Universal Current Losses in Perovskite Solar Cells Due to Mobile Ions

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Efficient mixed metal lead-tin halide perovskites are essential for the development of all-perovskite tandem solar cells, however they are currently limited by significant short-circuit current losses despite their near optimal bandgap ($\approx 1.25$ eV). Herein, the origin of these losses is investigated, using a combination of voltage dependent photoluminescence (PL) timeseries and various charge extraction measurements. It is demonstrated that the Pb/Sn-perovskite devices suffer from a reduction in the charge extraction efficiency within the first few seconds of operation, which leads to a loss in current and lower maximum power output. In addition, the emitted PL from the device rises on the exact same timescales due to the accumulation of electronic charges in the active layer. Using transient charge extraction measurements, it is shown that these observations cannot be explained by doping-induced electronic charges but by the movement of mobile ions toward the perovskite/transport layer interfaces, which inhibits charge extraction due to band flattening. Finally, these findings are generalized to lead-based perovskites, showing that the loss mechanism is universal. This elucidates the negative role mobile ions play in perovskite solar cells and paves a path toward understanding and mitigating a key loss mechanism.

1. Introduction

Perovskite solar cells have undergone major development from their first discovery in 2009, to a viable technology that is approaching commercialization.[1] One of their most interesting assets is the wide range of bandgaps which can be fabricated by changing the perovskite composition, opening up the possibility to produce all-perovskite multijunction cells that can overcome the Shockley–Queisser (SQ) limit of single junctions. For a tandem cell, the ideal bandgaps for the top and bottom cell are $1.7–1.9$ and $0.9–1.2$ eV, respectively.[2] Fully lead-based perovskites are widely investigated and have reached power conversion efficiencies (PCEs) of up to $25.5%$. In order to achieve ideal bandgaps for the low-gap cell in all-perovskite tandem photovoltaics, a mixture of lead and tin atoms at the B-site of the ABX$_3$ perovskite structure is required. This allows metal halide perovskites to reach bandgaps as low as $1.2$ eV.[4,5] While many studies in the literature focus their efforts into improving the open-circuit voltage ($V_{OC}$) and fill factor (FF) of perovskite solar cells (PSCs), there are less reports that investigate the loss in short-circuit current density ($J_{SC}$). In fact, high-performing perovskites have been shown to have “only” moderate ($\approx 5–15\%$) $J_{SC}$ losses compared to the SQ limit making them competitive in this regard with established technologies such as c-Si and GaAs, as shown in Figure 1a. In many cases, this loss is quickly overlooked and treated as a result of suboptimal light management in the cell which could be solved by optimizing the thickness of the solar cell stack or by using more complex light management strategies such as, for example, textured substrates,[6,7] cavities & plasmon resonances,[8] or carefully designed anti-reflective layers.[9,10] However, as we will show, suboptimal light management is not the only cause of $J_{SC}$ losses in perovskite solar cells, even in well performing mixed-cation mixed-halide perovskite cells. Tin-based and mixed PbSn perovskite solar cells are particularly affected by short-circuit current losses and their efficiencies lag behind those of their full-lead equivalents, despite having a band gap closer to the ideal for single junctions, with the best mixed lead/tin cells only reaching certified PCEs.
of a bit over 20%.[11–14] Considering reported bandgaps of 1.22 eV for a 50:50 Pb:Sn mixture, this would allow a maximum short-circuit current density of \( \approx 37.1 \text{ mA cm}^{-2} \) if we assume that an average external quantum efficiency of 95% can be achieved as demonstrated in the best Pb-perovskite cells.[15,16] However, even the best APbSnI\(_3\) perovskites achieve significantly lower currents, for example, 32 mA cm\(^{-2}\) have been demonstrated for a bandgap of 1.22 eV in ref. [13]. In most other reports, PbSn perovskites with similar bandgaps delivered even lower short-circuit current (<30 mA cm\(^{-2}\)).[17–19] This discrepancy between two apparently similar technologies is not often discussed and it is currently not clear why Sn(II) containing perovskites cannot achieve as high currents as their lead counterparts relative to their SQ limits.

Generally, it is well known that Sn(II)-containing metal halide perovskites are more prone to oxidation to Sn(IV) than their Pb(II) counterparts, due to the inert pair effect stabilizing the 6s electrons in Pb(II). This propensity to oxidize has led researchers to conclude that this is likely the origin of performance losses in PbSn perovskites. In turn, significant efforts have been undertaken to prevent this oxidation, or reduce its negative effects, such as the addition of metallic Sn to the solution to reduce Sn\(^{4+}\) through comproportionation,[13] addition of antioxidants and reducing agents,[14,20,21] or addition of excess Sn\(^{2+}\) by using salts such as SnF\(_2\), which also acts as a reducing agent.[22] Recently, it was also proposed to move away from using dimethylsulfoxide (DMSO) as a co-solvent, as this could oxidize Sn\(^{2+}\) to Sn\(^{4+}\) in solution.[23] However, the exact effect of the increased concentration of “oxidation-induced” mobile charges in the system has only been investigated by a few researchers.[24–26]

On the one hand, there has been substantial evidence of a large increase in the dark conductivity of Sn based perovskites upon exposure to oxygen, which is most likely due to electronic doping. For example, in ref. [27,28], a background hole carrier concentration of \(10^{10}\) to \(10^{16}\) cm\(^{-3}\) has been reported. This led to the conclusion that it is largely the \(p\)-doping that is responsible for the significant current losses.[29,30] For example, a high concentration of doping-induced carriers could reduce the lifetime and diffusion length of photoinduced charge or screen the
built-in field, which would in turn reduce the charge extraction efficiency, thereby causing short-circuit current losses.\(^{[27,31,32]}\) Although it is expected that high levels of doping can undermine the device performance, the exact underlying mechanisms have not been studied thoroughly experimentally, and the concentration of charge carriers required to induce detrimental effects is not precisely known. Moreover, the charge collection losses at short-circuit conditions in Sn-based perovskites can be caused by an insufficient charge carrier diffusion length due to electronic defects, which would also negatively affect the open-circuit voltage.

On the other hand, the performance losses could be caused by mobile ions, which may cause screening (or more precisely, a redistribution) of the internal field. Several groups have attempted to quantify mobile ion concentrations in different perovskites, and their outcomes are generally in the range of \(10^{15}\) to \(10^{19}\) \(\text{cm}^{-3}\)\(^{[33–36]}\) Indeed, the presence of mobile ions is expected in PbSn perovskite thin-films. For example, Leijtens et al.\(^{[37]}\) recently investigated the mechanism of oxidation of Sn and PbSn perovskites through X-ray diffraction (XRD), thermogravimetric analysis (TGA), and UV–vis, and demonstrated that mobile ions such as FA\(^+\) or I\(^-\) are likely formed. However, the effect of mobile ions on the short-circuit current losses in perovskites has, in general, not been investigated as intensively as, for example, their effect on the \(V_{OC}\)\(^{[38]}\) the hysteresis,\(^{[39–41]}\) and device stability.\(^{[42–44]}\) In order to further improve PbSn and Pb-based perovskite solar cells and other electronic devices,\(^{[45,46]}\) it is vital to gain a more detailed understanding of the mechanism causing short-circuit current losses and the exact effects of electronic doping and mobile ions on the device operation.

In this work, we investigated short-circuit current losses in low bandgap, mixed PbSn (FA\(_{0.83}\)Cs\(_{0.17}\)Pb\(_{0.5}\)Sn\(_{0.5}\)I\(_3\)) and other lead-based perovskite cells. In particular, we first aimed to understand whether the charge transport losses under short-circuit conditions in mixed PbSn perovskites (FA\(_{0.83}\)Cs\(_{0.17}\)Pb\(_{0.5}\)Sn\(_{0.5}\)I\(_3\)) are a result of electronic doping or mobile ions, before generalizing the results to other Pb-based systems. To this end, we recorded the temporal evolution of the current transient and determined a concurrent rise in the photoluminescence (PL) emission intensity after switching the voltage from \(V_{OC}\) to short-circuit, which implies an accumulation of electronic charge in the perovskite bulk. We hence attribute the reduced current-density to a reduced charge extraction efficiency. The decay in current directly translates into a loss of the steady-state maximum power point output of the device on the same timescales and to a current loss at slow scan speeds. To distinguish whether background doping or mobile ions are responsible for this loss, we performed bias assisted charge extraction (BACE) and charge extraction by linearly increasing voltage (CELIV) measurements, which allowed us to investigate the density and dynamics of extracted electronic and ionic charges. Overall, these measurements underline the extraction of electronic (bias-induced injected) charges on the \(\mu\)-timescales, while the characteristic features of mobile ions appear on the ms–s timescales, as observed in the current decay transients. Importantly, the ionic charge density (>\(1 \times 10^{15}\) \(\text{cm}^{-3}\)) was found to exceed the injected and photogenerated electronic charge density (\(5 \times 10^{15}\) \(\text{cm}^{-3}\)) present at \(V_{OC}\) by several orders of magnitudes, therefore dominating the observed recombination losses in the transient current decay. Moreover, the density of doping induced equilibrium charges (\(>6 \times 10^{14}\) \(\text{cm}^{-3}\)) was found to be negligible compared to the capacitive charge density (\(6 \times 10^{15}\) \(\text{cm}^{-3}\)), hence the density of doping-induced charge, in contrast with the mobile ion density, is insufficient to screen or redistribute the built-in potential. Furthermore, we could reproduce both the transient and steady-state performance of the device using numerical simulations, which further corroborated the understanding obtained from the experimental results. Finally, we demonstrated that PbSn based perovskites are not unique with respect to ion-induced current losses, but the same losses appear in various other perovskite compositions and architectures. Overall, the mobile ion induced losses limit the power conversion efficiency of our devices by 1–3% absolute. As such, this work underlines the importance “ion-management” to overcome band flattening and to minimize the recombination losses under maximum power point losses and improve device stability.

2. Results

Here we studied, low bandgap FA\(_{0.83}\)Cs\(_{0.17}\)Pb\(_{0.5}\)Sn\(_{0.5}\)I\(_3\) perovskite photovoltaic devices. The device stack is comprised of spin-coated poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) hole transporting layer (HTL) on a glass substrate coated with an indium-doped tin oxide (ITO) conductive layer. On top of that, the perovskite layer with a thickness of 470 nm is deposited via spin-coating. The stack is completed by an electron transporting layer (ETL) comprised of evaporated C\(_{60}\) (30 nm) and bathocuproine (BCP) (8 nm), with a copper (Cu) electrode on top. A detailed description of the device preparation can be found in Supporting Information. A cross-section of a complete device is displayed in Figure 1b. A JV scan of a characteristic efficient device can be seen in Figure 1c, while more detailed characteristics and statistics can be found in Figure S1, Supporting Information. From the device absorption and the external quantum efficiency (EQE), displayed in Figure 1d, the different current losses in the device can be determined. First of all, the optical losses of the device, as determined from the total reflectance \(R\) of the device, are significant. This is caused by the relatively low absorption coefficient of the lead-tin perovskite near the band edge (Figure S2, Supporting Information) and the absorber layer being too thin to absorb all the incident photons with energies above the bandgap. On top of that, the lead-tin perovskite devices suffer from significant additional collection losses (≈2 m\(\text{Acm}^{-2}\)), which can be determined from the difference between the device absorption minus parasitic losses in the ITO, PEDOT:PSS and copper (i.e., 1-\(R_{\text{parasitic}}\)) and the device EQE. The parasitic losses were estimated using a transfer matrix code developed by McGehee, et al.\(^{[47]}\) Although the optical losses can be largely reduced in thicker ≈800 nm devices (Figure S3, Supporting Information), the \(J_{SC}\) cannot be improved due to enhanced collection losses. Therefore, it can be concluded that the combination of relatively large optical losses in 470 nm thick devices and the large collection losses in our thicker devices (e.g., ≈800 nm), possibly due to traps resulting in an insufficient carrier diffusion length, are among the main
reasons for the relatively low $J_{SC}$ of the PbSn-perovskite as compared to Pb-based perovskites, with respect to what is expected from their different band gaps. In the following, however, we focus on understanding the observed charge collection losses at 0 V in the optimum 470 nm-thick devices, which are poorly understood and also significantly contributing to the $J_{SC}$ loss.

To investigate these collection losses at 0 V, we first measured the time dependence of the photoluminescence quantum yield (PLQY) and the short-circuit current density ($J_{SC}$) immediately after switching from open-circuit (OC) to short-circuit (SC) at $t = 0$ s as shown in the inset. b) The photoluminescence (PL) trace over the same time, taken while switching from OC to SC. c) The maximum height of the PL peak a function of time, where $t = 0$ is the moment where the bias of the device was switched from OC to SC. It can be seen that the PL is initially almost completely quenched, due to efficient charge extraction. However, it quickly comes back up again, indicating that the charge extraction is becoming less efficient and that photogenerated charges accumulate in the perovskite layer. d) The corresponding temporal evolution of the relative device efficiency loss under maximum power point tracking under AM1.5G illumination. e) A schematic representation of the band flattening that is presumably causing the decay in current upon switching to SC conditions. A more elaborate overview of the change in band structures can be found in Figure S4, Supporting Information. Comparing panels (a), (c), and (d) highlights that the decay of the current and the MPP happens on the same timescales as the PL increases.

Figure 2. a) The measured (blue line) and simulated (dashed blue line) current decay of a FA$_{0.83}$Cs$_{0.17}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ perovskite pin-type solar cell device after switching from open-circuit (OC) to short-circuit (SC) at $t = 0$ s as shown in the inset. b) The photoluminescence (PL) trace over the same time, taken while switching from OC to SC. c) The maximum height of the PL peak a function of time, where $t = 0$ is the moment where the bias of the device was switched from OC to SC. It can be seen that the PL is initially almost completely quenched, due to efficient charge extraction. However, it quickly comes back up again, indicating that the charge extraction is becoming less efficient and that photogenerated charges accumulate in the perovskite layer. d) The corresponding temporal evolution of the relative device efficiency loss under maximum power point tracking under AM1.5G illumination. e) A schematic representation of the band flattening that is presumably causing the decay in current upon switching to SC conditions. A more elaborate overview of the change in band structures can be found in Figure S4, Supporting Information. Comparing panels (a), (c), and (d) highlights that the decay of the current and the MPP happens on the same timescales as the PL increases.

To investigate these collection losses at 0 V, we first measured the time dependence of the photoluminescence quantum yield (PLQY) and the short-circuit current density ($J_{SC}$) immediately after switching from $V_{OC}$ to 0 V, while the sample remains under continuous illumination. As can be seen in Figure 2a, the $J_{SC}$ falls during the initial few seconds of operation at 0 V before eventually reaching a steady-state. On average, we find that freshly prepared FA$_{0.83}$Cs$_{0.17}$Pb$_{0.5}$Sn$_{0.5}$I$_3$ devices experience current density losses of 1.4 mA cm$^{-2}$. This equals about 5% of the initial current density. To reveal the reason for the loss in current, we simultaneously measured the emitted PL from the cell as a function of time. The temporal evolution of the PL spectra is displayed in Figure 2b, while the corresponding peak height is displayed in Figure 2c. It can be seen that, when the device bias is changed to 0 V at $t = 0$ s, the PL is initially nearly completely quenched, due to efficient charge extraction. However, it quickly comes back up again, indicating that the charge extraction is becoming less efficient and that photogenerated charges accumulate in the perovskite layer. d) The corresponding temporal evolution of the relative device efficiency loss under maximum power point tracking under AM1.5G illumination. e) A schematic representation of the band flattening that is presumably causing the decay in current upon switching to SC conditions. A more elaborate overview of the change in band structures can be found in Figure S4, Supporting Information. Comparing panels (a), (c), and (d) highlights that the decay of the current and the MPP happens on the same timescales as the PL increases.
or defects. At the time of stabilization, the PL has increased up to ≈6% of the PLQY value at open circuit conditions. Importantly, the decrease in current density and increased PL yield leads also to a direct loss in efficiency, that is, in the initial phase of maximum power point (MPP) tracking measurements, as displayed in Figure 2d. This has important implications as it indicates that the observed effect also influences cell performance under steady-state working conditions. Figure 2e displays the field screening due the accumulation of mobile ions at the interfaces over time, which is expected to cause the observed $J_{sc}$ and MPP losses and the increase of the PL on the same timescales. The simplified time dependent band structures displayed in Figure 2e are extracted from our numerical device simulations (details about the simulations are discussed further below). The corresponding time-dependent simulated band structures are presented in Figure S4, Supporting Information, which also includes a more detailed description of the movement of mobile ions in the performed experiments. Interestingly, as shown in Figure S5, Supporting Information, we find that there is an approximately linear relationship between the current decay and the increase in PL at 0 V. To explain this, we consider that the PL yield is proportional to the radiative recombination current ($j_{rad} = \epsilon \phi_{nl}$), while the current decay is mostly governed by non-radiative recombination (as the overall PLQY yield of the sample is only $10^{-4}$). Therefore, a linear relationship between the current decay and the PL increase implies that the radiative and non-radiative recombination losses are directly proportional to each other. In other words, the field screening-induced accumulation of electronic charges in the active layer increases the radiative and non-radiative recombination losses in the same way, which is consistent with the findings of our previous study.$^{[50]}$ It is important to note that the current losses can occur even if the charge carrier diffusion length in the perovskite exceeds the film thickness. This is because the transport layers can limit the extraction from the device and also interfacial recombination can increase if more charges accumulate in the active layer. To describe the current decay more quantitatively, we performed numerical drift–diffusion simulations of the cell, using the commercially available SETFOS 5.1 software package provided by FLUXiM. The input parameters for the simulations shown in Table S1, Supporting Information were partially based on our previous simulation work of pin-type triple cation perovskites,$^{[51,52]}$ and parameters tailored for lead-tin using the literature specified in Table S1, Supporting Information and our own extraction measurements, as discussed further below. The fit from the numerical simulations is shown in Figure 2a by the dashed line, which highlights that both the kinetics of the decay can be reproduced with the experimentally obtained effective ion diffusion coefficient ($≈10^{-10}$ cm$^2$ s$^{-1}$) and density ($≈10^{17}$ cm$^{-3}$) as well as the overall magnitude of the current losses. Figure S6, Supporting Information demonstrates the simulated current decay for other mobile ion densities.

In the following we demonstrate that the time dependent losses of the short-circuit current are also present in JV hysteresis measurements at slow scan speeds. To clearly visualize this important fact, we performed “fast hysteresis” measurements, where the JV is measured in forward and reverse direction over several orders of magnitude in scan speed (100 mV s$^{-1}$ to 800 V s$^{-1}$) after keeping the cell under open-circuit conditions and constant AM1.5G illumination. The details of this measurement are presented in Supporting Information. Figure 3 plots the short-circuit current density obtained as a function of scan speed range. At the fastest scan speeds (here, 1 ms per scan, or

Figure 3. a) The current density as obtained from JV scans in forward and reverse direction as a function of scan speed (100 mV s$^{-1}$ to 800 V s$^{-1}$). b) exemplifies the JV scans in forward and reverse direction at the slowest (top) and fastest scan speed (bottom). At fast enough scan speeds (scan time $\ll$ ion transit time), the mobile ions in the perovskite layer are not able to react to the change in the applied voltage, and hence the obtained efficiency can be regarded as a proxy of the ion-free efficiency. At slow scan speeds, however, mobile ions are able to screen the built-in field. This lowers the device efficiency, primarily through increased short-circuit current losses in case of the studied cells. Panel (a) shows lower current density for JV scans taken at slower scan speeds, as opposed to the “mobile-ion free” JV scans taken at the fastest scan speeds. Hence, the current losses also appear in the JV-measurements at slow scan speeds that are representative for steady-state conditions, as shown in Figure 2.
800 V s⁻¹), the mobile ions do not have enough time to react to the change in the external voltage, hence an “ion-free current density” is obtained if the ions are roughly homogeneously distributed at the starting voltage (V_OC). However, at slower scan speeds (e.g., 1 s per scan), the mobile ions are able to follow the change in internal field by moving from their equilibrium positions toward the transport layers, where they start to screen the field causing the losses in the J_SC. Indeed, at the slowest scan speeds (10–1 V s⁻¹), a decrease in J_SC of about 1.5 mA cm⁻² is observed with respect to the fast-scan (800 V s⁻¹). As such, the temporal current decay shown previously in Figure 2a.

In order to distinguish between different processes that could cause the observed current losses and the suspected band flattening, and to elucidate the density and kinetics of free electronic and ionic charge, we performed different charge extraction measurements. Figure 4a shows the extracted charge as a function of time from bias assisted charge extraction (BACE), where the (displacement) current is recorded upon a switch from V_OC to 0 V. The charge inside the active layer is thereby obtained by integrating the displacement current over time. It is important to note that mobile ions are not extracted from the device rather transported to the transport layers or electrodes, which however, causes an external displacement current. As can be seen in Figure 4a, the obtained temporal evolution of the charge density displays two features; an initial rise at ≈1 µs and a second rise at ≈300 ms. The initial rise consists itself of two contributions, the extraction of electronic charge and the RC decay due to the electrode (capacitive) charge (CU, where U is the V_OC). As shown in Figure S7, Supporting Information, using a separate setup with a home-built amplifier with a relatively low resistance (≈5 Ω), we can distinguish the contribution of these two initial processes to the first bump. As shown in Table 1, we obtain

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**Figure 4.** a) Bias assisted charge extraction (BACE) measurement (solid line) upon a switch from open-circuit to short-circuit, including the associated change in the electrode charge (i.e., the capacitance-voltage product 6 × 10¹⁵ cm⁻³) and the injected charge at open-circuit conditions (2 × 10¹⁵ cm⁻³). The extraction of both electronic charge and ionic charge occurs at very different timescales, where the extraction of mobile ions coincides with the current decay observed in Figure 1. b) Current extraction by linearly increasing voltage (CELIV) measurements confirm the results from the BACE measurements, showing that electronic charge extraction occurs much faster than ionic charge, and that the latter occurs on timescales of ms. c) Photo-CELIV transients after a laser excitation with given photocarrier concentrations. The graph demonstrates that a (photogenerated) carrier density of about 1 × 10¹⁵ cm⁻³ would create an initial bump in the transient response. Considering that the bump is absent in the dark measurement confirms that the doping-induced equilibrium carrier density is significantly lower than this threshold which is consistent with lateral conductivity measurements. d) Simulated stabilized current and current decay as a function of the mobile ion concentration (solid lines) and the doping concentration (dashed lines), respectively.
an injected charge carrier density of $2 \times 10^{15}$ cm$^{-3}$, while the electrode charge divided by the perovskite volume equals to $6 \times 10^{15}$ cm$^{-3}$ at 0 V (if the $V_{OC}$ is equal to the built-in field). Furthermore, upon applying a constant background illumination with a 1-sun equivalent intensity, the same measurement allows us to quantify the photogenerated charge carrier density that is present at $V_{OC}$. Figure S8, Supporting Information. The details of the measurement are discussed more elaborately in the captions of the corresponding figures in Supporting Information. Coming back to Figure 4a, the second increase in the extracted (or transported) charge is assigned to the mobile ion density in the system with a characteristic effective displacement time of 300 ms. This corresponds to the timescale observed in the current decay and PL increase. Note, this corresponds to an effective ion mobility of $4 \times 10^{-9}$ cm$^2$ V$^{-1}$ s$^{-1}$ and a diffusion coefficient of $1 \times 10^{-10}$ cm$^2$ s$^{-1}$. Importantly, the obtained ion density in the system is $2 \times 10^{15}$ cm$^{-3}$, which is significantly larger than the electronic charge in the system, including the electrode charge (per volume) that creates the built-in potential. Hence, a significant redistribution of the built-in field is expected due to the obtained ion density (as already shown above in Figure 2e). We note again, that the obtained ion diffusion coefficient and density was used as an input parameter for the numerical simulations, which allowed us to fit the current decay shown in Figure 2a.

In order to further corroborate the BACE measurements, we performed charge extraction by linearly increasing voltage (dark-CELIV) measurements, which are shown in Figure 4b. In this measurement, the linearly increasing voltage leads to a constant charging current of the electrodes. For a dielectric capacitor in the absence of mobile charges in the active layer, the response to the CELIV voltage pulse is a step function. Any additional charge present, for example, doping induced equilibrium charges or mobile ions (or photogenerated charges with background light), will cause a “bump” in the transient response, which allows us to estimate their density with respect to the electrode charge ($C_{V_{max}}$, where $V_{max} = 0.4$ V is the maximum applied voltage of the triangular pulse in this case). Hence, the absence of an initial bump in the dark-CELIV response, shown in Figure 4b, indicates that the doping density is insignificant with respect to $C_{V_{max}}$ per cell volume ($\approx 5 \times 10^{15}$ cm$^{-3}$). To further highlight this important point, we performed a photo-CELIV measurement, where we intentionally photogenerally generated a charge carrier density of e.g. $1 \times 10^{15}$ cm$^{-3}$ in the perovskite cell. As shown in Figure 4c, this photo-generated charge carrier density can nicely be seen in the current response and is roughly in the correct ratio compared to the $C_{V_{max}}$ charge. Moreover, the extraction of the photo-generated charge carrier density happens on the order of 1 μs, which further confirms the timescale of electronic charge transport. We note the relatively long extraction time is likely limited by the transport layers rather than bulk transport through the perovskite layer, as has been previously shown. To quantify the doping density in the PbSn perovskite, we performed lateral conductivity measurements which revealed a dark conductivity of $9 \times 10^{-5}$ S cm$^{-1}$ (Figure S9, Supporting Information). Assuming a long-range charge carrier mobility of roughly 1 cm$^2$ V$^{-1}$ s$^{-1}$ (which is lower than the short-range charge carrier mobility as obtained from optical-pump terahertz-probe spectroscopy measurements in ref. [18], since we consider grain boundaries), this would correspond to a doping-induced charge carrier density of $6 \times 10^{14}$ cm$^{-3}$, which is consistent with the absence of a doping-induced feature in the CELIV response. Turning our attention again to the dark-CELIV transient in Figure 4b, after $1 \mathrm{ms}$ the signal rises again just as observed in the BACE measurements due to the presence of mobile ions until beyond 100 ms, which represents the detection limit of our current setup. Considering that the current does not saturate, only a lower mobile ion density of $1.5 \times 10^{16}$ cm$^{-3}$, can be specified upon integration of the dark-CELIV signal. Therefore, these transient measurements demonstrate that the mobile ion concentration is much larger than the photogenerated charge carrier density, the injected charge at $V_{OC}$ and the doping induced charge, and sufficiently large to redistribute the device built-in electric field. In contrast, it is important to note that the doping density is much smaller than the $CU$ charge per cell volume ($6 \times 10^{15}$ cm$^{-3}$), which is too low to screen the electric field. To further highlight this point, we performed numerical simulations, the results of which, displayed in Figure 4d, demonstrate that the doping density will only start to make a significant impact at densities exceeding $1 \times 10^{16}$ cm$^{-3}$, at which point the built-in field becomes screened. Moreover, it can be seen that electronic doping, although it can affect the device performance at higher concentrations, as is displayed in Figure S10, Supporting Information, never leads to a temporal current decay, whereas for mobile ions, temporal current decays are observed for a range of concentrations. Interestingly, we also found that when the mobile ion concentration reaches a certain threshold, the stabilized current still decreases with increasing mobile ion densities, but the temporal decay disappears. We attribute this to the fact that at these high mobile ion densities, the ion concentrations at the TL interfaces are already large enough at $t = 0 \mathrm{s}$ to fully screen the field. The simulation results displayed here are for the case of only one mobile ion species. In Figure S11, Supporting Information, results for the case were there are two types of mobile ion present are displayed. Overall, the experimentally measured timescales and carrier densities allow us to conclude that the collection losses of the current stem from the ionic movement in the perovskite causing a redistribution of the internal field, rather than from electronic doping.

In order to find out whether the loss mechanism described above is unique for tin-containing perovskites, or if it also occurs for other perovskite compositions or architectures, we investigated several different lead-based perovskite systems. Surprisingly, as shown in Figure 5a, we observed that the exact same charge transport losses are indeed present for
all other studied lead-based perovskites, including methyl ammonium lead triiodide, two triple cation Cs$_{0.05}$(FA$_x$MA$_y$)$_{0.95}$Pb(I$_x$Br$_y$)$_3$ devices made from different $x/y$ ratios as well as for a triple cation perovskite in a nip-configuration based on TiO$_2$ and Spiro-OMeTAD. Further details of the device fabrication are presented in the Supporting Information. Also for these systems, as displayed in Figure 5b, the transient current decay is accompanied by an increase in PL over time at 0 V, while the timescales of the current loss and deterioration in charge extraction efficiency corresponds to the timescales at which the ions move in the respective systems. Figure 5c displays the effects of different scan speeds on the obtained short-circuit current confirming that the current at slow scan speeds is significantly lower than the “ion-free” $J_{SC}$ fast-scan speeds. This confirms that the finding that ionic charge movement is responsible for the observed current losses can be generalized beyond tin-based perovskites to lead halide perovskites. The formation of field-free regions in the perovskite bulk due to mobile ions is thus not only responsible for the $JV$ hysteresis, but also for significant current and efficient losses under realistic operating conditions. The latter is shown in Figure 5d, which highlights the MPP tracking of several devices with a high time resolution ($\approx$10 ms). Each of these devices displays a quick initial decrease in maximum power output (which might be easily overlooked when tracking the device efficiency over longer times). We point out that light soaking has also shown to have an impact on ion migration and hysteresis.$^{[55]}$ In order to distinguish between light soaking effects and the studied current losses, we have checked whether the scan-rate dependent hysteresis is reversible, or if there are permanent/light-induced changes in the device performance. Figure S12, Supporting Information shows that for the pin-type perovskite cells studied here, the current losses observed are not linked to light soaking induced changes in the device performance. However, on longer timescales, light soaking may have more pronounced effects. Finally, we note that we found the mobile-ion-induced
losses were overall quite similar in PbSn- and Pb-perovskite, hence we attribute the difference in the $J_{SC}$ loss in these two systems more to the difficulties in obtaining thicker active layers in PbSn-perovskites, which are required due to their lower absorption coefficient at the band edge. Nevertheless, preventing the fast-field screening and the corresponding current losses by minimizing the mobile ion density in all studied perovskites, would thus allow a significant improvement of the current in steady-state and in turn a substantial PCE improvement of between 1.5–3% absolute, even in our optimized devices.

3. Conclusions

To summarize, we have demonstrated that the charge collection losses in mixed lead-tin perovskites are caused by an accumulation of electronic charge in the active layer due to a reduction in the charge extraction efficiency over the first few seconds of operation, which simultaneously increases the emitted PL from the device. Through a series of transient electronic measurements and numerical modeling, we identified this collection loss to be due to the presence of mobile ions in these systems which redistribute the internal field within the first few seconds of operation, rather than an recombination rate of photogenerated carriers with doping-induced background charges or increased defect densities. As far as we could assess in this work, doping of (non-oxidized) mixed lead-tin perovskite is not directly causing current losses through band flattening as the doping density is too low to screen the electric field. Going beyond mixed-lead-tin systems, to lead-based perovskites, we show that the same process also occurs for a range of different mixed-ion lead-based perovskite solar cells. As with the low bandgap materials, we again find that the timescales of the current loss correspond to the timescales of ion motion in these different systems. Our findings demonstrate that even in what appear to be “hysteresis-free” perovskite solar cells at typical scan speeds ($\approx 100 \text{ mV s}^{-1}$), the role of mobile ions cannot be neglected, since they still have a large and negative impact on device performance. Considering that the ion-free current (measured at fast scan speeds) is typically $1.5 \text{ mA cm}^{-2}$ larger, this constitutes a significant PCE loss. In order to reduce charge collection losses both in mixed lead-tin perovskites, but also in neat lead-based perovskites, it is important to gain further understanding of how to reduce the mobile ion density, or how to engineer the devices so that the charge collection is insensitive to the redistribution of the ions. This will then enable us to move closer to the radiative efficiency limit.

Supporting Information

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

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Conflict of Interest

H.J.S. is co-founder and CSO of Oxford PV Ltd.

Data Availability Statement

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

Keywords

current losses, mobile ions, non-radiative recombination, perovskite solar cells, Sn perovskite, transient photoluminescence

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