Electronic Supplementary Information

Dye-sensitized solar cells with inkjet-printed dyes

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Estimation of the dye loading from the transmittance of complete DSSC

The *absorptance* of the dyed TiO₂ photoelectrode film in a complete DSSC was approximated as

$$A_{\rm PE} = 1 - T_{\rm PE} = 1 - f \frac{T_{\rm cell, PE}}{T_{\rm cell, EL}}$$
(SE1)

where $T_{cell,PE} = T_{PE-sub}T_{PE}T_{EL}T_{Pt}T_{CE-sub}$ and $T_{cell,EL} = T_{PE-sub}T_{EL}T_{Pt}T_{CE-sub}$ are respectively the transmittance measured through the photoelectrode and the electrolyte edge region next to it (**Figures S1 and S2 a-c**), each modeled as the product of the transmittances of the cell components through which the light beam goes in each measurement ("PE" stands for photoelectrode, "sub" for substrate, "EL" for electrolyte, "Pt" for the Pt catalyst layer, and "CE" for counter electrode). See ¹ for a similar optical model.

Note that, because in equation SE1 $T_{cell,PE}$ is divided with the 'background' measurement $T_{cell,EL}$ taken from the same sample, the division not only factors out the transmittance of the electrolyte (T_{EL}) , substrate (T_{PE-sub}, T_{CE-sub}) and platinum (T_{Pt}) , but also compensates for the sample-to-sample variations in them. In addition to this, the correction factor *f*, defined as

$$f = \frac{T_{\text{cell,EL}}(\lambda = 800 \text{ nm})}{T_{\text{cell,PE}}(\lambda = 800 \text{ nm})}$$
(SE2)

is used to compensate for spatial variations in the amount of Pt (T_{Pt}) and presence of air bubbles and other possible imperfections in the Surlyn sealing at the CE side (T_{CE-sub}), by normalizing the absorbance to zero at 800 nm (900 nm in the case of the black dye) where the absorptance by the dye is known to be non-existent.

Equation (1) neglects reflectance at the material layer interfaces, which are low due to relatively good refractive index matching, as well as the reflectance of the photoelectrode layer, which is negligible near the absorption maximum at 535 nm, where the already low back scattering of light

¹ J. Halme, P. Vahermaa, K. Miettunen, P. Lund, Adv. Mater., 2010, 22, E210-E234.

form the film (due to absence of scattering particles) is further attenuated by the intense light absorption².

The photoelectrode absorptance spectra obtained this way are shown in **Figure S2 d-f**. Example spectra were selected from it to the Figure 3 of the paper.

The dye loading (mol cm⁻²) in photoelectrode film was calculated as

$$n_{\rm dye} = \frac{Abs_{\rm PE}(\lambda = 535 \,\rm nm)}{\varepsilon_{\rm dye}(\lambda = 535 \,\rm nm)}$$
(SE3)

where ε_{dye} is the molar attenuation coefficient of the dye ($\varepsilon_{dye} = 1.75 \times 10^3 \text{ m}^2 \text{ mol}^{-1} = 17.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, taken from ³, and assumed to correspond to decadic attenuation, at the absorption maximum of the dye at 535 nm, and Abs_{PE} is the decadic *absorbance* (Figure S2 g-i) of the photoelectrode calculated from the *absorptance* of equation SE1 as

$$Abs_{\rm PE} = -\log_{10}(T_{\rm PE}) = -\log_{10}(1 - A_{\rm PE})$$
(SE4)



Figure S1. Photographs of the gradient (a) and two-color (b) DSSCs showing approximate positions and size of the light beam when measuring the transmittance through the center of each photoelectrode segment ($T_{cell,PE}$) and the free electrolyte region next to it ($T_{cell,EL}$). Two photoelectrode measurement ("a" and "b") were taken from each segment of the gradient DSSC and one from the two-color DSSC.

² J. Halme, G. Boschloo, A. Hagfeldt, P. Lund, J. Physic. Chem. C., 2008, 112, 5623-5637.

³ M. Wang, S. Plogmaker, R. H. Baker, P. Pechy, H. Rensmo, S. M. Zakeeruddin, M. Gratzel, *Chem Sus Chem.*, 2012, **5**, 181–187.



Figure S2. (a - c) Measured UV-VIS transmittance spectra ($T_{cell,PE}$ and $T_{cell,EL}$) of the small complete DSSCs, and calculated photoelectrode absorptance (d - f, equation SE1) and absorbance (g - i, equation SE4) spectra of their 7 µm thick TiO₂ photoelectrodes dyed with inkjet printing (C101 dye) with (a, d, g) or without (b, e, h) washing with DMF after printing, and the same for reference cells dyed by drop-casting the same dye solution in identical TiO₂ films (c, f, i). The absorbance data in figures (g - i) were used for calculating, with equation SE3, the dye loading shown in Figure 4 of the paper.



Figure S3. a) Device *transmittance* and b) photoelectrode *absorptance* values of the small semitransparent DSSCs at 550 nm wavelength (used as a reference for visible transparency), and c) the corresponding photoelectrode *absorbance* at 535 nm peak absorption wavelength (used for calculating the dye loading with equation SE3), corresponding to the spectra shown in Figures S2a, d, and g. Figures a and b also show the overall small sample-to-sample variation (three samples of each type) in the data, not discernible form selected spectra shown in the Figures 3a and d in the paper.



Figure S4. The inkjet-printer used in this study. a) Fuji Film's Dimatix Material Printer, Model DMP-2800, and b) printer cartridge filled with dye C101 solution.

Estimation of the dye loading with dye desorption from the TiO₂ films

The *absorbance of the dye desorption* solutions was calculated by subtracting the background level $Abs_{sol,meas,bg}$ from the measured absorbance $Abs_{sol,meas}$

$$Abs_{sol} = Abs_{sol,meas} - Abs_{sol,meas,bg}$$
 (SE5)

The background level $Abs_{sol,meas,bg}$ was determined separately for each absorbance spectrum as the average absorbance between 780 nm and 860 nm, where the dye is known to have negligible absorption. This corresponds to the similar correction made for solar cell transmittance data in equation (SE1). The resulting absorbance spectra are shown in **Figure S5**.

The dye loading (mol cm⁻²) in the photoelectrode film (Figure 4c in the paper) was calculated as

$$n_{\rm dye} = \frac{Abs_{\rm sol}(\lambda = 535\,\rm nm)}{\varepsilon_{\rm dye}(\lambda = 535\,\rm nm) \cdot L} \cdot \frac{V_{\rm sol}}{A_{\rm film}}$$
(SE6)

where V_{sol} is the volume of the desorption solution ($V_{sol} = 4 \text{ ml}$), L is the optical path length of the cuvette (L = 1 cm), and A_{film} is the area of the photoelectrode films ($A_{film} = 0.4 \text{ cm}^2$).



Figure S5. UV-VIS absorbance spectra of the dye desorption solutions (C101 dye), from which the dye loading shown in Figure 4c of the paper were calculated with equation SE6. The figure shows the spectra obtained after subtracting the background according to equation (SE5). The dyed TiO₂ films were 7 μ m thick and had 0.4 cm² area. The dye was desorbed from them to a solution volume of 4 ml, and measured with in a cuvette with 1 cm optical path.

Statistical analysis of the IV results: initial performance

Nomenclature and details of the statistical testing are given in the end of the document.

Initial performance of all prepared cells

All cells initial	N					
Printed	7	J _{SC} (mA/cm²)	V _{oc} (V)	FF	η (%)	R _{cell} (Ω)
P	'1	14.1	0.659	0.721	6.68	33.8
P	2	14.2	0.637	0.723	6.52	30.4
P	3	14.0	0.658	0.719	6.64	37.1
P	4	14.0	0.652	0.689	6.29	45.7
P	5	14.1	0.642	0.722	6.55	33.1
P	6	13.7	0.653	0.677	6.05	50.3
P	7	13.8	0.639	0.655	5.79	55.3
av	e	14.0	0 0.649	0.701	6.36	6 40.8
st	d	0.2	2 0.009	0.027	0.33	9.6
std/av	e	1.2 %	% 1.4 %	۵.9 %	% 5.2 %	6 23.5 %
sei	n	0.1	1 0.003	0.010	0.13	3 3.6
95% (CI	0.2	2 0.008	0.025	5 0.31	8.9
Reference	5	J _{sc} (mA/cm²)	V _{oc} (V)	FF	η (%)	R _{cell} (Ω)
R	1	14.1	0.650	0.724	6.62	31.8
R	2	13.6	0.639	0.648	5.63	55.8
R	3	13.9	0.665	0.693	6.39	43.9
R	4	13.4	0.664	0.718	6.40	38.2
R	5	14.0	0.652	0.645	5.87	59.3
av	e.	13.	B 0.654	0.686	6.18	3 45.8
SI	d	0.3	3 0.011	0.037	0.41	l 11.6
std/av	e	2.0 %	<u>% 1.7 %</u>	5.5%	6.7 %	<u>% 25.4 %</u>
Sei	n	0.1	1 0.005	0.017	0.18	3 5.2
95% (از	0.3	3 0.013	0.046	0.51	14.5
e 1. Comparison	of tv	vo different o	ell types - in	itial perform	ance	
	٨	l J _{sc} (mA/c	m²) V _{oc} (r	nV)	η (%)	R _{cell} (Ω)
performance						
Print	ed 7	' 14 ± 0.2	2 649 :	±9 70±3	6.4 ± 0.3	41 ± 10
Referen	ce 5	5 13.8 ± 0	.3 654 ±	11 69 ± 4	6.2 ± 0.4	46 ± 12
Differen	се	1.4 %	-0.8	% 2.2 %	2.8 %	<u>-10.8 %</u>

Differences in the initial performance (Table 1)

p-value

The results show no statistically significant differences (p < 0.05) between the two types of cells, for any of the IV parameters. The differences in the average values are also practically insignificant (< 5 %), except for the R_{cell} which shows relatively high variance between the samples.

0.41

0.47

0.46

0.21

0.46

Statistical analysis of the IV results: aging test at 1 Sun and 35 C

All but the following four samples (two in each series) were put to a 1000 h aging test.

Printed	2	J _{sc} (mA/cm ²	²) V _{oc} (V)	FF	η (%)	$R_{\text{cell}}(\Omega)$
P6		13.7	0.653	0.677	6.05	50.3
dif from ave		-2.1	% 0.7	% -3.4	% -4.8	% 23.3 %
P7		13.8	0.639	0.655	5.79	55.3
dif from ave		-1.1	% -1.4	% -6.5	% -8.9	% 35.4 %
Reference	2	J _{sc} (mA/cm ²	²) V _{oc} (V)	FF	η (%)	$R_{\text{cell}}(\Omega)$
R2		13.6	0.639	0.648	5.63	55.8
dif from ave		-2.8	% -1.5	% -7.5	% -11.4	% 36.8 %
R5		14.0	0.652	0.645	5.87	59.3
dif from ave		-0.1	% 0.5	% -8.0	% -7.7	% 45.3 %
Notes	Seve and agin	en cells with prin characterized, c a study respec	nted dye (P1…P7 of which five and t tively. The exclud) and five referen hree highest effic ed lower efficienc	ce cells (R1R5 ciency cells were s cy cells (P6, P7, R) were prepared selected for the 22, R5) had high

Samples excluded from the aging test

Seven cells with printed dye (P1...P7) and five reference cells (R1...R5) were prepared and characterized, of which five and three highest efficiency cells were selected for the aging study, respectively. The excluded lower efficiency cells (P6, P7, R2, R5) had high Rcell, most likely due to bad electrical contacts, and therefore lower FF. P6 and P7 had addionally slightly lower Jsc than the top five cells in the same group. The excluded P6 and R5 were aged in parallel, at the same conditions, while monitoring their performance with an in-situ measurement set-up, and exhibited similar aging behaviour as the rest of the cells (data not shown). P7 and R5 were stored and not used for further measurements.

Aging test

0	Hours		Ν										
	Printed		5	J _{sc} (m	A/cm²)	Vo	_{ic} (V)		FF		η (%)	R	_{cell} (Ω)
		P1		14.1		0.659		0.721		6.68		33.8	
		P2		14.2		0.637		0.723		6.52		30.4	
		P3		14.0		0.658		0.719		6.64		37.1	
		P4		14.0		0.652		0.689		6.29		45.7	
		P5		14.1		0.642		0.722		6.55		33.1	
		ave			14.1		0.650		0.715		6.53	;	36.0
		std			0.1		0.010		0.014		0.15	5	5.9
	:	std/ave			0.5 %	1	1.5 %	1	2.0 %		2.3 %	, D	16.4 %
		sem			0.0		0.004		0.006		0.07	,	2.6
		95% CI			0.1		0.012		0.018		0.19)	7.3
	Reference		3	J _{sc} (m	A/cm²)	Vo	_{ic} (V)		FF		η (%)	R	_{cell} (Ω)
		R1		14.1		0.650		0.724		6.62		31.8	
		R3		13.9		0.665		0.693		6.39		43.9	
		R4		13.4		0.664		0.718		6.40		38.2	
		ave			13.8		0.660		0.712		6.47	,	37.9
		std			0.3		0.008		0.016		0.13	6	6.0
	:	std/ave			2.5 %	I	1.3 %	1	2.3 %		2.0 %	, 0	15.9 %
		sem			0.2		0.005		0.010		0.08	3	3.5
		95% CI			0.8		0.021		0.041		0.32	2	15.0

250	Hours		N									
	Printed		5	J _{SC} (mA/cm ²)	V _{oc}	(V)	F	F		η (%)	R	_{cell} (Ω)
		P1		13.4	0.674		0.723		6.53		35.3	
		P2		14.6	0.636		0.715		6.63		28.8	
		P3		13.7	0.665		0.717		6.53		36.0	
		P4		14.8	0.648		0.685		6.56		36.7	
		P5		14.2	0.657		0.716		6.67		30.2	
		ave		14.1		0.656		0.711		6.58		33.4
		std		0.6	i	0.015		0.015		0.06		3.6
	st	d/ave		4.1 %	, D	2.3 %	1	2.1 %		0.9 %)	10.9 %
		sem		0.3		0.007		0.007		0.03		1.6
	95	5% CI		0.7		0.018		0.018		0.08		4.5
	Reference		3	J _{SC} (mA/cm²)	V _{oc}	(V)	F	F		η (%)	R	_{cell} (Ω)
		R1		14.4	0.662		0.719		6.86		31.8	
		R3		14.2	0.665		0.703		6.66		36.5	
		R4		14.1	0.664		0.710		6.67		34.8	
		ave		14.3		0.664		0.711		6.73		34.3
		std		0.1		0.001		0.008		0.11		2.4
	st	d/ave		1.0 %	, D	0.2 %	1	1.1 %		1.7 %)	6.9 %
		sem		0.1		0.001		0.005		0.07		1.4
	95	5% CI		0.3		0.003		0.020		0.28		5.9

500	Hours		Ν									
	Printed		5	J _{SC} (mA/cm ²)	Va	_{bc} (V)	F	F		η (%)	R	_{cell} (Ω)
		P1		13.9	0.673		0.720		6.73		34.5	
		P2		14.9	0.633		0.711		6.72		30.0	
		P3		14.0	0.656		0.716		6.57		33.2	
		P4		14.9	0.638		0.687		6.51		35.6	
		P5		14.1	0.653		0.716		6.60		31.2	
		ave		14.	3	0.651		0.710		6.63		32.9
		std		0.	5	0.016		0.013		0.10		2.3
		std/ave		3.5 %	%	2.4 %)	1.9 %	1	1.5 %)	7.0 %
		sem		0.2	2	0.007		0.006		0.04		1.0
		95% CI		0.0	6	0.020		0.016		0.12		2.8
	Reference		3	J _{SC} (mA/cm²)	V	_{oc} (V)	F	F		η (%)	R	_{æll} (Ω)
		R1		14.4	0.666		0.723		6.94		29.6	
		R3		13.7	0.669		0.711		6.53		33.8	
		R4		14.3	0.668		0.712		6.80		32.4	
		ave		14.	2	0.667		0.715		6.76		32.0
		std		0.4	4	0.002		0.007		0.21		2.1
		std/ave		2.6	%	0.2 %)	0.9 %	1	3.1 %	1	6.6 %
		sem		0.3	2	0.001		0.004		0.12		1.2
		95% CI		0.9	9	0.004		0.017		0.52		5.3

750	Hours		N									
	Printed		5	J _{SC} (mA/cm ²)	Vo	_c (V)	F	F		η (%)	R	_{cell} (Ω)
		P1		13.6	0.661		0.729		6.53		32.6	
		P2		15.2	0.634		0.700		6.74		30.6	
		P3		13.7	0.655		0.713		6.39		34.7	
		P4		14.8	0.623		0.691		6.37		34.5	
		P5		14.2	0.646		0.716		6.56		29.2	
		ave		14.3	3	0.644		0.710		6.52		32.3
		std		0.7	7	0.015		0.015		0.15		2.4
	std	ave		4.9 %	6	2.4 %		2.1 %		2.3 %)	7.4 %
	s	sem		0.3	3	0.007		0.007		0.07		1.1
	95%	∕₀ CI		0.9	9	0.019		0.018		0.19		3.0
	Reference		3	J _{SC} (mA/cm²)	Vo	_c (V)	F	F		η (%)	R	_{cell} (Ω)
		R1		14.2	0.661		0.725		6.80		31.0	
		R3		13.0	0.674		0.724		6.36		34.8	
		R4		13.1	0.674		0.725		6.39		35.4	
		ave		13.4	1	0.670		0.725		6.52		33.8
		std		0.7	7	0.008		0.001		0.25		2.4
	std	ave		5.0 %	6	1.2 %		0.1 %		3.8 %)	7.0 %
	s	sem		0.4	1	0.005		0.000		0.14		1.4
	95%	6 CI		1.7	7	0.020		0.001		0.62		5.9

1000	Hours	

Hours		Ν									
Printed		5	J _{sc} (mA/cm ²)	v _o	_c (V)		FF	η	(%)	R	_{cell} (Ω)
	P1		13.8	0.662		0.724		6.62		32.7	
	P2		14.4	0.632		0.703		6.39		31.8	
	P3		13.5	0.635		0.718		6.14		34.0	
	P4		15.1	0.616		0.690		6.43		32.1	
	P5		14.4	0.637		0.720		6.63		28.1	
	ave		14.	2	0.636		0.711		6.44		31.8
	std		0.	6	0.017		0.014		0.20		2.2
	std/ave		4.5	%	2.6 %		2.0 %		3.1 %)	7.1 %
	sem		0.	3	0.007		0.006		0.09		1.0
	95% CI		0.	8	0.021		0.018		0.25		2.8
Reference		3	J _{sc} (mA/cm²)	V o	_c (V)		FF	η	(%)	R	_{æll} (Ω)
	R1		13.8	0.664		0.718		6.58		32.4	
	R3		12.2	0.691		0.715		6.04		38.4	
	R4		13.3	0.662		0.728		6.41		33.0	
	ave		13.	1	0.672		0.720		6.34		34.6
	std		0.	8	0.016		0.007		0.28		3.3
	std/ave		6.1	%	2.4 %		1.0 %		4.4 %)	9.6 %
	sem		0.	5	0.009		0.004		0.16		1.9
	95% CI		2.	0	0.040		0.018		0.69		8.3

Table 2. Comp	aris	on of the two typ	e of cells dur	ing the aging	test	
	N	J _{sc} (mA/cm²)	V _{oc} (mV)	FF (%)	η (%)	R _{cell} (Ω)
<u>0 h</u>						
Printed	5	14.1 ± 0.1	650 ± 10	71.5 ± 1.4	6.53 ± 0.15	36 ± 6
Reference	3	13.8 ± 0.3	660 ± 8	71.2 ± 1.6	6.47 ± 0.13	38 ± 6
Difference		2.1 %	-1.5 %	0.4 %	1.0 %	<u>-5%</u>
<i>p</i> -value		0.29	0.19	0.80	0.57	0.69
<u>250 h</u>						
Printed	5	14.1 ± 0.6	656 ± 15	71.1 ± 1.5	6.58 ± 0.06	33 ± 4
Reference	3	14.3 ± 0.1	664 ± 1	71.1 ± 0.8	6.73 ± 0.11	34 ± 2
Difference		-1.0 %	-1.2 %	0.1 %	-2.2 %	-3%
<i>p</i> -value		0.62	0.31	0.94	0.14	0.67
<u>500 h</u>						
Printed	5	14.3 ± 0.5	651 ± 16	71 ± 1.3	6.63 ± 0.1	33 ± 2
Reference	3	14.2 ± 0.4	667 ± 2	71.5 ± 0.7	6.76 ± 0.21	32 ± 2
Difference		1.3 %	-2.5 %	-0.7 %	-2.0 %	3.0 %
<i>p</i> -value		0.57	0.08	0.49	0.39	0.58
<u>750 h</u>						
Printed	5	14.3 ± 0.7	644 ± 15	71 ± 1.5	6.52 ± 0.15	32 ± 2
Reference	3	13.4 ± 0.7	670 ± 8	72.5 ± 0.1	6.52 ± 0.25	34 ± 2
Difference		<u>6.3 %</u>	-3.9 %	-2.1 %	-0.02%	-4.3 %
<i>p</i> -value		0.16	<u>0.02</u>	0.09	0.99	0.45
<u>1000 h</u>						
Printed	5	14.2 ± 0.6	636 ± 17	71.1 ± 1.4	6.44 ± 0.2	32 ± 2
Reference	3	13.1 ± 0.8	672 ± 16	72 ± 0.7	6.34 ± 0.28	35 ± 3
Difference		<u>8.6 %</u>	<u>-5.3 %</u>	-1.3 %	1.5 %	<u>-8.3 %</u>
<i>p</i> -value		0.11	<u>0.04</u>	0.27	0.63	0.27

Table 3. Comp	arisc	on final vs. initial	performance	e for each <u>typ</u>	e of cells	
	N	J _{SC} (mA/cm²)	V _{oc} (mV)	FF (%)	η (%)	R _{cell} (Ω)
Printed						
0 hours	5	14.1 ± 0.1	650 ± 10	71.5 ± 1.4	6.53 ± 0.15	36 ± 6
Rel. stdev		0.5 %	1.5 %	2.0 %	2.3 %	<u>16.4 %</u>
1000 hours	5	14.2 ± 0.6	636 ± 17	71.1 ± 1.4	6.44 ± 0.2	32 ± 2
Rel. stdev		4.5 %	2.6 %	2.0 %	3.1 %	<u>7.1 %</u>
Difference		1.2 %	-2.0 %	-0.5 %	-1.4 %	<u>-11.9 %</u>
<i>p</i> -value		0.58	0.14	0.46	0.47	0.17
<u>Reference</u>						
0 hours	3	13.8 ± 0.3	660 ± 8	71.2 ± 1.6	6.47 ± 0.13	38 ± 6
Rel. stdev		2.5 %	1.3 %	2.3 %	2.0 %	<u>15.9 %</u>
1000 hours	3	13.1 ± 0.8	672 ± 16	72 ± 0.7	6.34 ± 0.28	35 ± 3
Rel. stdev		<u>6.1 %</u>	2.4 %	1.0 %	4.4 %	<u>9.6 %</u>
Difference		-4.9 %	1.9 %	1.3 %	-1.9 %	<u>-8.7 %</u>
<i>p</i> -value		0.30	0.27	0.37	0.39	0.24

Differences between the two types of cells during the aging test (Table 2)

At the end of the aging test at 1000 h, V_{oc} was 5 % lower in the printed dye cells compared to the reference cells (4 % lower at 750 h), whereas all the other IV parameters, and the conversion efficiency, do not show any statistically significant differences between the two types of cells.

Aging behavior of each cell type (Table 3)

Table 3 compares the initial and final (1000 h aged) performance of each type of cell. The statistical testing (paired Student's t-test at 95 % confidence) shows no significant aging in either of the cell types. The final data differ less than 5 % from the initial data for all IV characteristics, except for R_{cell} , which decreased by 7 % in the printed dye cells and 9 % in the reference cells, however as already mentioned, these changes are not statistically significant. Accordingly, the changes in the average values of the IV parameters and efficiency were similar or smaller than the standard deviations. We can therefore conclude that if any degradation happened, it was less than the standard deviations, which were only a few percent for all the IV parameters. In more practical terms: no significant aging took place.

Finally, we note that the R_{cell} has relatively high standard deviation (underlined in the table), possibly due to a problem occurred in the preparation of the electrical contact to the cells, but this did not inflate the standard deviations of the other parameters, nor the efficiency. Aging also increased the standard deviation of J_{sc} , V_{oc} and η , but it remained less than 5 % in all the cases, except for the J_{sc} of the aged reference cells (6%).

About statistical analysis in Tables 1, 2, and 3

Statistical testing

Statistical confidence level **95%** α : **0.05**

Criteria for practically significant difference and acceptable sample-to-sample variation (rel. stdev)

Criteria	J _{SC} (mA/cm ²)	V _{oc} (mV)	FF (%)	η (%)	R _{cell} (Ω)
Practically signif. difference	5%	same	same	same	same
Acceptable Rel. stdev	5%	5%	5%	10%	15%

Underlined in the tables are:

- *p*-values lower than or equal to α (e.g. 0.05 for 5 % significance)

- Differences larger than the practical significance level

- Relative standard deviations larger than the acceptable value

Nomenclature	
Ν	Number of samples
ave	Average
std	Standard deviation
std/ave, Rel. stdev	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: Printed vs reference, or Batch 2 vs Batch 1.
<i>p</i> -value	Calculated with two-tailed two-sample t-test with unequal variances. A paired t-test was used for comparing the initial and final data of the same batch of cells.
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 $V_{\rm OC}$)

Statistical analysis of the EIS results

The tables 4 - 6 below show results from the electrochemical impedance spectroscopy of the printed dye and reference DSSCs. See ref [MO] for the description and definitions of the equivalent circuit impedance model and its parameters shown in the tables. The results are commented with conclusions below the tables in the panel "Notes".

Initial data	N	SERIES R		P	HOTOELE	ECTRODE				со	UNTER EL	ECTRODE	-		[DIFFUSION	N	TOTAL R
Printed	5	$R_{\rm S}(\Omega)$	$R_{\rm PE}(\Omega)$	Q CPE, PE	$\boldsymbol{\beta}_{CPE,PE}$	C _{PE} (F) *	$ au_{ ext{PE}}$ (s) *	f [*] _{PE} (Hz) *	$R_{CE}(\Omega)$	Q CPE,CE	$\boldsymbol{\beta}_{CPE,CE}$	C _{CE} (F) *	$ au_{ ext{CE}}$ (s) *	f [*] _{CE} (Hz) *	$R_{\rm D}(\Omega)$	$ au_{ m D}({ m s})$	f [*] _D (Hz) *	$R_{\text{TOT}}(\Omega)$
P1		11.360	12.250	3.824E-04	0.986	3.535E-04	4.330E-03	36.75	3.321	1.679E-04	0.646	2.765E-06	9.182E-06	173 <mark>33</mark>	6.456	1.765	9.017E-02	33.39
P2		9.308	10.450	4.037E-04	0.993	3.877E-04	4.051E-03	39.29	2.355	<mark>5.39</mark> 8E-05	0.784	4.591E-06	1.081E-05	14720	6.744	1.788	8.901E-02	28.86
P3		12.940	12.720	4.019E-04	0.971	3.437E-04	4.372E-03	36.40	3.226	<mark>5.702</mark> E-05	0.711	<mark>1.72</mark> 4E-06	5.561E-06	28619	6.155	1.466	1.086E-01	35.04
P4		13.850	13.260	3.993E-04	0.997	3.926E-04	5.206E-03	30.57	4.895	1.645E-04	0.559	<mark>5</mark> .894E-07	2.885E-06	55164	7.238	1.713	9.291E-02	39.24
P5		8.604	13.030	4.418E-04	0.965	3.666E-04	4.776E-03	33.32	2.025	<mark>3.5</mark> 64E-05	0.824	4.659E-06	9.434E-06	168 <mark>7</mark> 0	6.614	1.628	9.776E-02	30.27
ave		11.2	12.3	4.058E-04	0.982	3.688E-04	4.547E-03	35.3	3.16	9.581E-05	0.705	2.866E-06	7.575E-06	26541	6.64	1.67	9.568E-02	33.4
std		2.3	1.1	2.182E-05	0.014	2.115E-05	4.501E-04	3.4	1.12	6.480E-05	0.107	1.781E-06	3.262E-06	16894	0.40	0.13	7.950E-03	4.1
std/ave		20.1 %	9.1 %	5.4 %	o 1.4 %	5.7 %	9.9 %	9.6 %	35.2 %	67.6 %	5 15.1 %	62.2 %	43.1 %	63.7 %	6.0 %	7.8 %	8.3 %	12.3 %
sem		1.0	0.5	9.756E-06	0.006	9.460E-06	2.013E-04	1.5	0.50	2.898E-05	0.048	7.965E-07	1.459E-06	7555	0.18	0.06	3.555E-03	1.8
95% CI		2.8	1.4	2.709E-05	0.017	2.627E-05	5.589E-04	4.2	1.38	8.045E-05	0.132	2.211E-06	4.051E-06	20977	0.50	0.16	9.871E-03	5.1
Reference	3	$R_{s}(\Omega)$	$R_{PE}(\Omega)$	Q CPE, PE	$m{eta}_{CPE,PE}$	C _{PE} (F) *	au _{PE} (s) *	f [*] _{PE} (Hz) *	$R_{CE}(\Omega)$	Q CPE, CE	$m{eta}_{CPE,CE}$	C _{CE} (F) *	$ au_{ ext{CE}}$ (s) *	f_{CE}^{*} (Hz) *	$R_{\rm D}(\Omega)$	$ au_{ m D}({ m s})$	f [*] _D (Hz) *	$R_{\text{TOT}}(\Omega)$
R1		7.640	13.140	4.108E-04	0.977	3.633E-04	4.774E-03	33.34	3.257	7.607E-05	0.750	4.758E-06	1.550E-05	10 <mark>269</mark>	6.360	1.614	9.861E-02	30.40
R3		13.330	12.290	3.739E-04	1.008	3.902E-04	4.796E-03	33.19	4.364	1.758E-04	0.619	<mark>2.107</mark> E-06	9.196E-06	173 <mark>07</mark>	6.422	1.492	1.067E-01	36.41
R4		11.750	12.140	3.694E-04	0.985	3.407E-04	4.136E-03	38.48	4.205	1.426E-04	0.640	<mark>2.215</mark> E-06	9.313E-06	170 <mark>89</mark>	6.025	1.517	1.049E-01	34.12
ave		10.9	12.5	3.847E-04	0.990	3.647E-04	4.568E-03	35.0	3.9	1.315E-04	0.670	3.027E-06	1.134E-05	14888	6.27	1.54	1.034E-01	33.6
std		2.9	0.5	2.271E-05	0.016	2.482E-05	3.750E-04	3.0	0.6	5.079E-05	0.070	1.501E-06	3.605E-06	4002	0.21	0.06	4.240E-03	3.0
std/ave		26.9 %	4.3 %	5.9 %	1.6 %	6.8 %	8.2 %	8.6 %	15.2 %	38.6 %	10.5 %	49.6 %	31.8 %	26.9 %	3.4 %	4.2 %	4.1 %	9.0 %
sem		1.7	0.3	1.311E-05	0.009	1.433E-05	2.165E-04	1.7	0.3	2.933E-05	0.041	8.664E-07	2.081E-06	2310	0.12	0.04	2.448E-03	1.8
95% CI		7.3	1.3	5.641E-05	0.040	6.165E-05	9.315E-04	7.5	1.5	1.262E-04	0.175	3.728E-06	8.956E-06	9941	0.53	0.16	1.053E-02	7.5

Table 4. Difference in the initial EIS characteristics

* Quantities marked with "*" are calculated from the unmarked values in the previous columns. The unmarked values were obtained by fitting an equivalent circuit model to the measured EIS data.

Comparison of two groups																		
		SERIES R			PHOTOELE	CTRODE				C	OUNTER EL	ECTRODE				DIFFUSION		TOTAL R
	N	$R_{\rm S}(\Omega)$	$R_{\rm PE}(\Omega)$	Q _{CPE,PE} (·10 ⁻³)	$\boldsymbol{\beta}_{CPE,PE}$	C _{PE} (mF) *	$ au_{\rm PE}$ (ms) *	f [*] _{PE} (Hz) *	$R_{CE}(\Omega)$	Q _{CPE,CE} (·10 ⁻³)	$\boldsymbol{\beta}_{CPE,CE}$	С _{СЕ} (µF) *	τ _{CE} (μs) *	f_{CE}^{*} (kHz) *	$R_{\rm D}(\Omega)$	$ au_{ m D}({ m s})$	f [*] _D (mHz) *	$R_{\text{TOT}}(\Omega)$
Initial data																		
Printed	5	11.2 ± 2.3	12.3 ± 1.1	0.41 ± 0.02	0.98 ± 0.01	0.37 ± 0.02	4.5 ± 0.5	35 ± 3	3.16 ± 1.12	0.1 ± 0.06	0.7 ± 0.11	2.9 ± 1.8	7.6 ± 3.3	27 ± 17	6.6 ± 0.4	1.67 ± 0.13	96 ± 8	33 ± 4
std/ave		<u>20%</u>	9%	5%	1%	6%	10%	10%	<u>35%</u>	<u>68%</u>	<u>15%</u>	<u>62%</u>	43%	<u>64%</u>	6%	8%	8%	<u>12%</u>
Reference	3	10.9 ± 2.9	12.5 ± 0.5	0.38 ± 0.02	0.99 ± 0.02	0.36 ± 0.02	4.6 ± 0.4	35 ± 3	3.94 ± 0.6	0.13 ± 0.05	0.67 ± 0.07	3 ± 1.5	11.3 ± 3.6	15 ± 4	6.3 ± 0.2	1.54 ± 0.06	103 ± 4	34 ± 3
std/ave		<u>27%</u>	4%	6%	2%	7%	8%	9%	<u>15%</u>	<u>39%</u>	<u>10%</u>	<u>50%</u>	<u>32%</u>	<u>27%</u>	3%	4%	4%	9%
Difference		2.8 %	-1.4 %	5.5 %	-0.8 %	1.1 %	-0.5 %	0.8 %	-19.7 %	<u>-27.1 %</u>	5.3 %	-5.3 %	-33.2 %	78.3 %	5.9 %	8.5 %	-7.5 %	-0.8 %
p-value		0.886	0.769	0.263	0.522	0.824	0.946	0.914	0.247	0.424	0.595	0.896	0.214	0.204	0.137	0.108	0.124	0.916

* Quantities marked with "*" are calculated from the unmarked values in the previous columns. The unmarked values were obtained by fitting an equivalent circuit model to the measured EIS data.

Notes

Rs and all CE parameters have high relative standard deviations in both type of cells. This means that the experimental accuracy of these parameters is somewhat limited, limiting also the comparison between the two types of cells with respect to these parameters. For example st/Jave is 35% and 15% for Rce in printed and reference cells respectively. However, in this study the PE performance is a more relevant subject for comparison. Moreover, the Rce is so low that the large variation in its value is practically insignificant from the point of view of device performance as a whole. None of the EIS parameters show statistically significant differences between the two types of cells. For example for the PE parameters this means that any differences that might exist are smaller than the relative standard deviations, which were less than 10 % in all cases.

1000h	N	SERIES R		Р	HOTOELE	CTRODE				со	UNTER EI	ECTROD	E			DIFFUSIO	N	TOTAL R
Printed	5	$R_{\rm s}(\Omega)$	$R_{\rm PE}(\Omega)$	Q CPE, PE	$\beta_{\text{CPE,PE}}$	C _{PE} (F) *	$ au_{ ext{PE}}$ (s) *	f [*] _{PE} (Hz) *	$R_{CE}(\Omega)$	Q CPE,CE	$\beta_{\text{CPE,CE}}$	C _{CE} (F) *	au _{CE} (s) *	f [*] _{CE} (Hz) *	$R_{\rm D}(\Omega)$	$\tau_{D}(s)$	f [*] _D (Hz) *	$R_{\text{TOT}}(\Omega)$
P1		9.553	11.860	4.228E-04	0.992	4.056E-04	4.811E-03	33.08	2.895	6.30 <mark>5E-05</mark>	0.730	<mark>2.632</mark> E-06	7.619E-06	20889	6.668	1.967	8.091E-02	30.98
P2		7.130	11.720	5.096E-04	0.977	4.529E-04	5.308E-03	29.99	1.821	<mark>5.47</mark> 4E-05	0.793	4.923E-06	8.965E-06	17753	5.718	1.568	1.015E-01	26.39
P3		9.636	13.010	4.472E-04	0.980	4.035E-04	5.250E-03	30.32	2.397	5.000E-05	0.736	<mark>1.96</mark> 4E-06	4.707E-06	33812	6.355	1.650	9.646E-02	31.40
P4		9.748	11.410	4.671E-04	0.998	4.618E-04	5.269E-03	30.21	2.474	2.188E-04	0.624	<mark>2.36</mark> 0E-06	5.838E-06	27263	6.705	1.738	9.157E-02	30.34
P5		7.220	11.090	4.562E-04	0.988	4.287E-04	4.754E-03	33.48	2.125	1.257E-04	0.678	<mark>2.505</mark> E-06	5.322E-06	29902	6.420	1.664	9.565E-02	26.86
ave		8.7	11.8	4.606E-04	0.987	4.305E-04	5.078E-03	31.4	2.34	1.024E-04	0.712	2.877E-06	6.490E-06	25924	6.37	1.72	9.322E-02	29.2
std		1.4	0.7	3.191E-05	0.008	2.660E-05	2.715E-04	1.7	0.40	7.185E-05	0.064	1.171E-06	1.758E-06	6557	0.40	0.15	7.732E-03	2.4
std/ave		15.7 %	6.2 %	6.9 %	0.8 %	6.2 %	5.3 %	5.5 %	17.1 %	70.1 %	9.0 %	40.7 %	27.1 %	25.3 %	6.2 %	8.9 %	8.3 %	8.2 %
sem		0.6	0.3	1.427E-05	0.004	1.190E-05	1.214E-04	0.8	0.18	3.213E-05	0.029	5.238E-07	7.864E-07	2932	0.18	0.07	3.458E-03	1.1
95% CI		1.7	0.9	3.962E-05	0.010	3.303E-05	3.371E-04	2.1	0.50	8.922E-05	0.079	1.454E-06	2.183E-06	8141	0.49	0.19	9.601E-03	3.0
Reference	3	$R_{\rm s}(\Omega)$	$R_{\rm PE}(\Omega)$	Q CPE, PE	$\boldsymbol{\beta}_{CPE,PE}$	C PE (F) *	$ au_{ ext{PE}}$ (s) *	f [*] _{PE} (Hz) *	$R_{CE}(\Omega)$	Q CPE,CE	$\boldsymbol{\beta}_{CPE,CE}$	C CE (F) *	au _{CE} (s) *	<i>f</i> [*] _{CE} (Hz) *	$R_{\rm D}(\Omega)$	$ au_{D}(s)$	f [*] _D (Hz) *	$R_{\text{TOT}}(\Omega)$
R1		7.886	13.750	4.777E-04	0.971	4.109E-04	5.650E-03	28.17	2.477	1.805E-05	0.901	6.021E-06	1.491E-05	10671	6.577	2.013	7.906E-02	30.69
R3		9.094	14.410	3.815E-04	0.986	3.534E-04	5.093E-03	31.25	3.563	<mark>6.52</mark> 0E-05	0.748	<mark>3.899E-</mark> 06	1.389E-05	11457	6.529	1.540	1.033E-01	33.60
R4		9.327	12.830	4.081E-04	0.983	3.726E-04	4.780E-03	33.30	3.418	6.38 <mark>4E-05</mark>	0.732	<mark>2.899</mark> E-06	9.910E-06	16059	6.006	1.670	9.530E-02	31.58
ave		8.8	13.7	4.224E-04	0.980	3.790E-04	5.174E-03	30.9	3.2	4.903E-05	0.794	4.273E-06	1.291E-05	12729	6.37	, 1.74	9.257E-02	32.0
std		0.8	0.8	4.970E-05	0.008	2.926E-05	4.406E-04	2.6	0.6	2.684E-05	0.093	1.594E-06	2.644E-06	2911	0.32	2 0.24	1.237E-02	1.5
std/ave		8.8 %	5.8 %	11.8 %	0.8 %	7.7 %	8.5 %	8.3 %	18.7 %	54.7 %	11.8 %	37.3 %	20.5 %	22.9 %	5.0 %	<mark>ه 14.0 %</mark>	13.4 %	4.7 %
sem		0.4	0.5	2.869E-05	0.005	1.689E-05	2.544E-04	1.5	0.3	1.549E-05	0.054	9.204E-07	1.526E-06	1680	0.18	0.14	7.142E-03	0.9
95% CI		1.9	2.0	1.235E-04	0.019	7.268E-05	1.094E-03	6.4	1.5	6.667E-05	0.232	3.960E-06	6.567E-06	7230	0.79	0.61	3.073E-02	3.7

Table 5. Difference in the final (1000 h aged) EIS characteristics

* Quantities marked with "*" are calculated from the values unmarked values in the previous columns. The unmarked values were obtained by fitting an equivalent circuit model to the measured EIS data.

Comparison of two groups																		
		SERIES R			PHOTOELE	CTRODE				c	OUNTER EL	ECTRODE			DIFFUSION TOTA			TOTAL R
	N	$R_{\rm S}(\Omega)$	$R_{\rm PE}(\Omega)$	Q _{CPE,PE} (·10 ⁻³)	$m{eta}_{CPE,PE}$	C _{PE} (mF) *	$ au_{ m PE}$ (ms) *	f [*] _{PE} (Hz) *	$R_{CE}(\Omega)$	$Q_{CPE,CE}$ (-10 ⁻³)	$m{eta}_{CPE,CE}$	С _{СЕ} (µF) *	$ au_{ ext{CE}}$ (µs) *	f_{CE}^{*} (kHz) *	$R_{D}(\Omega)$	$ au_{ m D}$ (s)	f [*] _D (mHz) *	$R_{\text{TOT}}(\Omega)$
<u>1000h</u>																		
Printed	5	8.7 ± 1.4	11.8 ± 0.7	0.46 ± 0.03	0.99 ± 0.01	0.43 ± 0.03	5.1 ± 0.3	31 ± 2	2.34 ± 0.4	0.1 ± 0.07	0.71 ± 0.06	2.9 ± 1.2	6.5 ± 1.8	26 ± 7	6.4 ± 0.4	1.72 ± 0.15	93 ± 8	29 ± 2
std/ave		16%	6%	7%	1%	6%	5%	5%	17%	70%	9%	<u>41%</u>	27%	25%	6%	9%	8%	8%
Reference	3	8.8 ± 0.8	13.7 ± 0.8	0.42 ± 0.05	0.98 ± 0.01	0.38 ± 0.03	5.2 ± 0.4	31 ± 3	3.15 ± 0.59	0.05 ± 0.03	0.79 ± 0.09	4.3 ± 1.6	12.9 ± 2.6	13 ± 3	6.4 ± 0.3	1.74 ± 0.24	93 ± 12	32 ± 1
std/ave		9%	6%	<u>12%</u>	1%	8%	9%	8%	<u>19%</u>	55%	<u>12%</u>	37%	20%	23%	5%	<u>14%</u>	<u>13%</u>	5%
Difference		-1.3 %	-13.5 %	9.0 %	0.8 %	13.6 %	-1.9 %	1.6 %	<u>-25.7 %</u>	<u>108.9 %</u>	-10.3 %	-32.7 %	-49.7 %	103.7 %	0.0 %	-1.4 %	0.7 %	-8.7 %
<i>p</i> -value		0.887	0.030	0.319	0.263	0.067	0.756	0.781	0.122	0.189	0.270	0.271	0.032	0.008	0.992	0.890	0.940	0.091

* Quantities marked with "*" are calculated from the values unmarked values in the previous columns. The unmarked values were obtained by fitting an equivalent circuit model to the measured EIS data.

Notes

Statistically significant difference is found only for the printed cells vs. reference cells: Rpe (-13.5%) and CE time constant (-50%). The difference in Rpe is modest though. Since also Voc showed statistically significant difference in this case (-5.3%) definite analysis for the difference in Rpe is beyond the scope of this data. Considering the high relative standard deviations in the CE parameters, the 50 % lower CE time constant in printed cells, could well be a false positive. We can thus conclude that the printed cells do not markedly differ from the reference cells after the aging test, in terms of their EIS characteristics measured at open circuit condition under one Sun equivalent illumination.

Table 6. EIS aging behavior of each cell type

Comparison of each group before and after aging

			SERIES R	RIES R PHOTOELECTRODE						COUNTER ELECTRODE						DIFFUSION		TOTAL R	
		N	$R_{\rm s}(\Omega)$	$R_{PE}(\Omega)$	Q _{CPE,PE} (·10 ⁻³)	$\beta_{\text{CPE,PE}}$	C PE (mF) *	$\tau_{\rm PE}$ (ms) *	f [*] _{PE} (Hz) *	$R_{CE}(\Omega)$	Q _{CPE,CE} (·10 ⁻³)	$\boldsymbol{\beta}_{CPE,CE}$	С _{СЕ} (µF) *	τ _{ce} (μs) *	f [*] _{CE} (kHz) *	$R_{D}(\Omega)$	τ _D (s)	f [*] _D (mHz) *	R _{TOT} (Ω)
Printed																			
Initial		5	11.2 ± 2.3	12.3 ± 1.1	0.41 ± 0.02	0.98 ± 0.01	0.37 ± 0.02	4.5 ± 0.5	35 ± 3	3.2 ± 1.1	0.1 ± 0.06	0.7 ± 0.11	2.9 ± 1.8	7.6 ± 3.3	27 ± 17	6.6 ± 0.4	1.67 ± 0.13	96 ± 8	33 ± 4
st	td/ave		20 %	9 %	5 %	1 %	6 %	10 %	10 %	35 %	68 %	<u>15 %</u>	62 %	43 %	64 %	6 %	8 %	8 %	<u>12 %</u>
1000h		5	8.7 ± 1.4	11.8 ± 0.7	0.46 ± 0.03	0.99 ± 0.01	0.43 ± 0.03	5.1 ± 0.3	31 ± 2	2.3 ± 0.4	0.1 ± 0.07	0.71 ± 0.06	2.9 ± 1.2	6.5 ± 1.8	26 ± 7	6.4 ± 0.4	1.72 ± 0.15	93 ± 8	29 ± 2
st	td/ave		<u>16 %</u>	6 %	7 %	1 %	6 %	5 %	5 %	17 %	70 %	9 %	<u>41 %</u>	27 %	25 %	6 %	9 %	8 %	8 %
Difference			<u>-22.8 %</u>	-4.2 %	13.5 %	0.5 %	16.7 %	11.7 %	-10.9 %	<u>-26.0 %</u>	6.9 %	1.1 %	0.4 %	-14.3 %	-2.3 %	-4.0 %	2.7 %	-2.6 %	-12.5 %
p-	value		<u>0.007</u>	0.445	<u>0.023</u>	0.467	<u>0.000</u>	0.093	0.096	0.127	0.851	0.865	0.987	0.398	0.934	0.317	0.581	0.594	<u>0.026</u>
Reference																			
Initial		3	10.9 ± 2.9	12.5 ± 0.5	0.38 ± 0.02	0.99 ± 0.02	0.36 ± 0.02	4.6 ± 0.4	35 ± 3	3.9 ± 0.6	0.13 ± 0.05	0.67 ± 0.07	3 ± 1.5	11.3 ± 3.6	15 ± 4	6.3 ± 0.2	1.54 ± 0.06	103 ± 4	34 ± 3
st	td/ave		27 %	4 %	6 %	2 %	7 %	8 %	9 %	<u>15 %</u>	39 %	10 %	50 %	32 %	27 %	3 %	4 %	4 %	9 %
1000h		3	8.8 ± 0.8	13.7 ± 0.8	0.42 ± 0.05	0.98 ± 0.01	0.38 ± 0.03	5.2 ± 0.4	31 ± 3	3.2 ± 0.6	0.05 ± 0.03	0.79 ± 0.09	4.3 ± 1.6	12.9 ± 2.6	13 ± 3	6.4 ± 0.3	1.74 ± 0.24	93 ± 12	32 ± 1
st	td/ave		9 %	6 %	<u>12 %</u>	1 %	8 %	9 %	8 %	19 %	<u>55 %</u>	12 %	37 %	20 %	23 %	5 %	<u>14 %</u>	<u>13 %</u>	5 %
Difference			-19.6 %	9.1 %	9.8 %	-1.0 %	3.9 %	13.3 %	-11.7 %	<u>-20.0 %</u>	<u>-62.7 %</u>	18.5 %	<u>41.2 %</u>	13.8 %	-14.5 %	1.6 %	13.0 %	-10.5 %	-5.0 %
p-	value		0.242	0.146	0.159	0.238	0.638	0.069	0.063	0.000	<u>0.033</u>	<u>0.020</u>	0.060	0.430	0.372	0.274	0.194	0.149	0.232

* Quantities marked with "*" are calculated from the values unmarked values in the previous columns. The unmarked values were obtained by fitting an equivalent circuit model to the measured EIS data.

Notes

High relative standard deviations are observed for Rs and the CE paramaters. Statistically significant difference of the EIS parameters after aging compared to their initial values is found only for Cpe (+17%) and Rtot (-12.5%) of the printed cells and Rce (-20%) of the reference cells. Note that no change in the Rpe was observed, which means that any changes that might have occured to the PE parameters are smaller then the relative standard deviations, which were less than 10 % for all PE parameters. This stability of the EIS characteristics is well in line with the stability of the IV characteristics, showing that neither the printed nor the reference cells showed any significant degradation of their electrochemical characteristics. Quite the contrary, the only (abovementioned) statistically significant changes in the EIS parameters were all performance **improvements**.

About statistical analysis

Criteria for practically signifigant difference and acceptable sample-to-sample variation (relative standard deviation, std/ave)

Criteria **	$R_{s}(\Omega)$	$R_{\rm PE}(\Omega)$	Q _{CPE,PE}	$oldsymbol{eta}_{CPE,PE}$	C _{PE} (F) *	$ au_{ ext{PE}}$ (s) *	f [*] _{PE} (Hz) *	$R_{CE}(\Omega)$	Q CPE,CE	$\boldsymbol{\beta}_{CPE,CE}$	C _{CE} (F) *	$ au_{ ext{CE}}$ (s) *	f^{*}_{CE} (Hz) *	$R_{\rm D}(\Omega)$	$ au_{D}(s)$	f [*] _D (Hz) *	$R_{\text{TOT}}(\Omega)$
Acceptable std/ave.	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %	10 %
Practically signif. difference	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %	20 %

* Quantities marked with *** are calculated from the values unmarked values in the previous columns. The unmarked values were obtained by fitting an equivalent circuit model to the measured EIS data.

** These criteria are subjectively chosen by the researcher to set a criteria for satisfactory repeatability of one type of sample and practically relevant difference between different type of samples

Statistical testing

Statistical confidence level	95 %
α	0.05

The p-value is calculated with two-tailed paired t-test

Underlined in the comparison table are:

- Relative standard deviations (std/ave) larger than or equal to the acceptable value (also highlihted with pink in in the data table)

- Differences larger than or equal to the practical signifigance level

- p -values lower than or equal to α (e.g. 0.05 for 5 % signifigance)

Nomenclature

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: Printed vs reference, or Batch 2 vs Batch 1.

	N				
Initial	5	J _{SC} (mA/cm ²)	V _{oc} (V)	FF	η (%)
P1		10.7	0.711	0.775	6.15
P2		11.8	0.674	0.759	6.38
P3		11.6	0.689	0.751	6.32
P4		11.9	0.684	0.747	6.38
P5		11.6	0.691	0.761	6.39
ave		11.5	0.690	0.759	6.32
std		0.5	0.013	0.011	0.10
std/ave		4.3 %	1.9 %	1.4 %	1.6 %
sem		0.2	0.006	0.005	0.05
95% CI		0.6	0.017	0.013	0.13
170 hours	5	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)
P1		11.0	0.697	0.785	6.25
P2		12.9	0.633	0.725	6.14
P3		11.9	0.679	0.743	6.14
P4		12.5	0.661	0.734	6.21
P5		11.7	0.684	0.758	6.26
ave		12.0	0.671	0.749	6.20
std		0.7	0.025	0.024	0.06
std/ave		<u>5.9 %</u>	3.7 %	3.1 %	0.9 %
sem		0.3	0.011	0.011	0.03
95% CI		0.9	0.031	0.029	0.07
	Э	J _{SC} (mA/cm)		<i>FF</i>	η (%)
P1		11.9	0.673	0.782	0.45
P2		12.8	0.625	0.738	6.10
		12.2	0.035	0.731	0.21
F		12.3	0.664	0.742	6.40
ave		12.3	0.652	0.754	6.27
std		0.3	0.019	0.017	0.15
std/ave		2.7 %	2.9 %	2.3 %	2.4 %
sem		0.1	0.008	0.008	0.07
95% CI		0.4	0.023	0.021	0.19
530 hours	5	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)
P1		12.6	0.664	0.774	6.60
P2		14.0	0.621	0.718	6.40
P3		12.8	0.645	0.736	6.20
P4		13.2	0.635	0.733	6.28
P5		13.0	0.655	0.738	6.49
ave		13.1	0.644	0.740	6.39
std		0.5	0.017	0.021	0.16
std/ave		4.2 %	2.6 %	2.8 %	2.5 %
					0.07
Selli		0.2	0.008	0.009	0.07

Statistical analysis of the IV results: aging test at half Sun and 60 C

986 hours	5	J _{sc} (mA/cm²)	V _{oc} (V)	FF	η (%)
P1		12.7	0.637	0.768	6.52
P2		13.2	0.604	0.726	6.11
P3		13.2	0.625	0.721	6.29
P4		13.0	0.614	0.724	6.05
P5		12.4	0.636	0.733	6.06
ave		12.9	0.623	0.734	6.21
std		0.3	0.014	0.019	0.20
std/ave		2.6 %	2.3 %	2.6 %	3.2 %
sem		0.2	0.006	0.009	0.09
95% CI		0.4	0.018	0.024	0.25
1154 hours	5	J _{sc} (mA/cm²)	V _{oc} (V)	FF	η (%)
P1		13.7	0.631	0.710	6.42
P1 P2		13.7 13.6	0.631 0.599	0.710 0.715	6.42 6.17
P1 P2 P3		13.7 13.6 12.7	0.631 0.599 0.620	0.710 0.715 0.729	6.42 6.17 6.01
P1 P2 P3 P4		13.7 13.6 12.7 13.1	0.631 0.599 0.620 0.606	0.710 0.715 0.729 0.717	6.42 6.17 6.01 6.02
P1 P2 P3 P4 P5		13.7 13.6 12.7 13.1 12.9	0.631 0.599 0.620 0.606 0.630	0.710 0.715 0.729 0.717 0.736	6.42 6.17 6.01 6.02 6.25
P1 P2 P3 P4 P5 ave		13.7 13.6 12.7 13.1 12.9 13.2	0.631 0.599 0.620 0.606 0.630 0.617	0.710 0.715 0.729 0.717 0.736 0.721	6.42 6.17 6.01 6.02 6.25 6.17
P1 P2 P3 P4 P5 ave std		13.7 13.6 12.7 13.1 12.9 13.2 0.4	0.631 0.599 0.620 0.606 0.630 0.617 0.014	0.710 0.715 0.729 0.717 0.736 0.721 0.011	6.42 6.17 6.01 6.02 6.25 6.17 0.17
P1 P2 P3 P4 P5 ave std std/ave		13.7 13.6 12.7 13.1 12.9 13.2 0.4 3.1 %	0.631 0.599 0.620 0.606 0.630 0.617 0.014 2.3 %	0.710 0.715 0.729 0.717 0.736 0.721 0.011 0.011	6.42 6.17 6.01 6.02 6.25 6.17 0.17 2.8 %
P1 P2 P3 P4 P5 ave std std/ave sem		13.7 13.6 12.7 13.1 12.9 13.2 0.4 3.1 % 0.2	0.631 0.599 0.620 0.606 0.630 0.617 0.014 2.3 % 0.006	0.710 0.715 0.729 0.717 0.736 0.721 0.011 0.011 0.005	6.42 6.17 6.01 6.02 6.25 6.17 0.17 2.8 % 0.08

Table 7. All aging data and t-test for initial and last data set											
		N	J _{SC} (mA/cm²)	V _{oc} (mV)	FF (%)	η (%)					
Initial		5	11.5 ± 0.5	690 ± 13	76 ± 1	6.3 ± 0.1					
	170 hours	5	12 ± 0.7	671 ± 25	75 ± 2	6.2 ± 0.1					
	386 hours	5	12.4 ± 0.3	652 ± 19	75 ± 2	6.3 ± 0.2					
	530 hours	5	13.1 ± 0.5	644 ± 17	74 ± 2	6.4 ± 0.2					
	986 hours	5	12.9 ± 0.3	623 ± 14	73 ± 2	6.2 ± 0.2					
	1154 hours	5	13.2 ± 0.4	617 ± 14	72 ± 1	6.2 ± 0.2					
	Difference		<u>-0.13</u>	<u>0.12</u>	<u>0.05</u>	0.02					
	<i>p</i> -value		<u>0.01</u>	<u>0.00</u>	<u>0.01</u>	0.25					

Aging behavior of the printed dye cells in the additional 1154 hours at half Sun at 60 °C type (Table 7)

Table 7 shows that the efficiency of the five DSSCs did not degrade at all in the additional aging test carried out at half Sun at 60 °C for 1154 hours: the drop from 6.3 % to 6.2 % is within the standard deviation of the five cells, which was relatively low. Statistically significant decrease of V_{OC} and *FF* was nevertheless observed, however, their effect on the cell efficiency was compensated by a significant increase of J_{SC} during the aging. It therefore seems the photoelectrochemical properties of the photoelectrode changed, however, without affecting the photovoltaic efficiency.

Nomenclature	
N	Number of samples
ave	Average
std	Standard deviation
std/ave, Rel. stdev	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: Printed vs reference, or Batch 2 vs Batch 1.
<i>p</i> -value	For two different groups of samples, the p-value is calculated with two-tailed
	two-sample t-test with unequal variances, whereas for the comparison of same
	before and after certain aging it is calculated with paired t-test.
J _{sc}	Short circuit current density
V _{oc}	Open circuit voltage
FF	Fill factor
η	Efficiency

About statistical analysis in Table 4

Statistical testing

Statistical confidence level	95 %	α:	0.05		
Criteria for practically signific	ant difference	and acceptable	sample-to-sample	e variation (I	rel. stdev)

Criteria	J _{SC} (mA/cm²)	V _{oc} (mV)	FF (%)	η (%)
Practically signif. difference	5 %	same	same	same
Acceptable rel. stdev	5 %	5 %	5 %	5 %

Underlined in the tables are:

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