Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting information –

Origin of thermal induced variation in performance and negative reactance of inorganic $CsPbI_2Br$ perovskite solar cells.

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1. Supporting data

The in-situ measurements were done according to the following temperature profile:

[25°C > 65°C > 105°C > 65°C > ~25°C > 65°C > 105°C > 65°C > ~25°C > 65°C > 105°C > 65°C > ~25°C] Where possible the heating and cooling rate was done at 5°C/min. A dwell time of 10 minutes was allowed after each target temperature is reached before the measurements were taken. For the in-situ IS, the following cycling profile was used.

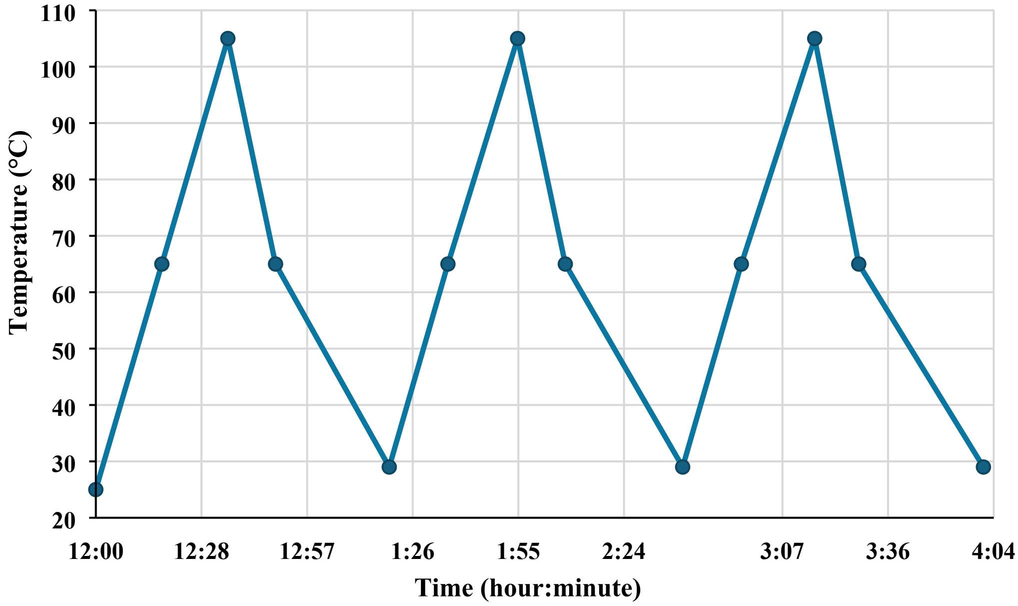

Figure S1 Temperature profile based on time stamp of in-situ IS measurements

Cycling profile

The 105°C high temperature is in line with the maximum temperature used for thermal cycling, according to IEC TS 63126:2020 IEC: Guidelines for qualifying PV modules, components and materials for operation at high temperatures - [4.4 Thermal cycling test (MQT 11, level 2)]. The 63126 version is the modified guideline standard PV testing IEC 61215-2:2016, but for higher temperatures. Usually, for certification, the common max thermal cycling temperature is 85 ± 2°C, with the certification requirement of 200 cycles; the 63126 increases this temperature requirement, setting the cycling temperature to 95 ± 2°C as level 1 and level 2 for max temperatures of 105°C ± 2°C. [1]

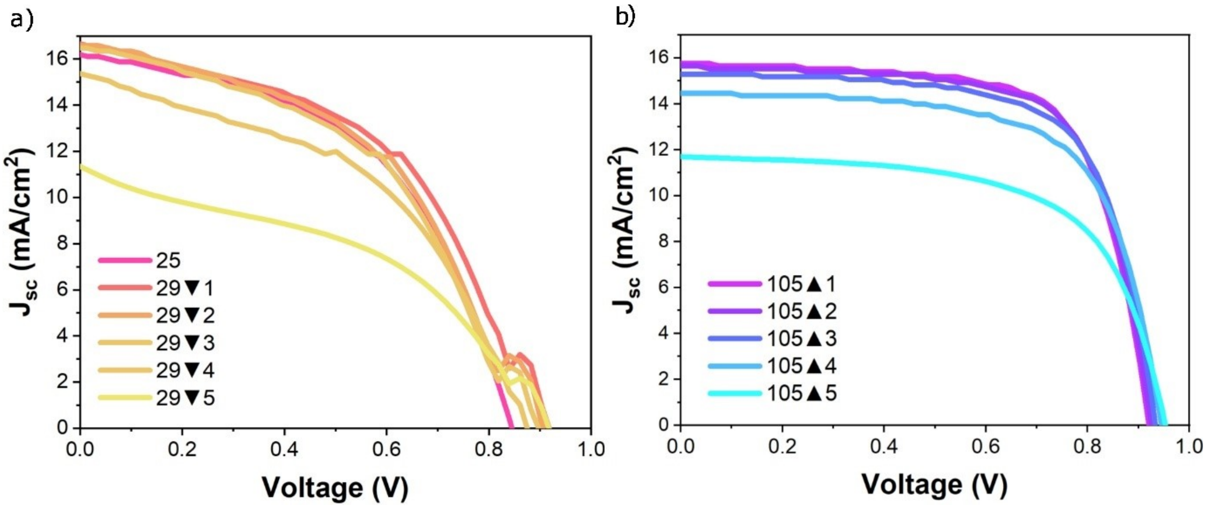

Figure S2 REV scan J-V curve of five thermal cycles of the PSCs, a) at room temperature (~25-29°C) after cooling denote by ▼ and b) at 105°C.

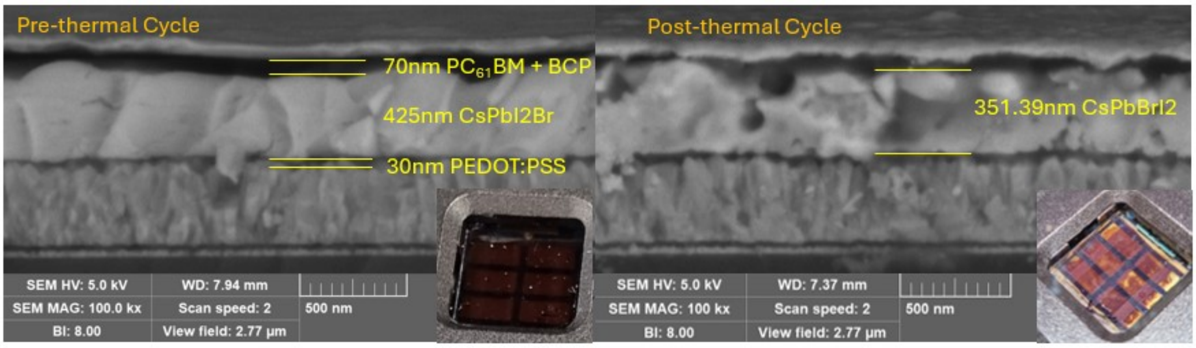

Figure S3 SEM pre and post three thermal cycles

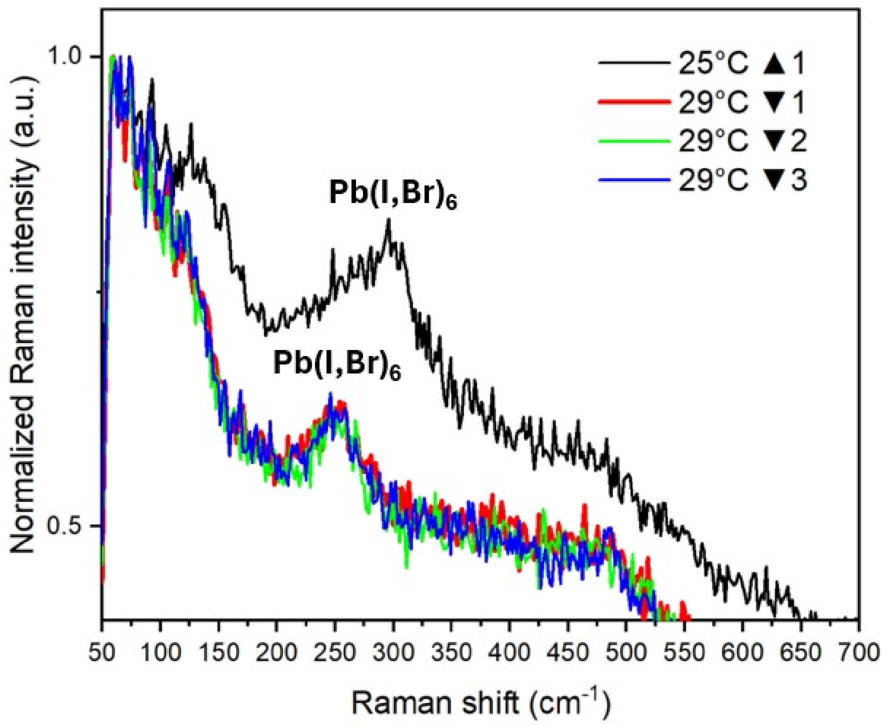

Figure S4 Raman spectroscopy showing vibrational mode 300 cm^{-1}shifing to 250 cm^{-1}post first cycling. Indicating bond shortening and octahedral tilting of $Pb(X)_6$.

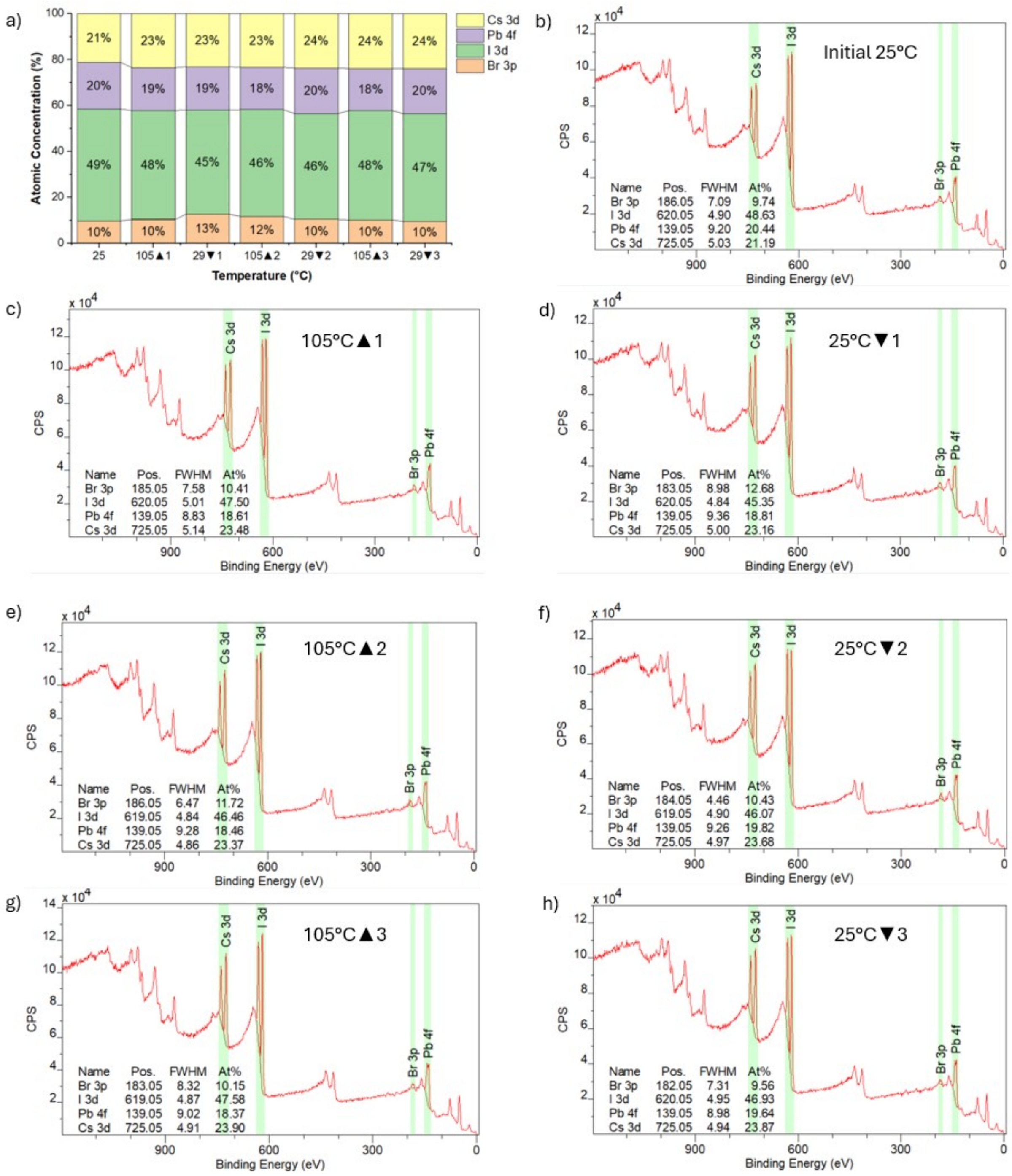

Figure S5 XPS – atomic concentration percentage relative to cesium

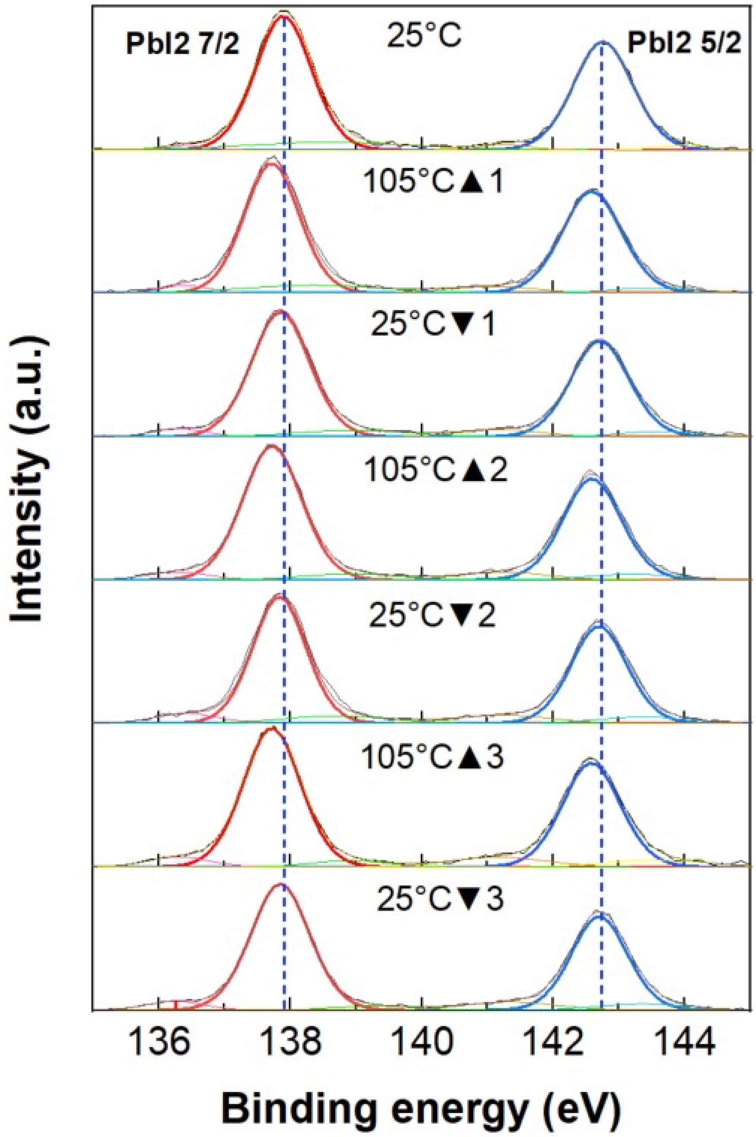

Figure S6 High resolution XPS of Pb4f through three cycles

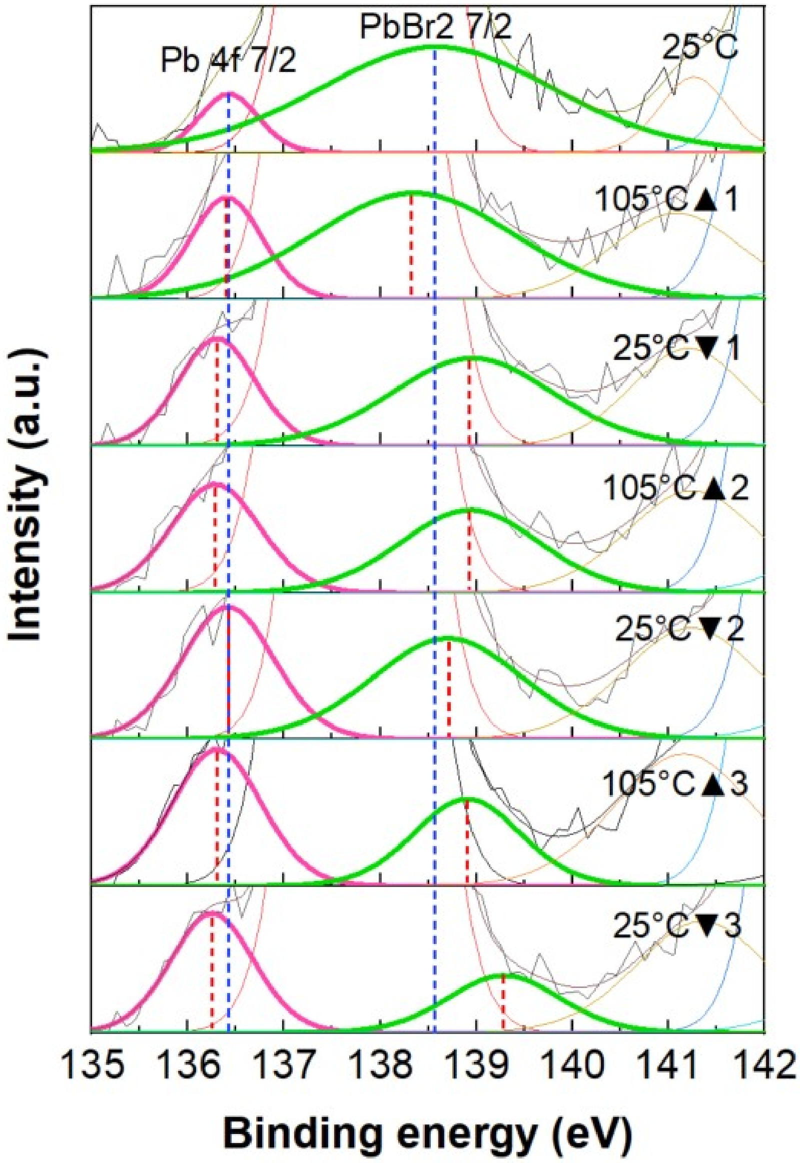

Figure S7 High resolution XPS of Pb4f – Close up on PbBr2 7/2 convolution through three thermal cycles.

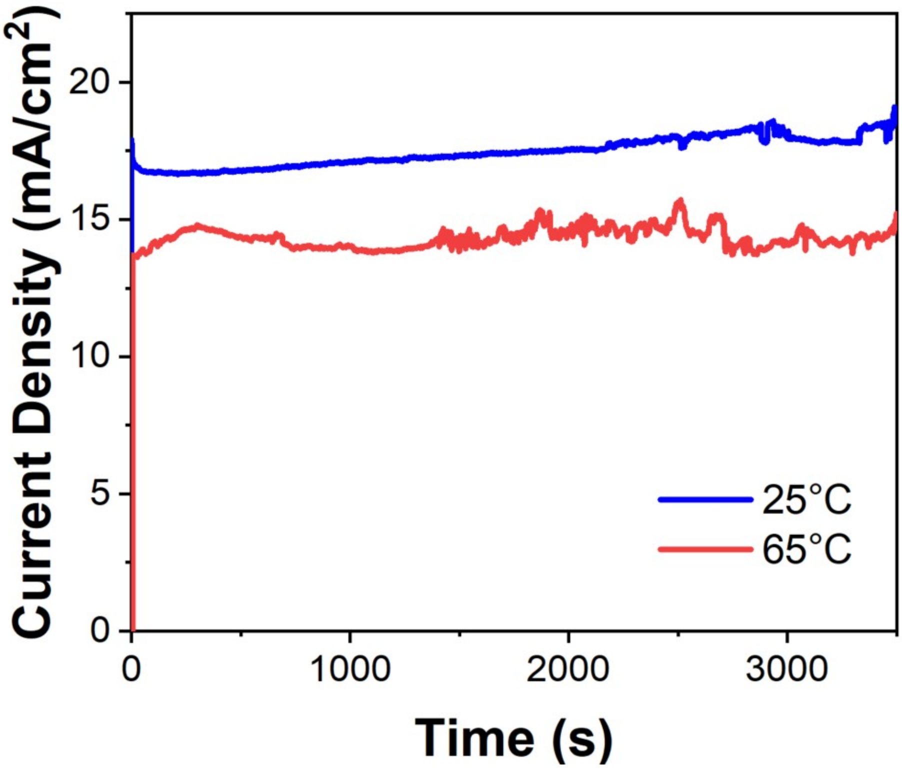

Figure S8 Jsc of the PSCs at MPP test as a function of illumination duration measured at 25^{o}C and 65^{o}C.

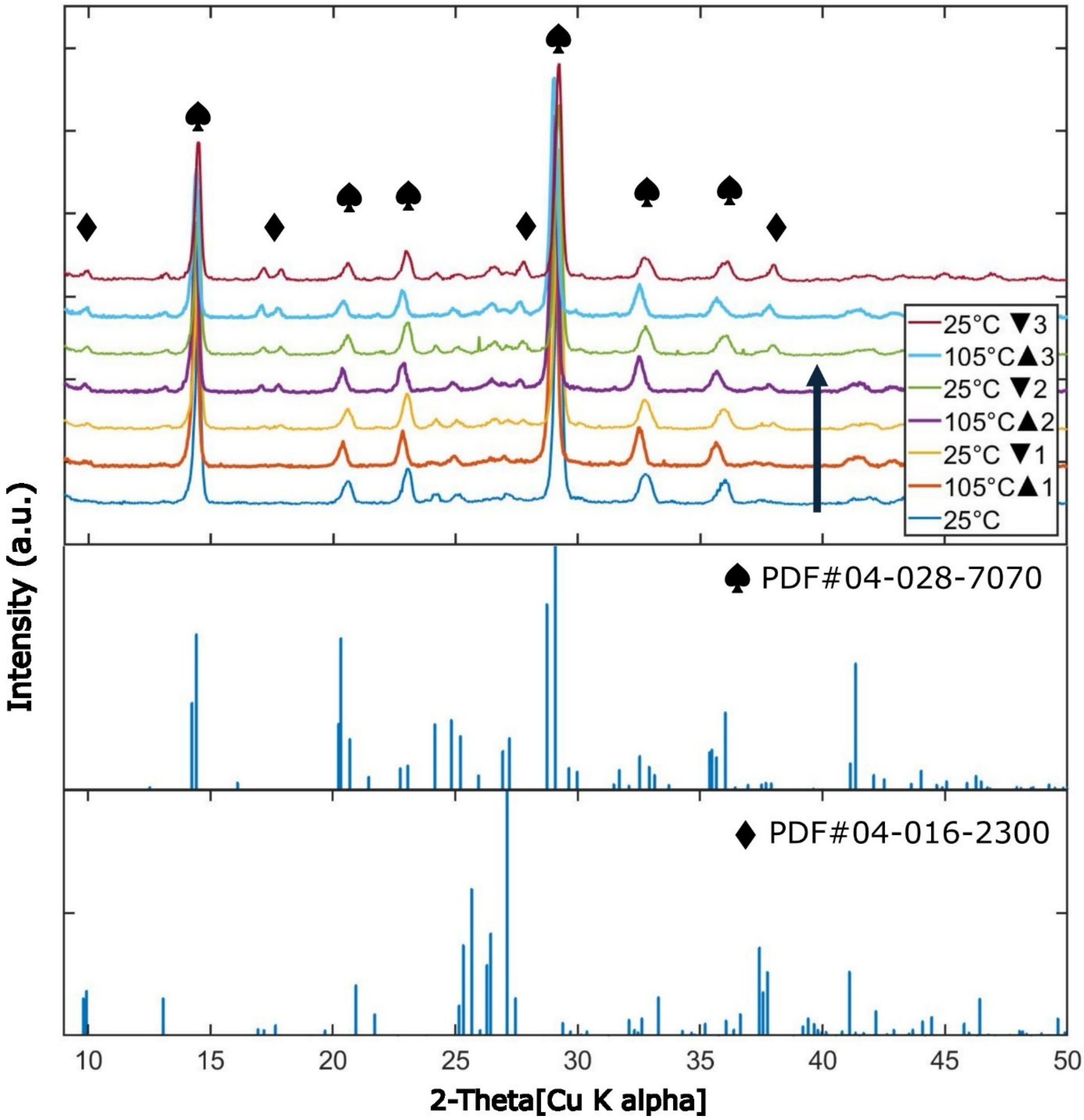

Figure S9 XRD match with Powder Diffraction File (PDF) references. Matching with primary phase (♠) of PDF# 04-028-7070 (Space Group: Pnma, a = 8.77 Å, b = 12.42 Å, c = 8.58 Å) and secondary phase (♦) of PDF# 04-016-2300 (Space Group: Pnma, a = 10.46 Å, b = 4.80 Å, c = 17.78 Å).

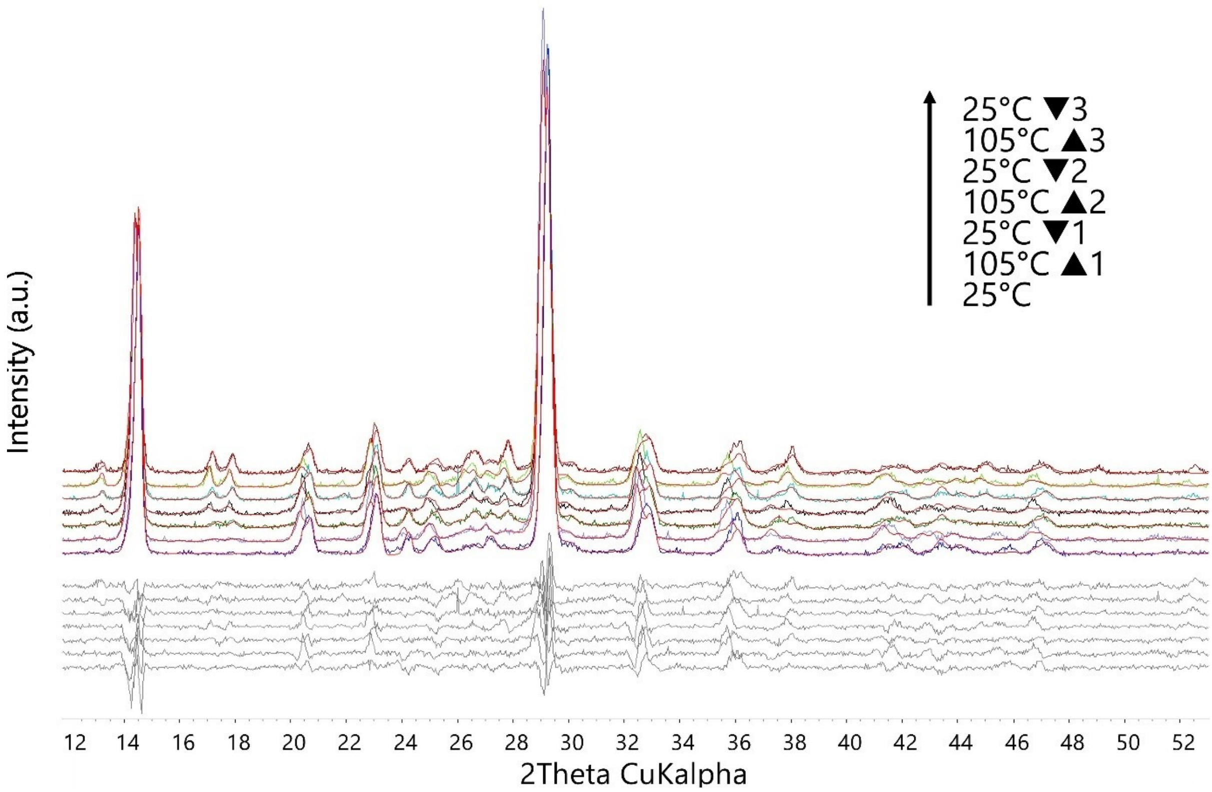

Figure S10 Batch Pawley fitting of XRD spectra for anisotropic analysis

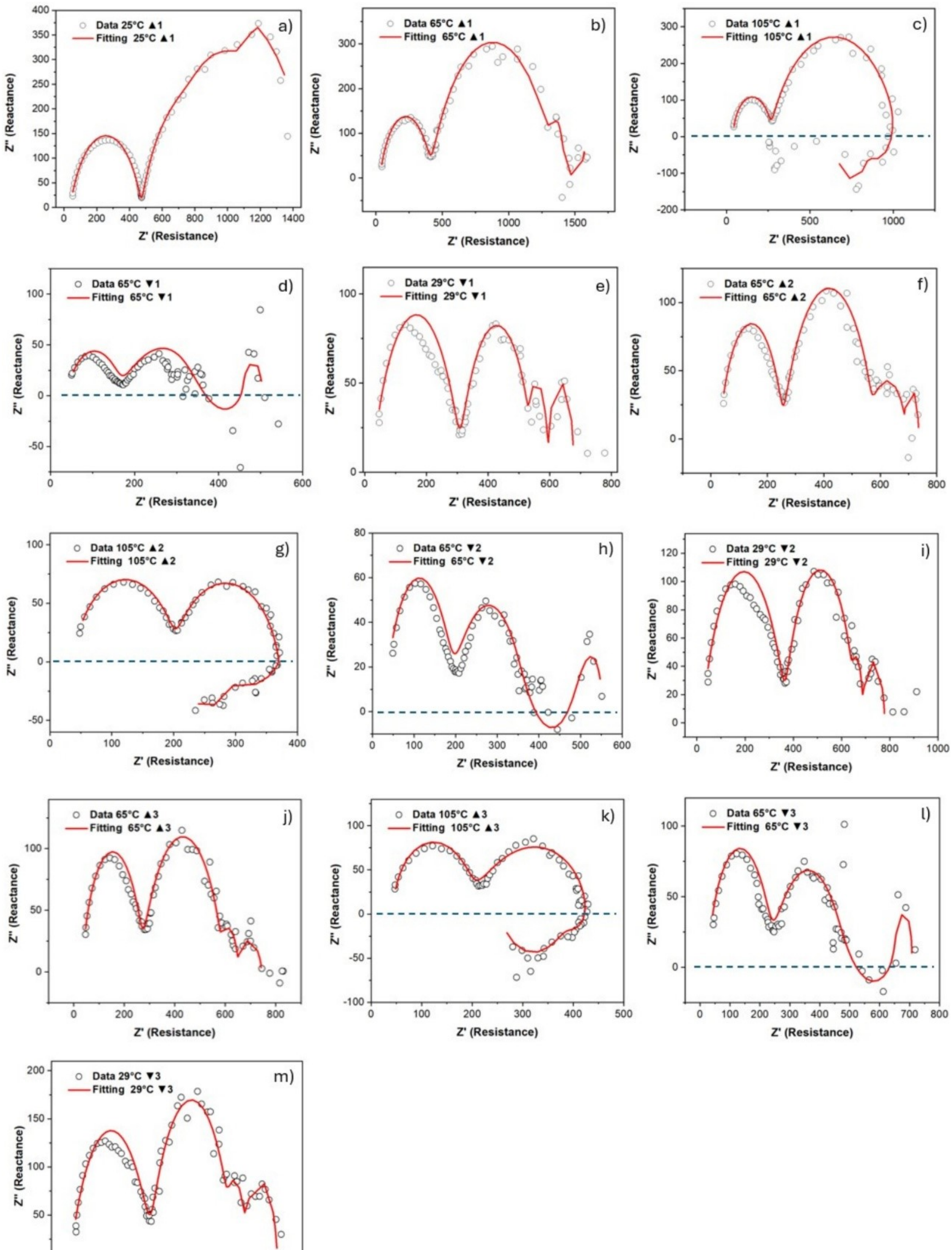

Figure S11 IS measurement during thermal cycling with Zview fitting. Fitting parameters in Table S2

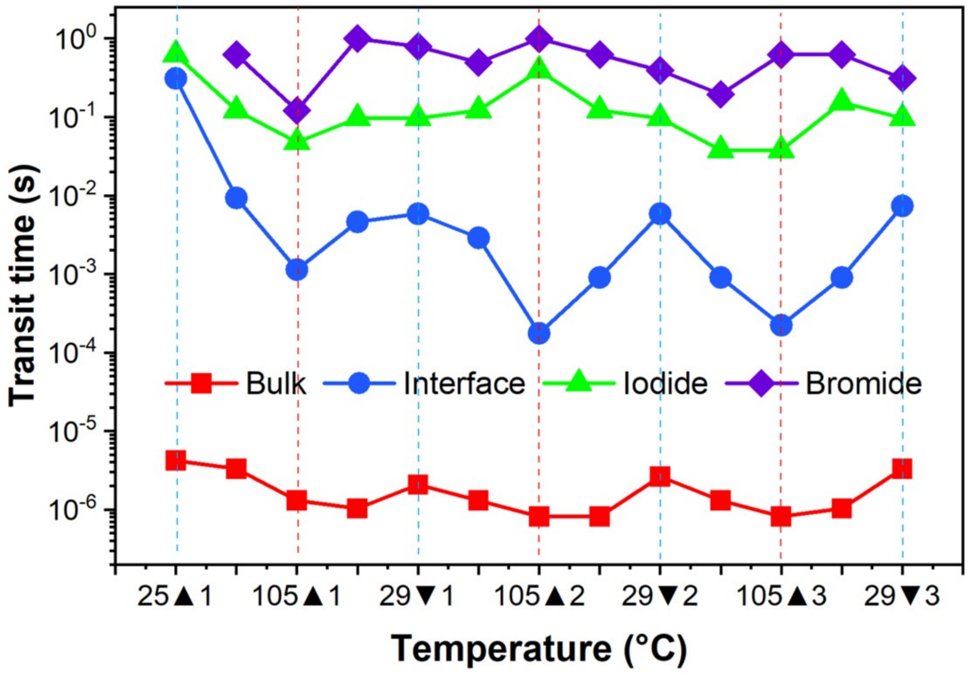

Figure S12 Transit time of each carrier component during thermal cycling

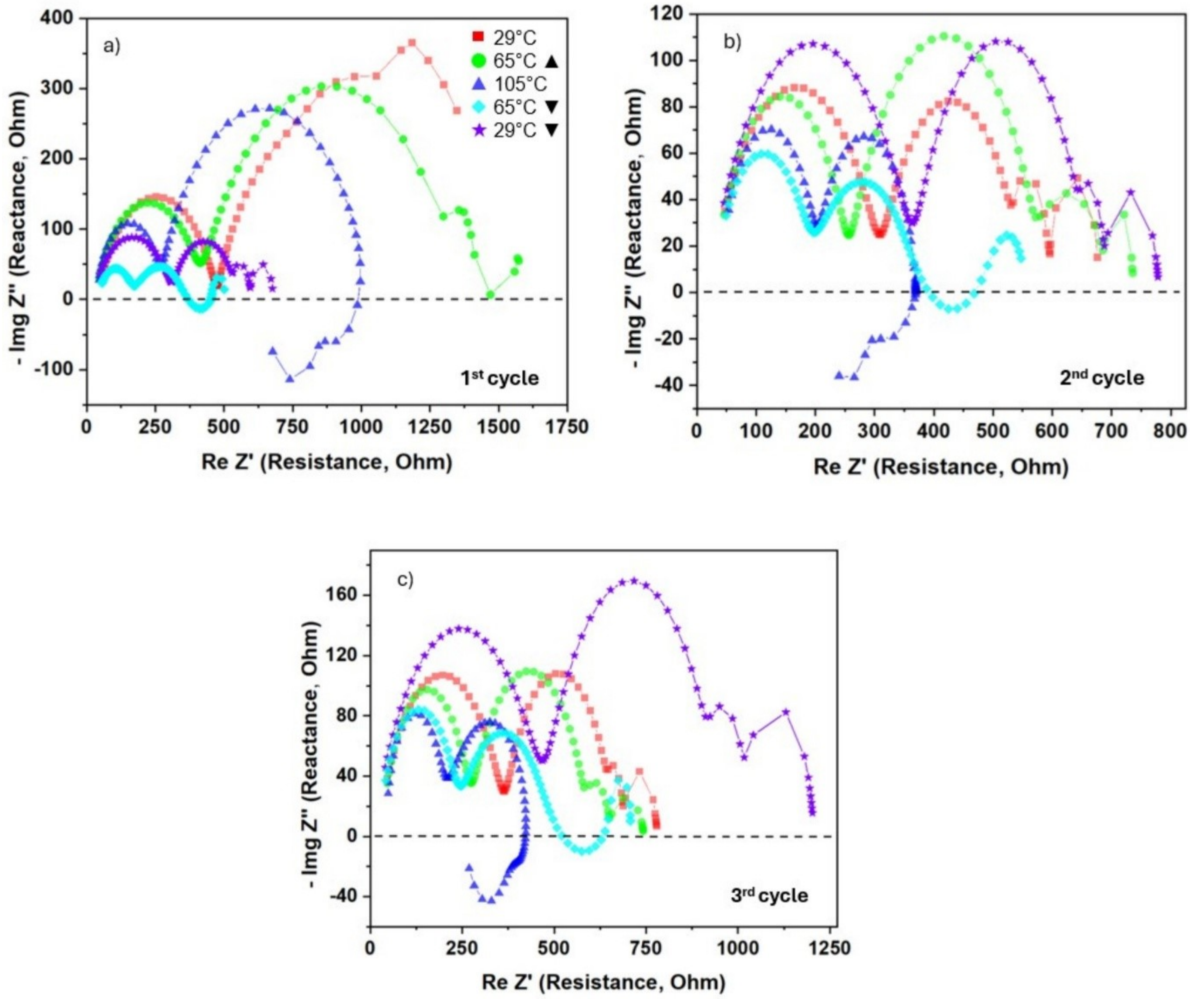

Figure S13 Three IS thermal cycles: a) First cycle, b) second cycle, and c) third cycle. Colour coded in sequence: room temperature of 25-29°C (red), heating to 65°C▲ (green), high temperature 105°C (blue), cooling to 65°C▼ (cyan), then post-heating room temperature (purple).

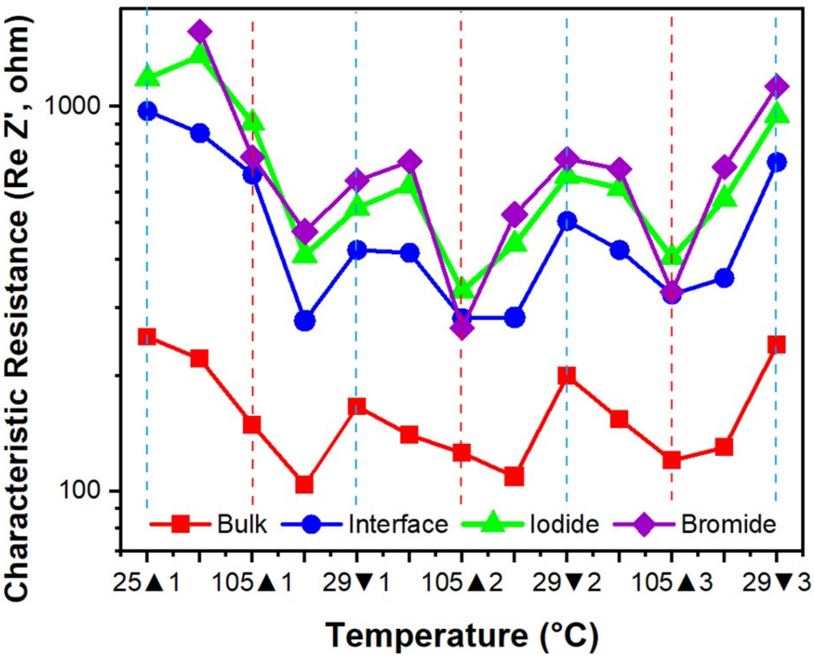

Figure S14 Characteristic Resistance of carrier component vs thermal cycling

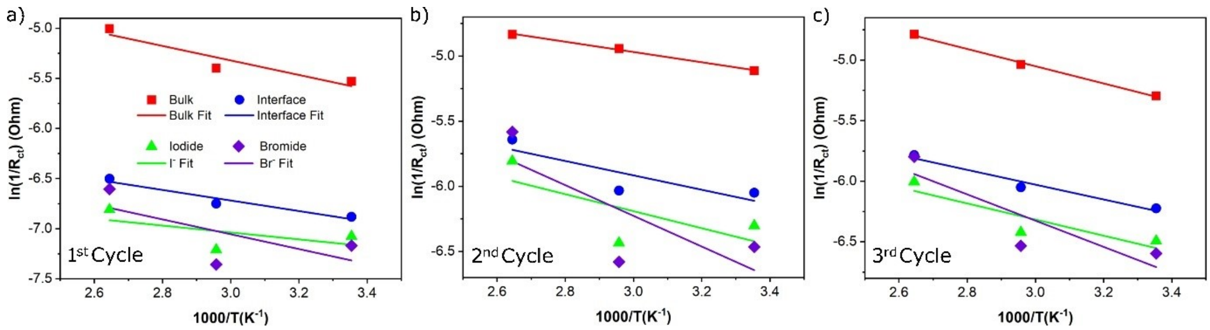

Figure S15 Arrhenius plot for calculating activation energy.

Table S1 XPS Atomic percentage ratio, relative to Cesium. Idealised $CsPbI_2Br$ is 1:1:2:1

Temperature Cycle (°C)	Cs	Pb	I	Br
25	1.00	0.95	2.29	0.56
105▲1	1.00	0.79	1.99	0.59
29▼1	1.00	0.80	1.92	0.72
105▲2	1.00	0.78	1.99	0.60
29▼2	1.00	0.82	1.95	0.59
105▲3	1.00	0.75	1.96	0.59
29▼3	1.00	0.81	2.01	0.56

Table S2 IS fitting parameters

Cycle Temp	R1	CPE1-T	CPE1-P	R2	CPE2-T	CPE2-P	R3
	Series	Bulk			Interface		
25 RT	38.49	2.16E-07	0.7509	435.2	3.41E-04	0.7518	725.3
65▲1	32.37	1.24E-07	0.7905	382.8	3.86E-05	0.7275	938.9
105▲1	40.99	9.04E-09	0.9691	225.5	5.99E-06	0.7845	400.8
65▼1	38.74	2.13E-07	0.7600	126	3.21E-04	0.4991	246
29▼1	22.95	3.91E-07	0.6974	289.4	8.98E-05	0.7604	238
65▲2	29.91	7.25E-08	0.8152	226.2	3.92E-05	0.7487	328.6
105▲2	38.4	2.05E-08	0.8933	165.8	4.21E-06	0.8464	10.54
65▼2	29.04	8.92E-08	0.7964	163.2	7.55E-05	0.6049	179.9
29▼2	20.26	3.51E-07	0.7000	349	6.03E-05	0.8004	292.8
65▲3	33.48	3.21E-08	0.8679	239.1	1.74E-05	0.7498	323.6
105▲3	39.15	1.04E-08	0.9505	174.8	3.46E-06	0.8366	46.44
65▼3	25.21	4.00E-08	0.8468	211.8	5.42E-05	0.6190	254.5
29▼3	8.148	4.53E-07	0.6717	471.8	4.43E-05	0.7797	472.5

Cycle Temp	CPE3-T	CPE3-P	R4	CPE4-T	CPE4-P	R5
	Iodide			Bromide		
25 RT	7.88E-04	1.257	179.8	4.57E-05	7.02	144.9
65▲1	9.32E-10	7.069	99.53	1.41E-05	6.951	148.6
105▲1	-5.221	-3.202	177.6	-38.89	-2.823	184.8
65▼1	-6.30E-03	0.4326	56.2	7.80E-02	1.52	16.9
29▼1	0.2805-6	4.956	52.23	3.15E-03	5.02	78.22
65▲2	8.32E-07	4.445	109.6	2.28E-05	9.037	44.9
105▲2	-0.00925	-2.999	75.88	0.6183	-4.363	79.44
65▼2	-2.26E-04	1.589	142.7	1.25E-02	1.2	38.97
29▼2	2.81E-07	4.956	32.58	2.92E-06	8.725	86
65▲3	4.74E-09	4.574	58.18	1.41E-08	8.451	88.92
105▲3	-0.05274	-2.849	119.8	0.39242	-1.235	38.08
65▼3	-1.85E-04	1.6	193.4	1.95E-02	1.6	26
29▼3	2.13E-07	4.77	84.81	1.27E-07	8.591	171.4

*CPE – non ideal geometric capacitance

Table S3 Characteristics RC Parameters of IS fitting. Arrows indicate heated (▲) and cooled (▼)

Temp (°C)	*Bulk*		*Interface*		*Iodide*		*Bromide*	
Cycle	*Resistance (Ohm)*	Capacitance *(nF)*	Resistance *(Ohm)*	Capacitance *(nF)*	Resistance *(Ohm)*	Capacitance *(nF)*	Resistance *(Ohm)*	*Cycle*
25 (initial)	*252.11*	*145.64*	*692.11*	*317.16*	*1054.00*	*365.21*	*n/a*	*25 (initial)*
65▲1	*221.02*	*137.56*	*854.23*	*303.02*	*1354.70*	*126.93*	*1568.40*	*65▲1*
105▲1	*148.90*	*108.03*	*666.31*	*271.61*	*907.30*	***-59.99***	*739.52*	*105▲1*
65▼1	*103.85*	*43.89*	*277.84*	*46.12*	*410.76*	***-13.15***	*474.16*	*65▼1*
29▼1	*166.11*	*88.12*	*423.96*	*82.31*	*545.80*	*48.06*	*642.68*	*29▼1*
65▲2	*140.11*	*84.46*	*416.86*	*110.43*	*623.43*	*42.73*	*720.79*	*65▲2*
105▲2	*125.73*	*70.25*	*281.85*	*67.21*	*332.49*	***-19.08***	*265.64*	*105▲2*
65▼2	*109.19*	*58.45*	*283.35*	*48.35*	*438.65*	***-6.14***	*524.04*	*65▼2*
29▼2	*199.45*	*106.63*	*504.40*	*108.11*	*660.39*	*46.89*	*732.28*	*29▼2*
65▲3	*153.85*	*97.53*	*423.95*	*109.56*	*614.95*	*35.47*	*687.63*	*65▲3*
105▲3	*120.16*	*81.38*	*325.07*	*75.92*	*405.37*	***-15.47***	*329.55*	*105▲3*
65▼3	*130.15*	*80.23*	*358.72*	*68.60*	*575.14*	***-9.89***	*697.29*	*65▼3*
29▼3	*240.20*	*137.71*	*717.65*	*169.51*	*949.98*	*86.11*	*1130.10*	*29▼3*

Reference

[1] International Electrotechnical Commission (2020). *IEC TS 63126:2020 ED1 Guidelines for qualifying PV modules, components and materials for operation at high temperatures, International Electrotechnical Commission*.