Supplementary Information for

How transport layer properties affect perovskite solar cell performance: insights from a coupled charge transport/ion migration model

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A   Details of Supplementary Videos

The videos each show simulation results for a current-voltage (J-V) scan of a three-layer perovskite solar cell after 4 seconds preconditioning at an applied voltage of 1.2 V. The top two panels show the evolution of the electric potential (black, left axes), ion vacancy density (magenta, right axis) and carrier densities (blue for electrons, red for holes, right axis, logarithmic) during the scan, while the bottom two panels simultaneously trace out the reverse and then forward scan of current density and the electric field at the midpoint of the perovskite versus voltage.

Video S1: Simulation results for a 0.75 V/s J-V scan of a PSC described by the parameters in Tables 1 and 2(a) of the main text except that the ion diffusivity $D_I = 10^{-16} \mathrm{m^2 s^{-1}}$.

Video S2: Equivalent to S1 but for the recombination parameters in Table 2(b) of the main text.

Video S3: Simulation results for a 1.78 V/s J-V scan of a PSC described by the parameters in Tables 1 and 2(a) of the main text except for the high doping densities of $d_E = d_H = 5 \times 10^{25}$ m^{-3} and the ion diffusivity $D_I = 10^{-16} \mathrm{m^2 s^{-1}}$.

Video S4: Equivalent to S3 but for the low doping densities of $d_E = d_H = 5 \times 10^{23}$ m^{-3}, *i.e.* it is an animation corresponding to Figure 5(c) in the main text.

Videos S5 and S6: Equivalent to S3 and S4, respectively, but for the recombination parameters in Table 2(b) of the main text.

B   Calculation of Current Density from Simplified DD Model

Following on from Section 3.5 of the main text, the J-V characteristics of a cell may be obtained from the surface polarisation model via solution of the following DD model for the charge carriers based upon the known internal electric potential. Here we follow the same procedure used previously (in approach (ii)) by Courtier *et al.*[1]

In order to calculate the total current $J(t)$, we consider the conservation equations for the electron and hole densities (n and p) in the perovskite layer ($0 < x < b$), given by equations (1)-(2) in the main text. However, as in Courtier *et al.*[1], we consider only the solution for the carriers (and the associated current densities) in the perovskite bulk, and do not solve explicitly in the very narrow Debye layers at

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the interfaces with the ETL (on $x = 0$) and HTL (on $x = b$). The electron and hole densities in the bulk, which we denote by $\bar{n}$ and $\bar{p}$ respectively, and the electron and hole currents in the bulk, which we denote by $\bar{j}_n$ and $\bar{j}_p$ are well approximated by equations (1)-(2) in the main text in which $-\frac{\partial \phi}{\partial x}$ is replaced by the known bulk electric field $E_{bulk}(t)$, calculated from the surface polarisation model; that is they satisfy

$$\frac{\partial \bar{p}}{\partial t} + \frac{1}{q}\frac{\partial \bar{j}_p}{\partial x} = G(x) - R(\bar{n}, \bar{p}), \qquad \bar{j}_p = -qD_p\left(\frac{\partial \bar{p}}{\partial x} - \frac{\bar{p}E_{bulk}(t)}{V_T}\right), \qquad (1)$$

$$\frac{\partial \bar{n}}{\partial t} - \frac{1}{q}\frac{\partial \bar{j}_n}{\partial x} = G(x) - R(\bar{n}, \bar{p}), \qquad \bar{j}_n = qD_n\left(\frac{\partial \bar{n}}{\partial x} + \frac{\bar{n}E_{bulk}(t)}{V_T}\right). \qquad (2)$$

Assuming that the carrier transport is fast in comparison to the timescale of ion vacancy motion, it is approximately true that the carriers are in a quasi-steady state, *i.e.*

$$\frac{1}{q}\frac{\partial \bar{j}_p}{\partial x} = G(x) - R(\bar{n}, \bar{p}), \qquad \bar{j}_p = -qD_p\left(\frac{\partial \bar{p}}{\partial x} - \frac{\bar{p}E_{bulk}(t)}{V_T}\right), \qquad (3)$$

$$-\frac{1}{q}\frac{\partial \bar{j}_n}{\partial x} = G(x) - R(\bar{n}, \bar{p}), \qquad \bar{j}_n = qD_n\left(\frac{\partial \bar{n}}{\partial x} + \frac{\bar{n}E_{bulk}(t)}{V_T}\right). \qquad (4)$$

These equations are supplemented by boundary conditions near to each interface which are calculated by assuming approximate thermal equilibrium of the carrier densities across the narrow Debye layers (which extend into the TLs) and substituting into the continuity and boundary conditions (10)-(12) (of the main text); they are

$$\bar{n}|_{x=0^+} = d_E k_E e^{-(V_1+V_2)/V_T}, \qquad \bar{j}_p|_{x=0^+} = -qR_l\left(d_E e^{-V_1/V_T}, \bar{p}|_{x=0^+} e^{-V_2/V_T}\right), \qquad (5)$$

$$\bar{p}|_{x=b^-} = d_H k_H e^{-(V_3+V_4)/V_T}, \qquad \bar{j}_n|_{x=b^-} = -qR_r\left(\bar{n}|_{x=b^-} e^{-V_3/V_T}, d_H e^{-V_4/V_T}\right). \qquad (6)$$

It follows from (1a) and (2a) that

$$\frac{\partial}{\partial x}(\bar{j}_p + \bar{j}_n) = 0, \quad \text{so that} \quad \bar{j}_p + \bar{j}_n = J(t), \qquad (7)$$

where $J(t)$ is the total current density flowing across the cell. This means that, for a known electric field $E_{bulk}(t)$, the value of $J(t)$ can be approximated at any point x in the domain from the numerical solution, using a solver such as MATLAB's `bvp4c`[2], of the boundary value problem (3)-(6) for $\bar{n}$ and $\bar{p}$.

C Extension of Numerical Scheme

Here, we follow the non-dimensional notation defined and used in Courtier *et al.*[3]. We introduce superscripts of E or H to denote the corresponding variables in the ETL or HTL, respectively.

C.1 Computational Grid

The complete computational grid is made up of three sub-grids; one for each of the three material layers. The equations in the perovskite layer are discretised onto N+1 grid points, denoted by $x = x_i$ for $i = 0, ..., N$, which partition the domain $x \in [0, 1]$ into N subintervals. To ensure that computational effort is expended where it is needed most (in the Debye layers) we position the grid points according to a Chebyshev distribution as follows.

$$x_i = \frac{1}{2}\left\{1 + \cos\left[\pi\left(\frac{i}{N} - 1\right)\right]\right\}, \qquad \text{for} \quad i = 0, ..., N. \qquad (8)$$

Similar grids are introduced for treatment of the equations in the TLs and these are defined by

$$x_i^E = \frac{b_E}{2b}\left\{\cos\left[\pi\left(\frac{i}{N_E} - 1\right)\right] - 1\right\}, \qquad \text{for} \quad i = 0, ..., N_E, \quad \text{where} \quad N_E = \text{round}\left(\sqrt{\frac{b_E}{b}}N\right), \qquad (9)$$

$$x_i^H = 1 + \frac{b_H}{2b}\left\{\cos\left[\pi\left(\frac{i}{N_H} - 1\right)\right] + 1\right\}, \qquad \text{for} \quad i = 0, ..., N_H, \quad \text{where} \quad N_H = \text{round}\left(\sqrt{\frac{b_H}{b}}N\right). \qquad (10)$$

The values of N_E and N_H are chosen to give approximately equal spacing either side of the interfaces. For the results presented in this paper, we use $N = 400$, and hence $N_E = 200$ and $N_H = 283$. For each of the three sub-grids we introduce a set of half-points which lie midway between the grid points. As such we write

$$x_{i+1/2} = \frac{x_{i+1} + x_i}{2}, \qquad \text{for} \quad i = 0, ..., N - 1, \tag{11}$$

for the perovskite layer, with equivalent definitions for the TLs.

C.2 Discretisation of Transport Layer Equations and Continuity Conditions

Within the ETL, the governing equations ensuring the conservation of electrons and Poisson's equation for the electric potential, along with the corresponding left-hand boundary conditions (*i.e.* those at the contact) are discretised in a precisely analogous way to those given in Courtier *et al.*[3]. We do likewise for the equations stating conservation of holes, Poisson's equation and right-hand boundary conditions in the HTL. In the interests of brevity, we do not reiterate the discretised system here and instead refer the interested reader to the relevant previous work.[3]

In order to preserve the second-order accuracy of the spatial discretisation achieved in our previous work[3], it is important to choose discretisations for the additional continuity conditions, introduced by the inclusion of the TLs, that also exhibit second order accuracy. Finding such discrete approximations is trivial for the conditions on the continuity of the potential and the prescribed ratios between carrier densities on either side of the respective interfaces. However, the electric field (E) and carrier currents (j^n, j^p) are only defined on the half-points (*i.e.* not directly on the interface where the conditions are to be applied) as follows

$$E_{i+1/2} = -\mathfrak{D}_{i+1/2}\left(\phi_{i+1}, \phi_i\right), \tag{12}$$

$${j^n}_{i+1/2} = \kappa_n \left(\mathfrak{D}_{i+1/2}(n_{i+1}, n_i) + \mathfrak{I}_{i+1/2}(n_{i+1}, n_i)E_{i+1/2}\right), \tag{13}$$

$${j^p}_{i+1/2} = -\kappa_p \left(\mathfrak{D}_{i+1/2}(p_{i+1}, p_i) - \mathfrak{I}_{i+1/2}(p_{i+1}, p_i)E_{i+1/2}\right), \tag{14}$$

for $i = 0, ..., N - 1$ and in which κ_n and κ_p are non-dimensional constants proportional to the relevant carrier diffusion coefficient. Definitions for the calligraphic operators can be found in Courtier *et al.*[3]. Equivalent expressions for the electric field and appropriate carrier current in each TL follow from identical considerations. The location of the half-points (away from the interfaces) necessitates extrapolating the relevant quantities, namely the electric field and carrier currents, to the interfaces at which the boundary conditions must be applied. Our extrapolation is linear and based on the values of the variables at the two nearest half-points. Hence, we apply the following set of 8 continuity conditions.

At the ETL/perovskite interface at $x = 0$,

$$\phi_{N_E}^E = \phi_0, \qquad\qquad k_E\, n_{N_E}^E = n_0, \tag{15}$$

$$\epsilon_E \left[E_{N_E - \frac{1}{2}}^E + \mathfrak{D}_{N_E-1}\left(E_{N_E-\frac{1}{2}}^E, E_{N_E-\frac{3}{2}}^E\right)\left(1 - x_{N_E-\frac{1}{2}}^E\right)\right] = \epsilon_p \left[E_{\frac{1}{2}} - \mathfrak{D}_1\left(E_{\frac{3}{2}}, E_{\frac{1}{2}}\right)x_{\frac{1}{2}}\right], \tag{16}$$

$$j^{n,E}_{N_E-\frac{1}{2}} + \mathfrak{D}_{N_E-1}\left(j^{n,E}_{N_E-\frac{1}{2}}, j^{n,E}_{N_E-\frac{3}{2}}\right)\left(1 - x_{N_E-\frac{1}{2}}^E\right) = j^n_{\frac{1}{2}} - \mathfrak{D}_1\left(j^n_{\frac{3}{2}}, j^n_{\frac{1}{2}}\right)x_{\frac{1}{2}} - R_l\left(n_{N_E}^E, p_0\right). \tag{17}$$

Similarly, at the perovskite/HTL interface,

$$\phi_N = \phi_0^H, \qquad\qquad p_N = k_H\, p_0^H, \tag{18}$$

$$\epsilon_p \left[E_{N-\frac{1}{2}} + \mathfrak{D}_{N-1}\left(E_{N-\frac{1}{2}}, E_{N-\frac{3}{2}}\right)\left(1 - x_{N-\frac{1}{2}}\right)\right] = \epsilon_H \left[E_{\frac{1}{2}}^H - \mathfrak{D}_1\left(E_{\frac{3}{2}}^H, E_{\frac{1}{2}}^H\right)x_{\frac{1}{2}}^H\right], \tag{19}$$

$$j^p_{N-\frac{1}{2}} + \mathfrak{D}_{N-1}\left(j^p_{N-\frac{1}{2}}, j^p_{N-\frac{3}{2}}\right)\left(1 - x_{N-\frac{1}{2}}\right) - R_r\left(n_N, p_0^H\right) = j^{p,H}_{\frac{1}{2}} - \mathfrak{D}_1\left(j^{p,H}_{\frac{3}{2}}, j^{p,H}_{\frac{1}{2}}\right)x_{\frac{1}{2}}^H. \tag{20}$$

References

[1] N. E. Courtier, J. M. Foster, S. E. J. O'Kane, A. B. Walker and G. Richardson, *Eur. J. Appl. Math.*, 2018, doi:10.1017/S0956792518000207.

[2] *MATLAB version 9.1.0.441655 (R2016b)*, 2016.

[3] N. Courtier, G. Richardson and J. M. Foster, *Applied Mathematical Modelling*, 2018, **63**, 329–348.