## **Supplementary Information**

# Interfacial Recombination Kinetics in Aged Perovskite Solar Cells Measured Using Transient Photovoltage Techniques

Jesús Jiménez-López<sup>1,2\*</sup> and Emilio Palomares<sup>1,3\*</sup>

- 1. Institute of Chemical Research of Catalonia-The Barcelona Institute of Science and Technology (ICIQ-BIST), Avda. Països Catalans 16, 43007 Tarragona, Spain
- Department d'Enginyeria Electrònica, Elèctrica i Automàtica, Univeristat Rovira i Virgili, Avda. Països Catalans 26, 43007 Tarragona, Spain
- 3. ICREA, Passeig Lluís Companys 23, 08010 Barcelona, Spain

\*Corresponding author, email: jjimenez@iciq.es ; epalomares@iciq.es

#### **Experimental methods**

#### Device fabrication

FTO films are first brushed with water and Hellmanex<sup>®</sup> soap, then, they are ultrasonicated with H<sub>2</sub>O/ Hellmanex<sup>®</sup>, acetone, and isopropanol. Finally, they are dried with an air flow.

Prior to compact TiO<sub>2</sub> (cTiO<sub>2</sub>) deposition, devices are treated with UV/O<sub>3</sub> for 30 minutes. Then, we deposit cTiO<sub>2</sub> by spin coating a 0.3 M Ti(iPrO)<sub>2</sub>(acac)<sub>2</sub> solution in 2-propanol using 4000 rpm, 1000 rpm/s for 25 s. The substrates are dried at 125 °C for 5 minutes and then calcined at 450 °C for 30 minutes. Once the substrates cool down, they are immersed into a 40 mM TiCl<sub>4</sub> solution at 70 °C for 30 minutes. After that, they are rinsed with H<sub>2</sub>O and ethanol and dried with an air flow.

The mesoporous TiO<sub>2</sub> layer (mTiO<sub>2</sub>) is also deposited by spin coating a 30 nm particle size paste (30NR-D, Greatcell) diluted in ethanol in a 1:7 weight ratio, with 6000 rpm, 1000 rpm/s for 30 s. The films are dried at 125 °C for 5 minutes and then annealed at 450 °C for 30 minutes. The substrates are then placed into the N<sub>2</sub> glovebox while they are still warm to avoid humidity.

We prepare a triple cation perovskite, CsFAMAPbIBr, by dissolving 1.2 M PbI<sub>2</sub>, 1.04 M formamidinium iodide (FAI), 0.16 M PbBr<sub>2</sub>, 0.16 M methylammonium bromide (MABr), and 0.1 M of CsI into DMF:DMSO (4:1, volume ratio). To help the dissolution, it is stirred at 60 °C for 30 minutes. Then, the solution is filtered and 40  $\mu$ l are spin coated with a two-step program, first 2000 rpm, 500 rpm/s and 12 s, and then 5000 rpm 500 rpm/s 25 s. 10 seconds before the end of the spinning process, 100  $\mu$ l of chlorobenzene are dropped in the center of the substrate while spinning. Then, the films are annealed at 100 °C/ 1 h. We prepare the devices with a continuous N<sub>2</sub> flow to remove the solvent atmosphere that can affect the perovskite morphology.

As hole transporting material (HTM), we pepare a 60 mM spiro-OMeTAD soluion. To this solution we add 4-tert-butylpyridine (TBP), LiTFSI (stock solution: 1.8 M in acetonitrile) and Co(III) TFSI (stock solution: 0.25 M) with a molar ratio 1 spiro-OMeTAD : 3.3 TBP : 0.5 LiTFSI : 0.05 Co(III) TFSI. 30  $\mu$ l of this solution are spin coated at 4000 rpm for 30 s.

Finally, 80 nm of Au are thermal evaporated under high vacuum conditions. Prior to Au deposition and after Au deposition, the devices are stored in air conditions with <10 % humidity.

### JV curves

The J-V curves were measured using a solar simulator (ABET 11000) and a source meter (Keithley 2400). The curves were registered under 1 Sun conditions (100 mW/cm<sup>2</sup>, AM 1.5G) calibrated with a Si-reference cell. The active area of the devices was  $0.09 \text{ cm}^2$ . The scan rate employed was 0.04 V/s (if different, it is stated). For the measurements with different light intensities, different optical filters were employed.

# Photo-induced transient photovoltage, transient photocurrent and charge extraction.

Photo-induced transient photovoltage (TPV), photo-induced transient photocurrent (TPC) and photo-induced charge extraction (CE) measurements were carried out using a white LED controlled by a programmable power supply and a control box that switches from open to short-circuit states. All the signals are recorded in an oscilloscope Yokogawa DLM2052 registering drops in voltage. Light perturbations pulses for TPV and TPC were provided by a nanosecond PTI GL-3300 nitrogen laser.

## **Photovoltaic parameters**

**Table S1.** Summary of the photovoltaic parameters of the cells tested in the study. The results were obtained under 1 Sun conditions (AM 1.5G, 100 mW/cm<sup>2</sup>) and a scan rate of 40 mV/s. Hysteresis index (HI) was calculated using HI =  $\left(\frac{P_{max,r}}{P_{max, f}}\right)$ -1.

Day	Sweep	J <sub>sc</sub> (mA/cm <sup>2</sup> )	Voc (V)	FF (%)	PCE (%)	HI
1	Forward	$21.3\pm1.3$	$0.960\pm0.026$	$50.6\pm3.3$	$10.3\pm0.8$	0.49
	Reverse	21.1 ± 1.3	$1.045\pm0.008$	$69.9\pm0.5$	15.4 ± 1.0	
2	Forward	$21.2 \pm 1.7$	$1.010\pm0.025$	$54.7\pm3.6$	11.7 ± 1.2	0.32
	Reverse	$20.8\pm1.6$	$1.063\pm0.011$	$69.7 \pm 1.8$	15.4 ± 1.5	
3	Forward	$22.4\pm0.6$	$1.043\pm0.015$	$55.8\pm3.4$	13.0 ± 1.2	0.31
	Reverse	$22.0\pm0.6$	$1.081\pm0.010$	$72.1 \pm 1.1$	17.1 ± 0.6	
21	Forward	$22.2\pm0.5$	$0.981 \pm 0.039$	$58.9\pm4.4$	12.9 ± 1.5	0.34
	Reverse	$22.4\pm0.5$	$1.078\pm0.014$	$71.8\pm0.9$	17.3 ± 0.5	
30	Forward	$21.8\pm0.6$	$1.090\pm0.007$	$64.0\pm3.3$	15.3 ± 1.0	0.06
	Reverse	$21.2\pm0.6$	$1.097\pm0.008$	$69.2\pm2.7$	16.1 ± 0.8	
45	Forward	$21.0\pm0.6$	$1.120\pm0.009$	$67.1\pm3.5$	15.8 ± 1.3	0.05
	Reverse	$20.8\pm0.5$	$1.132\pm0.009$	$70.6\pm2.2$	16.6 ± 0.8	



**Figure S1.** Scheme showing the possible band diagrams in different conditions. Dashed lines show the Fermi levels, complete lines show the valence band and conduction band of the perovskite, and the squared positive and negative symbols show the ions in the perovskite. (A) In dark conditions, when the selective contacts are deposited, a built-in voltage  $(V_{bi})$  is generated to compensate the difference in Fermi levels of the material. (B) Ions move to the interfaces until they screen the internal electric field, creating regions of accumulated ionic charge at both interfaces. (C) When light irradiates the cell, the Fermi levels split with an associated  $V_{oc}$ , and the electric field is of opposite sign respecting to the original internal electric field. The ions start moving, but, they do it slowly, so they will remain at the interfaces for some time, driving carriers in the opposite direction of extraction, creating regions with accumulated carriers (band valleys) where there is a greater degree of recombination, obtaining lower  $V_{oc}$  values. (D) Carrier accumulation will persist until ions redistribute, and the electric field that drives carriers in the opposite direction is canceled.



Figure S2. TPV transients at different light illumination times with a linear timescale measures on day 3 (A) and day 45 (B).



**Figure S3.** Amplitude of the negative transient deflection at different illumination times obtained from the TPV measured with a laser excitation wavelength of 590 nm.



Figure S4. TPV transients at different light illumination times for the devices measured on day 3, using different laser excitation wavelengths: 540 nm (A) logarithmic timescale,
(B) linear timescale; 590 nm (C) logarithmic timescale, (D) linear timescale; 660 nm (E) logarithmic timescale, (F) linear timescale.



Figure S5. TPV transients at different light illumination times for the devices measured on day 45, using different laser excitation wavelengths: 540 nm (A) logarithmic timescale, (B) linear timescale; 590 nm (C) logarithmic timescale, (D) linear timescale; 660 nm (E) logarithmic timescale, (F) linear timescale.



Figure S6. Examples of two different TPV decays used to obtain the small perturbation lifetime. The device is illuminated until we observe a stable  $V_{oc}$ . Then, the TPV is recorded. The decay is fitted to a monoexponential decay starting at the maximum point of the peak.



**Figure S7. (A)** JV curves under different light intensities for the device measured on day 3. **(B)** JV curves under different light intensities for the device measured on day 45. **(C, D)**  $J_{sc}$  values at different light intensities and the fitting to a power law dependence, in forward **(C)** and reverse **(D)** conditions. **(E,F)**  $V_{oc}$  dependence with the light intensity for forward **(E)** and reverse **(F)** conditions. It is used to calculate the ideality factor of the device.



**Figure S8.** Comparison of the small perturbation lifetime obtained at different light bias with TPV and their corresponding lifetimes for the capacitive discharge (dashed lines). This certify that in the range of voltages we are measuring, we are studying the charges in the bulk of the perovskite.



Figure S9. (A) Charge density obtained at different photovoltage using the CE technique.(B) The Small perturbation lifetime as a function of the charge density obtained from CE.



**Figure S10.** TPV and CE transient comparison at 1 Sun light intensity measured on day 3 (**A**) and day 45 (**B**). TPV transient comparison measured on days 3 and 45 at 1 Sun light intensity (**C**). CE transient comparison measured on days 3 and 45 at 1 Sun light intensity (**D**).



**Figure S11. (A)** Capacitance at different voltages (light bias) and **(B)** the charge obtained upon integration of the capacitance at the same voltages.



Figure S12. (A) Capacitance at different voltages (light bias) after the subtraction of the c at the contacts and (B) the charge obtained upon integration of the capacitance at the same voltages reflecting the charges stored in the bulk of the perovskite



**Figure S13.** Small perturbation lifetime obtained from TPV as a function of the charge density obtained from the integration of the differential capacitance after the subtraction of the geometric capacitance.

**Supplementary Note 1.**  $V_{oc}$  calculation from the fitting parameters obtained from the TPV and TPC analysis.

$$V_{oc} \text{ (calc)} = \frac{m K_B T}{q \delta} \ln \left( \frac{J_{sc} \tau_0}{Q_0} \right)$$
(1)

Where  $Q_0$  is the equilibrium charge density and m is the deviation from the thermal voltage (K<sub>B</sub>T/q) obtained from the exponential fitting of the lifetime as a function of the voltage (**Figure 4A** in the main text, Equation 2).

$$Q = Q_0 \exp\left(\frac{q V_{oc}}{m K_B T}\right)$$
(2)

d is the recombination order,  $\delta = \left(\frac{m}{\theta}\right) + 1$  that is the slope of the small perturbation as a function of the charge density (**Figure 4B**). And q and  $\tau_{\Delta n_0}$  are obtained from the exponential fitting of the lifetime as a function of the voltage.

$$\tau_{\Delta n} = \tau_{\Delta n_0} \exp\left(-\frac{q V_{oc}}{\theta K_B T}\right)$$
(3)

In the following table, table S2, we summarize the parameters obtained for the two devices and the final  $V_{oc}(calc)$ .

**Table S2.** Summary of the fitting parameters to calculate the  $V_{oc}$  obtained from the TPV and TPC techniques.

	Day 3	Day 45
m	2.3	2.2
θ	3.3	3.1
δ	1.7	1.7
$J_{sc}$ / $A \cdot cm^{-2}$	0.0221	0.0216
$\tau_{\Delta n0}$ / s	0.337	1.41
$Q_0$ / $C \cdot cm^{-2}$	$1.0 \cdot 10^{-16}$	$4.8 \cdot 10^{-17}$
V <sub>oc</sub> (calc) / V	1.109	1.132
V <sub>oc</sub> (exp) / V	1.087	1.139