions (*i.e.* when they stop migrating), the energy band diagram in short-circuit condition deviates from the “ideal” *n-i-p* band structure, and features a three-zone profile, labelled I, II, and III, see Figure 1c bottom. These zones recall the *drift* (I and III) and *diffusive* (II) transport regions of a silicon homojunction solar cell.^[18-19] In particular, the II region is characterized by a near-constant electrical potential profile, and can thus be considered as a quasi-neutral region. In essence, the creation of such a quasi-neutral region is a consequence of the narrowing of the lateral regions induced at the extraction layers. In turn, this narrowing is a consequence of the fact that the perovskite becomes effectively heavily doped at its contacts due to the accumulation of ions. Such heavily ‘doped’ surfaces resemble contact formation of silicon homojunction solar cells.

Carriers that are photo-generated in a quasi-neutral region can only be collected through diffusion (no electrical field is present to sweep them to the contacts). Consequently, *if* the carrier diffusion length $L_D < W_{\text{II}}$, the J_{sc} will mainly consist of contributions from the region I (ETL-transparent contact) and III (HTL-back contact), with most of its value coming from the light-incident side (region I). However, for our devices it is unlikely that the J_{sc} value of $\sim 23\text{ mA/cm}^2$ shown in the J-V curve of Figure 1b consists solely from the contribution of regions I

and III. This result suggests a sufficiently high L_D/W_{II} ratio in our devices,^[7b] thanks to limited bulk recombination in the quasi-neutral region.

To gain further insight into the mechanism underlying the current collection in PSCs we applied the transient photocurrent (TPC) technique to our devices. In TPC measurements, devices held in the dark are subjected to a white-LED light square pulse, tracking the subsequent transient current response. Various light intensities, pulse durations, and bias-voltage ranges can be used to investigate the role of the internal field and the carrier density respectively, free of the influence of any preconditioning typical of J-V curves. **Figure S1** shows the time sequence of the TPC experiment used to investigate the photocurrent response. The light intensity can be varied from 0.1 to 1 sun. The voltage bias can be varied from 0 (short circuit condition) to 1.1 V (close to the open circuit condition, see later). In recent works, TPC measurements were successfully applied to investigate charge dynamics and space-charge effects in organic, hybrid, and perovskite cells.^[18, 20] Figure 1d shows the rise in J_{sc} , following a 1-sun equivalent light pulse. We note that less than 2 s are required to reach the steady-state J_{sc} value. However, when zooming-in on the microseconds transient (see inset of Figure 1d), we find that this rise in the absolute value of the J_{sc} is not monotonic: after an initial steep increase of a few microseconds, the absolute value of the J_{sc} briefly *decreases* prior to a monotonic increase in the millisecond regime. This sharp local maximum was observed by Tress *et al.* in organic flat junction solar cells, and explained as complications in the extraction of photocarriers.^[21] In particular, a quick extraction of a electrons (holes) can generate a displacement current that piles-up holes (electrons) at the opposite transport layer, causing an over-shoot of current. In perovskites this phenomenon can be induced either by the presence of potential barriers (generated by accumulated ions), or by defect-assisted traps states.^[12b, 18, 22] To elucidate this effect, we

repeated the TPC study under different light intensities, from 0.1 to 1 sun with 100 μ s square light pulses (see **Figure S2**). Notably, the extent of the sharp local maximum is proportional to the irradiation intensity, as noted by Tress *et al.*, which supports the hypothesis of barriers in the extraction process. Similarly, the decay of the photocurrent depends on the light intensity, with longer decays for higher intensities. For reference, we compare the transient current of Figure 1c with the transient short-circuit photocurrent from a silicon homojunction solar cell (**Figure S3**). Because the dopants at the silicon contacts are immobile, and consequently the recombination and resistivity parameters that define the contacts are bias independent, the silicon homojunction solar cell's characteristics may give insight into the expected behaviour of the “ideal” PSC.^[19] We find that the TPC response of the silicon homojunction device features a sharp monotonic response when the light pulse is switched on, with a near instantaneous rise of the photocurrent to its short-circuit value.

2.2. Forward bias-below V_{oc}

To finalize our discussion on PSCs *without* contact passivation, we consider the influence of a positive voltage bias, below the open-circuit condition (**Scheme 1**). Here, in general, when a forward (i.e. *positive*) bias is applied to a solar cell (represented in the diagram by +0.6 V, green arrow), the photocurrent preserves the same *negative* direction of the J_{sc} , but decreases in magnitude due to the reduced slope of potential. By applying such a forward bias to a PSC that has charges accumulated at its ETL and HTL interfaces, the band structure changes from the dashed to the solid red lines in Scheme 1. As consequence, a reverse, *positive* current is now expected within region II. Again, the total extracted current (J_{tot}) results from the contribution of the currents generated in the three regions (J_I , J_{II} , J_{III} respectively). Thus, the sign of J_{tot} is dictated by the relative contributions of $J_{I,III}$ and J_{II} . If $J_{I,III} > J_{II}$, then J_{tot} is negative; if $J_{I,III} < J_{II}$, then J_{tot} is

positive. To confirm this mechanism, **Figure 2a** gives the TPC response recorded during a 2 s light pulse with a forward bias of 0.6 V. To emphasize the initial microsecond-scale region, we plot the transient response in a logarithmic time scale. Initially, a positive current rises until 10 μ s from the beginning of the light pulse (see inset in Figure 2a); after this point the positive current constantly decreases, and after $\sim$ 50 ms switches to negative values. Even after 2 s, the magnitude of the negative current is still increasing towards the values of the current obtained from the J-V curve of Figure 1b (comparative TPC experiments on a homojunction silicon reference cell, with an applied bias of +0.4V together with perovskite solar cells, are reported in **Figure S4**).

To gain further insight into this mechanism, we tested the J-V response from slow (0.1 V/s) to very fast (20000 V/s) scan rates (Figure 2b), where we find that the photocurrent response is strongly influenced by a high voltage scan rate.^[8c] Three observations can be made from Figure 2b. Firstly, the J_{sc} value is higher for slower scan rates. This is in agreement with the transient response of the J_{sc} discussed above. Despite this, the stabilization time of the J_{sc} in Figure 2b does not match the TPC transient of Figure 1d. This apparent discrepancy can be accounted for when considering the voltage-sweep direction used to record the J-V curve. In Figure 2b the voltage bias is swept in the reverse direction (*i.e.* from positive to negative values). This means that the short-circuit condition, which is reached at the end of such a voltage sweep, has been subject to a preconditioning process that involves all the preceding steps of voltage biasing. This phenomenon becomes irrelevant on a seconds time scale, where the hysteretic variation becomes smaller. However, in the micro-to-millisecond time scale it does affect the electrical properties of the devices and suggests a different time scale of the dynamics of the hysteresis, indicative of the multi-causal nature of the processes that define the extent of hysteresis in PSCs. Secondly, the

V_{oc} is higher for slower scan rates. Interestingly, this phenomenon is connected with the inversion time of the current, *i.e.* when the current changes from positive to negative direction. At the inversion time the $J_{tot}=0$ mA/cm², and the electric field along region II is compensated by that of region I and III. For the transient in Figure 2b (at +0.6 V) the inversion time is reached in 100 ms. However, the inversion time depends on the voltage applied as shown in Figure 2c which reports the inversion time obtained from a sequence of TPC measurements with voltage bias ranging from 0.3 to 1 V (we remand to **Figure S5** for the experimental setup, the TPC measurements and the extracted J/V curves). This phenomenon is linked to the integration time of the voltage points during the J/V curve. Indeed, if the integration time is shorter than the inversion time for the same specific forward bias, the corresponding current results positive and the V_{oc} “appears” at lower biases. To clarify this, Figure 2d reports the variation in the bands diagram when a bias of +0.6 V is applied (for sake of clarity only the CB is represented). In the very first microseconds, at a given positive voltage bias, J_{tot} is dominated by the contribution of J_{II} , resulting in a positive photocurrent. The electric field present in region II separates photo-generated carriers, sweeping holes closer to the ETL side of the devices, where negative ions were initially accumulated (similarly, electrons are swept to the HTL side of the devices, where positive ions were initially accumulated, see Scheme 1). After a certain time, the charge redistribution reaches the $J_{tot} = 0$ mA/cm² condition (*i.e.* $J_{I, III} = -J_{II}$), due either to the accumulation of free carriers in the potential valleys, or to a redistribution of the accumulated ionic charges along the device due to the variation of the electric field. Afterward, the negative values of J_{tot} denote the inversion of the band diagram and the stabilization of the standard characteristics of device.

The third observation relates to the presence of a plateauing step of constant photocurrent in the early microseconds range, independent of the applied voltage. This feature was not observed by Tress *et al.* at fast scan rate (100 V/s), but was reported by Belisle *et al.* by investigating the perovskite at even faster dynamics.^[8c, 18] According to Belisle *et al.* ^[18], this plateauing steps begins at biases where the photocurrent has maximum internal quantum efficiency. At higher biases, charges (both ionic and electronic) accumulate at the interface and screen the potential, therefore the photocurrent remains constant.^[18]

2.3. Role of passivating layers

We now shift our attention to the effect of contact passivation in PSCs and its relation to hysteresis. Recently, Peng *et al.* reported on the beneficial effects of passivating the *m*-TiO₂/perovskite interface with a polymer-fullerene interlayer (polymethylmethacrylate: phenyl-C61-butyric acid methyl ester, PMMA-PCBM respectively), inserted between the *m*-TiO₂ and perovskite.^[17] We tested the properties of such passivating-contact devices and compared them with those of non-passivated devices (labelled here as *pristine* device; **Figure S6** shows a histogram with the statistics of the results). The results clearly indicate enhanced performance for the passivated devices, including a suppression of the hysteresis. A representative J-V characteristic of a contact-passivated device is given in **Figure 3a**. The average short-circuit current is 22.9 mA/cm², V_{oc} of 1175 mV, 74.9 % FF and an overall PCE of 20.1% with a hysteresis factor of 0.9%. The stabilized PCE over 30 min is reported in **Figure S7**. To gain further insight into the observed hysteresis “quenching” we investigated the current dynamics by varying the voltage scan rate from slow (0.1 V/s) to extremely fast (20000 V/s) scan rates (Figure 3b), similar to Figure 2b. The current response of the passivated device differs markedly from that of its pristine counterpart. The major discrepancy is the absence of the plateau region

of positive current in the investigated range of voltages and scan rates and the presence of a higher V_{oc} , in particular at fast scan rates. **Table S1** reports the figures of merit for the pristine and passivated device at different scan rate. These two observations are evident by observing the TPCs measurements at different voltage biases (ranging from 0 to 1 V) over a 2s light pulse for the pristine (red) and passivated (blue) devices (Figure 3c). The pristine device shows the aforementioned behaviour, with positive photocurrents starting from +0.4 V biases. Then, in a time range from a few milliseconds to a half-second, depending on the bias applied, this photocurrent inverts its direction from positive to negative values, in agreement with the stationary J-V characteristic and with the inversion time. The passivating-contact device still features similar positive photocurrents from +0.4 V upward, proving that inversion of the current still happens. However, the inversion time is now three orders of magnitude shorter compared to the pristine case, as highlighted in the magnified view, shown in Figure 3d. From this, we conclude that the passivation layer does not affect the bulk of the perovskite, whose defects depend more on the crystallization process. Its effect must rather be sought in an interaction with the electrical charge accumulated at the interface with the transporting layers, responsible for the bands distortion. Indeed, the passivated device presents a shorter inversion time, absence of current overshoot at short circuit (see Figure 3d and **Figure S8**), and absence of the plateau current in the investigated range of voltages. We argue that these phenomena evidence a redistribution of the electronic charges which reduces the extraction barrier at the interfaces. Eventually, this results in a more selective passivated contact.

2.4. Numerical simulation

To extend our understanding on the ion migration and interface recombination, as well as the role of the passivating layer, we use a recently developed numerical semiconductor drift-diffusion model incorporating mobile ions.^[23] We simulate the transient photocurrent from a *n-i-p* PSCs with a population of mobile ions initially at equilibrium in the dark at short circuit, which is then subject to instantaneous illumination at a forward bias of 0.6 V. We based our calculation on the hypothesis that the mobile ion is a cation,^[24] but note that there is no conclusive evidence yet about the species of mobile ion in the quadruple cation mixture used in this work (or if there may be *multiple* mobile-ion populations). To test the role of the passivated interface we simulated a device in which trap-mediated recombination is limited to the perovskite/transport-layer interfaces. The simulation parameters are tabulated in the Supplementary Information, while full details of the model are provided elsewhere.^[23a] The simulation confirms that in equilibrium, the ion population will accumulate at one interface and deplete at the opposing interface to screen the bulk electric field, in agreement with the theory of ion accumulation described in the literature.^[11c, 25] In the dark at short circuit, the bulk electric field is at its maximum and is reduced by the application of voltage bias and illumination. Consequently, the simultaneous application of illumination and forward bias prompts a reduction in the accumulation of ionic charge by migrating away from the transport-layer interface. Our simulations confirm that the movement of ions is the driving force of the TPC response, as shown in **Figure S9**. We see that ion mobility significantly influences the rate at which the photocurrent reaches steady state. A higher ion mobility causes the ion population, and consequently the photocurrent, to stabilize more rapidly under the new bias conditions. By computing the recombination current at the transport-layer interfaces at several times in the TPC

response, we find that the increase in photocurrent is the result of a reduction in interface recombination, as shown in Figure S9b.

Figure 4, plots the concentration of charge carriers (ions, electrons and holes) at a period immediately following illumination (dark lines) and at the end of the TPC measurement (2 seconds, light lines), together with the relative change in concentration (dashed lines). Here, we observe the charge-carrier concentrations at the HTL interface, where the cations accumulate to screen the bulk electric field. Over the course of the measurement, cation accumulation, and consequently the concentration of minority-carriers (here electrons), decreases and the concentration of the majority carrier (holes) increases. The reduced concentration of electrons reduces the recombination at the interface, and consequently, less photocurrent is lost to interface recombination. This explanation is consistent with the hypothesis that the passivation of interface traps reduce hysteresis by reducing interface-recombination losses.

2.5. Discussion

From a broader perspective, we argue that all the described transients – the inversion of the photocurrent, the stabilization of the V_{oc} , and the plateau current – share the same root cause, namely the migration and accumulation of mobile ions at the perovskite/transport layer interfaces. Under illumination, these ions hinder charge extraction by altering the electric field distribution. This effect leads to an accumulation and subsequent recombination of photocarriers, affecting the performance of the device. This problem may be resolved in two ways: either by suppressing the migration of ions, or by neutralizing the accumulated charge. Firstly, to suppress ion migration there are two strategies: one is reducing the concentration of mobile defects during the perovskite formation, the other is by blocking the hopping paths of the ions through grain boundary engineering.^[26] Both routes have the optimization of the perovskite layer and

sophistication of its fabrication method as common focus. Secondly, to neutralize the accumulated charge at the interfaces, the charge-transport layers needs to be optimized by developing new materials or improving existing technologies. Here, an example is the use of contact-passivated m -TiO₂. Firstly, the extended surface area of the mesoporous scaffold is already an efficient strategy since it enhances the charge extraction. Therefore, the hysteresis index drops from 50% to 10% moving from flat junction devices (c -TiO₂/perovskite/Spiro) to mesoporous devices (m -TiO₂/perovskite/Spiro).^[8a, 8b] Secondly, the polymer/fullerene passivation of the m -TiO₂/perovskite interface further reduces the charge accumulation and facilitates charge extraction. Consequently, the hysteresis index drops further from 10% to negligible values.

3. Conclusion

In this article, we addressed the dynamics of transient photocurrent in the electrical properties of a hysteresis-free n - i - p PSC. We described the working mechanism of the solar cells in short circuit, and working conditions. We presented a process capable of suppressing the hysteresis and the relative dynamic responses. We found that n - i - p PSCs the presence of accumulated charges at the interface with transport layers alters the band structure compromising the formation of a reverse flow of photo-generated carriers in the first micro- to millisecond period. The electric field, either internal or external, can modify the accumulated charge distribution and ultimately the hysteretic response of the device on different time scales. Passivating the mesoporous/ perovskite interface suppresses the hysteretic behaviour of the device, which is reflected both in the transient behaviour and in the steady state properties. These results highlight the urgency to tailor and design a new class of transport layers with specific passivated surfaces, which will further enhance the performances of PSC.

4. Experimental Section

Device fabrication: Firstly, ~70 nm pure In-TiO₂ compact layers (*c*-TiO₂) were deposited on the pre-cleaned FTO (TEC-8) substrates (de-ionized water, acetone, isopropanol).^[9d] Secondly, ~100-nm-thick mesoporous TiO₂ layer (*m*-TiO₂) was deposited by spin-casting the TiO₂ solution at 5000 rpm with a ramp of 5000 rpm/s for 30 s, then sintered at 500 °C in air, where the 18 TiO₂ solution was prepared from the TiO₂ paste (30 NR-T, GreatCell Solar) diluted in anhydrous Ethanol (1:9, w/w). Lastly, before depositing the perovskite films, ultra-thin PMMA:PCBM passivation layers were deposited on top of the FTO/*c*-TiO₂/*m*-TiO₂ substrates by spin casting 4mg/ml PMMA:PCBM (1:3, w/w) blend solution in chlorobenzene. Then, the Cs_{0.07}Rb_{0.03}FA_{0.765}MA_{0.135}PbI_{2.55}Br_{0.45} perovskite films were deposited according to ref ^[17]. After depositing the perovskite films, Spiro-OMeTAD films were deposited via spin coating at 3000 rpm with a ramp of 3000 rpm/s for 30 s, where the Spiro-OMeTAD solution was prepared by dissolving 72.5 mg Spiro-OMeTAD, 28.5 uL 4-tert-butylpyridine and 17.5 μL lithium (trifluoromethanesulfonyl)imide solution (520 mg/ml in acetonitrile) in 1 mL chlorobenzene. The substrates were placed in air in a humidity-control box for >12 hours to ensure sufficient oxidation of the Spiro-OMeTAD. Finally, 95 nm gold electrodes were deposited through a shadow mask to define an active area of 0.16 cm².

Device characterization: The current density-voltage characteristics of perovskite solar cells were measured in a N₂ purged glovebox under standard simulated AM1.5 illumination using a solar simulator (Abet Technologies Sun 3000 Solar Simulator) equipped with Autolab Potentiostat/Galvanostat. Measurements were done using a custom-built measurement stage without aperture mask at room temperature. The light intensity is 100 mW/cm² as checked with a calibrated reference solar cell (RERA Technologies). Scanning rate was 50 mV s⁻¹ and voltage

step was 10 mV. No preconditioning protocol has been used before the characterization. The reverse scan was from 1.2 V to -0.1 V, and the forward scan was from -0.1 V to 1.2 V.

Transient photocurrent measurements: TPC measurements and fast scan rate J/V curves were collected using the all-in-one measurement system PAIOS 3.2 (Fluxim). PAIOS exploits a first function generator to control the light source (a calibrated white LED with a rise/fall time of 100 ns), and a second function generator to control the applied voltage bias. The output current is measured through a trans-impedance amplifier. More details about the TPC setup can be found in the Supporting Information (Figure S1 and **Figure S10**).

Transient photocurrent simulation: The transient photocurrent response was modelled using a numerical semiconductor drift-diffusion model of the perovskite absorber incorporating mobile ions. This model has been implemented in the semiconductor simulation software Quokka3. Electron and hole charge transport are modelled using the simplified drift-diffusion model. Ions are implemented as “inert” mobile electric charge. They do not act as trapping centres, and the concentration of traps is unaffected by ion migration. An equal population of anions and cations are implemented, but only one population is free to move. A finite-differences scheme on a non-equidistant mesh is applied, and the resulting system of nonlinear equations is solved by a Newton linesearch algorithm using the C++ library PETSC. The electron and hole transport layers (ETL and HTL) are simplified to a metal-semiconductor (MS) boundary condition characterized by an effective barrier height and surface recombination properties. Majority carrier transport over the boundary is defined via thermionic emission. The transient photocurrent response is replicated by initially assuming that the ion population is at equilibrium conditions in the dark at steady-state. Forward bias voltage and illumination are applied

simultaneously and the extracted photocurrent computed as the ion population migrates to the new steady state conditions. Further details of the model are provided in ref ^{[[23]]}.

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Figure 1. (a) Cross-sectional SEM image with the representative layers of the PSC. (b) J/V characteristics of a representative device. Black line: reverse scan, from 1.2 to -0.1 V. Red line: forward scan, from -0.1 to 1.2 V. Scan rate for both measurements: 50 mV/s. The inset table summarizes the photovoltaic parameters for the forward and reverse scan with the average values. (c) Band diagram of an ideal PSC (top) and after ion migration. Accumulated ions are represented at the interface with charge extraction layers by blue colored charges. The three regions affected by the accumulation of ions are denoted as I, II, and III. (d) TPC measurement in short-circuit condition for a light pulse of 2s. The inset graph shows a magnification on the first hundreds of microseconds.

Forward Bias Transient

Scheme 1. Schematic representation of the band diagram for an ideal device (blue) and a PSC (red) with accumulated ions. The short-circuit condition is represented by dashed lines, the green arrow represent a positive voltage applied to the ETL, the black arrows indicate the preferential direction of the current.

Figure 2. (a) TPC in log time scale with a voltage bias of 0.6V during a light pulse of 2s. In the inset is reported a magnification in linear time scale of the first microseconds. (b) J/V curves at different scan rates. The scan direction is from positive to negative voltages. To avoid any artefacts the device rests in the dark in open circuit for 60 s after each scan. (c) Inversion time at a specific bias extrapolated from the TPC measurements. (d) Temporal evolution of the bands diagram for PSC. At the initial point ($t=0$) the device is in short circuit condition. At $t>0$ a positive 0.6 V bias (green arrow) is applied to the ETL. For the sake of clarity only the conduction band is represented as a red line. Gray dotted lines represent the original band diagram in short circuit condition.

Figure 3. (a) J/V characteristics of a passivating-contact device. Black line: reverse scan, from 1.2 to -0.1 V. Blue line: forward scan, from -0.1 to 1.2 V. Scan rate for both measurements: 50 mV/s. In the table are reported the figures of merit for the forward and reverse scan with the average values. (b) J-V curves at different scan rate. Reverse scan direction. The device rests in dark in short-circuit 60 s prior the consecutive scan. (c) TPC measurements at different voltage bias (from 0 to 1 V) over a 2s light pulse for the pristine (dashed red) and passivated (solid blue) devices. d) Magnification of TPC over 200 μ s.

Figure 4. Electron, hole and cation concentration at $t=1$ ns and $t=2$ s (dark and light lines, respectively). Over this time, the cation concentration depletes from the HTL interface. This increases hole accumulation and increases electron depletion. Consequently, the interface

recombination reduces because of reduced availability of electrons (minority carriers). The relative change (Δ) in the populations between the two time points (t_1 and t_2) is calculated from $(C(z, t_2) - C(z, t_1)) / C(z, t_1)$, where C is the concentration (dashed lines). Thus, a positive number indicates an increase in the concentration over the course of the TPC measurement and vice versa.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Perovskite ions, under the influence of an electric field, migrate and accumulate at charge transport layer interfaces. This reduces the extraction of photo-generated carriers and induces hysteresis in the current/voltage scan. Here, we present a solution via a contact-passivation of the electron extraction layer. The passivating contacts significantly reduce the influence of the ions and greatly improve the overall performances of solar cells from ~18% to ~20%.

Keyword: Perovskites, solar cells, hysteresis, contacts passivation, ion migrations

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Interfacial dynamics and contact passivation in perovskite solar cells

Supporting Information

Interfacial dynamics and contact passivation in perovskite solar cells

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Figure S1: Schematic representation of the transient photocurrent experiment. The light rising time is 100 ns and the light pulse length is comprised between 1 μ s and 1000s. The time resolution of PAIOS is 16 ns. The white LED light source (100 mA) has been calibrated with a certified silicon reference: due to spectral mismatch we refer as “one sun” the LED intensity that give the same current that the one obtained via a solar simulator. The delay time is required to avoid artefact in the measurement due to the turn-on of the bias (as soon as the voltage is applied there is a short spike of current, recorded by the high resolution of PAIOS).

Figure S2: Normalized (left) and pristine (right) TPC at short circuit condition under different light intensities. The yellow square represents the turn on/off of the light pulse. The percentage is relative to the intensity of the diode power.

a

b

a

light

bias
(from -0.3 to +1 V)

+1 V

0 V

-0.3 V

time

Delay time
50 μ s

Irradiation

Follow up
20 μ s

b

Current Density (mA/cm^2)

Time (s)

TPC Bias (V)

-0.3
-0.2
-0.1
0
+0.1
+0.2
+0.3
+0.4
+0.5
+0.6
+0.7
+0.8
+0.9
+1

c

Current Density (mA/cm^2)

Bias (V)

3.3 μ s
10 μ s
100 μ s
1ms
10ms
100ms
1s
2s
J/V

25

results. The TPC results are plotted here as dotted red lines, the extrapolated J/V as a gradient green. The time scale is considered according to the value of the TPC. The J/V curves (scan rate 50 mV/s, reverse direction) obtained with PAIOS is reported as dotted gray line.

Figure S6: Statistics of the hysteresis index (HI) for a passivated (red) and pristine (black) devices. The HI is calculated as: $[1 - (\text{PCE}_{\text{forward scan}} / \text{PCE}_{\text{reverse scan}})] * 100$.

Figure S7: a) Stabilized PCE for the pristine device, and b) for the passivated device.

Figure S8: Normalized (left) and pristine (right) TPC at short circuit condition under different light intensities for a passivated device. The yellow square represents the turn on/off of the light pulse. The percentage is relative to the intensity of the diode power.

Scan rate (V/s)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)	Scan rate (V/s)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
20000	0.28	16.4	31.4	1.4	20000	0.80	18.2	27.1	3.9
5000	0.31	17.9	31.8	1.7	5000	0.87	17.8	24.7	3.8
1000	0.38	19.4	35.8	2.6	1000	0.91	21.0	26.8	5.1
200	0.47	20.1	38.1	3.6	200	0.98	22.2	34	7.4
50	0.57	21.1	39.2	4.7	50	1.05	21.7	39.4	9
10	0.66	21.5	44.8	6.4	10	1.10	21.6	43.8	10.4
2	0.77	21.6	52.4	8.7	2	1.13	21.8	48.4	12
0.5	0.90	21.7	58.9	11.5	0.5	1.15	22.0	53.1	13.5
0.1	0.96	21.7	61.3	12.8	0.1	1.17	22.2	58.3	15.1

Table S1: Figures of merit for the pristine (red) and passivated (blue) devices at different scan rates, obtained from PAIOS setup, in reverse direction. The mismatch in the performances respect to the solar simulator is attributed to the different light source of PAIOS, see Figure S10 for a comparison between solar simulator and PAIOS.

Figure S9. a) Simulated transient photocurrent from a n-i-p perovskite solar cell following simultaneous application of illumination and forward bias, as a function of the mobility of the mobile ion species. b) The photocurrent extracted from the cell, alongside the recombination current at the perovskite-transport layer interfaces during the TPC measurement. An increase in extracted photocurrent is the direct consequence of a reduction in interface recombination

Figure S10: a) Spectral irradiation of the PAIOS white LED, take with courtesy from <https://www.fluxim.com>. b) Qualitative comparison between the J/V curves obtained from the certified solar simulator and the PAIOS system for a passivated device under the same testing conditions (reverse scan, 30 mV/s scan rate). The J_{sc} and FF variations are induced by the different irradiation spectra of the two systems.

Simulation parameters

Summary of model parameters

Parameter	Symbol	Value	Reference
Perovskite absorber thickness		400 nm	
Device temperature	T	300 K	
Electron affinity	E_{EA}	3.8 eV	
Conduction Band Density of States	N_c	$2.2 \times 10^{18} \text{ cm}^{-3}$	[1] ^[27]
Valence Band Density of States	N_v	$1.2 \times 10^{19} \text{ cm}^{-3}$	[1] ^[27]
Band gap	E_g	1.7 eV	[2] ^[1c]
Relative permittivity	ϵ_r	25	[3] ^[28]
Electron mobility	μ_{electron}	30 cm^2/Vs	[4] ^[29]
Hole mobility	μ_{hole}	30 cm^2/Vs	[4] ^[29]
Radiative recombination coefficient	B	$6.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	[5] ^[30]
Auger recombination coefficients	C_n, C_p	$0.5 \times 10^{-28} \text{ cm}^6$	[6] ^[31]
Work Function, Electron Transport Layer	$W_{F,ETL}$	4.0 eV	
Work Function, Hole Transport Layer	$W_{F,HTL}$	5.3 eV	
Generation (uniform) ψ	G	$3.5 \times 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$	
Bulk trap density	N_t	0 cm^{-3}	
Net bulk doping	$N_A - N_D$	0	
Cation Concentration	C_{cat}	10^{19} cm^{-3}	
Anion Concentration	C_{an}	10^{19} cm^{-3}	

Cation mobility ^ψ	μ_{cat}	$10^{-9} \text{ cm}^2/\text{Vs}$
Anion mobility	μ_{an}	$0 \text{ cm}^2/\text{Vs}$ (immobile)

^ψ These parameters were adjusted to roughly fit the experimental data.

Details of the models used in the Quokka3 software are described elsewhere. ^[23b] However, with reference to figure 6a of the main manuscript, interface recombination current is modelled using the simplified SRH model:

$$J_{rec} = \frac{pn - n_{i,eff}^2}{S_{n0}(p_1 + p) + S_{p0}(n_1 + n)}$$

In this analysis, we have assumed equal values for S_{n0} and S_{p0} , that is symmetric electron and hole lifetimes for the interface traps.