Migration of cations induces reversible performance losses over day/night cycling in perovskite solar cells

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Perovskite solar cells performance parameters

Device	Voc	Jsc	FF	PCE
	(V)	(mA cm ⁻²)		(%)
1	1134	23.4	0.75	20.3
2	1140	23.3	0.76	19.8
3	1104	22.4	0.78	20.2
4	1117	22.8	0.76	20.1
5	1116	23.0	0.74	19.8
6	1117	22.8	0.76	20.2
7	1109	23.5	0.75	20.2
8	1103	22.6	0.77	19.8
9	1083	22.2	0.74	18.8
10	1107	23.2	0.77	20.7
11	1106	23.0	0.76	20.4
12	1107	23.1	0.73	19.4
13	1092	23.3	0.75	19.7
14	1110	23.2	0.73	19.4
15	1097	23.2	0.73	19.3
16	1110	23.1	0.75	20.0

We selected the best performing devices prepared over a period of 6 months following the same preparation procedure described in the Experimental Section of the main text. Device opencircuit voltage (Voc), short circuit current (Jsc), fill factor (FF) and power conversion efficiency (PCE) were extracted from the current density-voltage (J-V) curves collected under simulated solar light. The light source was a 450 W xenon lamp (Oriel) equipped with a SchottK113 Tempax sunlight filter (Praezisions Glas & Optik GmbH) to match the emission spectrum of the lamp to the AM1.5G standard. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cut-off filter (KG-3, Schott). The J-V curves were recorded by scanning the voltage at 0.01 V s^{-1} rate from forward bias to short circuit conditions with no preconditioning such as light soaking or holding the device under forward voltage bias beforehand. The cells were masked with a black metal mask (0.16 cm^2) to estimate the active area and reduce the influence of the scattered light.





Similar to what reported in the main text for mesoporous TiO₂-based device, the reversible losses can be measured also for mesoporous and planar SnO₂-based perovskite solar cells.

Mesoporous and planar SnO₂-based perovskite solar cells preparation: aluminum doped zinc oxide coated glass slides (Zhuhai Kaivo Optoelectronic Technology Co.) were cleaned by sonication in deionized water for 15 minutes. After rinsing with ethanol the substrates were again sonicated with isopropanol and rinsed with acetone. The substrates were treated with UV-ozone for 5 minutes and a 30 nm thick SnO₂ was deposited by spray pyrolysis at 450°C from a precursor solution of butyltin trichloride (250 mM) in anhydrous ethanol. For planar SnO₂ devices perovskite was spincoated directly on top of the SnO₂ compact layer. Mesoporous SnO₂ electrodes were synthesized using a structure directing block-copolymer. A tin oxide precursor sol was prepared by dissolving poly(1,4-isoprene-b-ethylene oxide) (25 mg,

Polymer Source, Mn: PIp(50000)-PEO(12000), Mw/Mn: 1.05) in tetrahydrofuran (1 mL), after which tin(IV) chloride pentahydrate was added (80 mg) and stirred for 30 minutes. The resulting solution was spin-coated (4000 rpm, 10 s) onto the substrate. The films were annealed on a programmable hotplate (2000 W, Harry Gestigkeit GmbH) using a 45 minutes ramp to 450 °C followed by a dwell time of 30 minutes to remove the block-copolymer template and crystallize SnO₂. Perovskite films were deposited from a precursor solution containing FAI (1 M), PbI₂ (1.1 M), MABr (0.2 M), PbBr2 (0.2 M) and CsI (0.075 M) in anhydrous DMF:DMSO 4:1 (v:v). The perovskite solution was spin-coated in a two-step program at 1000 and 6000 rpm for 10 and 20 s respectively. During the second step, 100 µL of chlorobenzene was poured onto the spinning substrate 5 seconds prior the end of the program. The substrates were then annealed at 100 °C for 1 hour in a nitrogen glove box. Subsequently, the substrates were cooled down for a few minutes and a spiro-OMeTAD (Luminescence Technology) solution (70 mM in chlorobenzene) doped with bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Aldrich), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III)tris(bis(tri uoromethylsulfonyl)imide) (FK209, Dyenamo) and 4-tert-butylpyridine (TBP, Aldrich) was spun at 4000 rpm for 20 s. The molar ratios of additives for spiro-OMeTAD were: 0.5, 0.03 and 3.3 for Li-TFSI, FK209 and TBP, respectively. Finally, 80 nm of gold was thermally evaporated under high vacuum on top of the device.

Reversible losses in inverted perovskite solar cells



Similar to what reported in the main text for mesoporous TiO₂-based device, the reversible losses can be measured also for so called inverted perovskite solar cells.

Inverted perovskite solar cells preparation: fluorine doped tin oxide (FTO) coated glass slides (Sigma-Aldrich) were cleaned by sonication in 2% Hellmanex soap solution for 15 minutes. After rinsing with deionized water and ethanol the substrates were again sonicated with isopropanol and rinsed with acetone. The substrates were then treated with UV-ozone for 5 minutes and brought into a nitrogen filled glovebox. A PTAA (EM Index, 15 mg/ml in toluene) solution doped with bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Aldrich) and 4-tert-butylpyridine (TBP, Aldrich) was spincoated on top of the FTO at 2000 rpm for 30 s. Perovskite films were deposited from a precursor solution containing FAI (1 M), PbI₂ (1.1 M), MABr (0.2 M), PbBr₂ (0.2 M) and CsI (0.075 M) in anhydrous DMF:DMSO 4:1 (v:v). The perovskite solution was spin-coated in a two-step program at 1000 and 6000 rpm for 10 and 20 s respectively. During the second step, 100 μ L of diethyl ether was poured onto the spinning substrate 5 s prior to the end of the program. The substrates were cooled down for a few minutes and a PCBM solution (20 mg/mL in chlorobenzene) was spun at 2000 rpm for 60 s. Finally, 80 nm of gold was thermally evaporated on top of the device.



Organic cation depth profiles by time of flight secondary ion mass spectrometry (ToF-SIMS)



Time of flight secondary ion mass spectrometry (ToF-SIMS) depth profiles comparing traces of **a** I_2^- , **b** Br_2^- , **c** CN^- ions for biased and control pixels of the sample shown in **Figure 2** in the main text. **d** and **e** show the same traces ploted in separate graphs for control and biased pixels respectively. The SnO⁻ ions coming from the fluorine doped SnO₂ (FTO glass) are used as a reference and all traces are normalized to their maxima.

Energy dispersive X-ray spectroscopy (EDX) depth profiles



Energy dispersive X-ray spectroscopy (EDX) depth profiles showing the traces of a I, b Br, d C and e N in biased and control pixels of the sample shown in Figure 2. c and f show the same traces plotted in separate graphs for control and biased pixels respectively. The Sn signal coming from the fluorine doped SnO_2 (FTO glass) is used as a reference. The traces are normalized to their maxima. Some of the traces from the biased pixel are interrupted. EDX was performed with Zeiss Merlin. Prior to cutting the sample was coated with carbon to avoid charging effect.



Date: Sun, Feb 21, 2016

Voltage (V)



Xe lamp: 450W/113 : 1000W is 22.20 mA/cm²; Estimated Mismatch; 1.29 % Osram: 18W/T8/840 @5001x is 70.7 µA/cm² Osram: 18W/T8/827 @5001x is 53.1 μ A/cm² Osram: 18W/T8/930 @5001x is 55.6 µA/cm² is 263.6 mA/cm²; Estimated Mismatch;-7.93 % Date: Tue, Sep 13, 2016 White LED M111: 1000W

1. Equivalent circuit representation of the PSC based on drift diffusion modelling

The purpose of this section is to predict the capacitance of the perovskite layer in a PSC, based on three different hypotheses for ion vacancy motion, and to use the results to compare to experimentally generated spectroscopy data. This comparison will, in turn, allow a comparison of hypotheses for ion vacancy motion. Based on DFT calculations [3] it is usually assumed that the most mobile vacancy species in the perovskite methylammoniumlead-trihalide are the positively charged halide vacancies and it is suspected that the motion of negatively charged methylammonium vacancies, though considerably less mobile than the halides, may still influence processes occurring on timescales of the order of 1s-10000s. In Richardson *et al.* [5] drift-diffusion models of vacancy motion are used to show that charge resides in narrow Debye layers, of the width around 2nm, at the edge of the perovskite layer and that away from these layers, in the perovskite bulk, there is almost exact charge neutrality with a balance between positive and negative vacancies. Charge neutrality in the perovskite bulk means that, with the exception of the Debye layers, the electric field is uniform (but may vary in time) throughout the perovskite. Significant charge densities in the Debye layers (caused by disparities in the concentrations of positive and negative ion vacancies) lead to rapid changes in the electric potential within these narrow regions and corresponding potential drops from one side of the Debye layer to the other. The behaviour of the device is thus almost entirely controlled by ion vacancy motion into and out of the Debye Layers.

If the mobile ion vacancies can redistribute themselves within the Debye layers more rapidly than changes occur to the external conditions (e.g. the applied potential) then, to a good approximation, the behaviour of the Debye layer can be characterised by a nonlinear capacitance relation [5], of the form $Q = Q_{dl}(V_{dl})$, which relates the charge Q stored in the layer to the potential drop \mathcal{V}_{dl} across it: defined as the potential in the perovskite, just inside the Debye layer, minus the potential in the adjacent blocking layer. Denoting the potential drop across the Debye layer at the interface with the electron transport layer (ETL) as \mathcal{V}_{-} and that across the Debye layer at the interface with the hole transport layer (HTL) as \mathcal{V}_{+} we see that the total potential drop across the two capacitances is $\mathcal{V}_{+} - \mathcal{V}_{-}$. If the charge in HTL Debye layer is defined as Q then charge conservation implies the charge stored in the ETL Debye layer is -Q. In order to determine the capacitance of the entire perovskite layer we need to consider the capacitance of both Debye layers in series. It follows that

$$Q = \mathcal{Q}_{dl}(\mathcal{V}_+),$$
 and $-Q = \mathcal{Q}_{dl}(\mathcal{V}_-)$

By defining the inverse of the function $\mathcal{Q}_{dl}(\mathcal{V})$ as $\mathcal{V}_{dl}(Q)$ it is possible to see that the total potential drop across both Debye layers $\mathcal{V}_c = \mathcal{V}_+ - \mathcal{V}_-$ is

$$\mathcal{V}_c(Q) = \mathcal{V}_{dl}(Q) - \mathcal{V}_{dl}(-Q). \tag{1}$$

The Debye layer capacitance C is then given by $C(Q) = 1/\mathcal{V}'_c(Q)$, where the prime denotes the derivative of the function $\mathcal{V}_c(Q)$.

The electrical behaviour of the cell can be described by the equivalent circuit shown in figure 1. Here the lower branch of the circuit (in red) provides the description of the vacancy motion within the perovskite and consists of a nonlinear capacitor (accounting for charge accumulation within both Debye layers) in series with a linear resistor which accounts for the resistance to vacancy motion within the perovskite.

Different capacitance relations are obtained depending on the assumptions made about the vacancy mobilities. At one extreme the assumption made in Richardson *et al.* [5] (which we term hypothesis (a)) is that, on the timescales of concern, the negatively charged methylammonium ions are completely immobile while the positively charged halide vacancies redistribute quickly within the narrow Debye layers into quasi-equilibrium configurations. These assumptions are backed up by the estimates of Eames *et al.* [3] for the activation energies required to move vacancies from one site on the perovskite crystal to an adjacent one (which suggest a much higher mobility for halide vacancies than for methylammonium vacancies). In [5] it is shown that this hypothesis leads to the following capacitance relation for a single Debye layer:

$$Q_{dl}(\mathcal{V}_{dl}) = \frac{A\varepsilon V_T}{L_d} \operatorname{sign}(\mathcal{V}_{dl}) \left[2\left(e^{\mathcal{V}_{dl}/V_T} - 1 - \frac{\mathcal{V}_{dl}}{V_T}\right) \right]^{1/2}, \quad \text{Hypothesis (a)}$$
(2)

where \mathcal{V}_{dl} is the potential drop across the Debye layer, ε the permittivity of the perovskite, V_T the thermal voltage, A the area of the cell and L_d the Debye length. In order to determine the capacitance of both Debye layers in series this relation is inverted to obtain $\mathcal{V}_{dl}(Q)$ which in turn is substituted into the relation (1) to obtain the total potential drop across both Debye layers \mathcal{V}_c as a function of the charge Q stored in them.

At the other extreme is the hypothesis that both sets of vacancies are sufficiently mobile so that they can redistribute quickly in the Debye layers into quasi-equilibrium configurations (which we term hypothesis (c)). This leads to a capacitance relation (as shown, for example, in [4]) for a single Debye layer of the form

$$Q_{dl}(\mathcal{V}_{dl}) = 2\sqrt{2} \frac{A\varepsilon V_T}{L_d} \sinh\left(\frac{\mathcal{V}_{dl}}{2V_T}\right), \qquad \text{Hypothesis (c).}$$
(3)

Once again the total potential drop across both Debye layers \mathcal{V}_c can be determined as a function of the stored charge Q by inverting this relation (to obtain $\mathcal{V}_{dl}(Q)$) and substituting into (1).

The spectroscopy experiments conducted in this work require that both the external illumination and the applied voltage are changed to their base values and then left for a period of 300s, in order to allow the vacancy distributions time to settle to an equilibrium within the PSC (it is somewhat doubtful whether 300s is sufficient to allow both sets of vacancy distributions to fully equilibriate). After this settling period a small oscillatory oscillation to the illumination is applied, with frequency in the range $10-10^{5}$ Hz, and the oscillatory response of the current flow to this perturbation in the illumination is measured and used to infer the dependence of the capacitance of the device on the base applied voltage V. The experiment is thus conducted on two very different timescales: the settling timescale



Figure 1: (a) The full nonlinear equivalent circuit (with nonlinear capacitor). (b) The linear equivalent circuit used to calculate the response to the addition of a small perturbation $i_{src}(t)$ to the photovoltaic generated current. Potential drops across various segments of the circuits shown by dashed lines with arrows.

of 300s and the spectrascopic timescale of less than 0.1s. This disparity in the experimental timescales leads us to pose an alternative vacancy motion hypothesis that may be appropriate to the spectrascopic experiments (we term this hypothesis (b)) and which is intermediate between hypotheses (a) and (c). In this scenario it is assumed that both vacancy species (halide and methylammonium) are sufficiently mobile so that they equilibriate within the Debye layers within the 300s settling period, but that on the much shorter spectrascopic timescale the methylammonium vacancies are effectively immobile (being frozen into the configuration obtained after the 300s settling period) while the more mobile halide vacancies are still mobile enough to equilibriate within the Debye layers, even on this short timescale. This hypothesis leads to the following linear capacitance relation relating the charge Q stored in the Debye layers to the total potential drop $\mathcal{V}_c = \mathcal{V}_+ - \mathcal{V}_-$ across both layers

$$Q(\mathcal{V}_c) = \frac{1}{2} \frac{A \varepsilon V_T}{L_d} \mathcal{V}_c, \qquad \text{Hypothesis (b).}$$
(4)

In figure 2(c) (main text) the total capacitance of both Debye layers, as defined by $C(Q) = 1/\mathcal{V}'_c(Q)$, is plotted for all three hypotheses as a function of V the potential drop across the cell at steady-state (here \mathcal{V}_c , the total potential drop across both layers, is equal to the total drop across the cell so that $\mathcal{V}_c = V_{bi} - V$). Notably hypothesis (a) gives a capacitance that increases with V while hypothesis (c) gives one that sharply decays with increases in V.

1.1 Derivation of the linearised equations describing the spectroscopy measurements

In the light intensity modulated spectroscopy experiments conducted whose results are plotted in figure 2(b) a steady source of illumination is applied to the cell at constant applied voltage V_{ap} and only after the experiment has been running for 300s is a small oscillatory perturbation to this light source applied. The aim of the following discussion is to predict the small oscillatory response of the current I produced by the device in response to the perturbation of the light source as a function both of the applied voltage V_{ap} and of the frequency ω of the perturbation. In order to do this we first consider the response of the device to the initial steady illumination source before linearising about this base state to derive a set of linear equations that can be used to analyse the response of the device to the oscillatory perturbation in light intensity.

A nonlinear equivalent circuit model for the PSC. An equivalent circuit description of the device, which is based on the asymptotic solution of a charge transport model for ion vacancy motion and electron and hole transport within a PSC given in [5], is shown in figure 1(a). In this description there are three components in parallel (i) the current source arising from photovoltaic generation, (ii) a diode that models recombination between electron and holes within the device and (iii) two nonlinear capacitors in series with a resistor that represent the flow of ion vacancies through the perovskite layer and in (and out of) the Debye layers on its edge.¹ The resistor in series with these three components can be assigned to the resistance of the contacts and the blocking layers. The total current I flowing through the circuit is thus the the sum of the currents flowing through the 3 components in parallel

$$I = I_{src} + I_d + I_{ion},\tag{5}$$

where $I_{src}(t)$ is the current source (a known quantity), I_d the current flowing thorough the diode and I_{ion} that flowing through the nonlinear capacitors and resistor in series. We characterise the two nonlinear capacitors in series by a single capacitance relation, as in (2)-(4) above, of the form

$$Q = \mathcal{Q}(\mathcal{V}_c)$$
 or equivalently by its inverse $\mathcal{V}_c = \mathcal{V}(Q).$ (6)

Here Q is the charge stored on the capacitors and $\mathcal{V}_c = \mathcal{V}_p - I_{ion}R_i$ is the total potential drop across the capacitors (in figure 1(a) a single capacitor with the properties of both capacitors in series is shown). On denoting the potential drop across the components in parallel by \mathcal{V}_p we obtain the following current voltage relations between I_{ion} and \mathcal{V}_p :

$$\mathcal{V}_p = \mathcal{V}(Q) + I_{ion} R_i, \tag{7}$$

$$\frac{dQ}{dt} = I_{ion}, \tag{8}$$

representing a sum of the potential drops across this arm of the circuit and conservation of charge within the capacitors, respectively. The current-voltage relation for the branch of the

¹It is relatively straightforward to see how the first and third of these components ((i) and (iii)) can be related to the asymptotic solution to the charge transport model give in [5], it is less clear that the electron-hole recombination can be described by a single diode (as in (ii)) but this is the usual way to represent this phenemenon in an equivalent circuit.

circuit containing the diode we model with a standard diode equation, namely

$$I_d = -\mathcal{I}_0 \left(\exp\left(-\frac{\mathcal{V}_p}{\mathcal{N}V_T}\right) - 1 \right),\tag{9}$$

where here V_T is the thermal voltage, \mathcal{I}_0 is the reverse saturation current and \mathcal{N} the ideality factor of the diode. Finally we sum the potential drop across the series resistor (resistance R_s) and that across the components in parallel and equate this to the total potential drop across the device $V_{bi} - V$ to obtain

$$\mathcal{V}_p + IR_s = V_{bi} - V,\tag{10}$$

where here V_{bi} is the built in voltage and V the applied potential (this terminology follows the convention in [5]). Equations (5)-(10) comprise five equations for the five unknowns \mathcal{V}_p , I_{ion} , I_d , I and Q (here I_{src} and V are specified).

The steady-state. We start by looking for a steady solution to the equivalent circuit model (which we denote by a tilde) for the situation when both the voltage V and the photovoltaic generated current I_{src} are held constant before linearising about this steady solution in order to model the situation in which there is a small sinusoidal perturbation is added to the photovoltaic generation term. At steady state the ionic current flow through the lower branch of the circuit is zero

$$\tilde{I}_{ion} \equiv 0. \tag{11}$$

The potential difference across the components in parallel $\tilde{\mathcal{V}}_p$, and across the capacitor $\tilde{\mathcal{V}}_c$, can be determined from (10) and (11), and are given by

$$\widetilde{\mathcal{V}}_p(\widetilde{I}) = V_{bi} - V - \widetilde{I}R_s, \qquad \widetilde{\mathcal{V}}_c = \widetilde{\mathcal{V}}_p.$$
(12)

It follows, from (5) and (9), that the steady-state current \tilde{I} is determined by the solution to the following equation

$$\tilde{I} = I_{src} - \mathcal{I}_0 \left(\exp\left(-\frac{\tilde{\mathcal{V}}_p(\tilde{I})}{\mathcal{N}V_T}\right) - 1 \right).$$
(13)

The steady state charge on the capacitor \tilde{Q} , obtained from the capacitance relation (6), is

$$\tilde{Q} = \mathcal{Q}(\tilde{\mathcal{V}}_p(\tilde{I})). \tag{14}$$

Linearising about the steady-state for small perturbations to the photovoltaic generation. Linearising the governing equations (5)-(10) about the steady-state solution leads to simplified equations for the perturbation induced by a small oscillation $i_{src}(t)$ to the photovoltaic generation term of the form

$$I_{src} = \tilde{I}_{src} + i_{src}(t). \tag{15}$$

This linearisation is achieved by writing the solution in the form

$$I_d = -\mathcal{I}_0 \left(\exp\left(\frac{\tilde{\mathcal{V}}_p(\tilde{I})}{\mathcal{N}V_T}\right) - 1 \right) + i_d, \qquad I_{ion} = i_{ion}, \qquad I = \tilde{I} + \iota,$$
$$Q = \mathcal{Q}(\tilde{\mathcal{V}}_p(\tilde{I})) + q, \qquad \qquad \mathcal{V}_p = \tilde{\mathcal{V}}_p(\tilde{I}) + v_p,$$

where the quantities i_d , i_{ion} , q, v_p and ι (all denoted by small letters) are small perturbations to the steady solution induced by $i_{src}(t)$. Substituting (16) into the equivalent circuit model (5)-(10) and linearising about the steady solution leads to the model

$$\iota = i_{src} + i_{ion} + i_d, \qquad v_p + \iota R_s = 0, \qquad v_p = i_d R_d(\tilde{\mathcal{V}}_p(\tilde{I})), \tag{16}$$

$$R_i \frac{di_{ion}}{dt} + \frac{1}{C(\tilde{\mathcal{V}}_p(\tilde{I}))} i_{ion} = \frac{dv_p}{dt}.$$
(17)

This model is equivalent to the linear equivalent circuit depicted in figure 1(b). Here the linear resistance R_d and the linear capacitance C are both functions of the steady state potential across the components in parallel $\tilde{\mathcal{V}}_p(\tilde{I}) = V_{bi} - V - \tilde{I}R_s$ and are defined by

$$R_d(\tilde{\mathcal{V}}_p(\tilde{I})) = \frac{\mathcal{N}V_T}{\mathcal{I}_0} \exp\left(\frac{\tilde{\mathcal{V}}_p(\tilde{I})}{\mathcal{N}V_T}\right), \qquad C(\tilde{\mathcal{V}}_p(\tilde{I})) = \mathcal{Q}'(\tilde{\mathcal{V}}_p(\tilde{I})).$$
(18)

where $\mathcal{Q}'(\cdot)$ is the derivative of the function $\mathcal{Q}(\cdot)$.

1.2 Solution of the linear model for sinusoidal perturbations to the photovoltaic generation

In order to mimic the light intensity modulated spectroscopy experiments carried out in the experimental part of this work we seek a solution to the linear equations (16)-(17) in which the perturbation to the photovoltaic generation is sinusoidal with the form

$$i_{src}(t) = i_0 \exp(i\omega t).$$

Substituting this forcing term into (16)-(17) and solving leads to the solution

$$i_{ion} = -i_0 M(\omega, V) \exp(i\omega t), \qquad v_p = -i_0 \frac{R_s R_d}{R_s + R_d} (1 - M(\omega, V)) \exp(i\omega t), \quad (19)$$

$$i_{d} = -i_{0} \frac{R_{s}}{R_{s} + R_{d}} (1 - M(\omega, V)) \exp(i\omega t), \qquad \iota = i_{0} (1 - M(\omega, V)) \frac{R_{d}}{R_{s} + R_{d}} \exp(i\omega t), \quad (20)$$

where

$$M(\omega, V) = \frac{\left(R_i + \mathcal{R}_{ef}\right)\mathcal{R}_{ef}\omega^2 C^2}{1 + \left(R_i + \mathcal{R}_{ef}\right)^2\omega^2 C^2} + i\frac{\mathcal{R}_{ef}\omega C}{1 + \left(R_i + \mathcal{R}_{ef}\right)^2\omega^2 C^2},\tag{21}$$

where the capacitance C and the effective resistance \mathcal{R}_{ef} , as defined by

$$\mathcal{R}_{ef}(\tilde{\mathcal{V}}_p) = \frac{R_s R_d(\mathcal{V}_p)}{R_s + R_d(\tilde{\mathcal{V}}_p)},\tag{22}$$

are both functions of $\tilde{\mathcal{V}}_p = V_{bi} - V - \tilde{I}(V)R_s$, and thus of V.

The key part of the solution required to compare to the experimental results (plotted in figure 2(b)) is the imaginary part of $\iota \exp(-i\omega t)$, which on using (20b), can be written

$$\operatorname{Im}\left(\iota \exp(-i\omega t)\right) = -\left(\frac{i_0}{R_s}\right) \frac{\mathcal{R}_{ef}^2 \omega C}{1 + \left(R_i + \mathcal{R}_{ef}\right)^2 \omega^2 C^2}.$$
(23)

This function has

a maximum modulus of
$$\frac{i_0 \mathcal{R}_{ef}^2}{2R_s \left(R_i + \mathcal{R}_{ef}\right)}$$
 for $\omega = \frac{1}{C \left(R_i + \mathcal{R}_{ef}\right)}$ (24)

The maximum of the imaginary part of the perturbation to the current only depends on the applied voltage V through \mathcal{R}_{ef} , via (12), (18) and (22). It is clear that as V increases from zero to the built in voltage V_{bi} so the linear resistance of the diode R_d decreases extremely rapidly (as expected). Typically the linear resistance of the diode is very large near shortcircuit (V = 0) but become comparable with the series resistance R_s near open-circuit (close to $V = V_{bi}$). Thus for sufficiently small V the effective resistance $\mathcal{R}_{ef} \approx R_s$ since $R_d \gg R_s$. As V increases there is then a small region of voltage in which R_d is comparable to R_s and then for larger applied voltages (where $R_d \ll R_s$) the effective resistance is approximated by $\mathcal{R}_{ef} \approx R_d$. The function $\mathcal{R}_{ef}(V)$ is thus a smoothed off step function which transitions from values close to R_s , for small enough V, to values close to zero, as V increases beyond a certain critical size. This type of behaviour is reflected in the experimental results plotted in the main paper figure 3(a). Here the maxima at V = -0.2, 0.2, 0.7 Volts are all very similar (presumably because $\mathcal{R}_{ef} \approx R_s$ for smaller values of V) however that for V = 0.9 Volts, which is close to $V = V_{bi}$, is about a factor of 10 smaller which could be explained by a considerably smaller value of \mathcal{R}_{ef} at this higher voltage. According to this theory the dependence of the experimental results on the capacitance of the Debye layers C, as the applied voltage V is changed, is reflected only through the position of the maximum as a function of frequency ω . In figure 3(a) of the main paper it can be seen that for the lower applied voltages (V = -0.2,0.2, 0.7 Volts) the position of this maximum changes little but for V = 0.9 Volts it is considerably decreased below that of the other voltages. This suggest that C must be an increasing function of $V(\text{since } (R_i + \mathcal{R}_{ef}) \text{ decreases, albeit probably only marginally, with } V).$ The only hypothesis consistent with this is hypothesis (a), reflected in the capacitance relation (2) and plotted in figure 3(b), which asserts that even on the long settling timescale of 300s there is minimal movement of methylammonium vacancies.

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Model Poisson drift-diffusion equations

The model cell is made up of a n-type layer in x < -1, a perovskite layer in -1 < x < 1 and a p-type layer in x > 1. The central assumptions used in the model will be: (i) that the blocking layers are sufficiently highly doped that their Fermi levels are flat (this justifies the use of Ohmic boundary conditions on th hole density at x = 1 and electron density at x = -1), and; (ii) that the electric field/potential is determined by the solely by the ion distribution and not the electrons/holes (this justified by the observation that there are orders of magnitude more ions than electronic charge carriers).

The ion problem: The equations that determine the distribution of positively charged defects (e.g. halide vacancies), P, and the electric potential, ϕ , are

$$\frac{\partial P}{\partial t} = D_0 \frac{\partial}{\partial x} \left(\frac{\partial P}{\partial x} + P \frac{\partial \phi}{\partial x} \right),\tag{1}$$

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{N_0 - P}{\lambda^2},\tag{2}$$

where, N_0 is the (fixed) density of the immobile negative vacancies (e.g. cation vacancies), λ is a small (dimensionless) parameter while we term the normalised Debye length and D_0 is the (dimensionless) diffusivity of negative defects.

Suitable boundary and initial conditions specify zero flux of positive defects at each boundary of the perovskite layer, a specified change in potential across the perovskite layer and that the initial density of positive and negative defects should be the same (thus ensuring net charge neutrality of the material). We therefore write

$$-D_0 \left(\frac{\partial P}{\partial x} + P \frac{\partial \phi}{\partial x}\right)\Big|_{x=-1,+1} = 0, \tag{3}$$

$$\phi|_{x=-1} = (V_{bi} - V)/2, \tag{4}$$

$$\phi|_{x=+1} = -(V_{bi} - V)/2, \tag{5}$$

$$P|_{t=0} = N_0. (6)$$

Here, V_{bi} and V are the built-in and applied voltages respectively, and (roughly speaking) $0 < V < V_{bi}$ corresponds to the power-generating regime.

The electronic problem: Once the ion problem, (1)-(6), has been solved we then determine the electronic current by solving the following system for the electron, n, and hole concentrations, p. The electric potential is, for the purposes of the solution of this system, taken to be a known function that was determined previously by solving the ionic problem. Since we are primarily interested in the dynamics on the timescale of ionic motion (much longer than the timescale for electron and hole motion), it is sufficient to solve only for the steady-state distribution of charge carriers. The equations are

$$D_{+}\left(\frac{\partial p}{\partial x} + p\frac{\partial \phi}{\partial x}\right) + G(x) - R(n, p, N, P) = 0,$$
(7)

$$D_{-}\left(\frac{\partial n}{\partial x} - n\frac{\partial \phi}{\partial x}\right) + G(x) - R(n, p, N, P) = 0,$$
(8)

where D_+ and D_- are the (dimensionless) diffusivitities of holes and electrons respectively, R(n, p, P) is the recombaintion rate (which we will specify later), and G(x) is the photo-generation rate. Suitable boundary conditions are Ohmic conditions on n and p at x = -1 and x = 1 respectively, accompanied by no flux conditions on n and p at x = -1 respectively:

$$n|_{x=-1} = n_0, (9)$$

$$-D_{+}\left(\frac{\partial p}{\partial x} + p\frac{\partial \phi}{\partial x}\right)\Big|_{x=-1} = 0, \tag{10}$$

$$p|_{x=1} = p_0, \tag{11}$$

$$-D_{-}\left(\frac{\partial n}{\partial x} - n\frac{\partial \phi}{\partial x}\right)\Big|_{x=1} = 0.$$
(12)

The current, J, is then give by the hole flux minus the electron flux; that is

$$J = D_{-} \left(\frac{\partial n}{\partial x} - n \frac{\partial \phi}{\partial x} \right) - D_{+} \left(\frac{\partial p}{\partial x} + p \frac{\partial \phi}{\partial x} \right).$$
(13)

The sum of equations (7) and (8) implies that this current is constant through the perovskite layer, and so the value of J may be determined by evaluating the right-hand side of (13) at any -1 < x < 1.

Recombination rate: The results shown here were computed for a recombination rate $R(n, p, N, P) = \gamma_1 np + \gamma_2 nN$, where γ_1 and γ_2 are constants. The model therefore accounts for two different recombination pathways. The first corresponds to traditional bimolecular recombination, at a rate proportional to np, whilst the second account for electron-dominated recombination via the cation vacancies at a rate proportional to nN. It is worth noting that qualitatively similar solutions are obtained for any recombination rate has the form $R(n, p, N, P) = \hat{\gamma}_1 R_1(n, p) + \hat{\gamma}_2 nN$, where R_1 could he Shockley-Reid-Hall, bimolecular, or direct recombination rates.

Computations: Solutions of the model equations were obtained using the chebfun software. More details on the using this software to solve similar Poission drift-diffusion systems can be found in [Foster et. al., SIAM J. Appl. Math, 74(6):1935–1966 (2014)].

Results — short circuit current decay: The model results in figure 4 were obtained by first solving (1)-(6) with: (i) the applied voltage V held fixed in either forward or reverse bias long enough for the P and ϕ to reach a steady-state; (ii) V was abruptly switched to zero and the resulting transients of P and ϕ were solved for, then; (iii) the equations for the electrons and holes, (7)-(12) were then solved taking ϕ as predicted by solving the transient problem in stage (ii). Finally; (iv) the current is computed (as a function of time) using (13).