Electronic supplementary data of the

Recovery of dye-sensitized solar cell's performance by heat treatment

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Abstract: The formation of iodine containing crystals with ageing in ionic liquid based dye-sensitized solar cells (DSSCs) containing an I_3^-/I^- redox couple has already been confirmed. In this report we show how the size of these crystals can reversibly change during operation and the effects this has on cell performance. We also show how heat treatment and applied forward and reverse current treatment influence crystal growth in the cell. Crystal growth was tracked using electroluminescence and transmittance imaging, while current-voltage characterization and electrical impedance spectroscopy was used to measure cell performance and follow the changes in I_3^- diffusion, charge transfer resistance, and recombinations occurring in the DSSCs. Results reveal that applying a reverse current to the DSSC leads to the rapid formation of H_2 bubbles while crystals grow rapidly when a forward current is applied. Additionally heat treatment at 80 °C can completely recover performance of a degraded cell showing visible defects and a large inhomogeneous active area.

Heat treatment

Table S1: The performance parameters (J_{SC}, V_{OC}, FF and η) of the reference DSSCs and the cells exposed to heat treatment at 60 °C or 80 °C for different time periods. Additionally the cell performance that were measured (a) 11 months prior the heat treatment, 9 months after the treatment and after additional heat treatment at 80 °C for 8 h (c) are given. For each temperature treatment two identical cells are presented.

cell	phase – time	J_{SC} (mA/cm²)	V_{OC} (V)	FF (%)	η (%)
cell 1	a	10.07	0.662	59.5	3.97
(ref.)	b – 0 min	8.99	0.693	68.1	4.24
	b – 5 min	9.42	0.702	65.6	4.34
	b – 15 min	9.43	0.702	65.8	4.36
	b – 30 min	9.44	0.703	65.9	4.37
	b – 60 min	9.47	0.704	65.6	4.37
	b – 120 min	9.46	0.705	65.3	4.35
	b – 240 min	9.32	0.707	65.1	4.29
	b – 360 min	9.34	0.706	65.0	4.29
	c – 1	8.97	0.695	66.7	4.16
	c – 2	9.73	0.666	65.0	4.21
cell 1a	a	10.35	0.662	61.1	4.18
(ref.)	b – 0 min	9.54	0.695	66.3	4.40
	b – 5 min	9.83	0.701	63.5	4.38
	b – 15 min	10.01	0.698	64.2	4.49
	b – 30 min	10.13	0.693	64.4	4.52
	b – 60 min	10.23	0.694	63.8	4.53
	b – 120 min	10.18	0.694	63.2	4.47
	b – 240 min	10.21	0.692	63.5	4.48
	b – 360 min	10.21	0.693	62.9	4.45
	c – 1	9.69	0.684	65.8	4.36
	c – 2	10.49	0.640	66.1	4.44

cell 2 (60 °C)	a	11.08	0.656	64.1	4.66
	b – 0 min	10.05	0.693	68.6	4.78
	b – 5 min	10.18	0.701	66.6	4.75
	b – 15 min	10.42	0.692	66.9	4.83
	b – 30 min	10.52	0.688	66.9	4.84
	b – 60 min	10.67	0.680	67.2	4.88
	b – 120 min	10.76	0.678	66.8	4.87
	b – 240 min	10.86	0.674	66.6	4.87
	b – 360 min	10.87	0.670	66.9	4.87
	c – 1	10.19	0.682	68.4	4.75
	c – 2	11.03	0.639	67.9	4.79
cell 2a (60 °C)	a	10.66	0.663	60.5	4.28
	b – 0 min	9.68	0.699	66.0	4.46
	b – 5 min	10.21	0.700	63.9	4.57
	b – 15 min	10.25	0.694	63.9	4.55
	b – 30 min	10.31	0.693	63.5	4.54
	b – 60 min	10.45	0.689	63.5	4.57
	b – 120 min	10.45	0.686	63.2	4.53
	b – 240 min	10.51	0.684	63.1	4.53
	b – 360 min	10.65	0.680	63.4	4.59
	c – 1	9.90	0.686	65.9	4.48
	c – 2	10.64	0.640	65.1	4.43
cell 3 (80 °C)	a	9.87	0.666	59.2	3.89
	b – 0 min	9.41	0.696	64.7	4.24
	b – 5 min	9.84	0.685	63.6	4.29
	b – 15 min	10.00	0.678	63.2	4.29
	b – 30 min	10.15	0.664	63.7	4.30
	b – 60 min	10.31	0.658	63.7	4.32
	b – 120 min	10.26	0.654	63.8	4.28
	b – 240 min	10.43	0.646	63.6	4.29
	b – 360 min	10.37	0.639	64.0	4.24
	c – 1	9.37	0.672	66.9	4.21
	c – 2	9.63	0.654	66.3	4.18
cell 3a (80 °C)	a	9.98	0.653	59.5	3.88
	b – 0 min	9.60	0.694	65.6	4.37
	b – 5 min	9.80	0.699	64.0	4.38
	b – 15 min	9.87	0.693	63.5	4.35
	b – 30 min	10.04	0.681	63.5	4.34
	b – 60 min	10.20	0.679	63.0	4.36
	b – 120 min	10.29	0.670	63.1	4.35
	b – 240 min	10.54	0.657	63.1	4.37
	b – 360 min	10.32	0.659	62.8	4.27
	c – 1	9.56	0.677	66.1	4.28
	c – 2	9.74	0.663	65.8	4.25

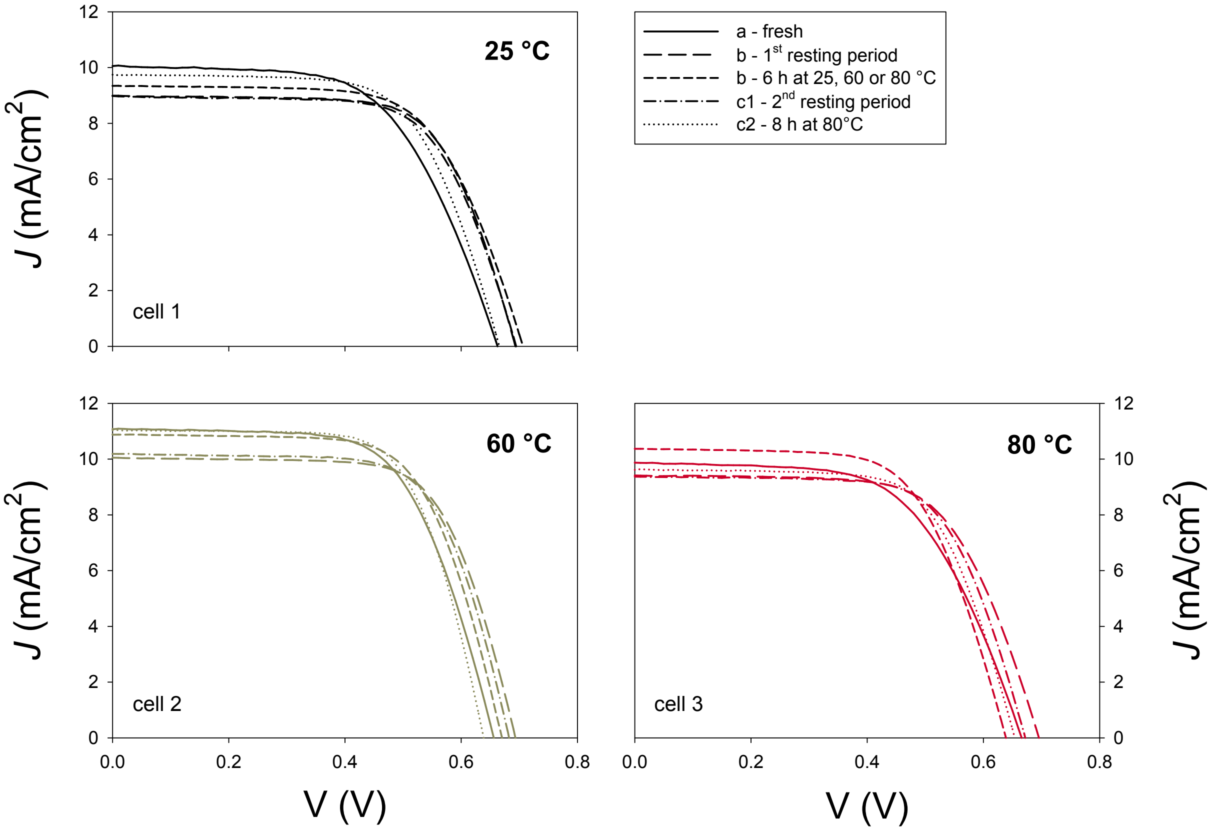

Fig. S1: The current-voltage scans (*I-V*) of the reference cell (cell 1) and cells exposed to the heat treatment at 60 °C or 80 °C (cells 2 and 3, respectively). The *I-V* scans were measured after production, after 1st resting period, after heat treatment at 25, 60 or 80 °C for 6 h, after 2nd resting period and after final heat treatment at 80 °C for 8 h.

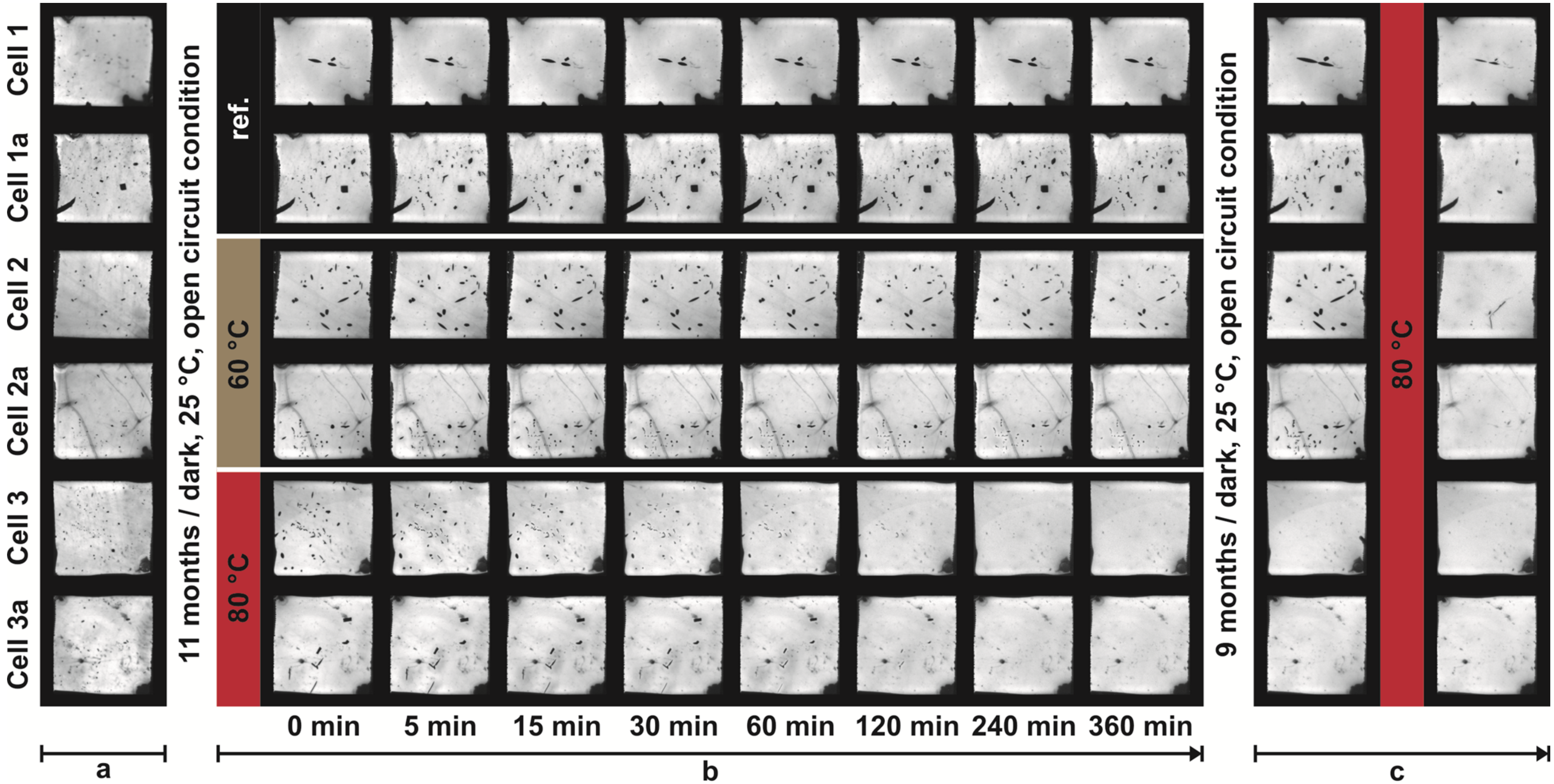

Fig. S2: The electroluminescence (EL) images of the reference cells and cells exposed to heat treatment at 60 °C or 80 °C. For each temperature treatment two identical cells are presented. The timeline of the heat treatment is given below (b). Additionally the EL images are given for the cells 11 months prior the treatment (a), 9 months after the treatment and after additional heat treatment at 80 °C for 8 h (c).

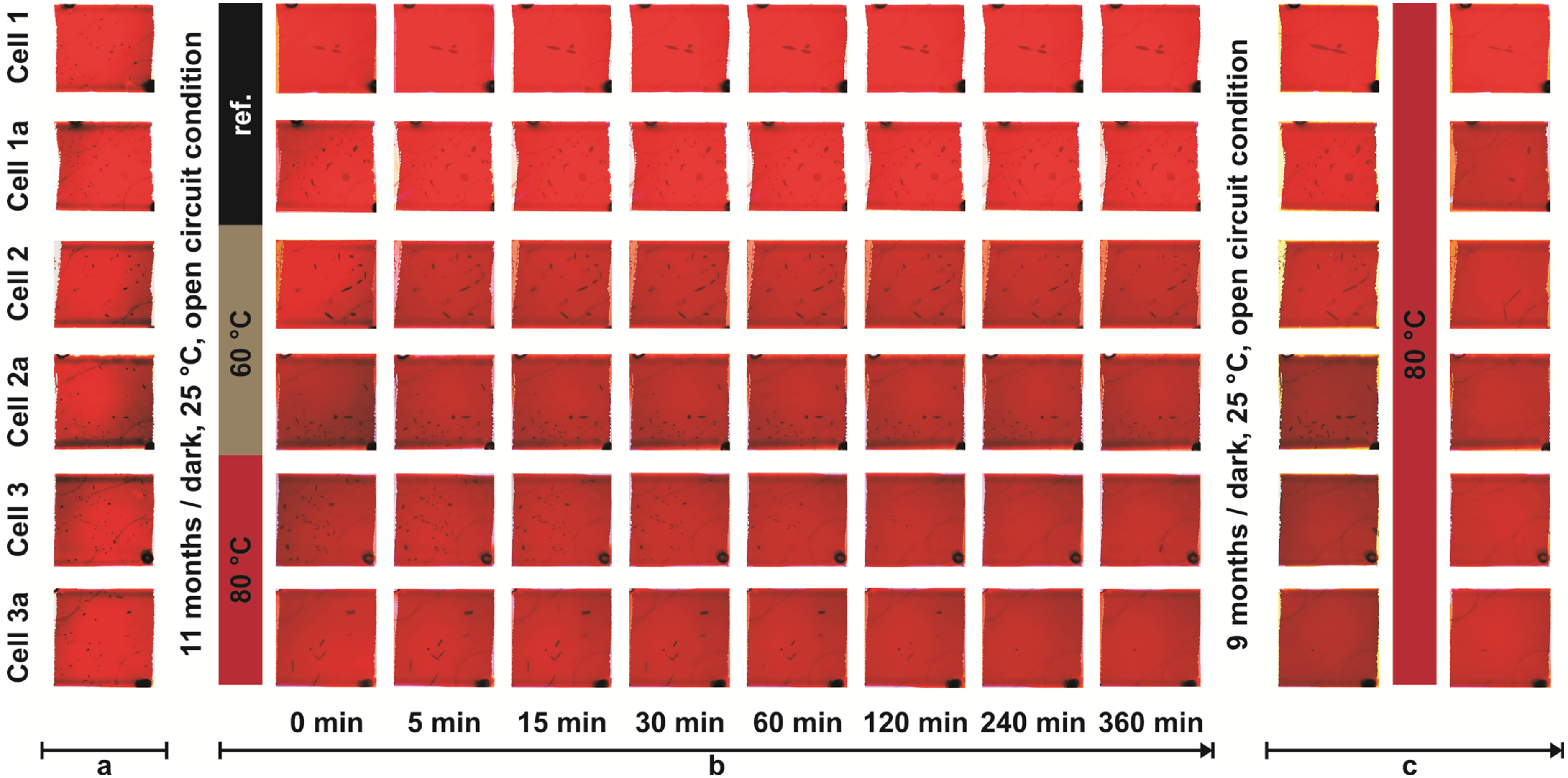

Fig. S3: The transmittance images (TI) of the reference cells and cells exposed to heat treatment at 60 °C or 80 °C. For each temperature treatment two identical cells are presented. The timeline of the heat treatment is given below (b). Additionally the TI images are given for the cells 11 months prior the treatment (a), 9 months after the treatment and after additional heat treatment at 80 °C for 8 h (c).

The electrical impedance spectra (EIS) were analysed according to the procedure described by M. Adachi, *et al.* [M. Adachi, *et al.*, *J. Phys. Chem. B* **110** (2006) 13872]. Fig. S4 shows a typical Nyquist plot of the EIS spectrum of illuminated DSSC measured under open-circuit conditions. The parameters determined from the spectrum are included in Fig. S4:

- The series resistance R_s equals the real part of the impedance measured at high frequency. It gives the sum of the TCO resistance and resistance outside of the cell like cables, contacts, *etc*.
- The charge transfer resistance R_{ct} is defined as the radius of the semicircle in a high frequency range. It gives the resistance for the electron transfer at the Pt (counter electrode)/electrolyte interface.
- The peak frequency of the semicircle in a high frequency range ω_1 is the angular frequency ($2\pi f$) where the impedance of the high frequency semicircle reaches the highest imaginary part (*i.e.* the maximal angle of the impedance). The ω_1 is inversely proportional to the capacitance at the counter electrode.
- The peak frequency of the central semicircle ω_2 is the angular frequency where the impedance of the central semicircle reaches the highest imaginary part. It is proportional to the effective recombination constant for the electrons k_{eff}.
- The charge transfer resistance related to the recombination of the photo generated electrons R_k equals to the radius of the central semicircle. Independently it does not describe any process in the dye-sensitized solar cell but in a combination with electron transport resistance in TiO_2 (fitted parameter) and k_{eff} it is possible to obtain the effective electron diffusion coefficient.
- The resistance correlated to the diffusion process of the tri-iodide ions in the electrolyte R_d equals the radius of the semicircle at a low frequency range.
- The peak frequency of the semicircle in a low frequency range ω_3 is the angular frequency where the impedance of the low frequency semicircle reaches the highest imaginary part. The ω_3 is proportional to the diffusion coefficient of the I_3^- ions in the electrolyte D_I.

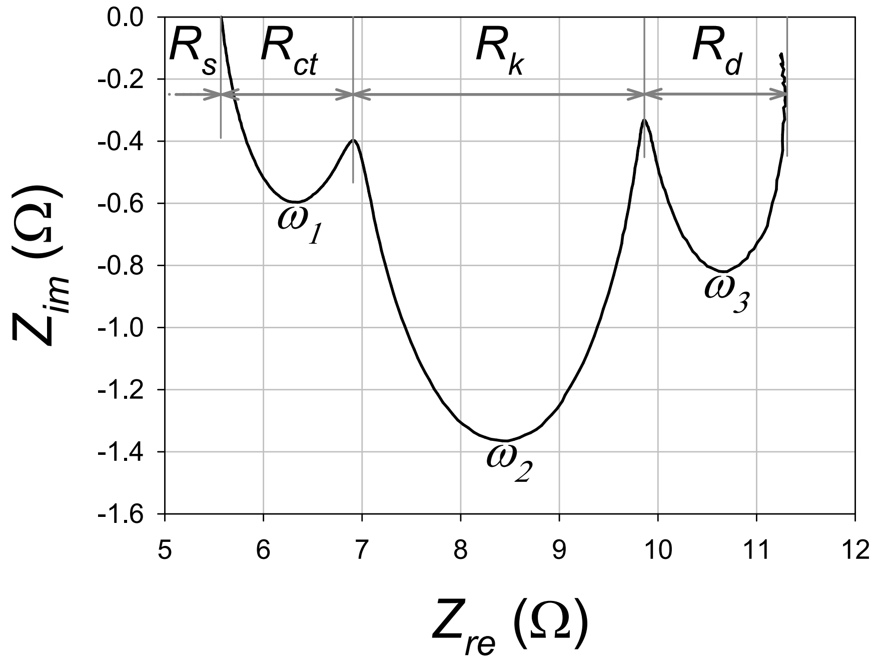

Fig. S4 A typical Nyquist plot of the EIS spectrum of illuminated DSSC under open-circuit condition.

Table S2: The parameters extracted from the Nyquist plots of the EIS spectra of the three identical DSSCs illuminated under open-circuit condition. The spectra of each cell were measured before heat treatment and after heat treatment at 80 °C for 4, 12 and 20 hours.

cell	time	R_s (Ω)	R_{ct} (Ω)	R_k (Ω)	R_d (Ω)	ω_1 [$10^3 s^{-1}$]	ω_2 [s^{-1}]	ω_3 [s^{-1}]
cell 1	before	5.63	1.42	3.38	1.03	60.7	487.8	1.55
	4 h	5.65	0.76	3.02	1.64	110.3	559.8	1.31
	12 h	5.65	0.75	3.66	1.35	82.9	659.4	1.26
	20 h	5.66	0.69	3.26	1.61	104.4	629.8	1.32
cell 2	before	5.70	1.87	3.59	1.39	50.5	487.8	1.83
	4h	5.70	1.24	3.31	1.43	72.9	510.7	1.73
	12 h	5.70	1.18	3.80	1.42	82.9	548.5	1.58
	20 h	5.69	0.93	3.39	1.43	90.9	523.8	1.73
cell 3	before	5.57	1.34	2.95	1.43	635.3	510.7	2.05
	4 h	5.58	0.83	2.83	1.39	100.6	559.8	2.05
	12 h	5.60	0.76	3.07	1.35	104.4	629.8	1.90
	20 h	5.63	0.58	3.01	1.34	119.8	601.4	2.09

Current treatment

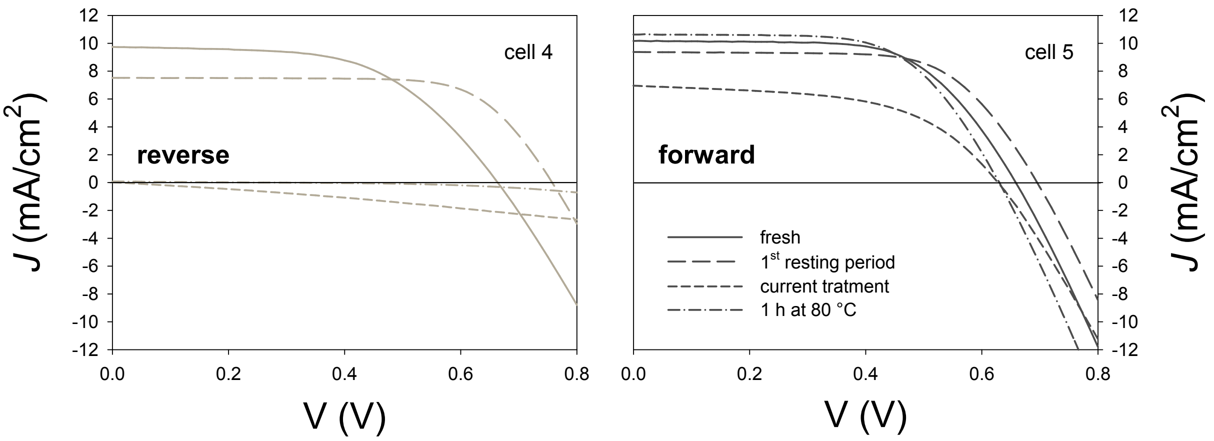

Fig. S5: The *I-V* scans of the cells exposed to reverse and forward bias current treatment (cells 4 and 5, respectively). The *I-V* scans were measured after production, after 1st resting period, after reverse or forward bias current treatment and after final heat treatment at 80 °C for 1 h.

The video clip showing the evolution of the spatial defects in the DSSCs that were exposed to reverse or forward bias current treatment is available online (http://www.rsc.org/suppdata/CP/C4/C4CP01463D/C4CP01463D3.mp4).

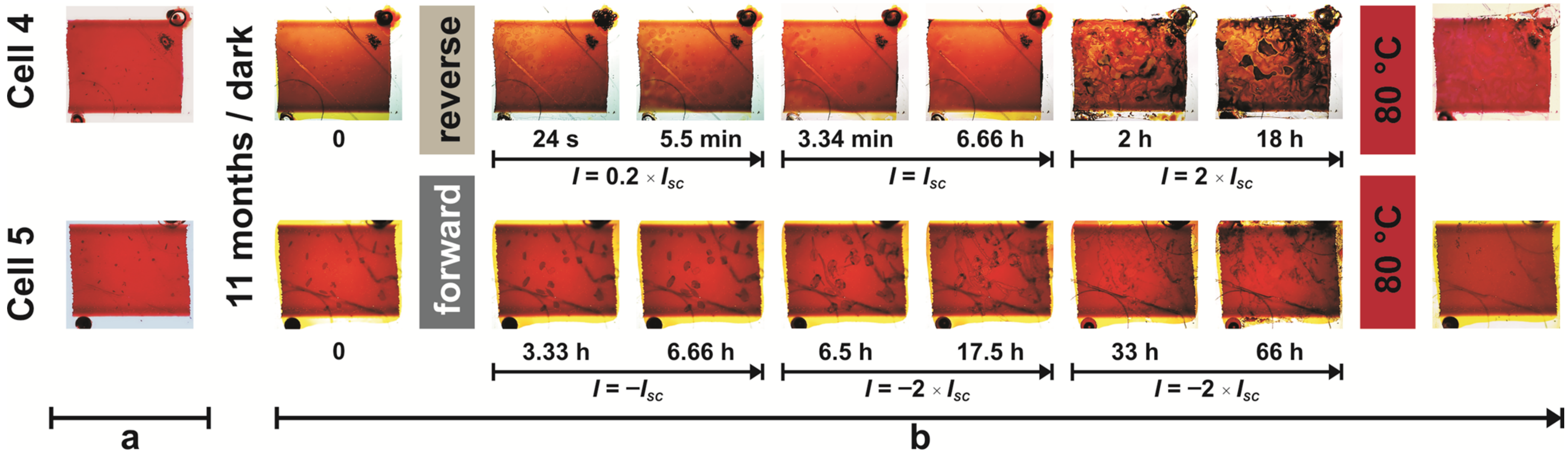

Fig. S6: The transmittance images (TI) of the DSSCs exposed to reverse or forward bias current, respectively. The timeline and the values of the applied current during the treatment are given below (b). Additionally, the TI images of the cells 11 months prior the treatment (a) and after the heat treatment at 80 °C for 8 h are given.