Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Long term stability of air processed inkjet infiltrated carbon-based printed perovskite solar cells under intense ultra-violet light soaking

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Experimental details

The CPSCs for this experiment were fabricated with the following sequence:

Fluorine doped tin oxide (FTO) coated glass substrates (10x10 cm^2, R_{SH} = 7 Ω/Sq, TCO22-7 from Solaronix) were first patterned with an automated laser and were cleaned sequentially in 1% aqueous solution of Hellmanex, acetone, and isopropanol respectively (15 min each) in an ultrasonic bath. After that TiO_2 compact layer (30-40 nm) was then deposited by coating a diluted solution of titanium di-isopropoxide bis (acetylacetonate) (75% in isopropanol, Sigma-Aldrich) in absolute ethanol (1:80) with spray pyrolysis technique using oxygen as a carrier gas over the patterned FTO glass substrates placed on a hot-plate which was kept at 500 °C. The non-active areas of the exposed substrates were protected with a glass mask. The substrates were then left to cool down to room temperature. Then the silver paste (Sun Chemical CRSN2442) was screen-printed and dried at 150 °C for 15 min to obtain conductive contacts for anode and cathode. After that, mesoporous TiO_2 layer (500 nm) was printed by screen-printing (Ti-Nanoxide T/SP diluted in terpineol, Solaronix) over the compact TiO_2 layer which was first dried at 150°C for 5 min and was then sintered at 500°C for 30 minutes. Then the insulating mesoporous ZrO_2 layer (1-2 µm) was printed again by screen-printing the ZrO_2 paste (Zr-Nanoxide ZT/SP, Solaronix) on the mesoporous TiO_2 layer and was again dried at 150 °C for 5 minutes and was then sintered at 500°C for 30 min followed by cooling down the substrate again to room temperature. The conductive porous carbon electrode was next deposited by screen-printing a carbon paste (Elcocarb B/SP, Solaronix), followed by drying at 150 °C for 5 min, and then sintering at 400 °C for 30 min. The substrates were then cooled down to room temperature before the inkjet infiltration of perovskite precursor ink.

Perovskite precursor ink formulation

0.53 g of PbI_2 (TCI Chemicals) was mixed with 0.19 g of methyl ammonium iodide (MAI, Dyesol) and 0.0176 g of 5-ammonium valeric acid iodide (5-AVAI, Dyesol) and all these ingredients were dissolved in 1 ml of gamma-butyrolactone (Sigma Aldrich) in a glass vial under a laboratory fume hood. The glass vial was sealed and placed for stirring for 30 min on a preheated (at 70 °C) hot-plate. A clear yellow solution was obtained that was allowed to cool down to room temperature before its infiltration in CPSCs. The ink was first filtered through a PTFE filter and was then transferred to the tank of the printer cartridge through the disposable syringe. The ink remained very stable both in glass vial and in the cartridge tank up to 4 weeks and no crystallization of the particles was observed.

Inkjet infiltration of perovskite precursor ink

Perovskite precursor ink was then permeated through carbon electrode of the PSCs with a drop-on-demand Dimatix materials inkjet printer (DMP-2831, Dimatix-Fujifilm Inc., USA, used before in our earlier reports [32-34]) with 15 µm drop spacing at 30 °C by applying a customized waveform with 18V amplitude and 1-8 kHz frequency. The relative humidity inside the printer hood was ~ 32% whereas the platen was kept at room temperature. After the automated infiltration of the perovskite precursor ink, the PSCs were transferred in a closed plastic box and were placed in a preheated oven at 50 °C for 30 minutes with lid on. After that the lid of the plastic box was removed and the PSCs were further heated for 1 more hour at 50 °C in the oven to ensure the complete the crystallization process of the perovskite absorber layer. Then the cells were removed from the oven and were then kept in vacuum prior measurements.

Epoxification of CPSCs

For batch 2 of the fabricated CPSC, the two components based commonly available epoxy (Strong Epoxy Professional, Casco-Finland) was applied manually through the popular doctor blading method including non-active area of the solar cells to block all possible pores. The contact areas were protected with the tape mask. The epoxified solar cells were dried overnight in the vacuum before the measurements and long term stability test. The thickness (150-160 μm) of epoxy over CPSCs was measured with a stylus-based programmable surface profiler measuring system (Model DEKTAK 6m, Veeco Instrument).

Measurements

The J-V curves of the fabricated PSCs were recorded in the Xenon lamp based solar simulator (Peccell Technologies, PEC-L01, Japan) under 1000 W/m2 light intensity equivalent to 1 Sun with a reference solar cell (PV measurements Inc) by employing black tape mask with an aperture area 0.16 cm^2. The incident photon to collected electron efficiency (IPCE) spectra were measured using a QEX7 spectral response measurement unit (PV Measurements Inc). X-ray diffraction (XRD) data was collected by microarea mapping the sample surfaces at a Rigaku Smart Lab X-ray diffractometer. A multilayer mirror was used to get Cu-Kα radiation which was cut with a collimator to 200 □m beam size. The diffractograms were obtained using a scanning rate of 1.5 □/min in the 1D-mode of a 2-dimensional HyPix-3000 detector. XRD measurements were performed for one fresh and one aged sample with and without epoxy sealing. The samples were analyzed from several different spots and the results were similar in different locations in the interior of the active area of the cells.

The photoluminescence (PL) lifetimes were determined by using a time-correlated single photon counting (TCSPC) apparatus equipped with a Picoharp 300 controller and a PDL 800-B driver for excitation, and a Hamamatsu R3809U-50 microchannel plate photomultiplier for detection in 90° configuration. All the samples were measured using a 650-660 nm excitation wavelength, and the PL decays were probed at 770 nm where the perovskite films have the peak emission. The PL decay traces were deconvoluted using a separately measured instrument response function, *i.e.* excitation pulse width, to increase accuracy of the calculated lifetimes near the instrument time resolution (about 110 - 200 ps excitation pulse width). The PL lifetimes were determined by fitting the decays with a 2- or 3-exponential decay function ($\Delta A = a_1 e^{-t/\tau 1} + a_2 e^{-t/\tau 2} + a_3 e^{-t/\tau 3}$) (different functions were required to obtain a reasonable fit quality). Multi-exponential decay curves demonstrate a complex PL decay dynamics of the perovskite films, due to different environments of individual emissive species. Table 1 presents the fit parameters and relative contributions of the components. The PL analysis was conducted on altogether six devices, three from each batch, and similar behavior was observed for all the cells of the batch.

The aging test

The long term stability test of the two batches of perovskite solar cells was executed by keeping the first and second batch for 751 hours and 1002 hours, respectively, at open circuit conditions at 40 ºC at approximately 45% relative air humidity in a weather chamber (Arctest-Finland ARC-150, Figure S1 a-b). The cells were illuminated by Osram Ultra-Vitalux 300 W UV + visible mercury lamps that generated 1.5 times the amount of UV light in AM1.5G spectrum during the tests. The spectrum of the lamps measured with Ocean Optics USB2000+ spectroradiometer is presented in Figure S2. The J-V curves were recorded periodically during the aging test in the abovementioned solar simulator. Additionally, the cells were photographed periodically according to the established procedure [35] with Olympus E-620 camera using white balancing, color calibration, and constant photographing settings and illumination. The pictures were analyzed only from the front side of the cells because the epoxy layer in batch 2 prevented the comparison of the two batches.

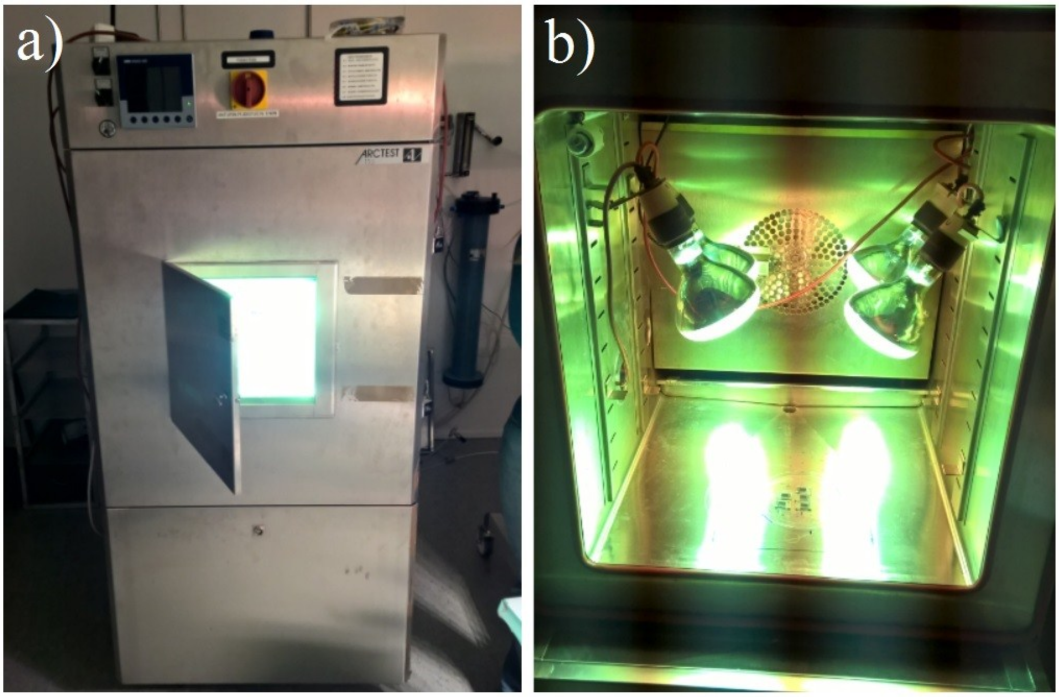

Figure S1: a) Weather chamber (Arctest-Finland ARC-150) used in this study (b) Inside view of the weather chamber where CPSCs are exposed to heavy UV-Illumination.

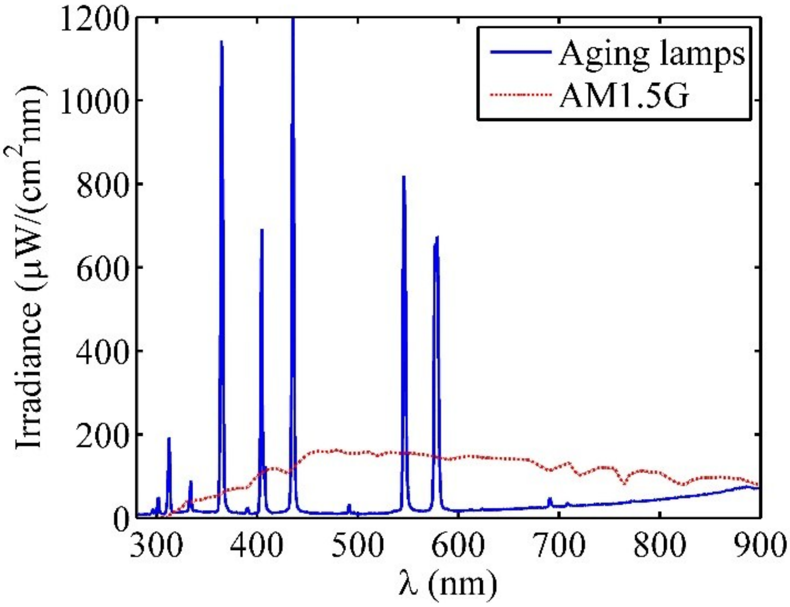

Figure S2: The irradiance of the UV lamps in comparison with AM1.5G spectrum. The irradiance of the lamps is 150% and 35% of the corresponding AM1.5G irradiance in UV area (300-380nm) and visible area (380-700 nm) respectively.

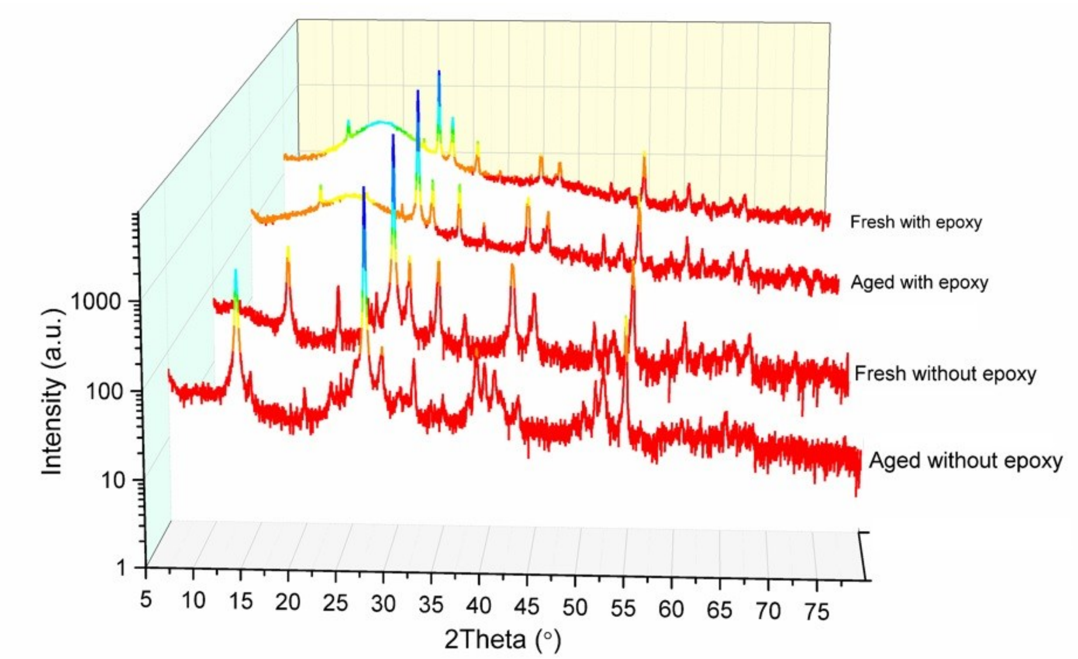

Figure S3: Full XRD data in logarithmic scale from the interior of the active area of four samples, aged or fresh, and with or without epoxy layer.

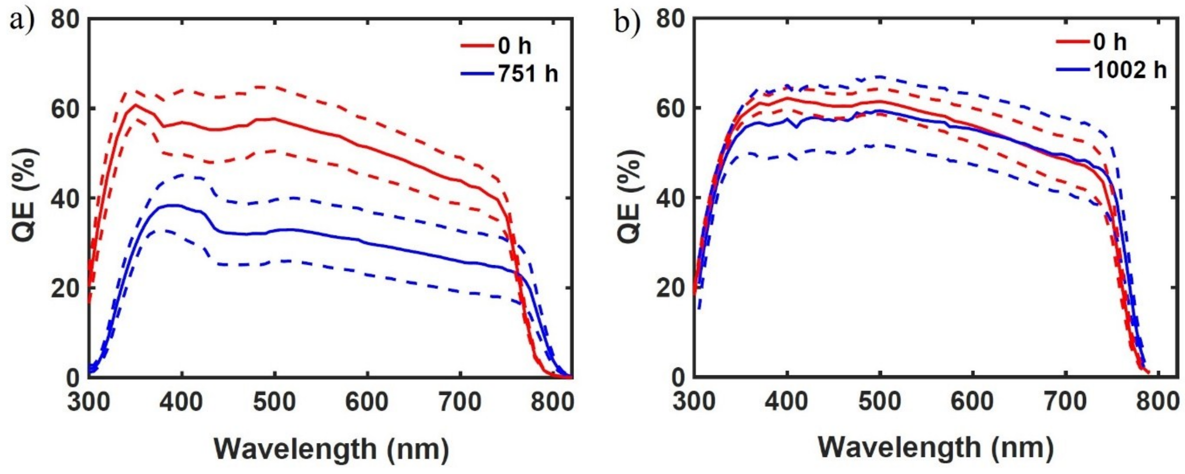

Figure S4: Incident photon to collected electron (IPCE) spectra of complete a) Batch 1 b) Batch 2. The solid lines represents the average values whereas the dashed lines represents the standard deviations.

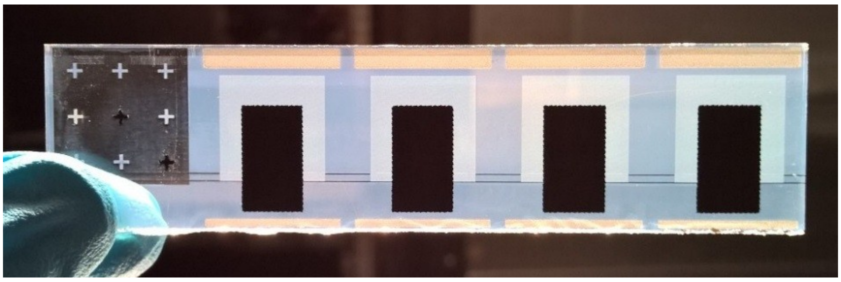

Figure S5: An array of 4 CPSCs (used in this study) before inkjet infiltration of perovskite precursor ink obtained through all scalable processes as described in our earlier report [20].

Statistical analysis of the IV results: aging test at 1.5 Sun and 40 °C (No epoxy)

Aging test

0 Hours

No epoxy	N 5	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P1		14.4	0.878	0.625	7.88	59.9
P10		13.2	0.861	0.605	6.86	58.5
P12		13.0	0.856	0.612	6.78	57.1
P13		13.4	0.795	0.665	7.06	45.6
P14		12.2	0.847	0.646	6.70	56.2
ave		**13.2**	**0.847**	**0.630**	**7.06**	**55.4**
std		**0.8**	**0.031**	**0.025**	**0.48**	**5.7**
std/ave		**5.8 %**	**3.7 %**	**3.9 %**	**6.8 %**	**10.2 %**
sem		0.3	0.014	0.011	0.22	2.5
95% CI		1.0	0.039	0.031	0.60	7.0

156 Hours

No epoxy	N 5	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P1		16.9	0.854	0.588	8.47	63.4
P10		15.5	0.865	0.596	7.98	60.0
P12		15.3	0.837	0.588	7.52	61.8
P13		14.8	0.782	0.639	7.38	45.5
P14		14.8	0.841	0.581	7.24	58.5
ave		**15.4**	**0.836**	**0.598**	**7.72**	**57.8**
std		**0.9**	**0.032**	**0.023**	**0.50**	**7.2**
std/ave		**5.5 %**	**3.8 %**	**3.9 %**	**6.5 %**	**12.4 %**
sem		0.4	0.014	0.010	0.23	3.2
95% CI		1.1	0.040	0.029	0.63	8.9

259 Hours

No epoxy	N 5	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P1		17.0	0.846	0.581	8.35	59.3
P10		14.5	0.867	0.603	7.59	59.4
P12		15.8	0.842	0.581	7.73	60.4
P13		14.9	0.790	0.624	7.34	48.4
P14		15.1	0.840	0.578	7.33	61.0
ave		**15.5**	**0.837**	**0.593**	**7.67**	**57.7**
std		**1.0**	**0.028**	**0.020**	**0.42**	**5.3**
std/ave		**6.2 %**	**3.4 %**	**3.3 %**	**5.4 %**	**9.1 %**
sem		0.4	0.013	0.009	0.19	2.4
95% CI		1.2	0.035	0.024	0.52	6.5

401 Hours

No epoxy	N 5	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P1		15.6	0.838	0.604	7.90	62.7
P10		13.5	0.857	0.614	7.09	65.0
P12		13.4	0.852	0.627	7.14	63.7
P13		9.3	0.788	0.666	4.90	65.9
P14		14.1	0.841	0.608	7.19	67.2
ave		**13.2**	**0.835**	**0.624**	**6.84**	**64.9**
std		**2.3**	**0.028**	**0.025**	**1.13**	**1.8**
std/ave		**17.6 %**	**3.3 %**	**4.0 %**	**16.6 %**	**2.7 %**
sem		1.0	0.012	0.011	0.51	0.8
95% CI		2.9	0.034	0.031	1.41	2.2

490 Hours

No epoxy	N	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
	5					
P1		14.7	0.846	0.588	7.33	69.4
P10		10.9	0.849	0.647	5.98	68.3
P12		12.6	0.845	0.609	6.50	70.2
P13		8.9	0.788	0.655	4.61	68.7
P14		11.6	0.841	0.601	5.85	76.7
ave		**11.8**	**0.834**	**0.620**	**6.06**	**70.7**
std		**2.1**	**0.026**	**0.030**	**0.99**	**3.5**
std/ave		**18.2 %**	**3.1 %**	**4.8 %**	**16.4 %**	**4.9 %**
sem		1.0	0.012	0.013	0.44	1.5
95% CI		2.7	0.032	0.037	1.23	4.3

751 Hours

No epoxy	N	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
	5					
P1		12.6	0.805	0.675	6.86	55.7
P10		7.9	0.823	0.694	4.52	82.0
P12		9.8	0.846	0.696	5.77	75.0
P13		6.3	0.801	0.676	3.41	92.2
P14		10.6	0.842	0.641	5.72	84.6
ave		**9.4**	**0.824**	**0.676**	**5.26**	**77.9**
std		**2.4**	**0.021**	**0.022**	**1.32**	**13.9**
std/ave		**25.9 %**	**2.5 %**	**3.3 %**	**25.1 %**	**17.8 %**
sem		1.1	0.009	0.010	0.59	6.2
95% CI		3.0	0.026	0.028	1.64	17.2

Table 1. Comparison final vs. initial performance for each type of cells

Show digits:		*1*	*0*	*1*	*2*	*0*
	N	J_{SC} (mA/cm^2)	V_{OC} (mV)	*FF* (%)	η (%)	R_{cell} (Ω)
No epoxy						
0 hours	5	13.2 ± 0.8	847 ± 31	63 ± 2.5	7.06 ± 0.48	55 ± 6
std/ave		5.8 %	3.7 %	3.9 %	6.8 %	10.2 %
751 hours	5	9.4 ± 2.4	824 ± 0	67.6 ± 0	5.26 ± 1.32	78 ± 14
std/ave		25.9 %	2.5 %	3.3 %	25.1 %	17.8 %
Difference		-28.6 %	-2.8 %	7.3 %	-25.5 %	40.5 %
p-value		0.02	0.17	0.07	0.03	0.05

Statistical analysis of the IV results: aging test at 1.5 Sun and 40 °C (with epoxy)

Aging test

0 Hours

Epoxy	*N* 7	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P5		9.3	0.825	0.630	4.83	56.6
P6		9.9	0.824	0.607	4.97	55.4
P7		9.8	0.839	0.667	5.51	48.5
P9		12.9	0.825	0.685	7.27	46.5
P10		12.6	0.830	0.685	7.14	52.2
P11		13.5	0.838	0.682	7.73	46.6
P12		12.0	0.816	0.653	6.41	56.3
ave		**11.4**	**0.828**	**0.659**	**6.26**	**51.7**
std		**1.7**	**0.008**	**0.030**	**1.17**	**4.5**
std/ave		**14.9 %**	**1.0 %**	**4.6 %**	**18.7 %**	**8.7 %**
sem		0.6	0.003	0.012	0.44	1.7
95% CI		1.6	0.007	0.028	1.08	4.2

163 Hours

Epoxy	*N* 7	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P5		12.3	0.765	0.617	5.82	62.8
P6		12.3	0.766	0.587	5.53	72.2
P7		10.5	0.772	0.598	4.86	82.5
P9		11.3	0.724	0.674	5.51	60.0
P10		10.3	0.718	0.647	4.78	80.2
P11		11.9	0.751	0.662	5.93	75.2
P12		12.2	0.733	0.626	5.58	70.8
ave		**11.5**	**0.747**	**0.630**	**5.43**	**72.0**
std		**0.9**	**0.022**	**0.032**	**0.44**	**8.4**
std/ave		**7.4 %**	**3.0 %**	**5.1 %**	**8.2 %**	**11.6 %**
sem		0.3	0.008	0.012	0.17	3.2
95% CI		0.8	0.020	0.030	0.41	7.7

277 Hours

Epoxy	*N* 7	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P5		13.1	0.816	0.578	6.17	75.4
P6		11.8	0.805	0.588	5.59	72.7
P7		12.1	0.816	0.610	6.02	74.7
P9		9.9	0.778	0.609	4.71	84.1
P10		10.7	0.771	0.612	5.04	75.0
P11		10.3	0.801	0.643	5.30	79.8
P12		16.1	0.773	0.590	7.33	63.1
ave		**12.0**	**0.794**	**0.604**	**5.74**	**75.0**
std		**2.1**	**0.020**	**0.021**	**0.87**	**6.5**
std/ave		**17.6 %**	**2.5 %**	**3.6 %**	**15.2 %**	**8.6 %**
sem		0.8	0.007	0.008	0.33	2.5
95% CI		2.0	0.018	0.020	0.81	6.0

373 Hours

Epoxy	*N* 7	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P5		11.9	0.846	0.631	6.35	63.5
P6		10.1	0.827	0.647	5.40	64.4
P7		10.9	0.839	0.650	5.96	64.0
P9		10.7	0.806	0.656	5.67	71.0
P10		9.9	0.795	0.664	5.21	81.6
P11		10.2	0.814	0.650	5.41	81.9
P12		14.6	0.777	0.631	7.14	66.0
ave		**11.2**	**0.815**	**0.647**	**5.88**	**70.3**
std		**1.6**	**0.025**	**0.012**	**0.68**	**8.2**
std/ave		**14.6 %**	**3.0 %**	**1.9 %**	**11.5 %**	**11.6 %**
sem		0.6	0.009	0.005	0.26	3.1
95% CI		1.5	0.023	0.011	0.63	7.6

441 Hours

Epoxy	N 7	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P5		11.6	0.829	0.645	6.23	55.2
P6		11.3	0.847	0.650	6.23	58.0
P7		11.5	0.870	0.628	6.27	62.1
P9		12.7	0.846	0.660	7.09	55.8
P10		11.9	0.839	0.630	6.28	69.2
P11		11.3	0.850	0.642	6.18	75.4
P12		15.5	0.806	0.615	7.69	62.7
ave		**12.3**	**0.841**	**0.639**	**6.56**	**62.6**
std		**1.5**	**0.020**	**0.015**	**0.59**	**7.4**
std/ave		**12.3 %**	**2.3 %**	**2.4 %**	**9.0 %**	**11.8 %**
sem		0.6	0.007	0.006	0.22	2.8
95% CI		1.4	0.018	0.014	0.54	6.8

795 Hours

Epoxy	N 7	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P5		12.7	0.816	0.627	6.50	54.8
P6		11.0	0.817	0.641	5.78	63.7
P7		12.1	0.837	0.628	6.36	65.9
P9		11.2	0.847	0.644	6.11	70.1
P10		11.3	0.843	0.623	5.95	86.8
P11		12.9	0.859	0.641	7.11	61.9
P12		15.7	0.830	0.622	8.10	51.5
ave		**12.4**	**0.836**	**0.632**	**6.56**	**64.9**
std		**1.6**	**0.016**	**0.009**	**0.81**	**11.6**
std/ave		**13.0 %**	**1.9 %**	**1.5 %**	**12.3 %**	**17.8 %**
sem		0.6	0.006	0.004	0.30	4.4
95% CI		1.5	0.015	0.009	0.75	10.7

1002 Hours

Epoxy	N 7	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	η (%)	R_{cell} (Ω)
P5		11.6	0.822	0.556	5.28	67.2
P6		12.0	0.804	0.506	4.86	80.6
P7		13.8	0.841	0.538	6.26	69.2
P9		12.7	0.851	0.579	6.26	81.0
P10		10.9	0.840	0.603	5.53	89.5
P11		13.1	0.861	0.608	6.86	75.2
P12		14.6	0.829	0.621	7.50	68.5
ave		**12.7**	**0.836**	**0.573**	**6.08**	**75.9**
std		**1.3**	**0.019**	**0.042**	**0.92**	**8.3**
std/ave		**10.1 %**	**2.3 %**	**7.3 %**	**15.2 %**	**10.9 %**
sem		0.5	0.007	0.016	0.35	3.1
95% CI		1.2	0.017	0.039	0.85	7.7

Table 3. Comparison final vs. initial performance for each type of cells

Show digits:		1	0	1	2	0
	N	J_{SC} (mA/cm^2)	V_{OC} (mV)	*FF* (%)	η (%)	R_{cell} (Ω)
Epoxy						
0 hours	7	11.4 ± 1.7	828 ± 8	65.9 ± 3	6.26 ± 1.17	52 ± 5
std/ave		14.9 %	1.0 %	4.6 %	18.7 %	8.7 %
1002 hours	7	12.7 ± 1.3	836 ± 19	57.3 ± 4.2	6.08 ± 0.92	76 ± 8
std/ave		10.1 %	2.3 %	7.3 %	15.2 %	10.9 %
Difference		10.7 %	0.9 %	-13.0 %	-3.0 %	46.7 %
p-value		0.15	0.26	0.00	0.64	0.00

Nomenclature (Include in report)

N	number of samples
ave	average
std	standard deviation
std/ave	relative standard deviation compared to average
sem	standard error of the mean
95% CI	half of the full 95 % confidence interval based on Student's t-distribution
Difference	relative difference of average values
***p*-value**	calculated with two-tailed two-sample t-test with unequal variances
J_{SC}	short circuit current density
V_{OC}	open circuit voltage
FF	fill factor
η	efficiency
R_{cell}	cell resistance (inverse slope of the IV curve at V_{OC})

About statistical analysis (Include in report)

Statistical testing

Statistical confidence level	**95%**	α: **0.05**
t-test of two independent groups (Batch 1 vs Batch 2):		**two-tailed, two-sample, unequal variances**
t-test of the same group before and after aging:		**two-tailed, paired t-test**

Criteria for practically significant difference and acceptable sample-to-sample variation (std/ave)

Criteria	J_{SC} **(mA/cm^2)**	V_{OC} **(mV)**	***FF*** **(%)**	η **(%)**	R_{cell} **(Ω)**
Practically signif. difference	5%	5%	5%	5%	5%
Acceptable level of std/ave	5%	5%	5%	10%	15%

Underlined in the comparison tables are

- p-values lower than or equal to α (e.g. 0.05 for 5 % signifigance)
- Differences larger than the practical significance level
- Relative standard deviations larger than the acceptable value

Notes (Leave out from in report)

Note 1: about the levels of significance

95 % confidence level is a typical in statistical testing. An alternative would be 99 %.
The practical significance level is up to your subjective decision, based on
what you consider practically relevant, meaningful difference.

Note 2: about further analysis opportunities

A more rigorous statistical test would perhaps be the Mann–Whitney U test:
http://en.wikipedia.org/wiki/Mann%E2%80%93Whitney_U_test
http://www.real-statistics.com/non-parametric-tests/wilcoxon-rank-sum-test/
Unfortunately, U test is not available as an Excel function. See the above tutorial link.
However, if you plan to use it, check if it is available in newest Excel versions.
Note however, that it may not give much added value in the end (See the Wikipedia link).

Note 3: Statistical tests for aging effect

Since the comparison of fresh and aged cells is between same devices, the statistical samples
of initial and aged data are not independent. In this case paired t-test should be used.