Supporting Information

Lead-binding biogenic polyelectrolyte multilayer coating for lead retention in perovskite solar cells

Authors

Fabian Körte[a], Cordula Daniela Wessendorf[b*], Thomas Schnabel[b], Markus Herrmann[a], Birgit Schröppel[a], Kathrin Stadelmann[a], Elsa Arefaine[a], Luisa Busch[b], Ruben Daum[a], Erik Ahlswede[b], Hanna Hartmann[a*]

* Corresponding authors

[a] NMI Natural and Medical Sciences Institute at the University of Tübingen, Markwiesenstraße 55, 72770 Reutlingen, Germany

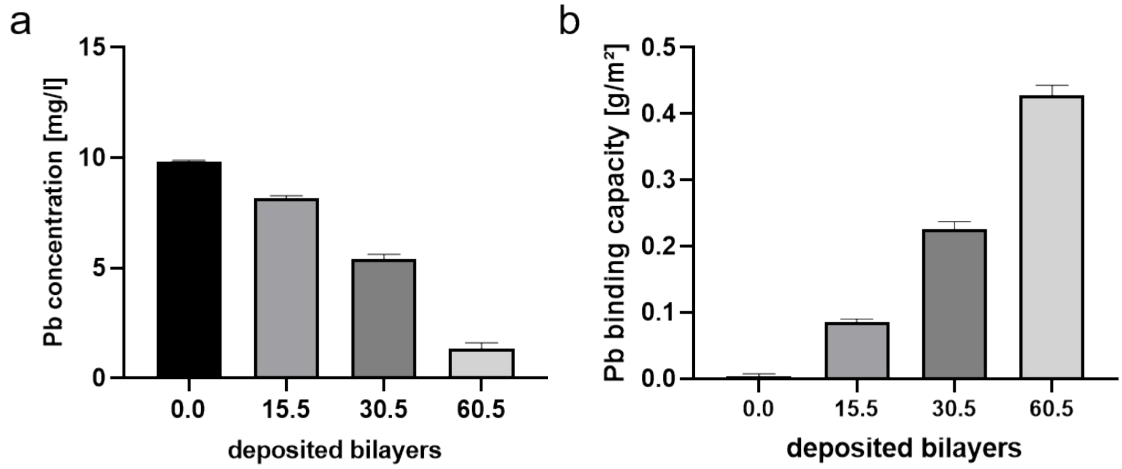
E-Mail: hanna.hartmann@nmi.de

[b] Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW) Baden-Württemberg, Industriestraße 6, 70565 Stuttgart, Germany

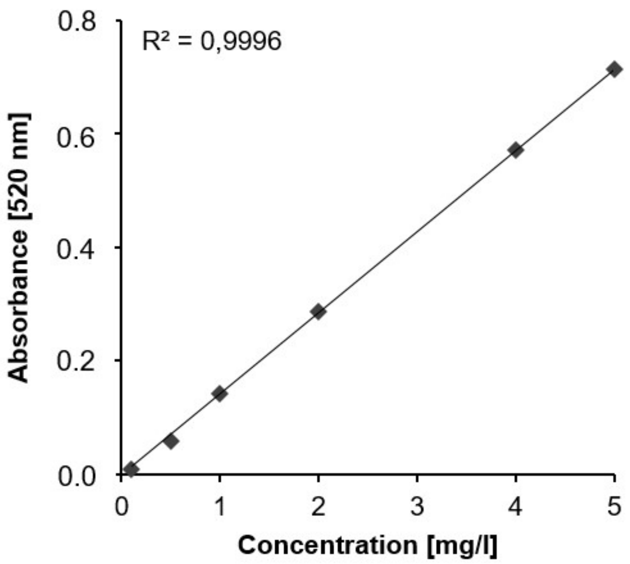
E-Mail: cordula.wessendorf@zsw-bw.de

Suppl. Table 1: lead binding properties of several differently functionalised biopolymers

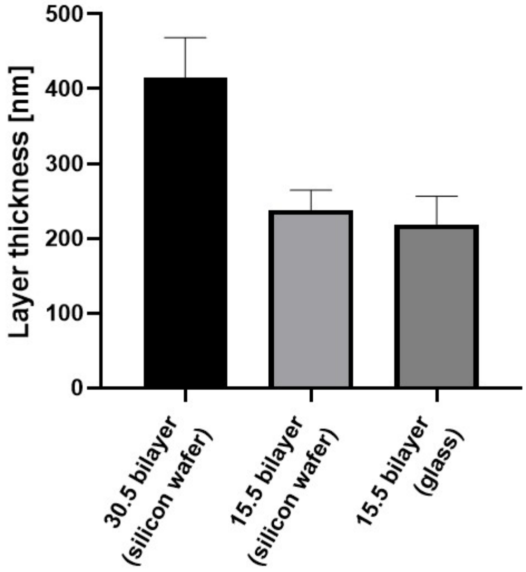
biopolymer	**Initial Pb conc. [mg/L]**	**Final Pb conc. [mg/L]**
Alginic acid	10.0	9.8 ± 0.2
Ca-alginate	10.0	**0.2 ± 0.0**
Polylysin (PLL, <30 kDa)	10.0	9.2 ± 1.1
hyperbranched PLL	10.0	**1.0 ± 0.3**
activated Charcoal	10.0	0.4 ± 0.3



Suppl. Fig. S1: Quantification of Pb-absorbing capabilities of PEM coated glass, crosslinked with $CaCl_2$ and soaked with PbI_2 aqueous solution.
(a) Quantification of unbound lead in solution after immersion of PEM coated glass with different numbers of bilayers, measured by a lead quantification kit (cuvette test).
(b) Lead binding capacity calculated from cuvette test data, dependent on the number of bilayers. Note the increasing lead binding with increasing number of bilayers.
The error bars represent the standard deviations from n=3 tests in triplicates.



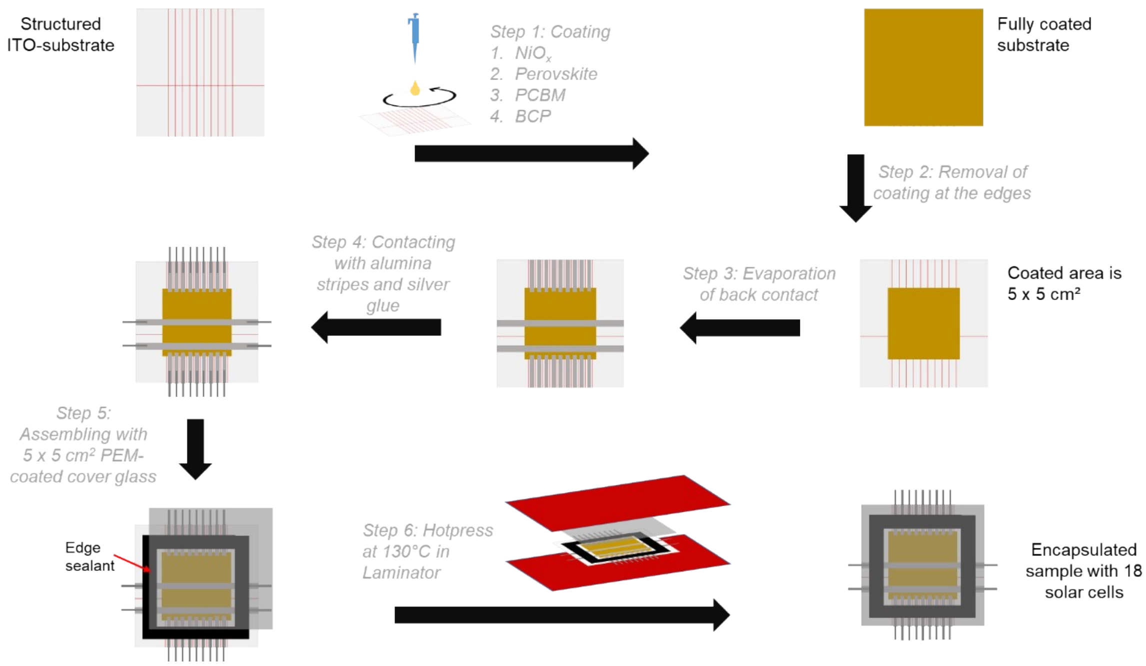
Suppl. Fig. S2: Quantification of lead concentration in aqueous solution using a cuvette test.
A standard solution of 1.07 g/l lead acetate in water was used to prepare a working solution of 10 mg/l at pH 5.5 which was then further diluted as shown. Note that the photometric quantification shows linear characteristics within the tested range of 0.10 – 5.00 mg/l P.



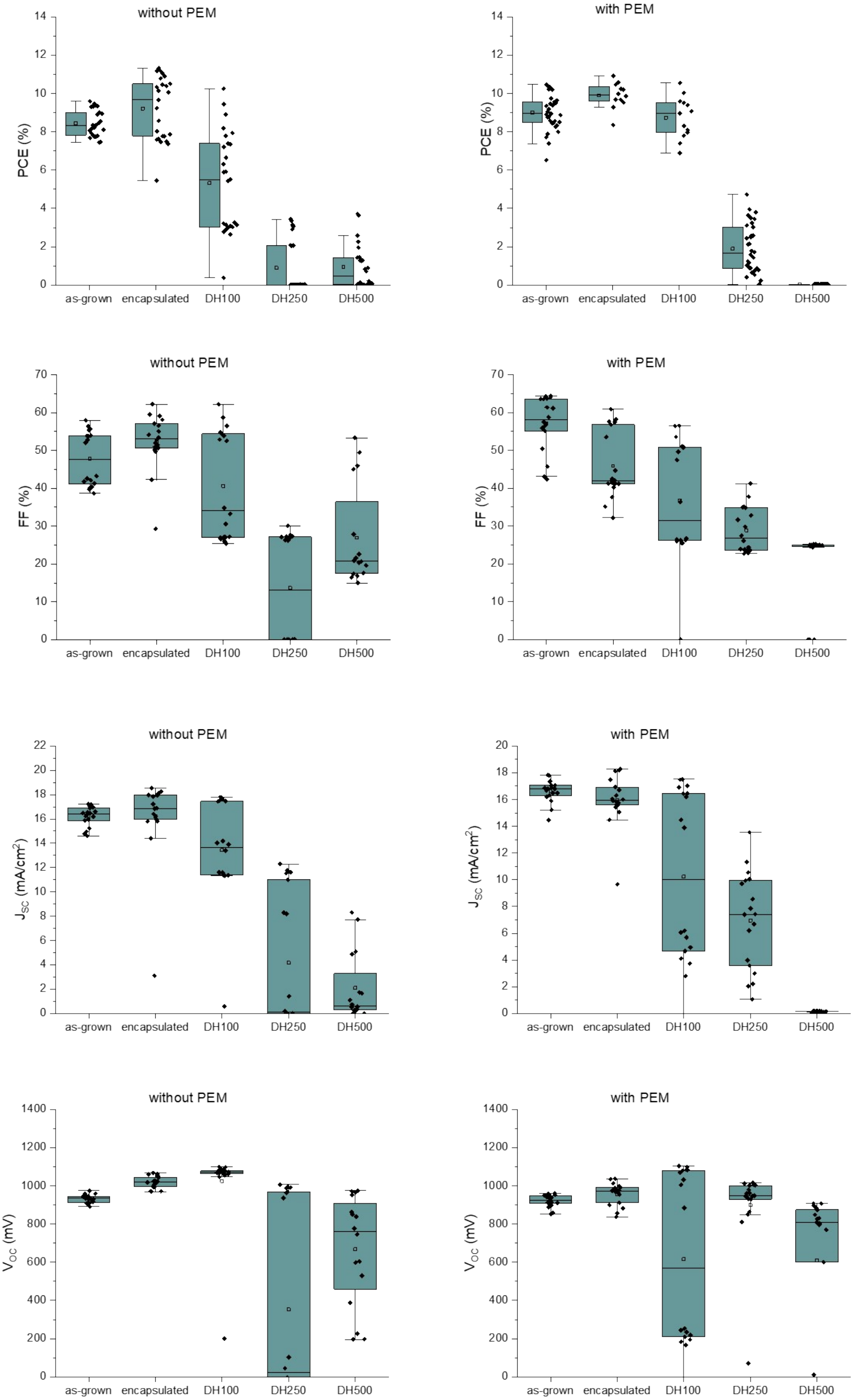
Suppl. Fig. S3: Quantification of the coating thickness.
The thickness of the coating was determined by ellipsometry (and profilomitry for glass) after build-up of 15.5 bilayers and 30.5 bilayers, respectively. Note the almost 2-fold increase in coating thickness when applying twice the number of bilayers.

Perovskite solar cell encapsulation procedure

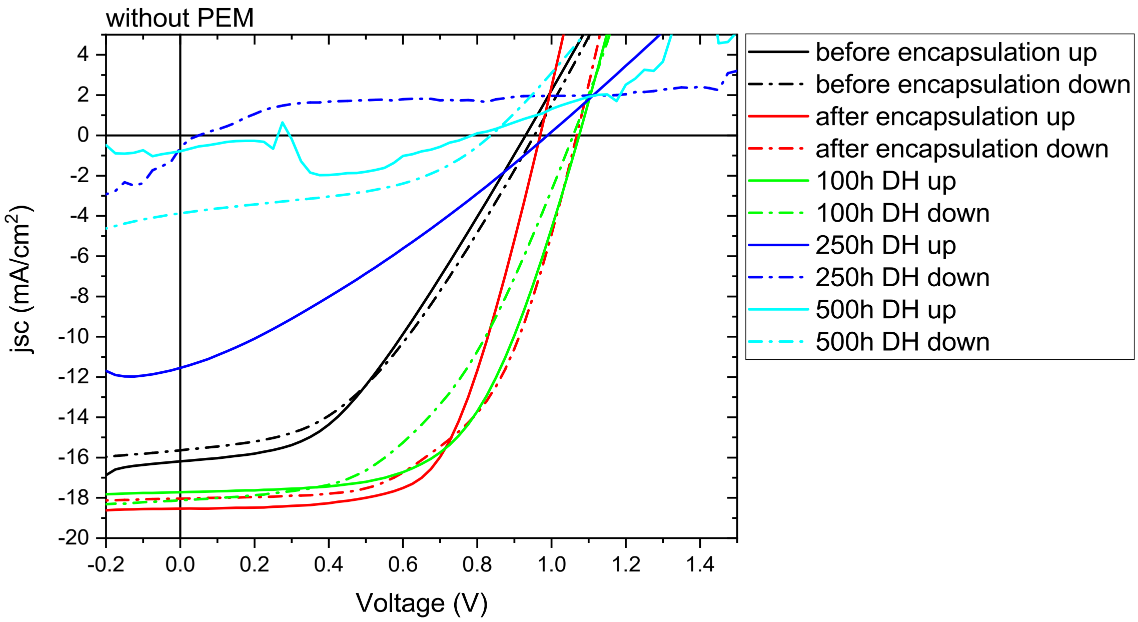
The perovskite solar cells were encapsulated with a butyl rubber edge sealant and either simple cover glass or with PEM-coated cover glass (Suppl. Fig. S4). After removal of the coating at the outer edges for contacting and sealing, the remaining coated area was 5 x 5 cm^2 for all samples. Therefore, each sample has 18 cells with an active area of 0.25 cm^2 each.

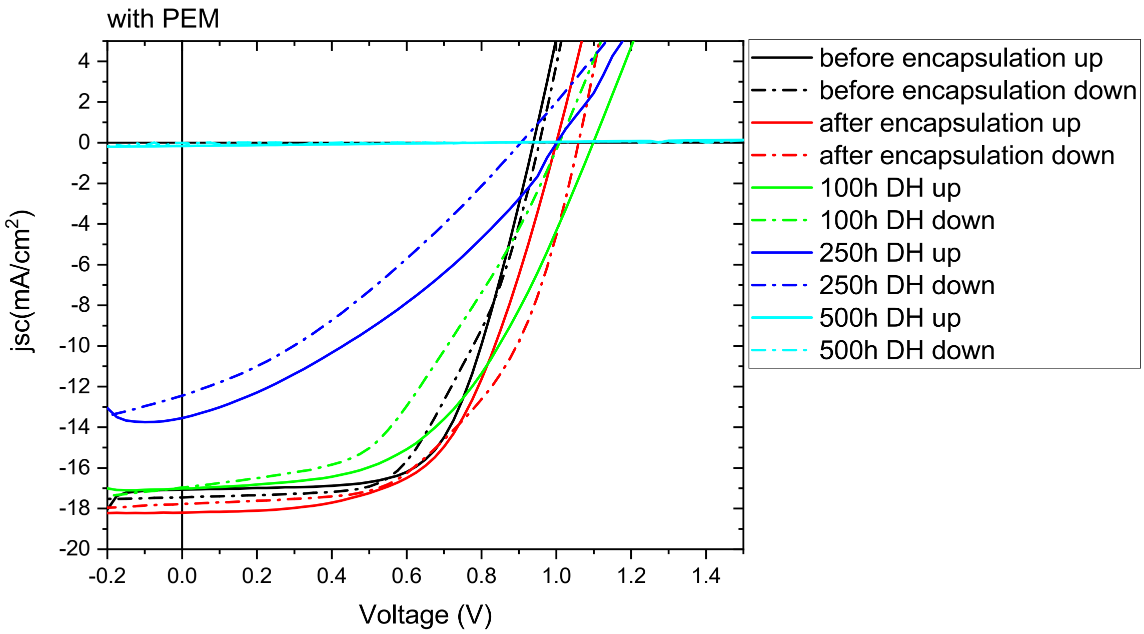


Suppl. Fig. S4: Fabrication process of encapsulated samples for stability tests.
Step 1: coating of the substrates, step 2: removal of coating at the edges, step 3: evaporation of back contact, step 4: contacting with alumina stripes and silver glue, step 5: assembling of glasses with edge sealant and (PEM-coated) cover glass, step 6: lamination process.

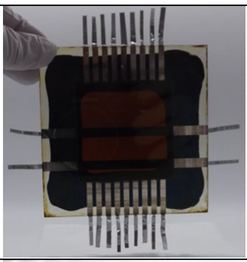
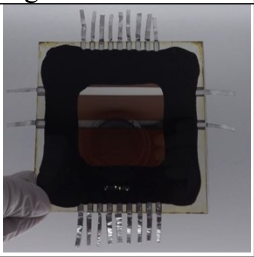
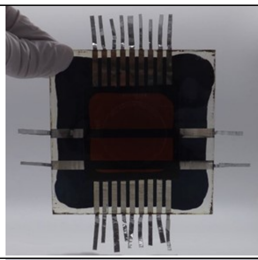
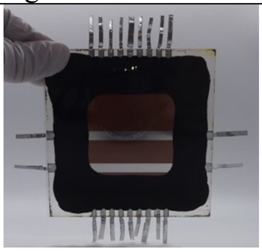
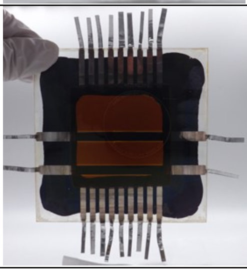
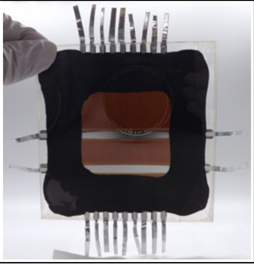
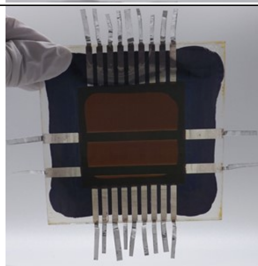
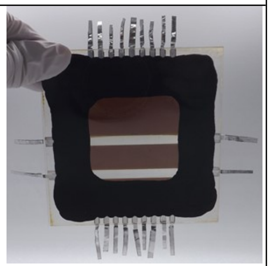


Suppl. Fig. S5: Power conversion efficiency (PCE), fill factor (FF), short current density (Jsc) and open circuit voltage (Voc) values for perovskite solar cells before and after encapsulation as well as after 100, 250 and 500h damp heat (DH) test at 85°C / 85% r. h. either without (left) or with (right) lead-absorbing PEM coating.





Suppl. Fig. S6: Exemplary IV-curves of 1 cell on a sample without PEM (top) and with PEM (bottom), respectively.

	Without PEM		With PEM	
	TCO-side	Ag-side	TCO-side	Ag-side
After encapsu-lation, before DH				
After 500 h DH				

Suppl. Fig. S7: Visual inspection of encapsulated samples before (top row) and after 500 h damp heat test (bottom row), either without PEM (left side) or with PEM layer (right side).

Influence of the PEMs on the solar cell efficiency and stability

The solar cell efficiencies for encapsulated perovskite cells with and without PEMs were measured before and after encapsulation and after 100, 250 and 500 h damp heat test (Suppl. Fig. S5). Before encapsulation the median efficiencies were at 8.4 % (without PEM) and 8.9% (with PEM). The rather low efficiencies derive from the fact that we spin coated a large area (substrate size was 9 x 9 cm^2) where usually more inhomogeneities and defects appear than on a small area can. Additionally, the distance to the contacts was larger than for normal single cells, which induces a higher series resistance and therefore limits the cell performance.

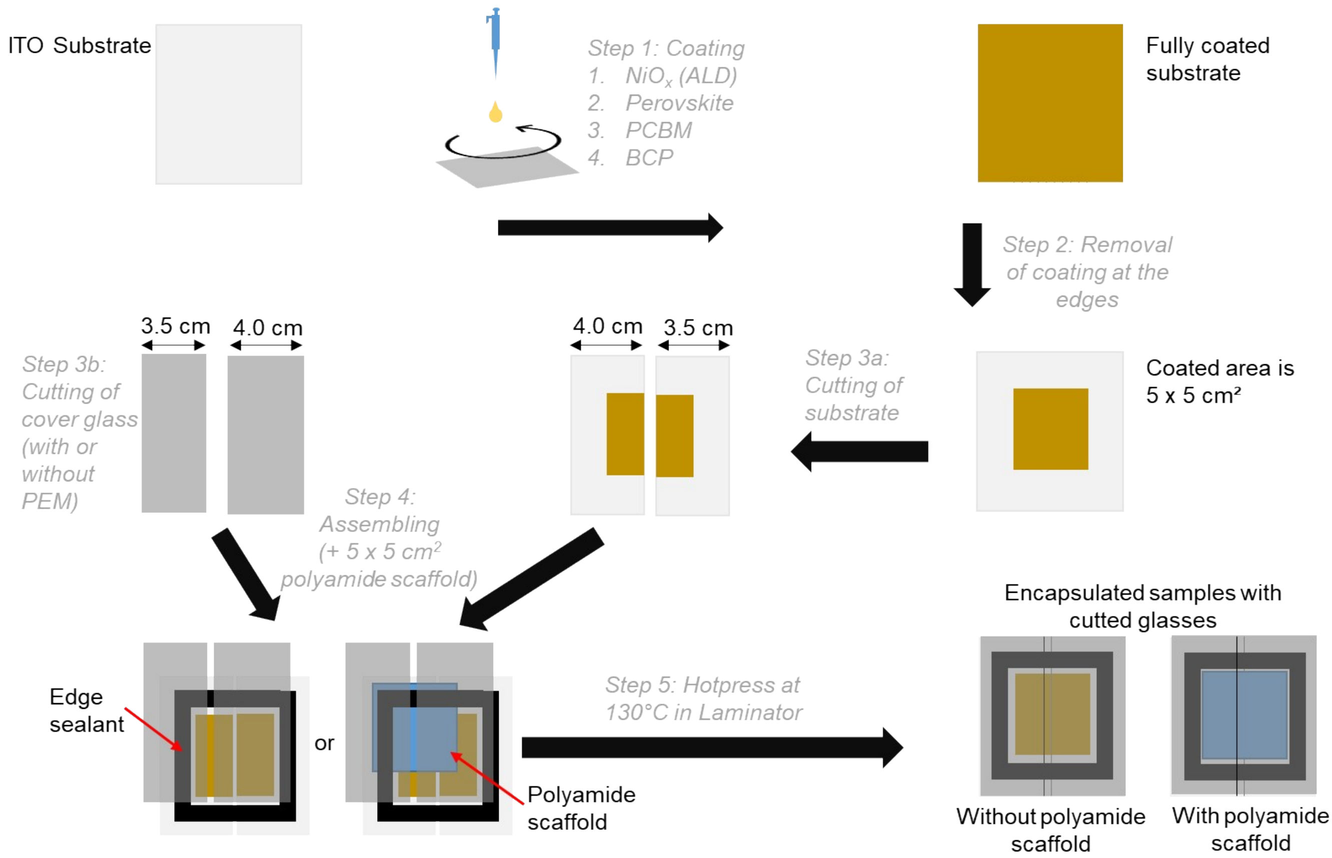
In both cases, after encapsulation the median efficiencies slightly increased to 9.7% and 10.0 %, respectively. At first this seemed quite surprising, because the encapsulation procedure was carried out at 130°C and perovskite solar cells are known to be sensitive to increased temperature. However, recently it was found out that at temperatures around 100°C defects like small cracks in the perovskite layer could be healed.[1]

After treating the perovskite solar cells in the climate chamber at 85°C and 85% relative humidity for 100h, the efficiencies of all cells decrease and the perovskite layer optically degraded, especially below and around the silver contacts. After 250h, all samples show a drastic decline in efficiency. After 500h only a few cells without the PEM coating show efficiencies of up to 4%, but the majority of the cells is destroyed and also optically strong degradation is observed.

This indicates that the edge sealing still has to be improved. The butyl rubber is optimised for a tight sealing in direct contact with glass. However, as we used alumina stripes for contacting the cells, we assume that the sealing around the alumina stripes was not tight enough and water vapour could enter the cells. Additionally, the PEM was not removed at the edges of the glass which causes a direct contact between the butyl rubber and PEM (Fig. 7). This is a clear difference to the samples without PEM, where the butyl rubber is in contact with the glass only and it could be an entry gate for humidity and oxygen. Nonetheless, the important message here is that the PEM-coating neither has a negative effect on the solar cell efficiency nor on its stability during a damp heat test. For further stability improvements, the edge sealing in combination with the contacts has to be optimised.

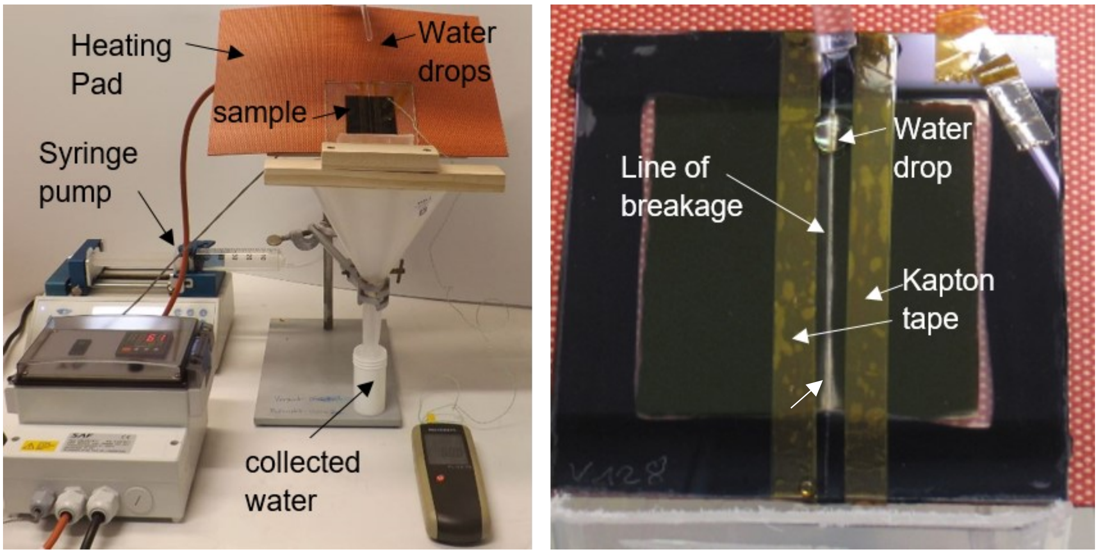
On-device Pb-sequestration capability

To investigate Pb-binding capacity of the PEM in a worst case scenario of broken encapsulation glass and subsequent elution of the contained lead by rain, the substrate glass was broken in the middle and laminated with a broken cover glass (Suppl. Fig. S8). To maintain the stability of the device, the two cracks had a lateral shift of 0.5 cm.

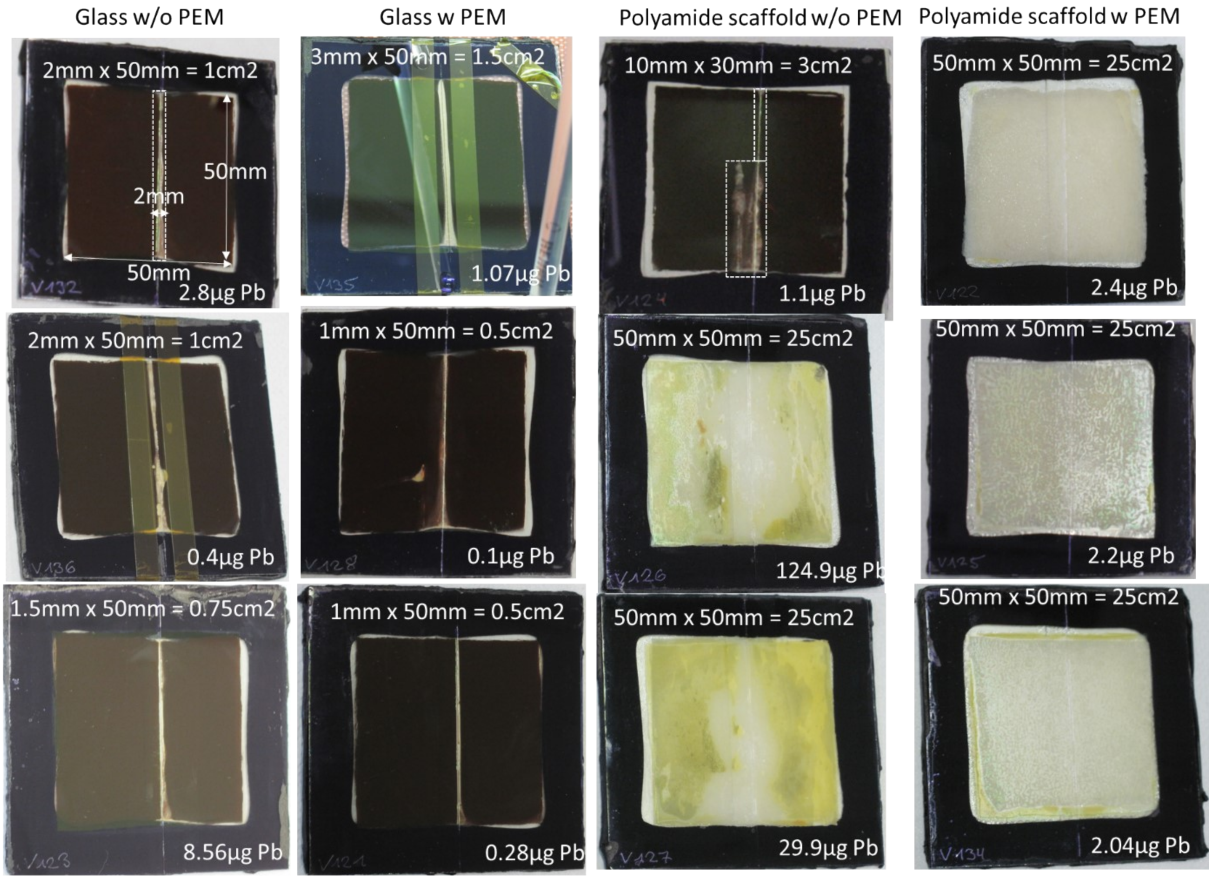


Suppl. Fig. S8: Fabrication process of encapsulated samples with broken encapsulation glasses for lead-elution tests.
Step 1: coating of the substrates, step 2: removal of coating at the edges, step 3: cutting of substrate and cover glasses, step 4: assembling of glasses with edge sealant and eventually integration of polyamide scaffold, step 5: lamination process.

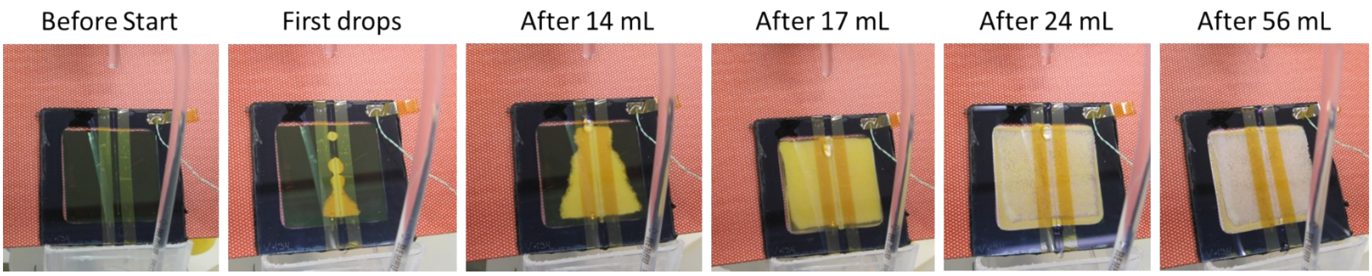
The samples were positioned in an angle of 45° on a hot pad (with 60°C to simulate the conditions of a solar cell in operation) and water with a pH of 4.5 was dropped with ~1 mL/min along the site of breakage of the substrate glass to simulate rain (Suppl. Fig S9 left). Two stripes of Kapton tape were placed ~2-3 mm next to the line of breakage to control the flow direction of the drops (Suppl. Fig S9, right).



Suppl. Fig. S9: Left: Self-made rain simulator with syringe pump and heating pad. The water has a pH of 4.5 to simulate sour rain and is dropped with 1 mL/min along the line of breakage of the cutted substrate glass of the sample. The heating pad has a temperature of 60°C to simulate the operating conditions of a solar cell. Right: Sample with water drop on line of breakage, 2 stripes of kapton tape were used to control way of water drops. Without polyamide scaffold, the optically degraded area is only 0.5 mm around the crack, (ca. 50 mm^2).



Suppl. Fig. S10: Pictures of all samples after simulated rain test, the size of the optically degraded area for each sample is given as well as the amount of eluted lead.



Suppl. Fig. S11: Photographs of a sample with PEM-coated polyamide scaffold during simulated rain test, the colour change from brown to yellow to white can be clearly seen.

References

1. Yadavalli, S.K., et al., *Facile healing of cracks in organic–inorganic halide perovskite thin films*. Acta Materialia, 2020. **187**: p. 112-121.