

Instability of p-i-n perovskite solar cells under reverse bias

Ricardo A. Z. Razera,^{a,b} Daniel A. Jacobs,^a Fan Fu,^{a,*} Peter Fiala,^a Marion Dussouillez,^d Florent Sahli,^a Terry C. J. Yang,^{a,‡} Laura Ding,^c Arnaud Walter,^a Adriano F. Feil,^d Henri I. Boudinov,^b Sylvain Nicolay,^c Christophe Ballif,^{a,c} and Quentin Jeangros^a

^a Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Microengineering (IMT), Photovoltaics and Thin-Film Electronics Laboratory (PV-Lab), Rue de la Maladière 71b, 2002 Neuchâtel, Switzerland

^b Universidade Federal do Rio Grande do Sul (UFRGS), Laboratorio de Microelectronica, Av. Bento Gonçalves 9500, Porto Alegre-RS, Brazil

^c CSEM, PV-Center, Jaquet-Droz 1, 2002 Neuchâtel, Switzerland

^d Pontificia Universidade Catolica do Rio Grande do Sul (PUCRS), Escola de Ciencias, Av. Ipiranga, 90619-900, 6681, Porto Alegre-RS, Brazil

* now at Swiss Federal Laboratories for Materials Science (Empa), Laboratory for Thin Films and Photovoltaics, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

‡ now at CSIRO Energy Centre, 10 Murray Dwyer Circuit, 2304 Mayfield West NSW, Australia

Supporting Information

Solar cell fabrication

First, the perovskite solution is prepared inside a N₂-filled glovebox (water and oxygen contents less than 1 ppm) by mixing powders of PbI₂ (TCI, 99.99 %), PbBr₂ (TCI, 98 %), FAI (Greatcell Solar) and CsBr (Abcr, 99.999%) in molarities of (1.14 ± 0.02) M, (0.216 ± 0.004) M, (1.08 ± 0.02) M and (0.216 ± 0.005) M, respectively. All powders are introduced in the same vial before adding the solvent (4:1 DMF:DMSO). Typically, 1.8 mL of solution is made for a batch of 16 samples. The solution is then heated to 75 °C until all powders are dissolved. The solution is prepared one day before the perovskite is deposited and is always stored in a sealed vial inside the N₂-glovebox.

Device fabrication starts by cleaning the 2.5 x 2.5 cm² indium tin oxide (ITO)/glass substrates (Kintec, sheet resistance of ~15 Ω/sq) with a 5 min-long oxygen plasma treatment followed by cleaning in an industrial glass washing machine. 20 nm of NiO is then deposited by sputtering. Before depositing the perovskite, the NiO is annealed at 300 °C for 15 min in air with a ramp of 15 min starting at room temperature. The substrates are then moved to a N₂-filled glovebox for perovskite deposition using the following spin-coating recipe: 1) speed=1000 rpm, time=10s, acceleration=200 rpm/s and 2) speed=6000 rpm, time=25s, acceleration=1000 rpm/s. 100 µL of perovskite solution is used for each substrate and the solution is dropped across the entire area. Chlorobenzene is used as antisolvent, with 200 µL applied at the center of the substrate some seconds before the end of the second step of the recipe. After spin-coating, the brownish samples

are immediately annealed at 105 °C for 1h in a pre-heated hot plate, where they quickly become black.

Then, still inside the glovebox, 1 nm of LiF (99.98%, Sigma-Aldrich) and 19 nm of C₆₀ (> 99.95%, NanoC) are thermally evaporated on top of the perovskite using a home-built system. The base pressure is 2.10⁻⁶ mbar or less. The rate of LiF deposition is ~0.2 Å/s and that of C₆₀ is ~0.5 Å/s, as monitored by a quartz crystal balance.

For semitransparent devices, the samples are then taken outside of the glovebox and moved to an Oxford Instruments atomic layer deposition system where 10 nm of SnO₂ is deposited using tetrakis(dimethylamino)tin and H₂O as precursors with the substrates at 100 °C. Then, 100 nm of indium tin oxide (ITO, sheet resistance of ~80 Ω/sq) is sputtered using an Evatec cluster tool. Alternatively, indium zinc oxide (IZO, ~30 Ω/sq) was also employed as transparent electrode (thickness varied up to 250 nm). Finally, except for cells without metal fingers, 130 nm of the metal electrode (Ag, Cu or a Ni/Al stack) is thermally evaporated on top of the ITO layer through a shadow mask in the form of a frame around the borders of the 0.5 x 0.5 cm² device area (see Figure S4 for the final layout). Each substrate contains 3 devices. For opaque cells, the back metal contact is directly evaporated on top of C₆₀ using a shadow mask and the back contact covers the entire area of the device.

All I-V measurements were taken using a homemade system. All semi-transparent cells are measured in superstrate configuration. The I-V curves are measured using Keithley's by increasing the applied voltage in steps and measuring the current after a determined delay. The light source is a combination of blue, green and red LEDs and halogen lamps calibrated to 1000 W/m² intensity using a standard c-Si cell. The spectrum is adjusted to AM1.5G by adjusting the relative intensity of the LEDs and halogen lamps.

The parameters used to make the IV curves are:

Voltage range: -0.1 V to 1.2 V in steps of 10 mV.

Delay at each step: 10 ms.

Integration time at each step: 10 ms.

For the reverse bias test protocol, after each step of reverse biasing, a forward scan (-0.1 V to 1.2 V) and then a reverse scan (1.2 V to -0.1 V) are taken. Note that fast I-V scans are acquired to capture the changes induced by the reverse bias. In the main text, all I-V curves shown are forward scans because these were taken first and therefore are more representative of the effects of the reverse bias treatments. Also, as a fast scan is used, some hysteresis is observed, as shown in Figure S3. However, both forward and reverse curves show qualitatively similar behaviors.

Samples were prepared for transmission electron microscopy (TEM) observations using the conventional focused ion beam lift-out procedure in a Zeiss NVision 40. Samples were then transferred quickly in air (<2 min) to a FEI Osiris TEM, where they were analyzed at 200 kV with a scanning TEM beam current of 250 pA. Energy-dispersive X-ray spectra were quantified using the Cliff–Lorimer method implemented in the Bruker Esprit software.

Photoluminescence (PL) spectra were acquired in a PL/Raman MonoVista Confocal system using a laser with a wavelength of 514 nm.

Supplementary Figures

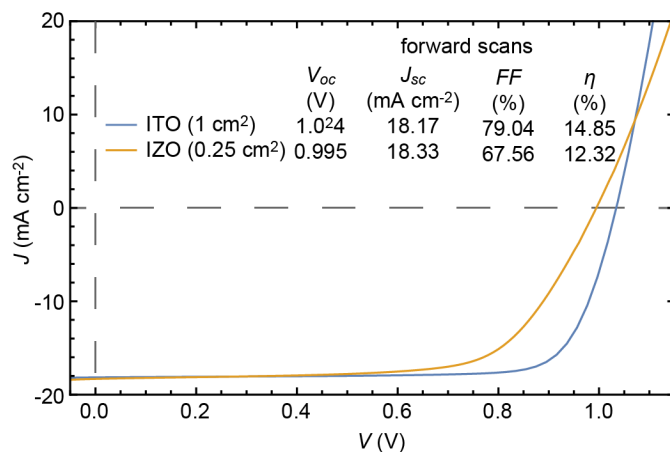


Figure S1: I-V properties of the ITO- and IZO-based cell analyzed in this study. The IZO electrode used here was 250 nm, while the optimized ITO one was 100 nm. The optimized ITO cell shown here covers an active area of 1 cm², while the IZO one is 0.25 cm².

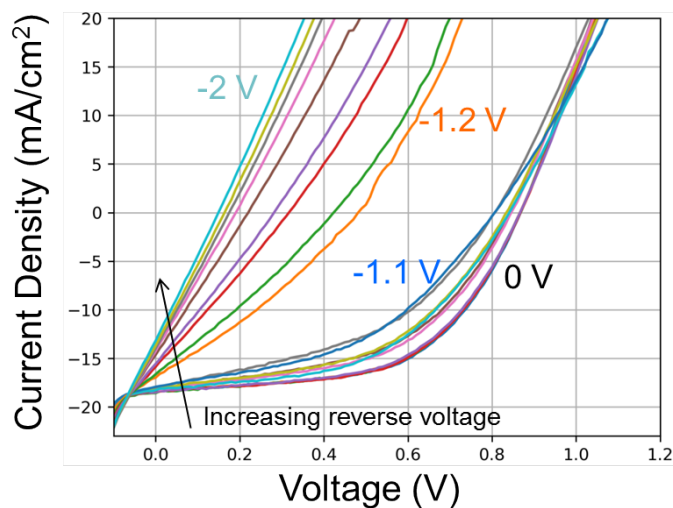


Figure S2: Typical evolution of the forward I-V scans when pre-biasing the device at progressively increasing reverse voltages. The shunt resistance decreases, while the series resistance increases.

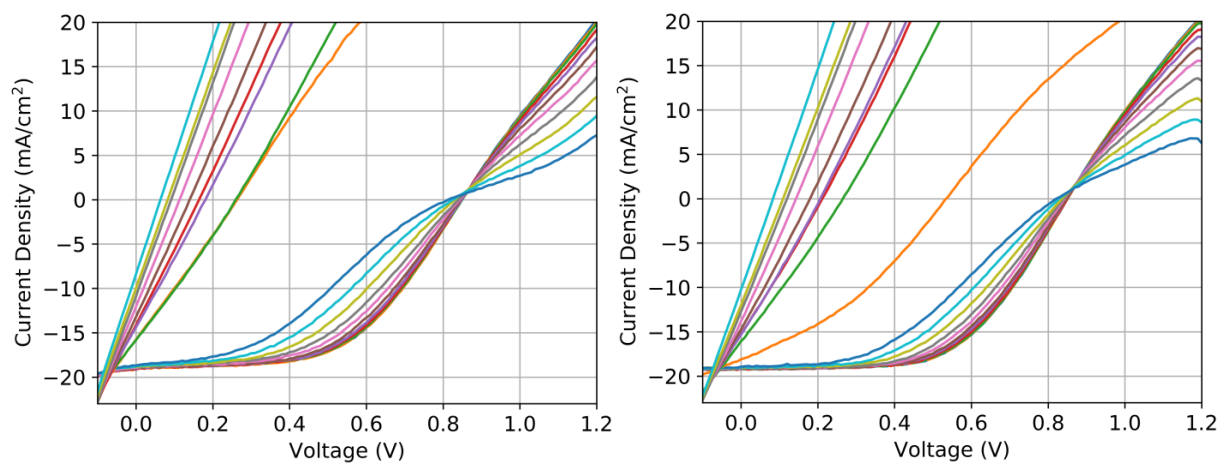


Figure S3: Forward (left panel) and reverse (right panel) scans taken after each reverse biasing step. Although hysteresis is present when measuring I-V scans in these conditions, both scans show qualitatively similar behaviors. The top figure is the same as Figure 1b of the main text and is shown for comparison with reverse scans.



Figure S4: a) semitransparent solar cell reverse biased from 0 V to -5 V in 3 min steps of -0.1 V showing visible burn marks. The top Ag contact can be seen from the glass side. b-c) Top view and focused ion beam-prepared cross-section scanning electron microscopy images of shunted areas.

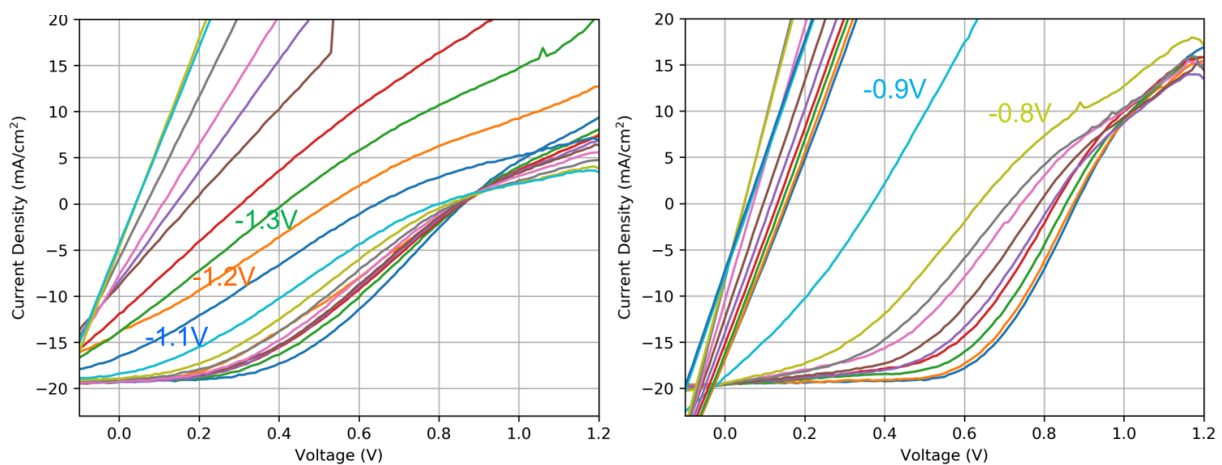


Figure S5: Evolution of the I-V curve after reverse biasing at increasing voltages for devices featuring a Cu (left panel) and a Ni/Al stack (right panel) as back electrode.

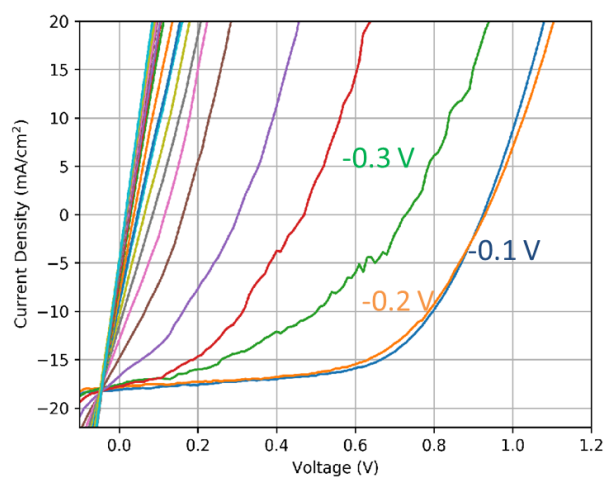


Figure S6: I-V curve evolution of an opaque solar cell, where the Ag back contact is directly on top of C_{60} and covers the entire area of the device.

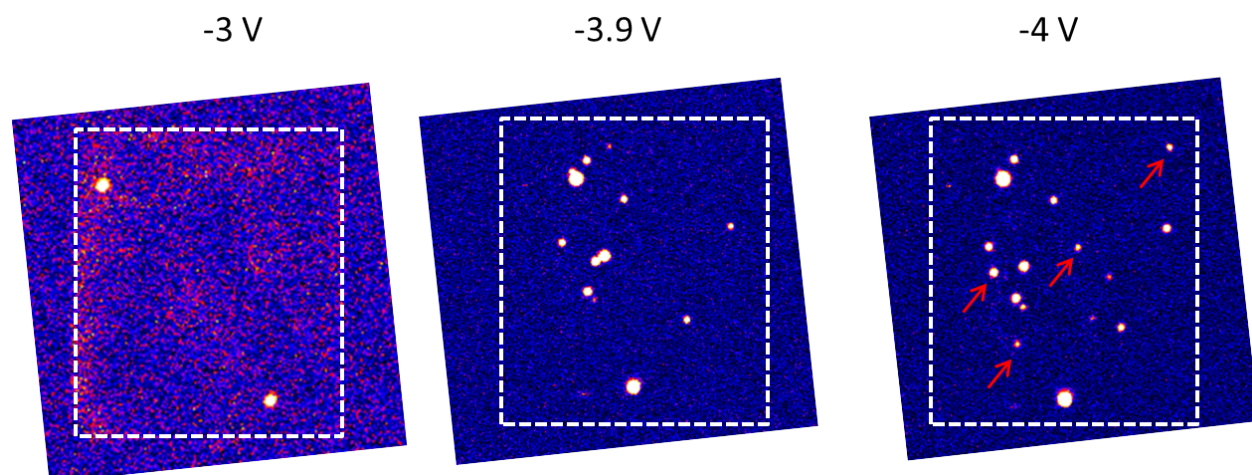


Figure S7: Hot spot formation observed with lock-in thermography in cells comprising no metallic top electrode (only ITO on top). The dashed white square delineates the region of the cell covered by the ITO electrode. At -3 V (left panel), two hot spots are observed, showing that even metal-electrode-free solar cells shunt under reverse bias, although only at heavier reverse biasing compared to cells with metal. In the middle and right panels, a comparison between images taken at -3.9 V and -4 V is shown. Arrows indicate hot spots that appeared abruptly during the biasing step to -4V. The fact that these hot spots were invisible during the previous biasing step is an indication that they were created by the reverse bias itself, as opposed to simply enlarging due to heat as in c-Si solar cells. These results indicate that the absorber layer itself also shunts under reverse bias, even in the absence of a metal electrode.

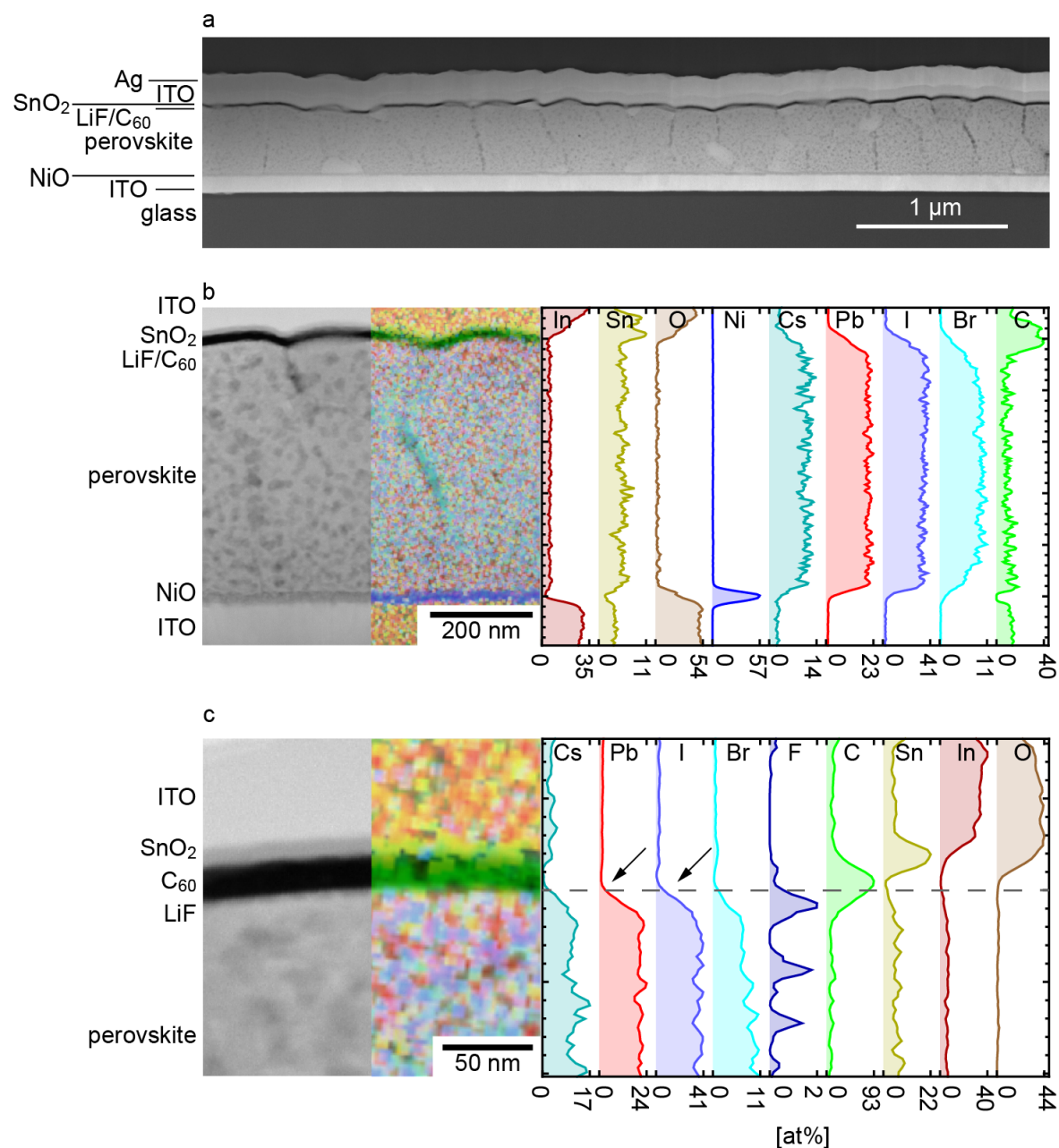


Figure S8: a) STEM HAADF image of a reference as-prepared device. The small voids are a consequence of the focused ion beam preparation of the TEM lamella. No double-layer structure is observed, contrary to Figure 2a of the main text (sample reverse biased at -5V). (b) EDX chemical map and corresponding concentration profile of the reference sample, showing no gradient in Br (unlike Figure 2b of the main text). (c) STEM HAADF and EDX data of the region close to the C_{60} layer. Note that the top edges of the Pb, I and Br distributions coincide in position and are well separated from the carbon peak of the C_{60} layer.

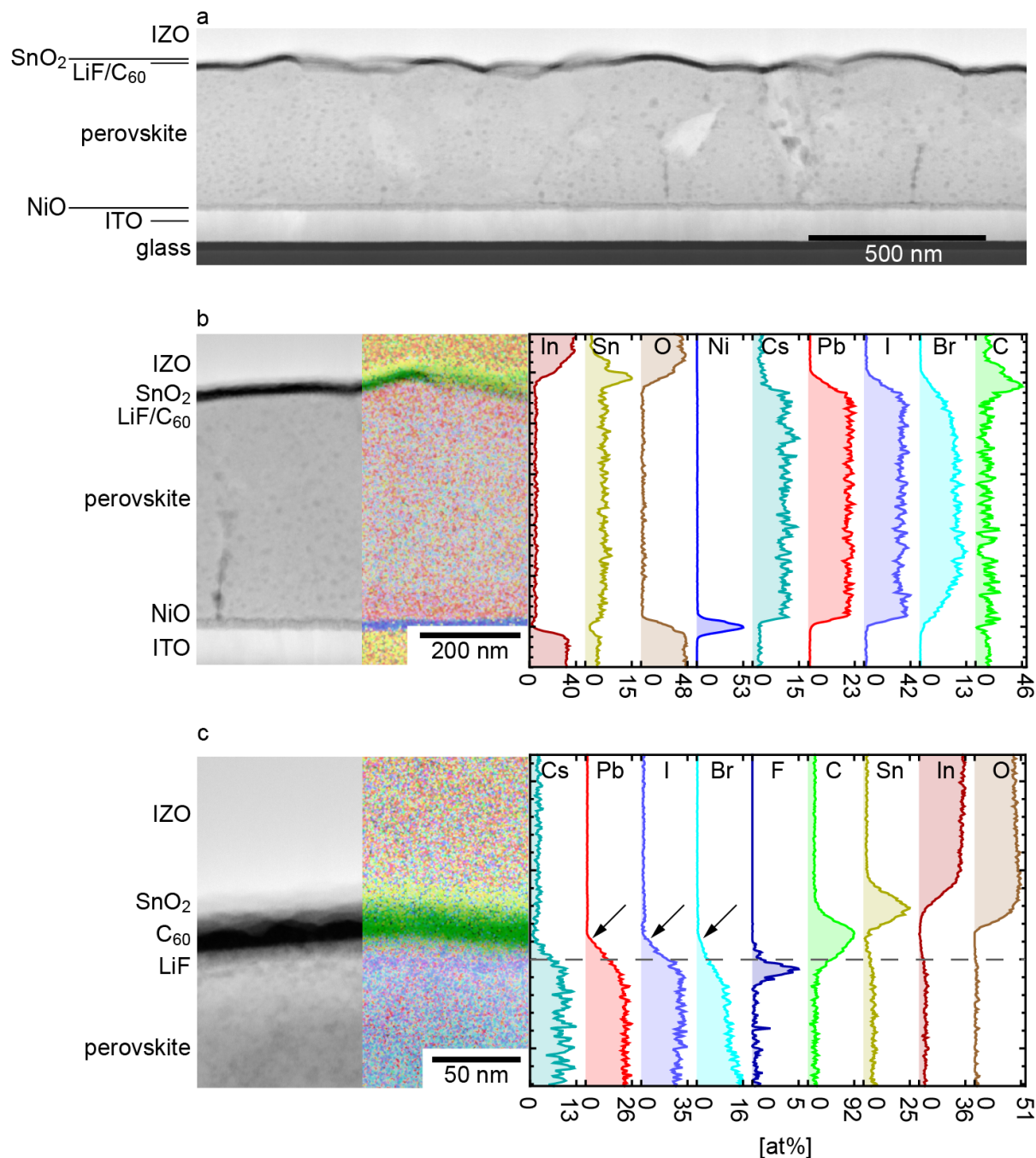


Figure S9: a) STEM HAADF image of an electrode metal-free device after recovering from an S-shape at MPPT. The small voids are a consequence of the focused ion beam preparation of the TEM lamella. (b) EDX chemical map and corresponding concentration profile of the recovered sample. (c) STEM HAADF and EDX data of the region close to the C_{60} layer. Note that the top edges of the Pb, I and Br distributions coincide in position and are well separated from the carbon peak of the C_{60} layer, corroborating our conclusion that it is the iodine inside the C_{60} layer that causes the S-shape.

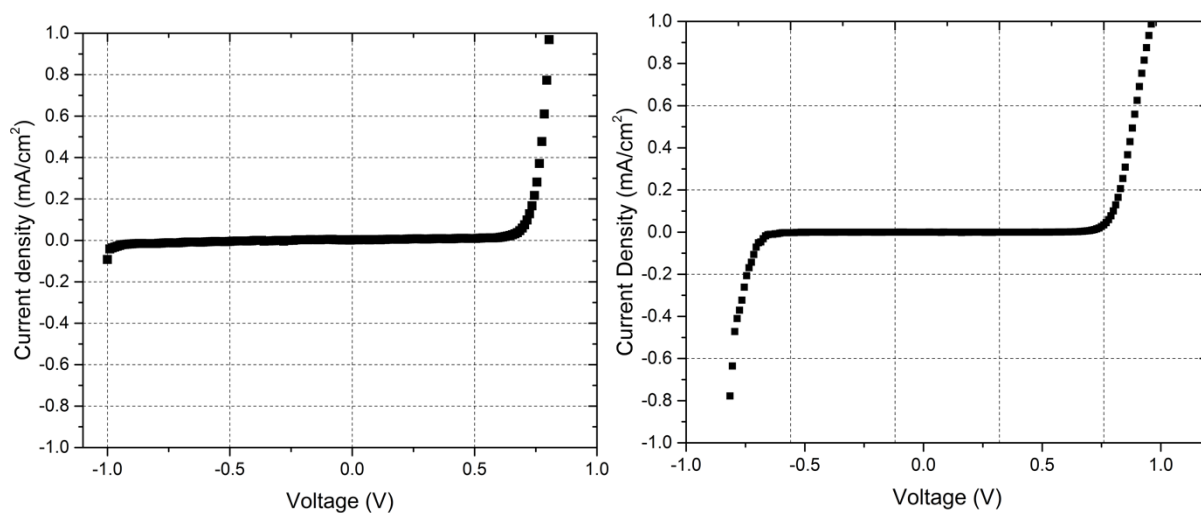


Figure S10: Dark I-V curves before degradation in reverse bias, showing the breakdown behavior. We take as definition of breakdown voltage the voltage at which the current is -1 mA/cm^2 , the definition used by Bowring et al, reference 9 of the main text. The cell corresponding to the left figure was then degraded at -5 V , a voltage higher than the breakdown voltage, while the cell corresponding to the right figure was degraded at -0.5 V , a voltage lower than the breakdown voltage. Phase segregation was observed only for the cell degraded at a voltage higher than the breakdown voltage.

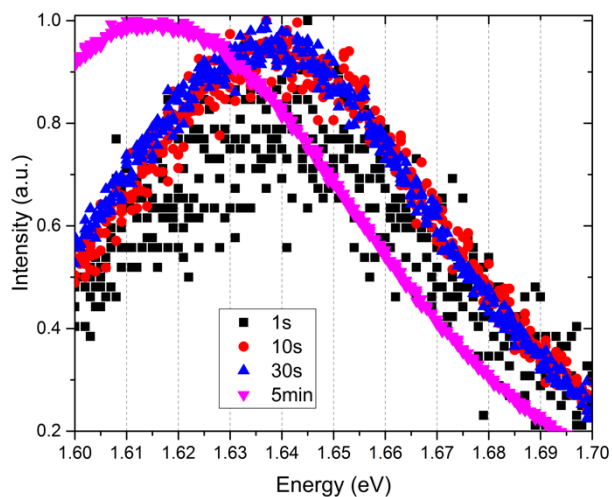


Figure S11: Normalized PL spectra measured with a light intensity of 1 sun for different exposure times for a perovskite solar cell not degraded in reverse bias.

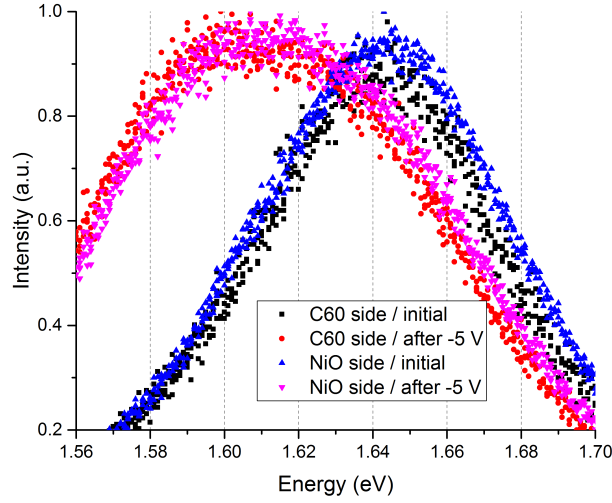


Figure S12: Normalized PL spectra of the perovskite taken from each side of a device degraded at -5 V for 30 min. A shift is observed after reverse biasing, irrespective of the side from which the spectrum is acquired.

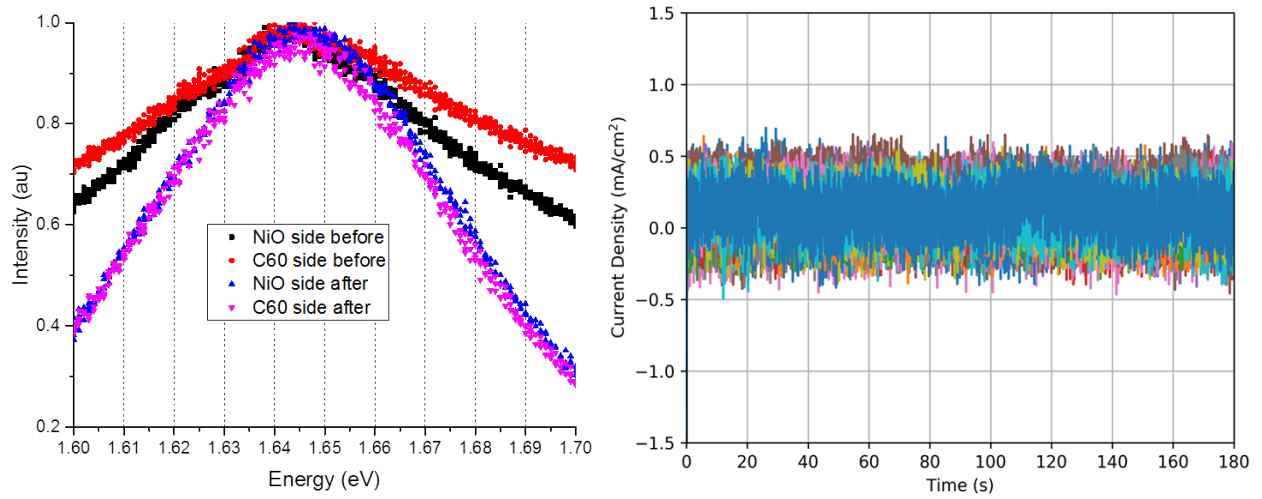


Figure S13: (Left panel) Normalized PL spectra comparing the perovskite before and after the reverse bias treatment shown in Figure 3a of the main text. Even though the S-shape was pronounced after reverse biasing, no bandgap shift and hence no phase segregation is observed, indicating that phase segregation is not the cause of the S-shape. (Right panel) Current as a function of time during the 3 min of reverse biasing for each step of the reverse bias protocol (0 V to -2 V in steps of -0.1 V) used in this work. The negligible current injected supports the fact that no phase segregation occurred in this sample.

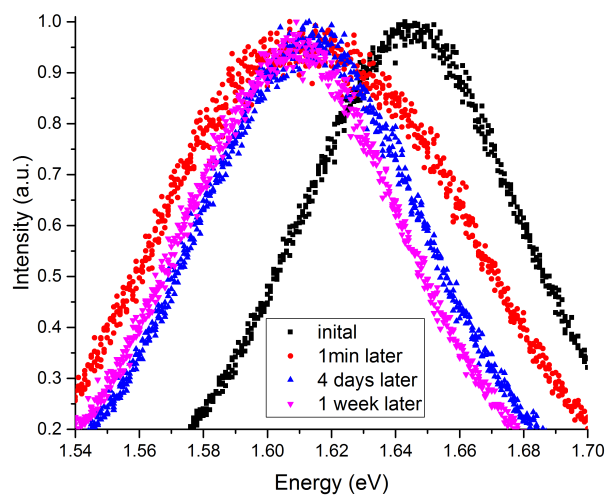


Figure S14: Normalized PL spectra measured at different times after the sample had been degraded at -5 V for 30 min, showing that the phase segregation persists even after one week after it was induced. These measurements were performed from the NiO side of the sample.