Modeling Anomalous Hysteresis in Perovskite Solar Cells

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Supporting Information

Abstract: Organic— inorganic lead halide perovskites are distinct from most other semiconductors because they exhibit characteristics of both electronic and ionic motion. Accurate understanding of the optoelectronic impact of such properties is important to fully optimize devices and be aware of any limitations of perovskite solar cells and broader optoelectronic devices. Here we use a numerical drift-diffusion model to describe device operation of perovskite solar cells. To achieve hysteresis in the modeled current—voltage characteristics, we must include both ion migration and electronic charge traps, serving as recombination centers. Trapped electronic charges recombine with oppositely charged free electronic carriers, of which the density depends on the bias-dependent ion distribution in the perovskite. Our results therefore show that reduction of either the density of mobile ionic species or carrier trapping at the perovskite interface will remove the adverse hysteresis in perovskite solar cells. This gives a clear target for ongoing research effort and unifies previously conflicting experimental observations and theories.

Research interest in organic—inorganic lead halide perovskite semiconductors has risen tremendously within the last 5 years due to their use in photovoltaics, already giving rise to power conversion efficiencies of >20%. despite this tremendous growth, knowledge of the perovskite material properties itself and the relevant physical processes is still lacking. Currently, one of the major issues holding back development of perovskite solar cells is the presence of hysteresis in the voltage-dependent photocurrent.7–10 Even solar cells exhibiting >20% efficiency exhibit some hysteresis, and the efficiency has been determined by taking the average of the forward and reverse scans or by holding the cell close to the maximum power point until stabilized steady-state power output is achieved. The physical origin of this hysteresis has been linked to a large variety of processes like (i) trapping of electronic carriers at the perovskite interface(s);11,12 (ii) ionic displacement;13 or (iii) ferroelectric effects.14,15 Experimental work supports these theories because, for instance, surface passivation of perovskites has led to a reduction in trap density and simultaneous reduced hysteresis.11,16 On the contrary, hysteresis has been shown convincingly to occur on time scales corresponding to ionic transport.13 Nevertheless, no clear and complete description exists of how such processes can eventually lead to hysteresis effects in these semiconductors while simultaneously considering all currently known processes governing device operation.

We use numerical modeling to investigate solar cell current voltage characteristics under light and dark, where the photoactive material includes both mobile ionic species and electronic trap sites. We show that hysteresis effects in perovskite solar cells originate from a combination of ionic transport throughout the perovskite and trapping of electronic carriers, most likely at the interface. Depending on the (history of the) biasing conditions, this combination can result in a significant loss in photocurrent due to trap-assisted recombination at the perovskite charge collection layer interface. This relatively high rate of recombination at the interface is sustained by large electron and hole densities due to (i) electronic compensation of ionic space charge and (ii) electronic traps. We could not reproduce any hysteresis via ionic transport or electronic traps alone, checked by calculations covering the reasonable limits of relevant parameters. Only when assuming an extraction barrier between the perovskite and its neighboring transport layer, could we “induce” hysteresis effects by including ionic transport alone, while excluding electronic traps; however, in this latter instance, hysteresis in open-circuit voltage, which is commonly observed in experiments, was not reproduced. This indicates that an extraction barrier can “amplify” hysteresis effects but is not its primary cause for the anomalous hysteresis observed in perovskite solar cells.

We show the energy level diagram of the modeled perovskite solar cell device in Figure 1. We use a numerical drift-diffusion model that was previously used in refs 17 and 18 to successfully describe the operation of light-emitting electrochemical cells, in which ionic and electronic transport are highly relevant. Here the model describes operation of typical perovskite solar cells including generation, recombination, transport, trapping, and injection of electronic and ionic charge carriers by calculating

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perovskite, leading to a change in the built-in voltage of the perovskite.\textsuperscript{15} Such a change in built-in voltage may lead to different $I$–$V$ characteristics, dependent on the bias history before the actual bias sweep.

To determine whether mobile ions alone can indeed cause hysteresis, we attempted to replicate the experiment reported by Tress et al.,\textsuperscript{13} which accurately shows the presence of hysteresis effects in perovskite solar cells. In their experiment, the perovskite solar cell was allowed to stabilize at varying bias voltages ($V_{\text{stabilized}}$) prior to performing a fast $I$–$V$ sweep. The stabilization allows the ions to redistribute. The subsequent $I$–$V$ sweep is sufficiently fast to not allow ions to redistribute again during the sweep. In our model, we reproduced this experiment by initially setting a homogeneous density of ions $a = c = 10^{18}$ cm$^{-3}$ in the perovskite, assuming only mobile anions with a mobility $\mu_a = 10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$, $V = V_{\text{stabilized}}$, and $G = 0$. Furthermore, we blocked ions at the interfaces, preventing ion exchange with the ETM or HTM. The consequence of this is that the quasi-steady state ion distribution is not affected by the ion mobility. We have thus had the liberty to choose an artificially high ion mobility to reduce computational time.\textsuperscript{24}

After the device reaches steady state after roughly $3 \times 10^{-8}$ s, we obtain the potential profiles that we show in Figure 2a. The potential drops at the perovskite interfaces prove the presence of ionic space charge screening the bulk of the perovskite from the externally applied electric field. Next, we set the anion mobility back to 0 to fix the ion distribution in the perovskite. This allows us to perform $I$–$V$ sweeps without ion redistribution or any need for knowledge on the ion mobility. In Figure 2b we show the potential profiles at $V = 0$ V and $G = 0$ to show the modified built-in voltage of the perovskite due to the induced ion distribution. In Figure 2c, respectively, we show the potential profiles and electron and hole density profiles at $V = 0$ V and $G = 2.5 \times 10^{21}$ cm$^{-3}$ s$^{-1}$. The subsequent $I$–$V$ characteristics, during which the ions were immobile at different values of $V_{\text{stabilized}}$ and $G = 2.5 \times 10^{21}$ cm$^{-3}$ s$^{-1}$, are plotted in Figure 3a. We observe that the modeled $I$–$V$ characteristics are all similar and thus independent of $V_{\text{stabilized}}$. This result is in contrast with expectations and the experiments,\textsuperscript{13} in which significant differences between $I$–$V$ characteristics with varying $V_{\text{stabilized}}$ are reported.

We can attribute the absence of any hysteretic effect in the $I$–$V$ curves in Figure 3a for different ion distributions, to the presence of a high ionic space charge (compare Figure 2b,c) of the ionic space charge by photogenerated electrons and holes. Close inspection of the modeling results shows a strong variation of the electron and hole densities (see Figure 2d) for varying $V_{\text{stabilized}}$. For $V_{\text{stabilized}} = 0$, $-0.5$, and $-1.0$ V, negative (positive) ionic space charge is formed at the interface between the ETM (HTM) and the perovskite. This negative (positive) ionic space charge is partially compensated by holes (electrons) in case $V_{\text{bias}} > V_{\text{stabilized}}$. For $V_{\text{stabilized}} = 1.2$ V, however, the ion distribution is reversed: positive (negative) ionic space charge sits at the interface with the ETM (HTM). Again the negative (positive) space charge is partially compensated by holes (electrons). The schematics in Figure 3b,c summarize this charge compensation mechanism and the flow of charge in the modeled perovskite solar cell including ion motion.

Because these results appear to contradict mounting experimental evidence pointing toward mobile ions being primarily responsible for hysteresis, we performed more simulations for varying initial ion densities in the perovskite, different types of mobile ions, and the inclusion of an extraction..

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**Table 1. General Device Model Parameters**

<table>
<thead>
<tr>
<th>property</th>
<th>unit</th>
<th>ETM</th>
<th>perovskite</th>
<th>HTM</th>
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</thead>
<tbody>
<tr>
<td>$\mu_p$</td>
<td>cm$^2$ V$^{-1}$ s$^{-1}$</td>
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<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>cm$^2$ V$^{-1}$ s$^{-1}$</td>
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<td>6.5</td>
<td>3</td>
</tr>
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<td>$I_{\text{pre}}$</td>
<td>1</td>
<td>$10^{-5}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$G$</td>
<td>cm$^{-3}$ s$^{-1}$</td>
<td>0</td>
<td>$2.5 \times 10^{21}$</td>
<td>0</td>
</tr>
<tr>
<td>initial $a$</td>
<td>cm$^{-3}$</td>
<td>0</td>
<td>$x$</td>
<td>$8 \times 10^{27}$</td>
</tr>
<tr>
<td>initial $c$</td>
<td>cm$^{-3}$</td>
<td>$8 \times 10^{27}$</td>
<td>$x$</td>
<td>0</td>
</tr>
<tr>
<td>initial $n$</td>
<td>cm$^{-3}$</td>
<td>$8 \times 10^{27}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>initial $p$</td>
<td>cm$^{-3}$</td>
<td>0</td>
<td>$8 \times 10^{27}$</td>
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</tr>
<tr>
<td>layer thickness</td>
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<td>48</td>
<td>472</td>
<td>48</td>
</tr>
</tbody>
</table>

(\textit{\textmu}_p) mobility was chosen, similar to literature values.\textsuperscript{19,20} The dielectric constant $\varepsilon_i$ was set at 6.5. (We note that we have compared with a dielectric of 30 in the SL).\textsuperscript{21} A weakened form of Langevin recombination was implemented via a prefactor $L_{\text{pre}} = 10^{-5}$ in the recombination rate equation, following estimates from experiments.\textsuperscript{22} Homogeneous generation $G$ of free electrons and holes was assumed throughout the perovskite layer of $G = 0$ or $2.5 \times 10^{21}$ cm$^{-3}$ s$^{-1}$ to model dark and light conditions, respectively.\textsuperscript{23} The properties of the HTM and ETM were chosen such that these resembled doped materials like TiO$_2$ and spiro-OMeTAD.\textsuperscript{15} Doping in these transport layers was modeled by a homogeneous density of immobile anions ($a$) or cations ($c$) which are electrostatically compensated by mobile electrons ($n$) and holes ($p$).

In various publications hysteresis in perovskite solar cells has been attributed to the movement of ions throughout the perovskite:\textsuperscript{13} Bias-dependent ionic redistribution results in the build up of ionic space charge at the interfaces of the perovskite, leading to a change in the built-in voltage of the perovskite.\textsuperscript{15}
barrier between the perovskite and the ETM (see SI). We do not observe hysteresis effects in the $I-V$ characteristics upon variation of the total ion density. The results are also independent of the type of ionic carrier that is mobile, for example, anions, cations, or both. In any of these three scenarios, the mobile ions are able to generate ionic space charge at both of the perovskite interfaces by a combination of ion accumulation and depletion. When we include a significant extraction barrier, that is, 0.3 eV between the perovskite and the ETM conduction bands, we do observe hysteresis effects (see SI); however, we only observe variations in the “fill-factor” of the $I-V$ curve (the fill factor describes how sharp the bend is in the $I-V$ curve), while $V_{oc}$ and $J_{sc}$ remain independent upon prebiasing conditions. The hysteresis effects originate from a reduced (increased) charge extraction under working conditions when $V_{stabilized} = -1.0$ V ($V_{stabilized} = 1.6$ V) by the induced negative (positive) ionic space charge at the ETM/perovskite interface. The reduced charge extraction results in a pile up of charge carriers in the bulk of the perovskite, enhancing recombination. For $V_{stabilized} = 1.6$ V, the induced positive ionic space charge at the ETM/perovskite interface compensates the effect of the poor extraction barrier, resulting in lower charge carrier densities in the bulk of the perovskite and hence a reduced recombination. The key observation we make here is that the modeled hysteresis does not resemble the hysteresis observed in experiments by Tress et al. nor do their experiments show an S-shaped $I-V$ characteristic around $V = V_{oc}$ which we observe in our modeled result. This indicates that

Figure 2. Modeled potential, electron, and hole density profiles for a typical perovskite device comprising ions but no traps. The shading in the background shows the device structure with from left to right: FTO, ETM, perovskite, HTM, and Au. Electric-field profiles can be found in the SI.

Figure 3. $J-V$ characteristics and interpretation of a perovskite solar cell with ions showing no hysteresis effects. (a) Modeled $J-V$ characteristics of a perovskite device comprising ions but no traps. (b,c) Schematics of the charge flow in the conduction (CB) and valence band (CV) of the perovskite in case (b) $V_{stabilized} < V_{oc}$ and (c) $V_{stabilized} > V_{oc}$ with 1. charge generation; 2. charge transport; and 3. charge extraction.
current and voltage hysteresis in perovskite devices must be explained by an alternative mechanism. In hind sight, we would not expect a modulation of the resistivity of a charge extraction barrier to induce voltage hysteresis but simply induce a more or less pronounced s-shape of the $I-V$ curve as our model predicts.25,26

Besides mobile ions, it is also known that there is a non-negligible trap density in these perovskite materials. Hence, we now also consider interfacial electronic traps as the origin of hysteresis. At first, we will consider only interfacial traps in the perovskite at the ETM/perovskite interface (see SI) and neglect mobile ionic species. Following literature, we take an interfacial trap state density $N_t = 10^{17}$ cm$^{-3}$ at the grid point in the perovskite that contacts the electron transport layer, with a trap energy $E_{\text{trap}} = 0.5$ eV.19 We describe the trapping rate (in m$^{-3}$ s$^{-1}$) by the product of the available trap density ($N_t - n_t$), the free electron density $n$ at the same grid-point, and a trapping coefficient $c_n$; $c_t$ can be approximated by the product of the site volume (i.e., $n_{\text{DOS}}^{-1} = 1/2.2 \times 10^{24} = 5 \times 10^{-25}$ m$^3$ following20) and the attempt frequency which can be approximated by a typical phonon frequency (10$^{10}$ to 10$^{12}$ s$^{-1}$). On the basis of these values, we used $c_t = 6 \times 10^{-13}$ m$^3$ s$^{-1}$ for the simulations.

We model trap-assisted recombination by a Langevin recombination rate of immobile trapped electrons and free holes, which is described by the product of the trapped electron density, the free hole density at the same grid-point, and a recombination coefficient $c_p$ (see SI).27 Following Langevin recombination and the material parameters of the perovskite used in the model, we calculated $c_p$ to be equal to $6 \times 10^{-13}$ m$^3$ s$^{-1}$.

In Figure 4a (dashed line) we show the modeled $I-V$ characteristic of a perovskite solar cell comprising electron traps at the ETM/perovskite interface without any mobile ions. We performed the calculations with the same parameters as previously described. The current stabilizes at each voltage point within $10^{-5}$ s, which directly shows that such interfacial trapping, by itself, is not the cause of hysteresis occurring on greater than milliseconds time scales.

Because neither mobile ions nor trap-assisted recombination alone can accurately reproduce the observed influence of prebiasing upon the current voltage curves, we seek to determine their combined effect. We repeat the modeling experiment where ions were allowed to stabilize at varying values of $V_{\text{stabilized}}$ under dark conditions before being immobilized, with the presence of traps. In Figure 4a we show the subsequent $I-V$ characteristics for $G = 2.5 \times 10^{21}$ cm$^{-3}$ s$^{-1}$ in the perovskite, where we observe a clear dependence of the $I-V$ characteristic on $V_{\text{stabilized}}$ which is strikingly similar to the experiments reported in ref 13.

We can explain the results in Figure 4a by a loss in photocurrent due to recombination in the perovskite of free holes with trapped electrons at the ETM/perovskite interface, as we illustrate in Figure 4c,d. For this loss to be significant, relatively large densities of free holes and trapped electrons are required. The trapped electron density is limited by the trap state density, that is, $10^{17}$ cm$^{-3}$ in this simulation, as well as the trapping rate relative to the recombination rate. The free hole density, shown in Figure 2d, depends strongly on $V_{\text{stabilized}}$ over roughly 6 orders of magnitude: We observe relatively large hole densities at the ETM/perovskite interface for $V_{\text{bias}} > V_{\text{stabilized}}$. Indeed, we observe in the $I-V$ characteristics in Figure 4a that the reduction in photocurrent takes place when $V_{\text{bias}} > V_{\text{stabilized}}$. We undertook further modeling, where we observe that this loss of photocurrent can be reduced by reduction of the trapping coefficient, the trap state density, and the recombination coefficient (see SI).

Following these results we also modeled $I-V$ characteristics with mobile ions to enable better comparison with regular $I-V$ sweeps of perovskite solar cells which exhibit hysteresis. Because of the long calculation time of the model, a relatively high sweep rate of 100 kV s$^{-1}$ was used in combination with relatively high anion mobilities, which we vary between $10^{-3}$ and $10^{-5}$ cm$^2$ V$^{-1}$s$^{-1}$. We made sure that at every voltage point during the sweep all electronic processes have reached steady...
state by allowing the model to continue calculations with \textit{immobilized} ions beyond the time dictated by the sweep rate. The variation of the ion mobility with a constant sweep rate can be regarded to be similar to a variation of the sweep rate with a constant ion mobility: Enhancement of the ion mobility is equivalent to a reduction of the sweep rate by the same factor, given we keep a constant ion density. We plot the results of these \textit{I–V} simulations for varying ion mobility in Figure 4b, which strongly resemble the experimental results reported in ref 13 (for varying sweep rate). For relatively low anion mobilities, that is, below $10^{-13}$ cm$^2$ V$^{-1}$ s$^{-1}$, the ions are hardly able to follow the varying electric field, resulting in a nearly hysteresis-free sweep. Furthermore, the ions are placed in a situation similar as illustrated in Figure 4d, resulting in hardly any losses in photocurrent. For relatively high anion mobilities, that is, $>10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, the ions can easily follow the changing electric field such that the forward and backward sweeps are the same as the ion distributions at each voltage point reach a steady state and are hence independent of the sweep direction. Our simulations show strong hysteresis at an anion mobility of $10^{-14}$ cm$^2$ V$^{-1}$ s$^{-1}$ and a sweep rate of 100 kV s$^{-1}$. Experiments in ref 13 require a sweep rate of 1 V s$^{-1}$ for the strongest hysteresis effects. Assuming similar mobile ion densities, we can estimate the ion mobility in the CH$_3$NH$_3$PbI$_3$ perovskite to be roughly $10^{-9}$ cm$^2$ V$^{-1}$ s$^{-1}$ or a diffusion coefficient of $2 \times 10^{-11}$ cm$^2$ s$^{-1}$. Recent work has suggested an $\Gamma$ diffusion coefficient of $10^{-12}$ cm$^2$ s$^{-1}$. The mismatch in 1 order of magnitude may be related to a difference in mobile ion density or may also be the difference in ion transport through the bulk of crystalline perovskite or through grain boundaries and is hence in reasonably good agreement.

We have shown above that the combination of mobile ions and electron traps at the ETM/perovskite interface can lead to hysteresis effects that accurately reproduce experimental observations, for a reasonable choice of material parameters. We did, however, consider alternative combinations to test the boundaries of hysteresis inducing factors. For instance, if we consider mobile ions combined with hole traps at the perovskite/HTM interface, we can also reproduce hysteresis effects as the description is physically identical to the case we have previously described. Moreover we also tested the combination of bulk traps and mobile ions (see SI section E). Here we found that substitution of interface traps for bulk traps can result in similar hysteresis effects. To do so, however, requires the assumption of relatively large bulk trap state densities as well as relatively high recombination coefficients. This can be justified by considering the results we present in Figure 2, where the regions of the perovskite film which are most strongly varying in ionic space charge density after prebiasing are the regions near the ETL and HTL interfaces. Hence hysteresis effects will be most strongly influenced by changes in trap densities in these regions.

These results show that to reduce hysteresis in perovskite solar cells and more importantly to improve their efficiency, it is required to reduce either the density of mobile ionic species or charge trapping. Reduction of the trap density in our model indeed reduces the hysteresis effect (see SI). This is in line with recent experimental work in which hysteresis has been reduced by passivation of traps at the perovskite interfaces. Furthermore, the trap density at the interface is very likely to depend on the type of charge-transport layers connecting the perovskite, especially if the charge-transport layers themselves are crystalline materials such as metal oxides, and the quality and structure of the perovskite itself which can strongly vary for different deposition methods. In addition, if any electronic doping of the perovskite occurs near the interfaces, we would expect this to strongly influence the charge carrier profiles and hence the hysteresis effects described in this letter. This could lead to a cell with low hysteresis despite large interfacial trap densities. Specifically considering devices incorporating mesoporous TiO$_2$ (or indeed mesoporous Al$_2$O$_3$), it has been observed that the Fermi level in the perovskite MAPbI$_3$ infiltrated into these mesoporous oxides is close to the conduction band, indicating it to be n-type-doped. This could be one of the reasons that cells with thin interlayers of mesoporous TiO$_2$ between the crystalline perovskite and compact TiO$_2$ layer can result in solar cells with low hysteresis.

We have shown that anomalous hysteresis effects in perovskite solar cells can be understood as the combined effect of ion migration through the perovskite and trapping of charge carriers at the perovskite interfaces. Both ion migration and charge trapping can cause large densities of electrons and holes at the perovskite interface, with the relative density dependent on the electronic bias history, trap density, and ionic density. For unfavorable biasing, a large density of trapped electrons and free holes accumulate at the perovskite ETM interface, inducing strong nonradiative trap-assisted recombination. The consequently large (nonradiative) recombination rate reduces the photocurrent and thereby the efficiency of the device. For favorable biasing, a low density of trapped electrons and free holes accumulates at this interface, good for more ideal solar cell operation. Ion migration or charge trapping alone cannot reproduce hysteresis effects. Hence, reduction of hysteresis and simultaneous improvement of efficiency should be achievable by reducing either the density of mobile ionic species or electronic defects responsible for trap-assisted recombination. Importantly, the new coherent insight we have derived from this model consolidates the previously perceived to be conflicting observations of anomalous hysteresis originating from different phenomena. We also note that it is not necessary to induce any consideration of ferroelectric effects to explain the observable hysteresis.

Although our model proves that interfacial traps and ion transport are both crucial to understand anomalous hysteresis in perovskite solar cells, it does not give any detail of the actual origin of the traps or the mechanism of ion transport throughout the perovskite. Hence to reduce hysteresis by reducing ion transport and interfacial traps, more research is required to gain more insight into these processes. Nevertheless, this model predicts that targeting these issues will lead to “ideal” solar cell operation.

More broadly, these results show that the presence of both mobile ions and traps in semiconductors can give rise to hysteretic effects, which reduce performance in electronic devices. Therefore, these results can be extended to other material systems like organic semiconductors, \textit{ionic transition-metal complexes}, or metal oxides, and they represent a sound platform for describing the operation of future devices.

### ASSOCIATED CONTENT

#### Supporting Information

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Notes
The authors declare no competing financial interest.

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Modelling anomalous hysteresis in perovskite solar cells

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A. The numerical model to describe perovskite solar cell operation

To model the device operation of perovskite solar cells a numerical model is used which describes carrier injection, transport, generation, recombination, and trapping for electronic and ionic charges. This model solves the Boltzmann transport equations and Poisson’s equation on a 2D grid by forward integration in time. In the next paragraphs a detailed description is given on the methods to describe charge transport, carrier injection and carrier recombination. Additional optional processes like i) charge trapping and ii) trap-assisted recombination are included in the numerical model as well. Parameters that need to be defined for each calculation are shown in Supplementary Table A1. Here CB and CV are the conduction band and valence band, respectively.
Supplementary Table A1. Input parameters for the numerical model of a perovskite solar cell.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
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<td>Mobility (electron; hole; anion; cation)</td>
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</tr>
<tr>
<td>CB and CV of semiconductors</td>
<td>( E_{\text{HOMO}}; E_{\text{LUMO}} )</td>
</tr>
<tr>
<td>Density of states of semiconductors</td>
<td>( N_0 )</td>
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<tr>
<td>Anion and cation density</td>
<td>( a; c )</td>
</tr>
<tr>
<td>Work function of contacts</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>Bias voltage</td>
<td>( V_{\text{bias}} )</td>
</tr>
<tr>
<td>Temperature</td>
<td>( T )</td>
</tr>
<tr>
<td>Relative dielectric constant</td>
<td>( \varepsilon_r )</td>
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A.1 Charge transport

In the 2D model a rectangular grid is used with grid points at the corners of each cell. The areas of the cells are determined by the widths of the columns and rows which can be specified per row or column. For each cell a material type is specified, either gate, contact, dielectric or semiconductor. Calculations of current, recombination, etc. are performed on the grid points. The 4 cells surrounding the grid point are in equilibrium with each other, which is effectuated by area-average weighting of these 4 cells. Consequently, a single quasi Fermi level is defined on each grid point.

Carrier transport is described by the following Boltzmann transport equations:

\[
J_i = -q\mu_i n_i \nabla \psi_{F,i}, \tag{S1}
\]

where \( q \) is the elementary charge, \( \mu_i \) and \( n_i \) are the mobility and density for free electrons \((n_i = n)\), free holes \((n_i = p)\), free anions \((n_i = a)\), or free cations \((n_i = c)\) and \( \psi_{F,i} \) is the quasi Fermi energy which is given by

\[
\psi_{F,n} = \psi_L - \frac{kT}{q} \ln \frac{n}{N_0}, \tag{S2}
\]

\[
\psi_{F,p} = \psi_H + \frac{kT}{q} \ln \frac{p}{N_0}, \tag{S3}
\]

\[
\psi_{F,a} = V - \frac{kT}{q} \ln \frac{a}{N_0} \tag{S4}
\]
\[ \psi_{F,C} = V + \frac{kT}{q} \ln \frac{c}{N_0}, \]  
(S5)

where \( \psi_L = E_{CB} + V \) and \( \psi_H = E_{VB} + V \) and \( V \) is the electrostatic potential. \( k \) is Boltzmann’s constant and \( T \) is the temperature. Einstein’s relation between the diffusion constant and the mobility is assumed to hold. The ion current is zero at the electrodes, for the electrodes are ionically blocking.

The continuity equations are

\[ \frac{d n}{d t} = \frac{1}{q} \frac{d J_n}{d x} - R, \]  
(S6)

\[ \frac{d p}{d t} = - \frac{1}{q} \frac{d J_p}{d x} - R, \]  
(S7)

\[ \frac{d a}{d t} = \frac{1}{q} \frac{d J_a}{d x}, \]  
(S8)

\[ \frac{d c}{d t} = - \frac{1}{q} \frac{d J_c}{d x}, \]  
(S9)

for electrons, holes, anions, and cations, respectively. Here \( J_i \) is the current density of particle \( i \) and \( R \) is the recombination rate. The potential profile throughout the device is calculated from Poisson’s equation:

\[ \nabla^2 V = - \frac{q}{\varepsilon_0 \varepsilon_r} (p - n + c - a), \]  
(S10)

where \( \varepsilon_0 \) and \( \varepsilon_r \) are the dielectric and the relative dielectric constant, respectively.

### A.2 Carrier injection

To describe the injection of electrons and holes into the semiconductors, the following parameters are of importance: the VB and CB levels of the semiconductor; the Fermi level of the contacts; and the charge carrier density in the semiconductor at the interface. The injection model is based on Boltzmann injection:
\[ n(1) = N_0 \exp \left( -\frac{q \varphi_n}{kT} \right), \]  

\[(S11)\]

where \( n(1) \) is the electron density at the first grid-point next to the electrode and \( \varphi_n \) is the injection barrier height. In this model injection is not affected by the grid-point spacing.

### A.3 Charge trapping

The charge trapping rate for electrons (\( T_n \)) is described by the product of the free electron density (\( n \)), the available trap density (\( N_t - n_t \)), and a trapping coefficient (in m\(^3\)s\(^{-1}\)):

\[ T_n = c_n \cdot (N_t - n_t) \cdot n. \]  

\[(S12)\]

Empty traps are considered neutral.

### A.4 Recombination

Free electrons and free holes recombine following a Langevin process in this model:

\[ R_f = L_{pre} \frac{q(\mu_n+\mu_p)}{\varepsilon_0\varepsilon_r} \cdot p \cdot n, \]  

\[(S13)\]

where \( R_f \) is the recombination rate of free carriers and \( L_{pre} \) is the Langevin prefactor.\(^5\)

Recombination between trapped electrons and free holes is also described by a Langevin process in the model:

\[ R_t = L_{pre,t} \frac{q(\mu_p)}{\varepsilon_0\varepsilon_r} \cdot p \cdot n_t = c_p \cdot p \cdot n_t. \]  

\[(S14)\]

where \( R_t \) is the recombination rate of free holes and trapped electrons, \( n_t \) is the trapped electron density, \( c_p \) is the recombination coefficient for this recombination process, and \( L_{pre,t} \) the Langevin prefactor for this specific recombination process.
A.5 Used parameters

The grid to model a perovskite solar cell is shown in Supplementary Figure A1. Although a smaller grid-point spacing is preferred, a 4 nm grid-point spacing was chosen to enable reasonable calculation times for the model without relevant changes in the outcome of the model. Independence of the results from the grid-point spacing was confirmed by modelling with a 2 nm grid-point spacing as well. A comparison between simulations with 2 nm and 4 nm grid-point spacing is shown in Figure A2.

Supplementary Figure A1. Grid layout of the modelled perovskite solar cell.

Supplementary Figure A2. Simulation comparison for varying grid-point spacings.

The energy level diagram is shown in Supplementary Figure A3.
**Supplementary Figure A3.** Energy level diagram in eV of the simulated perovskite solar cell.

Parameter values to model perovskite solar cell operation are shown in Supplementary Table A2. The used ion mobility in case the ions were set to be ‘mobile’ was $10^{-1} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$. We note that the chosen ion mobility is unimportant, and only influences the time to reach steady state in the calculation.
Supplementary Table A2. General device model parameters.

<table>
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<tr>
<th>property</th>
<th>unit</th>
<th>ETM</th>
<th>Perovskite</th>
<th>HTM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_p, \mu_n$</td>
<td>cm$^2$ V$^{-1}$ s$^{-1}$</td>
<td>0.02</td>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
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<td>6.5</td>
<td>3</td>
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<tr>
<td>$L_{pre}$</td>
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<td>$10^5$</td>
<td>1</td>
</tr>
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<td>$G$</td>
<td>cm$^{-3}$ s$^{-1}$</td>
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<td>$2.5 \times 10^{21}$</td>
<td>0</td>
</tr>
<tr>
<td>initial $a$</td>
<td>cm$^{-3}$</td>
<td>0</td>
<td>X</td>
<td>$8 \times 10^{17}$</td>
</tr>
<tr>
<td>initial $c$</td>
<td>cm$^{-3}$</td>
<td>$8 \times 10^{17}$</td>
<td>X</td>
<td>0</td>
</tr>
<tr>
<td>Initial $n$</td>
<td>cm$^{-3}$</td>
<td>$8 \times 10^{17}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>initial $p$</td>
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<td>0</td>
<td>$8 \times 10^{17}$</td>
</tr>
<tr>
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<td>472</td>
<td>48</td>
</tr>
<tr>
<td>$N_0$</td>
<td>cm$^{-3}$</td>
<td>$10^{20}$</td>
<td>$10^{20}$</td>
<td>$10^{20}$</td>
</tr>
</tbody>
</table>

A.6 Model operation

Initially no electrons or holes are present. Only at the electrodes electrons and holes are present due to the boundary conditions imposed by the injection model. In addition, the bias voltage is applied to one of the contacts (Au), whereas the other contact (FTO) is set at 0 V. For a defined number and size of time steps, the model then calculates the Fermi energy of all the carriers, solves the Boltzmann transport equations, accounts for electron-hole recombination, and solves the continuity equations to determine the new carrier densities at each grid point. A steady-state solution is obtained when the current, which is determined by the sum of current through the contacts, becomes constant.
B. Electric field profiles corresponding to Figure 2a-c

Supplementary Figure B1. Modelled potential and electric field profiles for a typical perovskite device comprising ions but no traps. The shading in the background shows the device structure with from left to right: FTO, ETM, perovskite, HTM, Au.
C. Additional simulations for perovskite solar cells comprising only mobile ions and no traps

For varying ion densities:

Supplementary Figure C1. Modelled $I$-$V$ characteristics of perovskite devices comprising ions and no traps for varying ion densities.
When including an extraction barrier of 0.1 eV and 0.3 eV, respectively, between the conduction bands of the ETM and the perovskite:

**Supplementary Figure C2.** Modelled $I$-$V$ characteristics of perovskite devices with different extraction barriers. Modelled $I$-$V$ characteristics of perovskite devices with an extraction barrier of (a) 0.1 eV and (b) 0.3 eV between the conduction band of the ETM and the perovskite, while including mobile ions in the simulation and excluding charge traps.

**Supplementary Figure C3.** Recombination and charge density profiles. (a) Recombination profile and (b) charge density profiles for simulations corresponding to Figure C2.
D. Additional simulations for perovskite solar cells comprising mobile ions and traps

Supplementary Figure D1. Modelled I-V characteristics of perovskite devices comprising ions and traps for varying (a) \(c_p\), (b) \(N_t\), and (c) \(c_n\). In (d) p-type traps were added at the perovskite/HTM interface similar to the n-type traps at the perovskite/ETM interface with the same trapping and recombination coefficients. The p- and n-type trap state density, \(P_t\) and \(N_t\), respectively, was varied as indicated in the figure.
**Supplementary Figure D2.** (a) Recombination profile and (b) charge density profiles for simulations corresponding to Figure 4a.

**Supplementary Figure D3.** Modelled $I$-$V$ characteristics for variation of the dielectric constant in the perovskite. Simulation parameters are the same as in the simulations shown in Figure 4a in the main text. The black curve is reproduced from Figure 4a.
Supplementary Figure D4. Modelled I-V characteristics for variation of the ion concentration in the perovskite. Simulation parameters are the same as in the simulations shown in Figure 4a in the main text. The black curve is reproduced from Figure 4a.
E. Bulk traps

Trapping of electrons in the bulk is described by equation S12. For bulk traps, a trap energy of 0.014 eV was used to simulate shallow traps. The trap state density was set at varying values of $10^{20}$, $10^{19}$, $10^{18}$ cm$^{-3}$. The trapping coefficient $c_n$ was set at $6 \cdot 10^{-16}$ m$^3$s$^{-1}$. Recombination between trapped electrons and free holes in the bulk perovskite was described by equation S14 where the recombination coefficient $c_p$ was set at $6 \cdot 10^{-14}$ m$^3$s$^{-1}$.

Similar simulations were performed here including bulk traps and mobile ions, as the simulations described in the main text including interface traps and ions. The results are shown in Supplementary Figure E1.

**Supplementary Figure E1.** J-V characteristics and interpretation of a perovskite solar cell with ions and bulk traps showing hysteresis effects. (a) Modelled J-V characteristics of a perovskite device comprising ions and bulk traps. (b-c) Schematics of the charge flow in the conduction (CB) and valence band (CV) of the perovskite in case (b) $V_{\text{stabilized}} < V_{\text{oc}}$ and (c) $V_{\text{stabilized}} > V_{\text{oc}}$ with 1. charge generation; 2. charge transport; 3a. charge extraction; 3b. charge trapping; 4. trap-assisted charge recombination.

The results show that besides traps at the interfaces, also traps in the bulk of the perovskite can lead to the occurrence of hysteresis in case mobile ions are present. For $V_{\text{stabilized}} < V_{\text{oc}}$, the ionic space charge...
at the interface enhances the carrier density in the device for $V > V_{\text{stabilized}}$. Consequently recombination throughout the bulk of the perovskite is enhanced. Note that the radiative recombination coefficient here is $c_p = 6 \cdot 10^{-14} \text{ m}^3\text{s}^{-1}$, which is relatively high compared to experimental values reported in literature for recombination in the bulk of these types of perovskites: Ref [6] reports $1.7 \cdot 10^{-16} \text{ m}^3\text{s}^{-1}$.

Variation of $c_p$ (for a trap state density of $10^{20} \text{ cm}^{-3}$) in Supplementary Figure E2 shows that for more realistic radiative recombination coefficients in the bulk, the effect of bulk traps on the occurrence of hysteresis becomes relatively weak.

Supplementary Figure E2. $J$-$V$ characteristics of a perovskite solar cell with ions and bulk traps showing hysteresis effects for a variation of the radiative recombination coefficient as shown in the legend.

On the basis of these simulations we can conclude that the combination of bulk traps and mobile ions in perovskite solar cells, can result in hysteresis. However, for hysteresis to appear, a relatively high radiative recombination coefficient and trap state density of the bulk perovskite must be assumed.
REFERENCES