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Supporting Information - Understanding equivalent circuits in perovskite solar cells. Insights from drift-diffusion simulation

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Figure S1: Simulated impedance spectra at V_{OC} under 100 W·m⁻² and 50 W·m⁻² of 465 nm monochromatic illumination using parameters included in Table SS1 and surface recombination of Table SS3.

Parameter	Value	Literature reference or justification		
Temperature (T)	298 K	Standard conditions		
Incident photon flux	$5 1000 \text{ W} \text{m}^{-2}$	Wide illumination range with the 1-sun equivalent power		
(F_{ph})	5 - 1000 W .m	as upper limit		
	Electron	transport layer (TiO ₂		
Work function (E_{fE})	(-) 4.0 eV	Ref. [1]		
Effective doping den-	$1.1.10^{26}m^{-3}$	Ref. [2–4]		
sity (d_E)	1.1.10 111			
Width (b_E)	$1.10^{-7} {\rm m}$	Direct measurement on similar devices		
Permittivity (ϵ_E)	$20 \epsilon_0$	Ref. [5]		
Electron diffusion co-	$5.14 \cdot 10^{-7} \text{ m}^2 \text{s}^{-1}$	Ref. [1]		
emcient (D_E)				
Width (b)	$\frac{10^{-7}}{2.10^{-7}}$	Direct measurement on similar devices		
$\frac{V(u(t))(0)}{V(t)}$	3.10 III	Direct measurement on similar devices		
$\frac{1 \text{ elimitativity } (\epsilon_p)}{\Lambda \text{ begen tion, coefficient}}$	24.1 t ₀			
at 465 nm (α)	$6.5 \cdot 10^6 \text{ m}^{-1}$	Direct measurement on similar devices		
Conduction band min-	$()$ 0 \mathbf{V}			
imun (E_c)	(-) 3.8 eV	Intermediate value between Ref. $[7]$ and $[1]$		
Valence band maxi-	() 54 oV	Dof [7]		
mum (E_v)	(-) 0.4 CV			
Electron difusion coef-	$5 \cdot 10^{-5} \text{ m}^2 \text{s}^{-1}$	Gives a CCE of 100% [8,9] with the bulk lifetime in		
ficient (D_n)		Table SS2. Value very close to the reported $(2.05 \cdot 10^{-5})$		
		m^2) by Wehrenfennig et al [10].		
Hole diffusion coeffi-	$5 \cdot 10^{-5} \text{ m}^2 \text{s}^{-1}$	Similar value to the perovskite electron diffusion coeffi-		
cient (D_p)		cient.		
Conduction band den-	$8.1 \cdot 10^{24} \text{ m}^{-3}$	Ref. [11]		
sity of states (g_c)				
Valence band density	$5.8 \cdot 10^{24} \text{ m}^{-3}$	Ref. [11]		
of states (g_v)				
Mean density of anion	$1.6 \cdot 10^{25} \text{ m}^{-3}$	Ref. [12]		
vacancies (N_0)				
Diffusion coefficient	$10^{-16}m^2s^{-1}$	Ref. [13]		
for amons (D_P)	tor amons (D_P)			
Hole transport layer (Spiro-OMeTAD)				
Work function (E_{fH})	(-) 5.22 eV	Kei. [1]		
Effective doping den-	$1.1 \cdot 10^{26} \mathrm{m}^{-3}$	Similar value to the effective doping density of ETL.		
Width (b_{rr})	3.10^{-7} m	Direct measurement on similar devices		
$\frac{V(U(H)(OH)}{V(CT)}$	3.60	Direct measurement on similar devices		
Holo diffusion $coefficients$	<u> </u>			
$\operatorname{cient}(D_n)$	$2.57 \cdot 10^{-9} \text{ m}^2 \text{s}^{-1}$	Ref. [14]		
cient (D_H)	2.57.10 ° m-s -	Rel. [14]		

Table S1: Standard parameter set for the layer properties in the DD simulations.

Parameter	Value	Literature reference or justification	
Electron pseudolife-	0.10^{-8} c	Chosen to match an approximate V_{OC} of 1 V under the	
time for SRH (τ_n)	9.10 8	1 sun equivalent illumination	
Hole pseudolifetime for SRH (τ_p)	3.10^{-9} s	Two orders of magnitude smaller than the electron pseu-	
		dolifetime, therefore this parameter does not affect the	
		calculations when the perovskite is p-type (i.e. when	
		there is a greater density of holes than electrons in the	
		perovskite layer).	

Table S2: SRH Recombination pseudolifetimes for electrons and holes for the simulated spectra with pure SRH recombination.

Parameter	Valuo	Literature reference or justification		
1 al allietel	value	Interature reference of Justification		
Electron recombina- tion velocity at ETL (v_{nE})	$10^5 m s^{-1}$	Make the electrons disappear as soon as they reach the ETL, simulating the injection into the selective contact		
Hole recombination velocity at ETL (v_{pE})	$50 {\rm ~m~s^{-1}}$	Recombination velocity to reach a similar V_{OC} under 1 sun equivalent illumination to the obtained with pure SRH recombination. Slightly faster than v_{nH} to repro- duce the differences on how selective both contacts are.		
Electron recombina- tion velocity at HTL (v_{nH})	$0.5 {\rm ~m~s^{-1}}$	Recombination velocity to reach a similar V_{OC} under 1sun equivalent illumination to the obtained with pureSRH recombination. Slightly slower than v_{pH} to reproduce the differences on how selective both contacts are.		
Hole recombination velocity at HTL (v_{pH})	$10^5 m s^{-1}$	Make the holes disappear as soon as they reach the HTL, simulating the injection into the selective contact		

Table S3: Surface Recombination velocities for electrons and holes at the ETL and the HTL for the simulated spectra with pure surface recombination.

Parameter	Original Value	Modified value			
Perovskite layer $(CH_3NH_3PbI_3)$					
Electron diffusion co- efficient (D_n)	$5 \cdot 10^{-5} \text{ m}^2 \text{s}^{-1}$	$8 \cdot 10^{-6} \text{ m}^2 \text{s}^{-1}$			
Hole diffusion coefficient (D_p)	$5 \cdot 10^{-5} \text{ m}^2 \text{s}^{-1}$	$8 \cdot 10^{-6} \text{ m}^2 \text{s}^{-1}$			
Conduction band den- sity of states (g_c)	$8.1 \cdot 10^{24} \text{ m}^{-3}$	$8.1 \cdot 10^{25} \text{ m}^{-3}$			
Valence band density of states (g_v)	$5.8 \cdot 10^{24} \text{ m}^{-3}$	$5.8 \cdot 10^{25} \text{ m}^{-3}$			
Mean density of anion vacancies (N_0)	$1.6 \cdot 10^{25} \text{ m}^{-3}$	$1.6 \cdot 10^{26} \text{ m}^{-3}$			
Diffusion coefficient for anions (D_P)	$10^{-16}m^2s^{-1}$	$3 \cdot 10^{-17} m^2 s^{-1}$			
Recombination parameters					
Electron pseudolife- time for SRH (τ_n)	9.10^{-8} s	$2 \cdot 10^{-7} \text{ s}$			
Electron recombina- tion velocity at ETL (v_{nE})	$10^5 m s^{-1}$ or de- activated	$10^5 m s^{-1}$			
Hole recombination velocity at ETL (v_{pE})	$50 \mathrm{~m~s^{-1}}$	$20 \mathrm{~m~s^{-1}}$			
Electron recombina- tion velocity at HTL (v_{nH})	$0.5 {\rm ~m~s^{-1}}$	7.5 m s^{-1}			
Hole recombination velocity at HTL (v_{pH})	$10^5 m s^{-1}$ or de- activated	$10^5 m s^{-1}$			

Table S4: Changes introduced in the parameter set to reproduce a real device.



Figure S2: Zoom in of the fit result (green line) reproducing the loop observed for pure SRH recombination simulations (red line) using the parallel equivalent circuit.



Figure S3: Charge collection efficiency obtained from applying Eq.4 to the resistances extracted from the 2-RC (up) and the parallel (bottom) equivalent circuits, for pure SRH recombination (left) and the pure surface recombination (right) scenarios, compared to the IQE calculated using Eq.10 with the JV curve resulting with a 0.01 mV·s⁻¹ scan rate using the parameters in Table SS1.



Figure S4: Simulated impedance spectra at V_{OC} under 100 W·m⁻² of 465 nm monochromatic illumination using parameters included in Table SS1 with the changes considered in Table SS4



Figure S5: Deviation between the CCE values obtained from R_{HF} and R_{rec} in Figure 8 compared to the steady state JV curve.

1 Appendix. Numerical conditions of the Drift-Diffusion model

IonMonger drift-diffusion model reproduces a three layers device, which, for the parameters chosen in this study, consists of an electron transport layer (TiO₂), a perovskite absorber layer ($CH_3NH_3PbI_3$) and a hole transport layer (Spiro-OMeTAD) [15]. In the perovskite layer (0 < x < b), the electronic carriers (electrons and holes) densities, n and p respectively, are driven in time, t, and one spatial dimension, x, via the continuity equations

$$\frac{\delta n}{\delta t} - \frac{1}{q} \frac{\delta j_n}{\delta x} = G - R, \qquad \qquad j_n = q D_n \left(\frac{\delta n}{\delta x} - \frac{n}{k_B T} \frac{\delta \phi}{\delta x} \right), \qquad (1)$$

$$\frac{\delta p}{\delta t} + \frac{1}{q} \frac{\delta j_p}{\delta x} = G - R, \qquad \qquad j_p = -q D_p \left(\frac{\delta p}{\delta x} + \frac{p}{k_B T} \frac{\delta \phi}{\delta x} \right), \tag{2}$$

where q is the elementary charge, G and R the generation and recombination rates, $D_{n,p}$ the respective diffusion coefficients for electrons and holes, k_B the Boltzmann constant and T is the absolute temperature. In addition, IonMonger considers one mobile anion species with a certain density, P, whose migration is restrained to the perovskite layer and is governed by the following equation

$$\frac{\delta P}{\delta t} + \frac{\delta F_p}{\delta x} = 0, \qquad F_P = -D_p \left(\frac{\delta P}{\delta x} + \frac{P}{k_B T} \frac{\delta \phi}{\delta x}\right), \qquad (3)$$

where F_P is the ionic flux and D_P is the anion vacancy diffusion coefficient. Eq. (1-3) are coupled to Poisson's equation for the electric potential

$$\frac{\delta^2 \phi}{\delta x^2} = \frac{q}{\epsilon_p} (N_0 - P + n - p) \tag{4}$$

Here, ϵ_p is the relative permittivity of the perovskite and N_0 is the uniform immobile cation vacancy density, which is equivalent to the mean anion vacancy density in order to ensure the electrical charge neutrality. Electrons and holes are generated in the perovskite layer according to the Beer-Lambert profile for a single wavelength (465 nm in this study) of light

$$G(x) = F_{ph} \alpha e^{-\alpha x} \tag{5}$$

where F_{ph} is the photon flux inciting on the device with energy above the bandgap of the absorptive material and α is the absorption coefficient of the perovskite. Recombination happening in the bulk of the perovskite is calculated using a combination of bimolecular (direct relaxation across the bandgap), which is deactivated in this study, and trap-assisted Shockley-Read-Hall (SRH) processes, given by

$$R(n,p) = (np - n_i^2) + \frac{(np - n_i^2)}{\tau_n p + \tau_p n + k_3}$$
(6)

Here, τ_n and τ_p are the SRH pseudo-lifetimes for electrons and holes and k_3 is a constant from the deep trap approximation used by Courtier et al [15] and n_i is the intrinsic carrier density determined by

$$n_i = g_c g_v \exp\left(-\frac{E_g}{2k_B T}\right) \tag{7}$$

where g_c and g_v are the density of states in the conduction and valence bands of the perovskite and E_g is its bandgap. For the cases where pure surface recombination was considered, this is determined at the ETL/perovskite interface by

$$R_l(n,p) = \frac{n|_{x=0^-}p|_{x=0^+} - n_i^2}{p|_{x=0^+}/v_{nE} + n|_{x=0^-}/v_{pE} + k_1}$$
(8)

In this case, v_{nE} and v_{pE} are the electron and hole recombination velocities within the ETL/perovskite interface and k_1 is a constant from the deep trap approximation at the

ETL/perovskite interface. As for the electron concentration at the interface of the ETL and the hole concentration at the interface of the perovskite are given by $n|_{x=0^-}$ and $p|_{x=0^+}$. respectively. In the same way, the recombination at the perovskite/HTL interface is defined by

$$R_r(n,p) = \frac{n|_{x=b^-}p|_{x=b^+} - n_i^2}{p|_{x=b^+}/v_{nH} + n|_{x=b^-}/v_{pH} + k_2}$$
(9)

where v_{nH} and v_{pH} are the electron and hole recombination velocities at the perovskite/HTL interface and k_2 is a constant from the deep trap approximation at the perovskite/HTL interface. The electron concentration at the interface of the perovskite is denoted by $n|_{x=b^-}$ while the hole concentration at the HTL interface is given by $p|_{x=b^+}$.

Anion migration, generation and bulk recombination are restrained to the perovskite layer. Thus, the conservation equations for electrons in the ETL $(-b_E < x < 0)$ are given by

$$\frac{\delta n}{\delta t} - \frac{1}{q} \frac{\delta j_n}{\delta x} = 0, \qquad \qquad j_n = q D_E \left(\frac{\delta n}{\delta x} - \frac{n}{k_B T} \frac{\delta \phi}{\delta x} \right) \tag{10}$$

with

$$\frac{\delta^2 \phi}{\delta x^2} = \frac{q}{\epsilon_E} (n - d_E) \tag{11}$$

Here, D_E is the electronic diffusion coefficient in the ETL and ϵ_E and d_E are the permittivity and effective doping density of the ETL. The conservation equations for holes in the HTL $(b < x < b + b_H)$ are given by

$$\frac{\delta p}{\delta t} + \frac{1}{q} \frac{\delta j_p}{\delta x} = 0, \qquad \qquad j_p = -q D_H \left(\frac{\delta p}{\delta x} + \frac{p}{k_B T} \frac{\delta \phi}{\delta x} \right) \tag{12}$$

with

$$\frac{\delta^2 \phi}{\delta x^2} = \frac{q}{\epsilon_H} (d_H - p) \tag{13}$$

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where D_H is the hole diffusion coefficient in the HTL and ϵ_H and d_H are the HTL permittivity and effective doping density respectively.

To simulate the physics behind a perovskite solar cell operation, a set of boundary conditions are applied to all the previously described equations. To model metal contacts at the ETL and HTL edges, the following conditions are applied

 $\phi|_{x=-b_E} = 0,$ $n|_{x=-b_E} = d_E,$ $\phi|_{x=b+b_H} = V_{ap} - V_{bi},$ $p|_{x=b+b_H} = d_H$ (14)

At the ETL/ $CH_3NH_3PbI_3$ interface

$$\phi|_{x=0^{-}} = \phi|_{x=0^{+}}, \qquad \epsilon_{E} \frac{\delta \phi}{\delta x}|_{x=b^{-}} = \epsilon_{H} \frac{\delta \phi}{\delta x}|_{x=b^{+}},$$
$$p|_{x=b^{-}} = k_{H} p|_{x=b^{+}}, \qquad j_{n}|_{x=b} = -q R_{l_{r}}, \qquad F_{p}|_{x=0} = 0$$
(15)

At the $CH_3NH_3PbI_3$ /HTL interface

$$\phi|_{x=b^-} = \phi|_{x=b^+}, \qquad \epsilon_p \frac{\delta\phi}{\delta x}|_{x=b^-} = \epsilon_H \frac{\delta\phi}{\delta x}|_{x=b^+}, \qquad p|_{x=b^-} = k_H p|_{x=b^+},$$

$$j_n|_{x=b} = -qR_{l_r}, \qquad F_P|_{x=0} = 0 \tag{16}$$

where k_E and k_H accounts for the ratio of the carrier densities at either side of the perovskite and transport layer interface. This is determined by

$$k_E = \frac{g_c}{g_{c,E}} \exp\left(-\frac{E_c - E_{c,E}}{qk_BT}\right), \qquad k_H = \frac{g_v}{g_{v,H}} \exp\left(-\frac{E_v - E_{v,H}}{qk_BT}\right)$$
(17)

Here, $g_{c,E}$ and $g_{v,H}$ are the density of states of the ETL conduction band and HTL valence band respectively, E_c and E_v are the energies of the conduction and valence bands of the perovskite layer while $E_{c,E}$ and $E_{v,H}$ are the energies of the conduction and valence bands of the ETL and HTL. In this study, it is assumed that the density of states of the selective transport layers are equal to the effective doping densities in those layers. This means $g_{c,E} = d_E$ and $g_{v,H} = d_H$. As a result of this, the band edges $E_{c,E}$ and $E_{v,H}$ are equal to the Fermi levels in the ETL and HTL, denoted by E_{fE} and E_{fH} . Considering this, the built-in voltage is determined by

$$V_{bi} = \frac{1}{q} (E_{fE} - E_{fH}) = \frac{1}{q} (E_{c,E} - E_{v,H})$$
(18)

The aforementioned equations with the given boundary equations were solved applying the open-source numerical solver *IonMonger* [16].

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