Supporting Information: Revealing Charge Carrier Mobility and Defect Densities in Metal Halide Perovskites via Space-Charge-Limited Current Measurements

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| Parameter                          | Symbol | Value                  |
|-----------------------------------|--------|------------------------|
| **Conduction Band**               | $E_c$  | 3 eV                   |
| **Valence Band**                  | $E_v$  | 5 eV                   |
| **Band gap**                      | $E_{gap}$ | 2 eV                  |
| Effective density of states       | $N_{cv}$ | $1 \times 10^{18}$ cm$^{-3}$ |
| **Mobility**                      | $\mu$  | $10$ cm$^2$ V$^{-1}$ s$^{-1}$ |
| **Relative dielectric constant**  | $\epsilon_r$ | 25.5                  |
| **Mobility**                      | $\gamma$ | $10^{-10}$ cm$^3$ s$^{-1}$ |
| **Trap density**                  | $n_t$  | 0 or $10^{11}$ – $10^{14}$ cm$^{-3}$ |
| **Trapping level depth below $E_c$** | $E_{trap}$ | 1 eV                  |
| **Contact**                       | $C_n(p)$ | $10^{-7}$ cm$^3$ s$^{-1}$ |
| **Contact work function**         |        | 3.0 eV                 |
Figure S1: (a-d) Density of electron, filled-traps, anion and cation for different applied voltage for a steady-state scan.
Figure S2: (a-d) Density of electron, filled-traps, anion and cation for different applied voltage for a pulsed scan where the ion distribution is kept fixed at 0 V condition. We can note that the distribution of filled traps and electron is not too different between steady-state and pulsed scan which explain the very similar JV-curves in figure 2 (b).
Figure S3: (a-d) Density of electron, filled-traps, anion and cation for different applied voltage for a backward scan where the ion distribution is kept fixed at 200 V condition. We can note that the distribution of filled traps and electron is significantly affected by the accumulation of cation at the injecting electrode which explain the difference between JV-curves in figure 2 (b).
Figure S4: Pulsed-SCLC JV-curves for 160, 210 and 465 µm thick MAPbI₃ single crystal.
Table S2: Parameters used in the drift-diffusion fit of the 160 $\mu$m thick single crystal MAPbBr$_3$ in figure 3 (a).

| Parameter                              | Symbol | Value          |
|----------------------------------------|--------|----------------|
| **Perovskite Layer**                   |        |                |
| Conduction Band                        | $E_c$  | 3.4 eV         |
| Valence Band                           | $E_v$  | 5.6 eV         |
| Band gap                               | $E_{gap}$ | 2.2 eV       |
| Effective density of states            | $N_{cv}$ | $1 \times 10^{18}$ cm$^{-3}$ |
| Thickness                              | L      | 160 $\mu$m    |
| Mobility                               | $\mu$  | 12.9 cm$^{-2}$ V$^{-1}$ s$^{-1}$ |
| Relative dielectric constant           | $\epsilon_r$ | 25.5        |
| Ion density                            | $n_{ion}$ | $1.09 \times 10^{13}$ cm$^{-3}$ |
| **Recombination**                      |        |                |
| Band-to-band recombination rate constant | $\gamma$ | $10^{-10}$ cm$^3$ s$^{-1}$ |
| Trap density                           | $n_t$  | $1.32 \times 10^{13}$ cm$^{-3}$ |
| Trapping level depth below $E_c$       | $E_{trap}$ | 0.54 eV      |
| Electron (hole) capture coefficient    | $C_n(p)$ | $10^{-7}$ cm$^3$ s$^{-1}$ |
| **Contact**                            |        |                |
| Contact work function                  |        | 3.82 eV        |
Figure S5: Simulated pulsed-SCLC JV-curves for n-Doping (a) and p-Doping (c) of the perovskite bulk. (b & c) Extracted net-charge using equation 4. We note again that V2 is the best point to take as $V_{net}$ and that the SCLC really describe the net charge such as $n_{net} = n_t - n_{ion} + N_A - N_D$
Figure S6: (a) Simulated pulsed-SCLC JV-curves for deep acceptor and donor type of traps showing that only charged traps affect the JV and can be resolved by the SCLC measurements. (b) & (c) also show that the traps need to be sufficiently deep to have any effect on the JV-curves and that shallow traps that are less than 0.2 eV from the band edge will not appear on the SCLC measurement. Overall equation 4 can be rewritten such as $n_{net} = n_{i}^{net} - n_{ion} + N_A - N_D$ with $n_{i}^{net}$ being the net charge sitting on the trap levels.
1 Drift-diffusion equations as a device model.

1.1 Drift-diffusion main equations

The device model used throughout this paper is based on 1D drift-diffusion equations. The so-called drift-diffusion simulations consist of three main sets of equations. The Poisson equation:

$$\frac{\partial}{\partial x} \left( \epsilon(x) \frac{\partial V(x)}{\partial x} \right) = -q \left( p(x) - n(x) + C_i(x) \right), \quad (S1)$$

with $x$ is the position in the device, $V$ the electrostatic potential, $n$ and $p$ the electron and hole concentrations, and $\epsilon$ the permittivity. $C_i$ can represent any other type of charges in the systems such as: (i) doping with $N_A^+$ and $N_D^-$ being the ionized p-type and n-type doping respectively, (ii) ions with $X_c$ and $X_a$ the cation and anion densities and (iii) the charged traps $\Sigma_T^+$ and $\Sigma_T^-$ for hole and electron traps. Such as the Poisson equation may be written as:

$$\frac{\partial}{\partial x} \left( \epsilon \frac{\partial V}{\partial x} \right) = -q \left( p - n + N_D^+ - N_A^- + X_c - X_a + \Sigma_T^+ - \Sigma_T^- \right) \quad (S2)$$

The current continuity equations:

$$\frac{\partial J_n}{\partial x} = -q (G - R)$$
$$\frac{\partial J_p}{\partial x} = q (G - R) \quad (S3)$$

with $J_{n,p}$ the electron and hole currents, $G$ and $R$ the generation and recombination rate respectively. The movement of these free charges is governed either by diffusion due to a gradient in carrier density or by drift following the electric field such as the electron and hole currents can be written as:[1]

$$J_n = -qn \mu_n \frac{\partial V}{\partial x} + qD_n \frac{\partial n}{\partial x}$$
$$J_p = -qp \mu_p \frac{\partial V}{\partial x} - qD_p \frac{\partial p}{\partial x} \quad (S4)$$

with $\mu_{n,p}$ the charge carrier mobilities and $D_{n,p}$ carrier diffusion coefficients. The carrier diffusion coefficients can be written following Einstein equation such as:[1]

$$D_{n,p} = \mu_{n,p} V_T \quad (S5)$$

with $V_T = k_B T / q$ the thermal voltage ($V_T = 25.69 \text{ mV}$ at $25^\circ \text{C} = 298.15 \text{ K}$) with $k_B$ the Boltzmann’s constant, $T$ the absolute temperature.

For the simulation we chose to place the cathode at $x = 0$ and the anode at $x = L$ as a convention, $L$ being the total thickness of the device.

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[1] Note that for notation convenience the $x$ dependence of the variables will be dropped in the following. However, in a multilayer stack not only densities values are meant to vary with $x$ but also values such as mobilities and dielectric constant...
In order to numerically solve the system of equation presented above we need to specify the boundary conditions for the carrier densities:

\[
\begin{align*}
n(0) &= N_c \exp \left( \frac{-\phi_n}{V_T} \right) \\
N_c \exp \left( \frac{E_g - \phi_p}{V_T} \right) \\
p(0) &= N_v \exp \left( \frac{-E_g - \phi_n}{V_T} \right) \\
N_v \exp \left( \frac{-\phi_p}{V_T} \right) \\
\end{align*}
\]  

(S6)

and the potential at the contacts:

\[
q \left( V(L) - V(0) + V_{\text{app}} \right) = W_c - W_a
\]  

(S7)

with \( N_c \) and \( N_v \) the effective density of states for the conduction and valence band respectively, here we chose \( N_c \) and \( N_v \) to be equal, \( \phi_n \) and \( \phi_p \) the electron and hole injection barrier at the cathode and anode, \( V_{\text{app}} \) being the externally applied voltage and \( W_a \) and \( W_c \) the anode and cathode work functions respectively. The built-in potential is then given by \( V_{bi} = (W_c - W_a)/q \).

The generation rate of charge \( G \), in equation S3, is usually obtained by measuring the complex refractive index of all the layers and performing transfer matrix modeling.\(^{[2]}\) As for the recombination rate \( R \), it is typically expressed by adding the contribution from the band-to-band recombination and SRH recombination from equations S8 and S9. More details on the numerical methods used to solve this system of equations can be found in Ref. 1,3–6.

1.2 Band-to-band recombination

Band-to-band recombination corresponds to the direct recombination of a free electron from the conduction band with a free hole from the valence band. This type of recombination is usually accompanied by the emission of a photon with the same energy as the bandgap and is, hence, also called radiative recombination.

The band-to-band recombination rate \( R_B \) is given by

\[
R_B = \gamma \left( np - n_i^2 \right),
\]  

(S8)

1.3 Trap-assisted recombination

Trap-assisted recombination consists of the recombination of an electron and a hole via a localized state within the bandgap. Under steady-state conditions, the trap-assisted recombination rate is described by the Shockley-Read-Hall (SRH) statistics\(^{[7,8]}\) such as:

\[
R_{SRH} = \frac{C_n C_p \Sigma_T}{C_n(n + n_1) + C_p(p + p_1)} \left( np - n_i^2 \right),
\]  

(S9)

where \( \Sigma_T \) is the trap density, \( n_1 \) and \( p_1 \) are constants which depend on the trap energy level \( (E_{\text{trap}}) \), and \( C_n \) and \( C_p \) are the capture coefficients for electrons and holes respectively. \( n_1 \) and \( p_1 \) are defined as followed:

\[
\begin{align*}
n_1 &= N_c \exp \left( -\frac{E_C - E_{\text{trap}}}{k_B T} \right) \quad \text{and} \quad p_1 = N_v \exp \left( -\frac{E_{\text{trap}} - E_V}{k_B T} \right)
\end{align*}
\]  

(S10)
2 Pulsed-SCLC are ions really fixed?

To confirmed that we can use steady-state drift-diffusion simulations to reproduced the pulsed-SCLC JV by fixing the ions in their position at 0 V we simulated the actual transient signal of a voltage pulse to reconstruct the pulsed-SCLC JV as done in the experiment, see figure 3 (a). Where the voltage on the x-axis is the final applied voltage of the pulse and the current on the y-axis is taken as the average current (over 20 ms) after the displacement current pic. Figure S7 shows an example of the output from the transient drift-diffusion for a pulse from 0 to 3 V.

By reconstructing the pulsed-SCLC JV from the transient simulations we can compare with the output from the steady-state simulations where the ions are kept fixed. Figure S8 shows that there is a perfect agreement between the steady-state and transient simulations when the ionic mobility is kept at values close to what was reported in the literature $10^{-12} - 10^{-8}$ cm$^{-2}$ V$^{-1}$ s$^{-1}$.[9–11] However, as the mobility gets higher ($10^{-4}$ cm$^{-2}$ V$^{-1}$ s$^{-1}$) the effect of ions start to influence the JV. Nevertheless, for common mobility values for ions and for electric-fields below $10^7$ V m$^{-1}$ the ions are indeed fixed to there position at 0 V, see figure S9-S11. Hence, our approach of simulating the pulsed-SCLC JVs using steady-state simulations is justified and will be used to perform the fitting of experimental JV as it is numerically either to solve and saves a lot of computational time.

We also checked if the pulsed-SCLC method could be applied to thin-films, see figure S13, by simulating and 300 nm thick single-carrier device. We again find a perfect agreement between the transient and steady-state simulations suggested the the approach described here could also be applied to thin film. However, it is worth noting that this approach only work for sufficiently high trap densities as specified by equation 3 in the main text.

Figure S7: Example of simulated current transient for a voltage pulsed from 0V to 3 V. The pulsed-SCLC JV is constructed by averaging the current after the displacement current (i.e. after 10 µs) for 20 ms.
Table S3: Parameters used in the drift-diffusion to compare pulsed-SCLC JV from steady-state or reconstructed from transient simulation for MAPbBr₃-like single crystal.

| Parameter                        | Symbol | Value                                      |
|----------------------------------|--------|--------------------------------------------|
| Perovskite Layer                 |        |                                            |
| Conduction Band                  | $E_c$  | 3.4 eV                                     |
| Valence Band                     | $E_v$  | 5.6 eV                                     |
| Band gap                         | $E_{gap}$ | 2.2 eV                                    |
| Effective density of states      | $N_{cv}$ | $1 \times 10^{18}$ cm$^{-3}$               |
| Thickness                        | $L$    | 10 µm                                      |
| Mobility                         | $\mu$  | 12.9 cm$^{-2}$ V$^{-1}$ s$^{-1}$            |
| Relative dielectric constant     | $\epsilon_r$ | 25.5                                      |
| Ion density                      | $n_{ion}$ | $10^{11} - 10^{14}$ cm$^{-3}$              |
| Ion mobility                     | $\mu_{ion}$ | $10^{-12} - 10^{-4}$ cm$^{-2}$ V$^{-1}$ s$^{-1}$ |
| Recombination                    |        |                                            |
| Band-to-band recombination rate constant | $\gamma$ | $10^{-10}$ cm$^3$ s$^{-1}$               |
| Trap density                     | $n_t$  | $10^{13} - 10^{14}$ cm$^{-3}$              |
| Trapping level depth below $E_c$ | $E_{trap}$ | 0.54 eV                                    |
| Electron (hole) capture coefficient | $C_n(p)$ | $10^{-7}$ cm$^3$ s$^{-1}$                |
| Contact                          |        |                                            |
| Contact work function            |        | 3.82 eV                                    |

Figure S8: Comparison between pulsed-SCLC JV from steady-state simulations (lines) and reconstructed from the simulation of the transient pulse (circles), here we see a perfect agreement between the steady-state and transient simulations. For different trap densities $10^{13}-10^{14}$ cm$^{-3}$ and different ions densities $10^{11}-10^{14}$ cm$^{-3}$. The ionic mobilities are also increased with (from left to right) $10^{-12}, 10^{-8}$ and $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. 
Figure S9: Time evolution of the ionic distribution in the perovskite during the voltage pulse for different pulsed voltages and electric field (E) with ionic mobilities of $10^{-12} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$. 
Figure S10: Time evolution of the ionic distribution in the perovskite during the voltage pulse for different pulsed voltages and electric field (E) with ionic mobilities of $10^{-8}$ cm$^{-2}$ V$^{-1}$ s$^{-1}$.
Figure S11: Time evolution of the ionic distribution in the perovskite during the voltage pulse for different pulsed voltages and electric field ($E$) with ionic mobilities of $10^{-4}$ cm$^{-2}$ V$^{-1}$ s$^{-1}$. 
Figure S12: Comparison between pulsed-SCLC JV from steady-state simulations (lines) and reconstructed from the simulation of the transient pulse (circles) for a thin-film perovskite (300nm), here we see again a perfect agreement between the steady-state and transient simulations.
3 Derivation equation 4

If we interpret the transition into the SCLC regime as the moment when the free electron density becomes higher than the density of traps (i.e. all traps are filled) and higher than the other types of charges present in the bulk of the system (dopants, ions) then before \( V_{fli} \) or really \( V_{\text{net}} \) in this case we have \( n_t - n_{\text{ion}} + N_A - N_D > n \). This is well illustrated by figure S1-S3 where we see that SCLC is reached at a voltage slightly above 100 V where the electron density is higher than the density of the types of charge carrier.

Starting from the Poisson equation, we have:

\[
\frac{dF}{dx} = \frac{\rho}{\epsilon}, \quad \text{(S11)}
\]

with \( F \) the electric field and \( \rho \) the net charge. If we now assume that \( F(0) = 0 \) then:

\[
F(x) = \frac{\rho x}{\epsilon}. \quad \text{(S12)}
\]

By integrating both side of the equation and with \( V = \int_0^L Fdx \) we get:

\[
V_{\text{net}} = \frac{q\rho L^2}{2\epsilon}, \quad \text{(S13)}
\]

which in the absence of doping can be written as:

\[
V_{\text{net}} = \frac{q(n_t - n_{\text{ion}})L^2}{2\epsilon} \quad \text{(S14)}
\]

Here, the \( n_{\text{ion}} \) represent the cations density as the anions are confined near the electrode and do not affect the space-charge in the middle of the material, as shown in figure S1-S3.
4 Experimental procedures:

Chemicals and Reagents: N,N-Dimethylformamide (DMF) (68-12-2), PbBr₂ (10031-22-8), and CH₃NH₃Br (6876-37-5) were purchased from Sigma-Aldrich. All salts and solvents were used as received and without any further purification.

Synthesis of MAPbBr₃ Single Crystals and Device Fabrication: MAPbBr₃ single crystals were fabricated from a seed MAPbBr₃ crystal by following a previously published experimental protocol.[12–14] PbBr₂ (3.67 g) and CH₃NH₃Br (1.11 g) were dissolved in 10 mL of DMF. The solution was stirred until fully transparent. This solution was filtered with a 25 mm diameter 0.45 µm PVDF filter. A 4 mL sample of the filtrate was placed in a vial which contained a seed MAPbBr₃ crystal. To control the thickness down to the micrometer scale, a small chamber was constructed using two thin glass plates of different thicknesses placed on the bottom of the glass vial with a gap in between and a cover glass on top. The vial was kept in an oil bath undisturbed at 80 °C for 5 h. A free-standing, millimetersized crystal was taken out of the vial once formed and quickly rinsed by pure DMF solvent.

Measurement and Characterization: The 120 nm gold electrodes were evaporated on both of the larger faces of the single crystal by an evaporator (Kurt J. Lesker, Nano36) at a 0.5 A s⁻¹ deposition rate. The JV traces were measured using a computer-controlled Series Keithley source meter in the dark under vacuum at room temperature. The vacuum pump (Leybold vacuum, PT 70 F-Compact) pumped the system down to 10⁻⁴ mbar.

Figure S13: Illustration of the synthesis process of the perovskite single crystal.
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